



HAL
open science

Héritage des activités métallurgiques et processus de remobilisation à long terme des métaux dans un district minier alpin (Alpes françaises du Nord-Ouest).

Floriane Guillevic

► To cite this version:

Floriane Guillevic. Héritage des activités métallurgiques et processus de remobilisation à long terme des métaux dans un district minier alpin (Alpes françaises du Nord-Ouest).. Géochimie. Université Savoie Mont Blanc, 2023. Français. NNT : 2023CHAMA014 . tel-04496155

HAL Id: tel-04496155

<https://theses.hal.science/tel-04496155v1>

Submitted on 8 Mar 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

THÈSE

Pour obtenir le grade de

DOCTEUR DE L'UNIVERSITÉ SAVOIE MONT-BLANC

Spécialité : **Sciences de la Terre, de l'Univers, et de l'Environnement**

Arrêté ministériel : 25 Mai 2016

Présentée par

Floriane GUILLEVIC

Thèse dirigée par **Fabien ARNAUD (EDYTEM)** et

codirigée par **Magali ROSSI (EDYTEM)**

codirigée par **Jérôme POULENARD (EDYTEM)**

préparée au sein du **Laboratoire Environnements, Dynamiques et Territoires de la Montagne (EDYTEM) - UMR 5204**
dans l'**École Doctorale Sciences, Ingénierie, Environnement (SIE)**

Héritage des activités métallurgiques et processus de remobilisation à long terme des métaux dans un district minier alpin (Alpes françaises du Nord-Ouest).

Thèse soutenue publiquement le 17 Mai 2023,
devant le jury composé de :

Mme. Alexandra COURTIN

Professeure des Universités, Université Paris-Saclay, GEOPS,
Rapporteuse

Mr. Vojtěch ETTLER

Professeur des Universités, Charles University (Prague), Institute of
geochemistry, mineralogy and mineral resources, Rapporteur

Mr. Luís CAMARERO

Chargé de recherche, Spanish Research Council (CSIC-CEAB),
Examineur

Mme. Sophia Veronica HANSSON

Chargée de recherche, CNRS, Université de Toulouse, LEFE,
Examinatrice

Mme. Anne-Véronique WALTER-SIMMONET

Maître de Conférences, Université de Franche-Comté,
CHRONO-ENVIRONNEMENT, Examinatrice et Présidente du jury

À ma grand-mère, Suzanne

Résumé

Les activités minières et métallurgiques sont parmi les activités industrielles les plus impactantes pour l'environnement et les organismes vivants. Pour transformer une roche minéralisée en métal plusieurs étapes industrielles (minéralurgie puis métallurgie) sont nécessaires, qui produisent chacune d'importantes quantités de déchets généralement porteurs d'éléments traces métalliques (ETM) potentiellement toxiques (Pb, Sb). Le panel des ressources internationales du programme des Nations Unis souligne l'important héritage environnemental des nombreux sites miniers anciens et abandonnés à travers le monde (van der Voet et al., 2013). Les différentes problématiques environnementales et sanitaires soulevées par l'héritage minier dans de nombreux pays, comme la France, représentent une opportunité pour mieux appréhender les effets à long terme de ses activités sur l'environnement.

Des centaines d'anciennes mines ont été exploitées par le passé dans les Alpes. Toutes ont été fermées et abandonnées entre le XIX^e et le XX^e siècles, laissant des déchets miniers et métallurgiques abandonnés en surface. La mine de Pb-Ag de Peisey-Nancroix (Savoie) fût l'une des plus importantes mines régionales entre XVII^e et le XIX^e siècles. Les activités minières et métallurgiques ont laissé sur place d'importantes quantités de roches stériles toujours riches en minerai et des scories métallurgiques enrichies en ETM. Des fumées pyrométallurgiques ont également été émises dans l'atmosphère pendant la pyrométallurgie. Cette thèse vise à évaluer la contamination engendrée par la dispersion des déchets dans l'environnement, la part de chacune des sources à la contamination et leur remobilisation potentielle depuis 200 ans. La mise en place d'une approche source-puits, multi-compartiments, multi-scalaire, basée sur la caractérisation des sources de la contamination (roches minéralisées, scories et fumées métallurgiques) et des puits potentiels de la contamination (sols, sédiments lacustres, eaux et sédiments de rivière) combinée à des analyses géochimiques, minéralogiques, sédimentologiques et isotopiques (Pb-Sb) a permis d'évaluer l'héritage à long-terme des activités minières et métallurgiques passées. L'étude des sols en aval de la zone de stockage de déchets révèle une contamination extrême en plomb (Pb) et modérée en antimoine (Sb) en surface, mais un transfert limité en profondeur. Les isotopes de Sb identifient les scories comme étant la principale source de contamination des sols sur le site. Les sédiments de rivière et les eaux à proximité du site minier montrent un enrichissement rapidement dilué par le régime torrentiel du Ponturin. Les sédiments lacustres du lac de La Plagne, situé 7 km en amont, enregistrent une contamination par les fumées pyrométallurgiques pendant la période d'activité de la mine 5 fois supérieure à la période pré-mine. Les sols du bassin versant du lac montrent toujours la persistance de ce Pb anthropique portant la signature du minerai local. L'érosion de ces sols depuis 200 ans contribue à remobiliser ce Pb anthropique vers l'aval : une petite partie du Pb anthropique remobilisé est piégé dans le lac de La Plagne, alors que la majorité est évacuée dans le Ponturin par l'exutoire du lac.

Cette étude montre la persistance et la remobilisation des ETM liés aux anciennes activités minières et métallurgiques. Les inventaires de Pb anthropiques générés demeurent assez importants pour que la trace laissée par ces activités soit mesurable sur le long terme, plusieurs siècles après l'arrêt des activités.

Abstract

Mining and metallurgical activities are among the industrial activities that have the greatest impact on the environment and living organisms. In order to transform a mineralized rock into metal, several industrial steps are necessary and produce large quantities of wastes, generally carrying potentially toxic trace metals. In this respect, the United Nations International Resource Panel recalls that many old and abandoned mining sites have left a serious environmental legacy throughout the world (van der Voet et al., 2013). The various environmental and health issues raised by the mining legacy in many countries, such as in France, represent an opportunity to better understand the long-term effects of these activities on the environment.

Hundreds of former mines were exploited in the French Alps, which closed down between the 19th and the 20th centuries, leaving mining and metallurgical waste heaps abandoned on the surface. The Pb-Ag mine of Peisey-Nancroix (Savoie) was one of the most important regional mines between the 17th and 19th centuries. Ore processing and metallurgical activities have left on site large quantities of ore-bearing waste rocks and metal-rich metallurgical slags. Pyrometallurgical fumes were also emitted into the atmosphere. This thesis aimed to assess the contamination generated by the dispersion of these wastes in the environment, the contribution of each source to the contamination and their potential remobilisation. The implementation of a source-sink, multi-compartments, and multi-scalar approach, based on the characterisation of the sources of the contamination (ore-bearing rocks, metallurgical slags and fumes) and the potential sinks of the contamination (soils, lake sediments, waters and river sediments), combined with geochemical, mineralogical, sedimentological and isotopic (Pb-Sb) methods, allowed evaluating the long-term legacy of past mining and metallurgical activities. The study of surface soils downstream of the waste storage area reveals extreme lead (Pb) and moderate antimony (Sb) contamination in the upper most horizons, with limited transfer in depth. Sb isotopes identified slags as the main source of soil contamination at the site. River sediments and waters collected in the vicinity of the mine site show enrichment that is rapidly diluted by the torrential regime of the river. The sediments of Lake La Plagne, located 7 km upstream, show a contamination from the pyrometallurgical fumes during the period of mine activity 5 times higher than during the pre-mine period. The soils of the lake catchment show the persistence of this anthropogenic Pb, with the signature of the local ore. For 200 years, the soil erosion contributes to remobilize this anthropogenic Pb downhill: only a small part of this anthropogenic Pb is being caught into the lake, whereas most of it is being evacuated downstream by the river.

This study shows the persistence and remobilisation of trace metals related to past mining and metallurgical activities. The anthropogenic Pb inventories generated remain large enough for the mining legacy to be measurable over the long term, even centuries after the activities have ceased.

Remerciements

Il y a certaines aventures dont on aimerait qu'elles ne finissent jamais, car les personnes rencontrées en ont fait une aventure hors du commun.

Je tiens à remercier dans un premier temps Alexandra Courtin et Vojtěch Ettler qui ont accepté d'être rapporteur et rapportrice de mon manuscrit de thèse, ainsi que pour leurs commentaires sur le manuscrit et les échanges au cours de ma soutenance de thèse. Pour ces mêmes raisons, je remercie également Anne-Véronique Walter-Simonnet, Sophia Veronica Hansson et Lluís Camarero pour leur rôle d'examineur et d'examinatrice lors de ma soutenance de thèse.

Mes plus grands remerciements s'adressent directement à mes trois directeurs de thèse, Magali Rossi, Fabien Arnaud et Jérôme Poulenard. Je crois qu'il m'aurait été difficile d'aller au bout de cette thèse sans eux. Magali, je n'ai toujours pas les mots pour te remercier. Ton accompagnement au cours de ces trois ans et demi de thèse a été exceptionnel, un support constant propice à mon épanouissement dans la recherche. Tu as su m'orienter vers les bonnes décisions et m'encourager lorsque j'en avais besoin. Fabien, je te remercie pour tes précieux conseils et les orientations que tu as su donner à ma thèse, avec cette volonté de toujours pousser nos raisonnements plus loin et avec plus de complexité. Jérôme, je te remercie pour ton soutien et ta bonne humeur quotidienne. Tu m'as transmis tes connaissances sur les sols, qui je l'espère me suivront encore longtemps. Vous avez formé un beau triptyque de raison et de fougue scientifique !

Plusieurs personnes ont également contribué de manière significative par leur expertise à mes travaux de thèse, réussissant à les porter à la croisée de plusieurs disciplines.

Grâce à la participation de Jean Martins et de Lorenzo Spadini, nous avons poursuivi les tests d'extraction chimiques débutés en amont de ma thèse. Je vous remercie tous les deux pour votre accueil au sein du laboratoire IGE.

Dès le début de ma thèse, Cécile Quantin s'est investie dans mon encadrement en participant à mon comité de thèse, et la collaboration s'est poursuivie au laboratoire GEOPS avec l'étude des isotopes du Pb et du Ni. Cécile, je te remercie pour la route vers l'isotopie que tu as fait prendre à ma thèse et surtout pour ta gentillesse et ton accueil à GEOPS. Je profite de ces remerciements parisiens pour remercier Gaël Monvoisin qui m'a formé et épaulé pendant quelques semaines de manips pour la mesure des isotopes du Pb.

Je ne peux pas parler d'isotopie sans mentionner Eléonore Resongles qui m'a fait découvrir le monde des isotopes de l'antimoine. Eléonore tu as pleinement contribué à la réussite du 3^{ème} volet

de ma thèse en utilisant une approche multi-isotopes qui nous a tous captivé. Je remercie également au laboratoire HSM Colin Ferrari et Rémi Freydier pour leur aide aux manips et aux mesures.

Je remercie également Géraldine Sarret et Françoise Elbaz-Poulichet pour leur participation et leurs conseils au cours de mon comité de thèse.

Mes travaux de terrain se sont concentrés dans la vallée du Ponturin, près du village de Peisey-Nancroix ; je remercie ainsi l'équipe municipale et les agriculteurs qui nous ont accompagnés au cours de ces années de thèse et nous ont permis de mener à bien ces travaux.

Je voudrais également remercier les membres du laboratoire EDYTEM d'avoir toutes et tous apporté une ambiance propice à la joie et au partage. Tout particulièrement, merci Anne-Lise d'avoir été présente chaque jour pour répondre à mes questions (incessantes ?) et de m'avoir accompagné dans toutes les étapes de ma thèse même lorsque je cassais les moules des pastilles XRF ! Merci à Fayçal pour ta bonne humeur quotidienne, tes petites blagues qui égayent nos journées au labo de sédimentologie et encore merci pour toutes les belles lames épaisses que tu m'as fournies pour ma thèse (et merci également à Wafaa qui a pris la relève). Merci également à Pierre de m'avoir aiguillé pour le modèle d'âge d'un lac, décidément pas facile à dater.

Et bien sûr, toutes celles et ceux sans qui cette aventure n'aurait pas été aussi extraordinaire... les doctorantes et doctorants du labo ! Nous avons su créer un environnement bienveillant et à l'écoute, et vous m'aurez toutes et tous apporté des petits joies quotidiennes. Ma camarade des premiers jours, Agathe, tu as été mon rayon de soleil, ton engagement et ta manière de mettre des mots sur les choses continueront de m'impressionner ; Stéphane et ses soliloques m'ayant presque donné envie de rempiler pour 3 ans de thèse en socio ; Maëva, pour tous ces thés, cafés, sucreries et discussions immo (haha) partagés, ainsi que nos covoiturages et de ces "que va-t-on faire nos vies ?", merci d'avoir été là. Yoann, secrétaire attitré au bureau des "mites" et légendes, ton flegme et calme olympien resteront un exemple pour moi ; Tanguy, pour ta gentillesse et tes attentions quotidienne et Giorgia, ta fougue italienne a grandement animé notre bureau lorsque tu étais parmi nous. Parce que la liste serait trop longue, merci aussi aux doctorants et doctorantes pour tous les bons moments partagés, au cours de déjeuners en salle thé, d'un verre en terrasse et des weekends docs : Lise, Louis, Jules, Julien, Aurélie, Julia, Andréa, Chloé, Camille et Noémie. Certains auront pris plus de place que d'autres dans ma vie, merci Juju d'avoir été là.

Une pensée aussi aux plus anciens (pas si vieux que ça non plus !) Ana, Tim, Mathieu et William qui nous ont très bien accueillis au sein d'EDYTEM. La bonne humeur a toujours été au rendez-vous. Ana tu resteras l'une de mes plus belles rencontres de ma thèse.

Le monde associatif et les personnes rencontrées (elles se reconnaîtront) m'ont énormément appris sur les enjeux environnementaux de l'industrie minière et sur le travail en collectif. Nous avons vécu des expériences inoubliables, merci à vous.

Ces 3 dernières années de thèse c'est aussi beaucoup de souvenir avec les amis et amies de plus longue date, toujours là pour faire la fête et écouter la « dure vie » de thésarde : merci aux copines et copains de Lasalle, Alice, Camille, Camie, Coco, Fred, Karl, Marion, Pauline, Thomas, Valentine mais aussi à ceux et celles de prépa et notamment à Flo qui m'a même suivi jusqu'en Savoie !

Et bien sûr pour terminer, merci à ma famille, mes parents et ma sœur d'être toujours présent année après année me soutenant même lorsqu'ils ne comprennent plus vraiment l'intérêt d'un énième diplôme. Merci de m'avoir donné le goût d'apprendre ! À croire que c'est de famille, ce sera bientôt ton tour Romane d'écrire ses remerciements.

Table des Matières

Résumé 1

Abstract 2

Chapitre 1 | Introduction générale : La mine et ses impacts environnementaux sur la zone critique.....19

1.1 Les ressources minérales et leur exploitation au cours du temps20

1.1.1 Les ressources minérales au fil du temps20

1.1.2 Evolution de la nature des minerais exploités.....20

1.1.3 Evolution des techniques de traitement du minerai.....22

1.2 L'activité minière et la production de déchets.....23

1.2.1 De la prospection à la découverte d'un gisement.....23

1.2.2 L'extraction du minerai.....24

1.2.3 Le traitement minéralurgique du minerai.....25

1.2.4 Le traitement métallurgique du minerai27

1.2.5 La fermeture et l'après-mine28

1.3 Les déchets miniers, sources de contaminations métalliques dans l'environnement29

1.3.1 Les éléments traces métalliques (ETM)29

1.3.2 Les différents modes de transfert des ETM dans la zone critique.....31

1.3.3 Les contaminations en ETM anthropiques de la zone critique.....33

1.4 Problématiques de la thèse et cadre méthodologique34

1.4.1 Problématique.....34

1.4.2 Approche et mise en œuvre.....37

1.5 Organisation du manuscrit.....38

Chapitre 2 | La mine de Pb-Ag de Peisey-Nancroix (Savoie)..... 43

2.1 Contexte géographique44

2.2 Contexte géologique.....46

2.3	Contexte historique	48
2.4	La mine de Peisey-Nancroix, le site idéal pour une étude multi-compartiments à différentes échelles.....	50
Chapitre 3 Modes de dispersion du Pb dans les sols miniers.....		53
3.1	Introduction	55
3.2	The Pb-Ag mine of Peisey-Nancroix (Savoy, France)	57
3.3	Material and methods.....	59
3.3.1	Contamination source materials.....	59
3.3.2	Soil sampling.....	59
3.3.3	Physical and chemical characterisation of soils.....	59
3.3.4	Quantitative analysis of soils by WDS-XRF	60
3.3.5	Mineralogical characterisation	61
3.3.6	Single extraction tests	62
3.3.7	Analytical data treatment.....	63
3.4	Results	63
3.4.1	Slags and waste rocks compositions.....	63
3.4.2	Soil properties	66
3.4.3	Pb contamination of soils	68
3.4.4	Pb-bearing phases in soils	72
3.4.5	Pb single extraction tests.....	74
3.5	Discussion.....	77
3.5.1	Remobilisation and long-term mobility of Pb.....	78
3.5.2	Pb dispersion processes in soils	79
3.5.3	The airborne portion of the Pb contamination	81
3.6	Conclusion.....	82
3.7	Acknowledgement.....	82
3.8	Supplementary material.....	83
Chapitre 4 Héritage à long-terme des fumées pyrométallurgiques.....		101

4.1	Introduction	103
4.2	Study area.....	104
4.3	Materials.....	106
4.3.1	Lake sediments	106
4.3.2	Surface and subsurface soil samples.....	106
4.4	Methods	107
4.4.1	High-resolution elemental EDS-XRF analyses.....	107
4.4.2	Carbonates and organic matter content.....	107
4.4.3	Major and trace element contents, and enrichment factor (EF)	108
4.4.4	Pb isotopes	108
4.4.5	Short-lived radionuclides (^{210}Pb , ^{137}Cs , ^{230}Am)	109
4.4.6	^{14}C dating.....	109
4.4.7	Anthropogenic Pb (Pb_{ANTH}) and accumulation rate ($\text{AR}_{\text{Pb_ANTH}}$).....	109
4.4.8	Inventory calculations.....	110
4.5	Results	111
4.5.1	Sedimentology of Lake La Plagne.....	111
4.5.2	Major elements	113
4.5.3	Trace elements and enrichment factor.....	114
4.5.4	Pb stable isotopes.....	117
4.5.5	Age-depth model of lake sediments	119
4.5.6	Anthropogenic Pb inventories	122
4.6	Discussion.....	124
4.6.1	Recording of local ore smelting activities	124
4.6.2	Long persistence of anthropogenic Pb in lake sediments.....	126
4.6.3	Long-lasting remobilisation of legacy Pb from soil.....	128
4.7	Conclusion.....	128
4.8	Acknowledgement.....	129
4.9	Supplementary Material.....	129

Chapitre 5 | Couplage isotopique Pb-Sb sur sols, sédiments et eaux de rivières 145

5.1 Introduction147

5.2 Material and methods.....150

 5.2.1 The Peisey-Nancroix mining site150

 5.2.2 Sampling and sample preparation.....152

 5.2.3 Sample analysis153

5.3 Results and interpretation.....157

 5.3.1 The potential sources of contamination157

 5.3.2 Soil, sediment samples and water.....158

5.4 Discussion.....165

 5.4.1 Spatial characterization of the Pb and Sb contamination.....165

 5.4.2 Antimony isotope fractionation during pyrometallurgy166

 5.4.3 Coupling of Pb and Sb isotopes.....167

 5.4.4 Quantification of the anthropogenic contamination169

5.5 Conclusion.....171

5.6 Acknowledgment.....171

5.7 Supplementary material.....172

Chapitre 6 | Inventaires du plomb à l'échelle du bassin versant 183

6.1 Choix du fond géochimique pour chacun des sites.....185

6.2 Stock de plomb anthropique généré par les haldes (sols du site minier).....186

 6.2.1 Méthode de calcul et d'interpolation187

 6.2.2 Inventaires de Pb interpolés188

6.3 Inventaire de plomb anthropique généré par l'émission de fumées lors de la pyrometallurgie.....189

 6.3.1 Reconstruction de l'inventaire de Pb anthropique déposé initialement sur les sols autour de Lac de la Plagne190

 6.3.2 Inventaire de Pb anthropique du lac de La Plagne issu de la remobilisation des sols par érosion.....191

6.4	Comparaison	193
Chapitre 7 Conclusion et Perspectives		197
7.1	Les contaminations des différents compartiments autour du site minier	197
7.2	Le problème de la caractérisation du fond géochimique local.....	198
7.3	La caractérisation des sources de contamination anthropique & des modes de dispersion 199	
7.3.1	L'apport du couplage isotopie Pb-Sb pour caractériser les sources de contaminants 199	
7.3.2	Dispersion des déchets miniers et métallurgiques sur le site	201
7.3.3	Dispersion des fumées pyrométallurgiques	202
7.4	Relations entre mobilité, biodisponibilité et minéralogie des ETM.....	202
7.5	Messages à retenir.....	204
7.6	Perspectives	204
7.6.1	Perspectives à l'échelle du site de Peisey-Nancroix.....	204
7.6.2	Perspectives globales.....	206
REFERENCES		209
ANNEXES 225		
ANNEXE A - Liste des laboratoires partenaires et collaborateur pour la réalisation des analyses 226		
ANNEXE B - Valorisation scientifique durant la thèse.....		227
ANNEXE C - Proceeding of the 16 th SGA Biennial Meeting.....		229

Table des figures

Figure 1.1: Ancienne tranchée d'exploitation de minerai de Pb-Ag en lisière du lac Blanc d'Huez	23
Figure 1.2 : Formation d'une anomalie géochimique en conditions de surface : la zone minéralisée (en gris), est oxydée au voisinage de la surface.	24
Figure 1.3 : Comparaison des techniques de concassage utilisées au cours du temps pour le traitement minéralurgique du minerai illustré l'étape du broyage.	26
Figure 1.4 : A) Carte des gisements, gîtes et indices en France. B) Carte des anciennes mines et exploitation en France	28
Figure 1.5: Schéma d'un site minier et métallurgique mettant en évidence les sources, les puits et les principaux modes de transferts des ETM dans les différents compartiments de la zone critique.	32
Figure 1.6 : Schéma synthétique de l'approche multi-compartiment et multi-scalaire mise en œuvre dans cette thèse.....	38
Figure 2.1 : Cartes de localisation de la mine de Pb-Ag de Peisey-Nancroix (Savoie, France).....	44
Figure 2.2 : Planche photographique détaillant l'environnement du site minier et métallurgique de Peisey-Nancroix.....	45
Figure 2.3: Plan général de la mine royale de Peiey en 1864.....	46
Figure 2.4 : A) Schéma structural des Alpes occidentales avec un carré représentant la localisation de la carte B (d'après Bertauts et al., 2022). B) Carte géologique de la zone Briançonnaise située entre les massifs de la Lauzière et de la Vanoise modifiée d'après la carte géologique de Moûtiers (1:50 000)	47
Figure 2.5 : Frise chronologique de l'exploitation de la mine de Peisey-Nancroix entre le XVII ^e et le XIX ^e siècle.....	48
Figure 3.1 : A) Location map of Peisey-Nancroix in the northern French Alps; B) Geological map of the Peisey-Nancroix Pb-Ag mine and its surroundings; C) Organisation of the old mine site, and infrastructures	58
Figure 3.2: Reflected light (A) and SEM images (B-K) of primary and secondary Pb-bearing phases identified in the ore (A), slags (B-C) and soils (D-K).	65

Figure 3.3 : A) Principal component analysis of the 117 samples based on major elements and soil organic matter (SOM) with Pb as an illustrative supplementary variable, allowing the characterisation of three soil types: carbonate-rich cambisols, carbonate-poor cambisols and highly contaminated soils; B) Distribution map of the three soil types.....67

Figure 3.4: A) Spatial distribution of the total Pb content in soils indicating that Pb content decreases down to the local pedo-geochemical background (blue points); B) the Pb enrichment factor and; C) the Pb geoaccumulation index.71

Figure 3.5: Spatial distribution of the Pb-bearing phases based on mineralogical observations73

Figure 3.6: Graph of the amount of extracted Pb (mg.kg^{-1}) using 3 extractants (distilled water, humic acid, and EDTA) as a function of the total soil Pb content (mg.kg^{-1}) on a logarithmic scale.75

Figure 3.7: Spatial distribution of the fraction of extracted Pb (%) for each extractant.....76

Figure 4.1 : Location maps of the study area.105

Figure 4.2: Dry bulk density (DBD) and $\text{LOI}_{550^\circ\text{C}}$ and $\text{LOI}_{950^\circ\text{C}}$ for discrete samples (units %) along the PLG-03 core as well as major and trace element content profiles measured by EDS-XRF with a 1-mm step.....112

Figure 4.3: Distribution map of surface soil around Lake La Plagne indicating EF_{Pb} , the total Pb content (in mg.kg^{-1}) and the anthropogenic Pb content (Pb_{ANTH} in mg.kg^{-1}).116

Figure 4.4: Pb isotope ratios of soils (surface and subsurface soils) and lake sediments compared to the Pb local ore.119

Figure 4.5: Age-depth model on the continuous sedimentation removed from events based on (from left to right) $^{210}\text{Pb}_{\text{ex}}$ activity (mBq.g^{-1}), ^{137}Cs activity (mBq.g^{-1}), ^{241}Am activity (mBq.g^{-1}) and the age model calculated from $^{210}\text{Pb}_{\text{ex}}$ on the real depth.120

Figure 4.6: Age-depth model of the master core combining ^{137}Cs and ^{231}Am peaks with ^{14}C dates.122

Figure 4.7: A) The ratio $\ln(\text{Pb}/\text{Rb})$ from XRF-EDS data according to time (age CE) divided into 3 periods : pre-smelting, smelting and post-smelting periods with $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 9 samples along PLG-03; B) Accumulation rate of anthropogenic Pb ($\text{AR}_{\text{Pb-ANTH}}$) calculated using both the elemental ratio (Rb) and Pb isotopes (equations 3 and 4); C) Historical timeline of the ore production from 1745 to 1865 yr cal CE.....123

Figure 4.8: Comparison between Lake La Plagne and Lake Anterne.....127

Figure 5.1: A) Location map of the Pb-Ag Peisey-Nancroix mine in the French northern Alps; B) Location map of the collected samples along the Ponturin river and the Arc stream; C) Map of interpolated Pb content of topsoils (package Autokrige;; R Core team 2022) of the mining site

showing the position of the soil profiles; D) Geological map of the mining site with positions of the soil profiles.....151

Figure 5.2: Distribution of Pb and Sb enrichment factors with depth (empty circles), and evolution of the $^{206}\text{Pb}/^{207}\text{Pb}$ and $\delta^{123}\text{Sb}$ isotopes for the P1, P3 and P5 soil profiles (grey circles).....162

Figure 5.3 : Diagrams showing the Pb isotopic compositions of the contamination sources (squares) , the soil horizons (circles) and sediments (diamonds).163

Figure 5.4 : Isotopic signatures of Sb (A) and $\delta^{123}\text{Sb}$ values versus $1/\text{Sb}$ (logarithmic scale, B) for potential contamination sources (squares), soil samples (circles) and sediments samples (diamonds).164

Figure 5.5: Coupling of Pb and Sb isotopes.....168

Figure 6.1: A) Distribution spatiale de la teneur en Pb totale et cadre restreint des points de sol de surface sélectionnés pour le calcul des inventaires. B) Distribution des points de mesure de masse volumique (densité apparente de terre fine), répartie entre la zone prairiale et la partie forestière.186

Figure 6.2: Cartes d'interpolation des inventaires (stocks) de Pb anthropique obtenus par krigeage standard (à gauche) et l'erreur standard associée en fonction de la densité apparente des sols considérée (à droite).....189

Figure 6.3: Schéma explicatif de la démarche de calcul de l'inventaire du Pb anthropique192

Figure 7.1 : Couplage des isotopes du Pb et de Sb montrant la signature des sédiments lacustres du lac de La Plagne201

Figure 7.2 : Inventaire du Pb anthropique ($\text{g}\cdot\text{m}^{-2}$) en fonction de l'inventaire du $^{210}\text{Pb}_{\text{ex}}$ ($\text{Bq}\cdot\text{m}^{-2}$) dans les sols de surface autour du lac de La Plagne.205

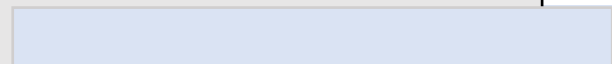
Table des tableaux

Table 1-1 : Dates approximatives du début des âges des métaux dans les différentes régions du monde	21
Table 3-1: Major and trace element contents of waste rocks and slags.....	64
Table 3-2: Basic statistics of the 3 groups of soil based on PCA and hierarchical clustering.....	69
Table 3-3: PTE content of site reference soils and rocks and guidelines.	70
Table 3-4: Spearman correlations between the Pb total content and major elements and constituents of soil.	71
Table 3-5: Classification of samples in groups of Pb extraction variability.....	78
Table 3-6: Spearman correlation coefficients between extracted Pb and soil properties (n = 20).	79
Table 4-1: Principal soil properties, trace elements and major contents for superficial soil in the surrounding of Lake La Plagne	114
Table 4-2: Pb isotopes (²⁰⁴ Pb, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb) of lake sediments, superficial and subsurface soils	118
Table 4-3: The ¹⁴ C dates collected in Lake La Plagne cores (PLG).....	121
Table 4-4: Inventories of anthropogenic Pb and ²¹⁰ Pb _{ex}	125
Table 5-1: Concentrations and isotopic signatures of Pb and Sb in soils and sediments samples and in potential contamination sources (slags, ore-bearing rocks, stack residues).....	159
Table 5-2 : Water properties and Pb and Sb content of water samples.	161
Table 5-3: Fractions of the contamination sources to horizons soil and dewatering sediments using $\delta^{123}\text{Sb}$ (in percents).....	170
Table 6-1: Teneurs élémentaires en plomb et éléments lithogènes et leurs ratios élémentaires associés.....	185
Table 6-2: Comparaison des inventaires de Pb _{TOTAL} et de Pb _{ANTH} intégrés sur la zone étudiée	188
Table 6-3: Flux moyen de Pb anthropique estimé d'après le taux d'accumulation du Pb anthropique dans les sédiments lacustres.....	191
Table 6-4 : Quantité initiale de Pb anthropique déposée sur les sols du bassin versant du lac de La Plagne.....	191

Chapitre 1 |

Introduction &

Approche méthodologique



Chapitre 1 | Introduction générale : La mine et ses impacts environnementaux sur la zone critique

Les activités minières et métallurgiques sont parmi les activités humaines les plus délétères pour l'environnement (Hudson-Edwards, 2016; Hudson-Edwards et al., 2011; Dudka and Adriano, 1997; Thornton, 1996) par la dégradation des habitats, par la modification de la circulation des eaux souterraines et par la contamination des sols, des eaux et des sédiments fluviaux et lacustres liée au stockage de déchets en surface et à l'émission de gaz et particules fines lors du traitement pyrométallurgique. En France, plusieurs études soulignent la présence de contamination en éléments traces métalliques (ETM) autour de sites miniers récemment fermés. L'ancienne mine d'or et d'arsenic de Salsigne (Aude) a généré la contamination des nappes souterraines en arsenic, entraînant celles des sols par infiltration et irrigation (Khaska et al., 2018). En Guyane, l'orpaillage illégal de l'or conduit à une augmentation de la concentration en mercure des poissons, et *in fine* chez les populations autochtones (Maury-Brachet et al., 2020). Ces activités peuvent donc être nocives pour les écosystèmes et les populations vivants sur d'anciens territoires miniers.

Malgré des impacts environnementaux et sanitaires avérés, les activités minières et métallurgiques demeurent actuellement inévitables pour subvenir à des besoins individuels et collectifs toujours croissants en matières premières minérales (métaux, minéraux industriels, sable, etc.). En effet, malgré une part de plus en plus importante du recyclage des métaux, celui-ci reste insuffisant pour subvenir aux besoins (Christmann, 2018). Si l'exploitation de nouvelles mines semble donc inéluctable, il apparaît nécessaire pour les mines du futur de limiter les impacts sociaux et environnementaux sur l'ensemble du cycle minier, depuis l'exploration jusqu'à la gestion de l'après-mine. Pour mieux appréhender l'héritage laissé par les mines, il est nécessaire de connaître les impacts environnementaux à (très) long-terme des exploitations minières et des traitements métallurgiques des minerais. L'étude des impacts environnementaux associés à des mines anciennes et abandonnées depuis plusieurs siècles permettrait de mieux appréhender les questions de contamination de la zone critique, de rémanence et de remobilisation des ETM sur le temps long, et ainsi de pouvoir anticiper au mieux les impacts des futures exploitations minières sur les territoires.

1.1 Les ressources minérales et leur exploitation au cours du temps

1.1.1 Les ressources minérales au fil du temps

La valeur d'une ressource repose sur l'utilité qui en est faite par les sociétés. Une ressource minérale est la concentration ou la présence d'une substance solide au sein de la croûte terrestre qui présente un intérêt économique. Son intérêt économique repose sur la forme, la teneur et la quantité de la ressource minérale qui la rend rentable (Jébrak and Marcoux, 2008). L'usage des métaux et minerais a varié d'un continent à l'autre de même qu'entre les pays (Table 1-1). En Europe, il est tout de même possible d'établir de grandes périodes chronologiques. Dès le Néolithique (à partir du VI^e millénaire avant notre ère), l'usage du cuivre natif se développe à travers le continent pour la réalisation d'outils (Killick and Fenn, 2012). La métallurgie apparaît peu de temps après. L'Age du Bronze (à partir du III^e millénaire avant notre ère) voit l'avènement de cet alliage de cuivre et d'étain pour la fabrication d'armes et de parures. A L'Age du Fer (I^{er} millénaire avant notre ère), les sociétés développent l'art de la forge pour créer une kyrielle d'outils destinés aux domaines du transport, de la construction ou de l'armement. Les métaux, dit nobles ont été exploités dès les premières sociétés mais c'est seulement durant ce dernier millénaire avant notre ère que leur utilisation explosa pour battre monnaie. La péninsule ibérique constituait alors très probablement la plus grande zone de richesses minérales en Europe occidentale (Craddock, 2009). On y exploitait principalement l'argent sous forme de jarosite et de minerai de plomb argentifère. Dès l'Antiquité (I^{er} s. av. J.C. – V^e s. ap. J.C.), le plomb est parmi les métaux les plus utilisés par les Romains, qu'ils utilisent pour leur monnaie (galène argentifère) mais aussi pour l'acheminement de l'eau ou l'armement par exemple. L'argent issu de la galène argentifère est récupéré pour la monnaie. Ainsi au fil des siècles, les besoins économiques et sociétaux ont évolué favorisant l'exploitation d'un métal à la faveur d'un autre. Aujourd'hui, presque tous les éléments du tableau périodique ont une utilité industrielle, que ce soit dans l'industrie aéronautique, hi-tech, ou autre¹.

1.1.2 Evolution de la nature des minerais exploités

Le *minerai* se réfère aux espèces minérales porteuses de substances utiles. Ainsi, la galène (PbS) est considérée comme étant le principal minerai de plomb. Dans une roche minéralisée, le minerai est associé à d'autres minéraux n'ayant aucune valeur économique qui constituent la *gangue* de la minéralisation (p. ex., cristaux de quartz auxquels est associé l'or natif). Les géologues miniers

¹ Se référer au site internet www.elements.wlonk.com/ElementsTable.html pour plus de détails.

appellent minerai la roche constituée de la gangue et des minéraux porteurs des métaux (minerai), ce qui peut amener à une certaine confusion. Nous utiliserons donc dans ce manuscrit le terme de minerai pour désigner uniquement les minéraux porteurs des métaux d'intérêts et le terme de *roche minéralisée* pour désigner l'assemblage *gangue + minerai*.

Table 1-1 : Dates approximatives du début des âges des métaux dans les différentes régions du monde (années av. J.C., hormis indication contraire ; d'après Tylecote, 2002)

Archaeological ages	Chalcolithic		Early Bronze	Middle/Late Bronze	Early Iron	Roman Iron	Late Iron
	Native copper ¹	Smelted copper	Early Bronze	Full Bronze			
Metal ages							
Anatolia	}	5000	3000	2000	1000	30	
Troad							
Egypt							
Palestine							
Mesopotamia	7000	4000	3500	2800	1200	AD 100	
Aegean		3300	2500	2000	1000	150	
Italy		3000	2000	1200	800	250	
Iberia		3000	1500	1000	700	200	
SE Europe	5000	4500	3000	1500	700	AD 100	
NW Europe		2200	1800	1200	500	50	AD 400
E Europe and Russia		2200	1500	700	400	-	
Far East			1500	1300	700	-	
West Africa					500	-	
East Africa (Nubia, Sudan)					200	AD 1	
South America		AD 700	AD 1000	AD 1400	-	-	
North America	4000						

¹earliest known use of

Initialement, les métaux ont été exploités sous forme d'éléments natifs (Cu, Ag), qui sont les plus faciles à exploiter et qui sont les plus rentables car contenant un unique élément chimique métallique (Table 1-1). Ces types de gisements étant aujourd'hui appauvris, on exploite désormais plutôt des minéraux porteurs de l'élément d'intérêt : p.ex. pour l'argent, la freibergite ($[\text{Ag,Cu,Fe}]_{12}[\text{Sb,As}]_4\text{S}_{13}$; 40% d'Ag) ou la galène argentifère (jusqu'à quelques pourcents d'Ag, Bertauts et al., 2022).

Dans les roches minéralisées comme dans le minerai, le métal d'intérêt est généralement associé à un cortège métallique qui a souvent été délaissé car, au moment de sa récupération, (i) il n'est pas valorisable économiquement (teneurs trop faibles), (ii) l'intérêt pour le métal n'est pas connu, ou

(iii) les techniques de récupération sont inexistantes. Un minerai métallique en tant que tel n'est pas une substance directement utilisable : seul le métal l'est. Il convient donc de séparer le minéral d'intérêt (minerai) de sa gangue (procédés minéralurgiques) puis de séparer le métal d'intérêt des autres éléments chimiques (procédés métallurgiques). Ainsi, la nature des roches minéralisées a évolué au cours du temps, passant de roches contenant des métaux natifs à des roches de moins en moins concentrées en métaux, nécessitant des développements technologiques constants, que ce soit pour l'extraction du minerai ou pour les procédés minéralurgiques et métallurgiques.

La teneur en métal d'une minéralisation correspond à la masse de métal divisée par la masse de roche minéralisée, exprimée en pourcents. On définit la *teneur de coupure* comme la teneur maximale en métal pour laquelle l'exploitation devient rentable (Lottermoser, 2010). Au fil du temps, la teneur de coupure a diminué au gré des développements technologiques et des coûts de production. Aujourd'hui, elle peut varier annuellement en fonction de l'évolution des marchés financiers et de la rentabilité de la production. Les *réserves* minérales correspondent à la partie économique exploitable des ressources minérales, exprimées en tonnes de métal (Jébrak and Marcoux, 2008). L'estimation des réserves est directement liée à la teneur de coupure : plus la teneur de coupure est basse, plus les réserves seront élevées.

1.1.3 Evolution des techniques de traitement du minerai

Les techniques de traitement du minerai sont devenues de plus en plus efficaces récupérant une part toujours plus importante de métal. Parallèlement à la diminution des teneurs observée dans les gisements actuels, les techniques de traitement du minerai ont permis d'accéder à ces faibles teneurs. La teneur de coupure a diminué conjointement à la teneur des gisements. La plus grande mine d'argent actuelle, la mine de Polkowice-Sieroszowice (Pologne), extrait 40g d'Ag par tonne de roche cuprifère. La récupération de ces teneurs repose sur un broyage micrométrique du minerai ($<75 \mu\text{m}$; Wills and Finch, 2016). Avant l'électrification des installations minéralurgiques et métallurgiques, seuls des moyens mécaniques permettaient d'exploiter des gisements argentifères d'une teneur pouvant atteindre alors 750 g/t d'Ag au XIX^e siècle (Tylecote, 2002). Aujourd'hui, nous pouvons noter aussi le développement du recyclage (mine secondaire) à partir des objets manufacturés de la mine primaire, qui représente actuellement 60% de la production de Pb (Wills and Finch, 2016).

1.2 L'activité minière et la production de déchets

Reprenant la définition de Lottermoser (2010), les déchets de la mine regroupent les déchets produits lors des activités minières d'extraction, du traitement du minerai et de la métallurgie. Ces déchets peuvent être solides, liquides ou gazeux.

1.2.1 De la prospection à la découverte d'un gisement

Jusqu'au Moyen-Age, l'exploitation de minerai était généralement le fruit de découverte de filons minéralisés affleurant en surface, et qui se poursuivaient en galeries sous la surface, pour les gisements les plus riches. Ces traces d'exploitation sont parfois encore visibles dans le paysage (Figure 1.1). Au Moyen-Age, on exploite de nouveau des gisements déjà connus ou exploités durant l'Antiquité.



Figure 1.1: Ancienne tranchée d'exploitation de minerai de Pb-Ag en lisière du lac Blanc d'Huez (mine du Lac Blanc, Isère ; © Cliché de Muriel Raveton, LECA), exploitée pendant le XII^e et XIV^e siècles (Peloux et al., 2015).

À partir du XIX^e siècle sont mises en place des techniques de prospection minéralogique. Lors de la ruée vers l'or du continent américain, les orpailleurs étaient à la recherche d'or alluvionnaire issu de l'érosion de gisements affleurants, et remontaient ensuite les rivières pour trouver les filons à exploiter. Toujours en cours aujourd'hui, la prospection géochimique se base sur la présence d'anomalies géochimiques en surface, résultant de l'érosion ou de l'altération chimique de la minéralisation affleurante comme souterraine (Figure 1.2). Plusieurs exemples de littérature documentent l'enrichissement naturel des sols de surface par l'altération de la zone minéralisée (par

ex. Galán et al., 2008; Morin et al., 2001). Désormais, la prospection géochimique consiste à analyser des sédiments de rivière ou des sols dans la région ciblée et à comparer leurs teneurs avec celle du fond (pédo-)géochimique local : des teneurs supérieures à celles du fond (pédo)géochimique local matérialisent une anomalie positive pouvant être liée à la présence d'une minéralisation d'intérêt potentiellement économique. Aujourd'hui, des techniques de prospection géophysiques sont également réalisées, afin de sonder le sous-sol à la recherche d'anomalies magnétiques, de résistivité électrique, de densité, etc. (Jébrak and Marcoux, 2008).

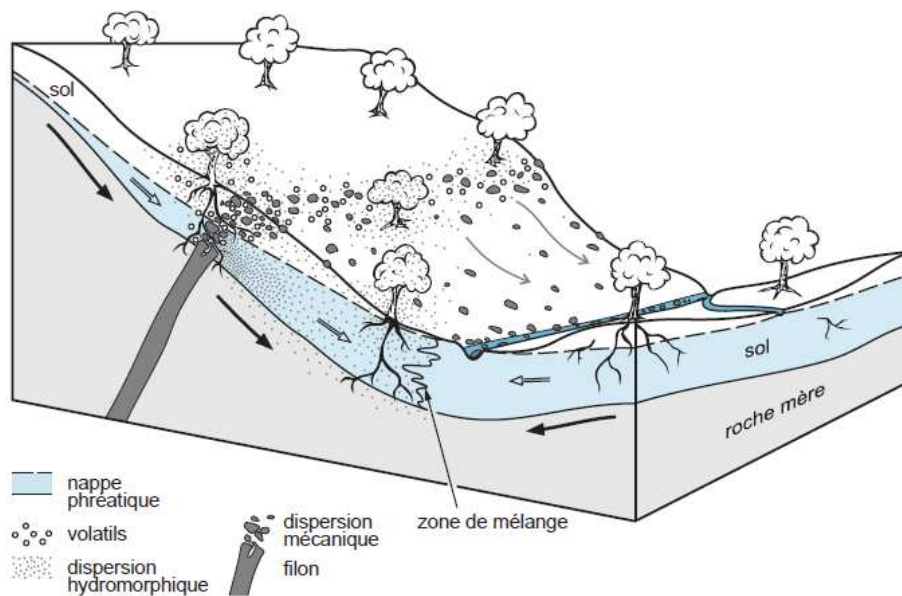


Figure 1.2 : Formation d'une anomalie géochimique en conditions de surface : la zone minéralisée (en gris), est oxydée au voisinage de la surface. Une partie des éléments est lessivée et dispersée par la nappe phréatique, formant une anomalie hydrogéochimique. Le pompage de l'eau par la végétation conduit à des enrichissements biogéochimiques. En surface, les particules sont dispersées dans les sols sous forme particulière et peuvent être transportées dans les vallons où leur accumulation engendrera des anomalies dans les sédiments (d'après Jébrak and Marcoux, 2008).

1.2.2 L'extraction du minerai

L'extraction du minerai consiste à excaver en surface le minerai du sous-sol. Les débuts de l'extraction minière ont eu lieu en surface où une multitude de fosses se juxtaposaient pour extraire le filon affleurant (Garçon, 1995). Ce n'est qu'au début du I^{er} millénaire av. J.C. que les avancées en mécanique et en hydraulique ont permis le développement de galeries de plusieurs centaines de mètres sous la nappe phréatique par pompage des eaux (Craddock, 2009). On peut noter aussi qu'à partir du XVII^e siècle, l'usage de la poudre dans les mines a supplanté les techniques d'abatage par le feu et l'usage d'outils en fer facilitant l'extraction du minerai (Ancel et Py, 2008).

Au Moyen-Age, les techniques d'extraction du minerai sont restées identiques, avec le développement de réseaux de galeries souterraines. Après des centaines d'années voire des millénaires d'exploitation, les ressources minérales métalliques considérées aujourd'hui comme peu profondes (<500 m), s'épuisent progressivement. Il existerait actuellement au moins 112 mines dans le monde dont la profondeur d'exploitation est supérieure à 1000 m (Li and Cai, 2021). Dans le cas des mines à ciel ouvert, l'emprise au sol tend également à s'accélérer depuis plusieurs décennies pour des fosses dépassant le kilomètre de diamètre.

La principale source de déchets produits lors de l'extraction de roches minéralisées est la roche dite « stérile ». Il s'agit de matériaux rocheux contenant peu ou pas de minerai, considérés comme stériles si leur teneur en métaux est inférieure à la teneur de coupure. Dans le cas, d'exploitations en fosse, à ciel ouvert, la couverture du sol et les déblais de roches, issus du décapage de l'emprise de la zone minéralisée en surface, représentent également de larges volumes de déchets.

1.2.3 Le traitement minéralurgique du minerai

Le traitement minéralurgique vise à séparer le minerai de la roche encaissante et de la gangue afin de produire un concentré de minerai (phases métalliques). Le traitement minéralurgique est encore aujourd'hui réalisé sur le site d'extraction afin de réduire le volume de matériel à transporter avant le traitement métallurgique. À l'époque romaine, les mineurs utilisent des outils en fer et en acier (pics, marteaux, coins, etc.), qui sont plus résistants que les outils en bronze, pour concasser les roches minéralisées et le minerai. Craddock (2009) mentionne également l'utilisation de marteaux à bascule, probablement actionnés par l'eau, pour broyer les roches minéralisées à une taille centimétrique. À partir du XVI^e siècle, l'emploi du bocard - moulin à pilons actionné par l'eau - s'est généralisé dans le travail des mines (Figure 1.3) L'alimentation électrique a remplacé l'eau au début du XX^e siècle (Lynch et Rowland, 2005).

À l'issue du broyage, le minerai de taille réduite est ensuite séparé de la gangue par des techniques de lavage, qui utilisent la différence de densité des particules : les particules les moins denses (stériles et gangue) sont entraînées par l'eau pour ne garder que les minéraux les plus denses (minerai). Des vestiges de laveries antiques sont encore visibles dans les célèbres mines grecques argentifères du Laurion (Craddock, 2009). Au début du XX^e siècle, différentes techniques de séparation du minerai voient le jour, telles que la séparation par processus magnétiques et électrostatiques, qui s'ajoutent à la séparation gravitaire (Lottermoser, 2010). Le développement de la flottation, à la fin du XIX^e siècle a permis de récupérer des phases métalliques finement disséminées (Lynch et Rowland,

2005). Ainsi, l'amélioration des performances du traitement minéralurgique a permis d'exploiter au cours des XX^e et XXI^e siècles, des minerais de moins en moins riches, généralement sous forme disséminée. L'exploitation de ces gisements, autrefois délaissés pour raisons technologiques, a provoqué l'augmentation du tonnage de roches minéralisées à traiter, générant de plus en plus de déchets.

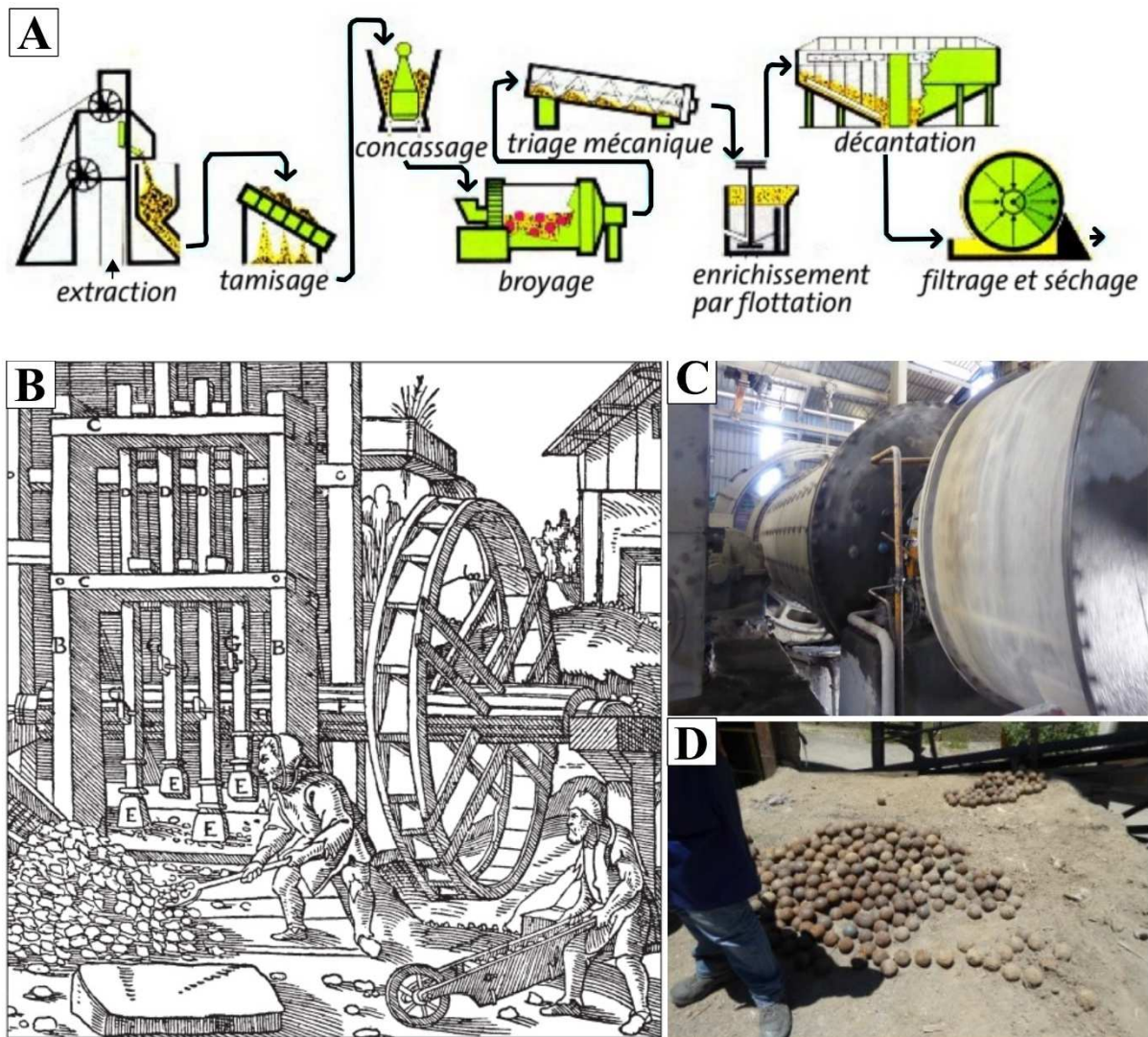


Figure 1.3 : Comparaison des techniques de concassage utilisées au cours du temps pour le traitement minéralurgique du minerai illustré l'étape du broyage. A) Schéma résumant les étapes actuelles du traitement du minerai (Poulard et al., 2017). B) Bocard du XVI^e siècle formé de pilons actionnés par un arbre à cames actionné par une roue hydraulique (Agricola, 1556). C) Concasseur à boulets de la mine de Pb-Zn-Ag de Tighza (Maroc). D) Boulets extrait du concasseur servant à concasser le minerai. © Clichés de Magali Rossi (EDYTEM).

Les déchets minéralurgiques, appelés aussi résidus miniers ou *tailings* en anglais sont essentiellement constitués de particules plus ou moins fines de roches encaissantes et de minéraux de gangue, qui peuvent encore contenir un peu de minerai et d'autres minéraux métalliques sans intérêts

économiques présents dans la minéralisation. Ces déchets sont traditionnellement stockés en surface. Historiquement, du fait de l'utilisation de l'énergie hydraulique pour la séparation, une partie de ces déchets était transportée et évacuée par les cours d'eaux adjacents.

1.2.4 Le traitement métallurgique du minerai

L'ensemble des procédés de fabrication des métaux correspond au traitement métallurgique du minerai. Ces procédés sont divisés en deux grandes catégories, la pyrométallurgie et l'hydrométallurgie. La *pyrométallurgie* correspond à la destruction de la structure cristalline du minerai par une chauffe à haute température (Lottermoser, 2010). Une première phase de chauffe, le *grillage*, permet la transformation des sulfures en oxydes (700 °C pour la galène) : la galène (PbS) est alors transformée en litharge ou massicot (PbO). Lors de la fusion oxydative du minerai (850 °C pour la galène), les éléments métalliques sont réduits en gouttelettes fondues de métal, ou d'un composé intermédiaire, se séparant du bain silicaté qui est moins dense. Dans le cas du plomb, une étape supplémentaire, appelée *cupellation*, permet la séparation de l'argent du plomb. Une étape de raffinage est souvent nécessaire pour enlever les métaux présents en impuretés. L'*hydrométallurgie* utilise des solvants chimiques qui vont casser la structure cristalline des minerais pour libérer le métal d'intérêt sous forme ionique ou de complexes en solution. L'exemple le plus connu est la lixiviation des minerais aurifères à partir d'une solution de cyanure de sodium. Les techniques d'hydrométallurgie s'étant développées tardivement, à la fin du XIX^e siècle (Habashi, 2005), nous nous focaliserons ici sur les techniques de pyrométallurgie qui étaient très largement majoritaires jusqu'à XX^e siècle.

Il est admis que jusqu'à l'Antiquité de simples fosses enfouies de 1 à 2 mètres de profondeur faisaient office de fourneau et permettaient de récupérer le cuivre, le plomb ou l'argent. Le développement au Moyen Age de soufflets à eau a permis une évolution vers des fourneaux plus larges. Au XVIII^e siècle, la méthode anglaise utilisant le four à réverbère remplace la méthode allemande utilisant des demi-hauts fourneaux, qui n'utilisent plus les soufflets (Garçon, 1995; Tylecote, 2002).

Les déchets pyrométallurgiques, appelés *scories*, correspondent aux roches issues de la vitrification des minéraux silicatés fondus. Il est courant de retrouver sur les sites miniers historiques des haldes à scories, puisque le minerai était généralement fondu sur place. Cependant, les méthodes passées étaient bien moins efficaces pour récupérer le métal d'intérêt (Hudson-Edwards, 2016), ce qui a engendré la production de déchets plus enrichis en ETM qu'aujourd'hui. Par ailleurs, le procédé

était optimisé pour récupérer le métal d'intérêt et non les co-produits également contenus dans le minerai. Ces co-éléments se retrouvent donc essentiellement piégés dans les scories. Enfin, les processus de pyroméallurgie émettent dans l'atmosphère des aérosols riches en soufre et en ETM lors de la combustion du minerai.

1.2.5 La fermeture et l'après-mine

Entre la fin du XIX^e et le XX^e siècles, l'activité minière décline en Europe, laissant de nombreuses mines abandonnées (Figure 1.4). Certains propriétaires ayant disparu ou bien fait faillite, la gestion des anciens sites miniers incombe dorénavant à l'Etat, qui est alors le garant des dommages causés par l'activité de l'exploitant. Des mouvements de terrain causés par l'effondrement de galeries souterraines, à la fin des années 1990, marquent le début de la gestion de l'après-mine en France. Les problèmes souterrains engendrés par la présence de galeries non travaillées et de circulation des eaux souterraines s'ajoutent à ceux de surface liés au stockage des déchets miniers et métallurgiques. Etant encore parfois riches en ETM, leur mise en sécurité très limitée conduit à la contamination diffuse en métaux des sols, des sédiments et des eaux sur le long terme (aspects sur lesquels se focalisera cette thèse) et potentiellement des écosystèmes (Leblanc et al., 2000; Camizuli et al., 2018; Kříbek et al., 2019). Enfin, l'impact environnemental attribué à l'émission de fumées métallurgiques a souvent été négligé.

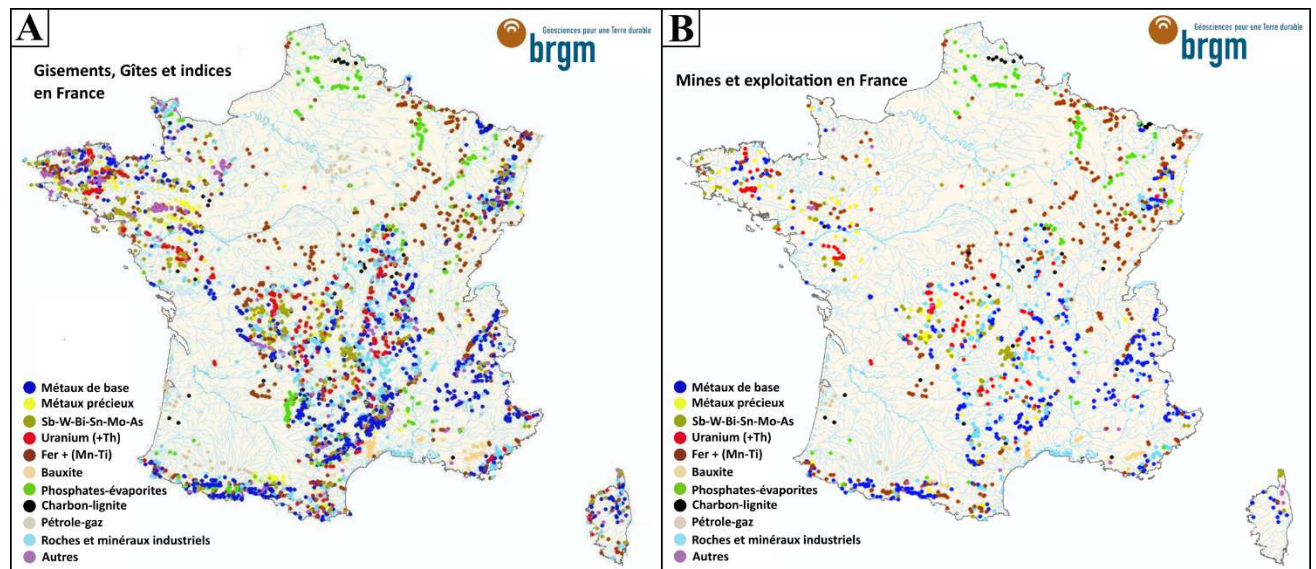


Figure 1.4 : A) Carte des gisements, gîtes et indices en France. B) Carte des anciennes mines et exploitation en France (modifié d'après le BRGM, www.brgm.fr)

Ainsi, cet héritage minier entraîne la modification des écosystèmes terrestres et aquatiques à différentes échelles spatiales et à plus ou moins long terme (Hudson-Edwards et al., 2011). L'évaluation et la gestion de cet héritage minier plusieurs centaines à milliers d'années après l'arrêt des activités minières et métallurgiques représente une problématique globale, car tous les pays ont ou bien ont connu une industrie minière (Hudson-Edwards, 2016).

1.3 Les déchets miniers, sources de contaminations métalliques dans l'environnement

La mine génère de vastes quantités de déchets (Allan, 1997) représentant un des principaux flux de déchets mondiaux (Hudson-Edwards et al., 2011), qui recouvreraient au total une surface d'environ 1 000 000 km² (Lottermoser, 2010). Le volume de déchets des sites historiques représente une faible part de ce total en comparaison de celui produit par les mines actuelles. Toutefois, leur gestion demeure problématique du fait de leur plus forte teneur en ETM (Lottermoser, 2010; Hudson-Edwards, 2016). Nous discuterons ci-dessous du potentiel de contamination des déchets miniers et métallurgiques (haldes à scories et roches stériles) abandonnés depuis plus d'un siècle, ainsi que des fumées produites durant la pyrométallurgie.

1.3.1 Les éléments traces métalliques (ETM)

Le groupe des éléments traces regroupe les éléments concentrés à l'état de traces (< 0.1 % ou < 1000 mg.kg⁻¹) dans les différents compartiments de l'environnement, se différenciant par leur teneur des 12 éléments majeurs, exprimés en pourcents (O, Si, Al, K, Na, Na, Mg, Fe, Ti, H, P, Mn). Dans la suite de la thèse, l'usage du terme ETM inclura aussi bien le groupe des métaux (p.ex., Pb, Cd, Hg, Cr, Co, Cu, Mn, Ni) que celui des métalloïdes (p.ex. As et Sb).

Tous les ETM ne sont pas intrinsèquement toxiques ; certains comme le Cu et le Zn sont des éléments essentiels au bon fonctionnement des plantes (Adriano, 2001). Les ETM sont considérés comme potentiellement toxiques dès lors que leur concentration dépasse le seuil de ce qui est considéré tolérable pour les organismes vivants de chacun des compartiments de la zone critique. On parle alors d'éléments traces potentiellement toxiques (ETPT ; p.ex., Pb, As, Sb). La spéciation des éléments, c'est-à-dire leur forme chimique, joue un rôle crucial dans la toxicité de l'élément et influence aussi sa mobilité et sa biodisponibilité (Semple et al., 2004; Rao et al., 2008). Dans le cadre de cette thèse, nous nous focaliserons sur la dispersion dans l'environnement du plomb, considéré comme l'un des ETM à risque pour la santé humaine parmi les 9 éléments proposées par

l'Académie des Sciences (1998), et de l'antimoine, considéré comme un contaminant émergent (Shotyk et al., 2005; Herath et al., 2017).

1.3.1.1 Le plomb (Pb) dans l'environnement

Le plomb est un élément qui n'est ni essentiel ni bénéfique pour les organismes vivants (Alloway, 2013). La valeur moyenne du Pb dans la croûte continentale est de 17 mg.kg⁻¹ (Rudnick and Gao, 2003). Dans les roches crustales, le plomb est présent essentiellement dans les feldspaths potassiques et les plagioclases, en remplacement du potassium (Heinrichs et al., 1980). Les principaux minéraux porteurs de Pb dans les zones minéralisées sont la galène (PbS) et la cérusite (PbCO₃; Jébrak et Marcoux, 2008). Baize (2000) définit une gamme de concentrations en Pb pour les sols français comprise entre 23 et 49 mg.kg⁻¹ (médiane = 34 mg.kg⁻¹), suggérant un léger enrichissement dans les sols par rapport au sous-sol. Au niveau européen, la valeur médiane des sols en Pb est de 23 ± 57 mg.kg⁻¹ (Salminen et al., 2005). Le Canada propose une valeur guide de 70 mg.kg⁻¹ Pb pour les sols agricoles visant à protéger la qualité des sols. Dans le cas spécifique d'un sous-sol minéralisé, le sol se retrouve également enrichi par le métal sous-jacent (Figure 2) : dans le cadre d'une forte anomalie, il peut atteindre des valeurs comprises entre 100 et 3000 mg.kg⁻¹ (Baize, 2000). C'est pourquoi, il est recommandé de définir le fond pédo-géochimique local avant toute évaluation d'une contamination métallique ; c.-à-d. de définir la concentration en ETM du sol issu des processus géologiques et pédologiques, en dehors de tout apport anthropique (Baize, 1997). Pour les sédiments de rivière, la teneur médiane observée est de 21 mg.kg⁻¹ Pb (± 207) pour une gamme de teneurs plus étendue que celle des sols (Salminen et al., 2005). Des valeurs guides pour les ETM ont été mises en place pour suivre la qualité des sédiments de rivière en France. Sont considérés de bonne qualité, les sédiments ayant des valeurs en Pb inférieures à 100 mg.kg⁻¹ (MacDonald et al., 2000; JORF, 2006). À partir de 170 mg.kg⁻¹ Pb, des effets toxiques sur les organismes aquatiques sont possibles (MacDonald et al., 2000). Pour les eaux, l'OMS définit une limite de potabilité égale à 0.01 mg. L⁻¹ ou 10 µg.L⁻¹ (Ineris, 2020; World Health Organization, 2022). Le transfert de Pb du sol vers les plantes est généralement limité, à l'exception des sols très contaminés (Adriano, 2001). Néanmoins, il peut facilement être assimilé par voie respiratoire ou digestive entraînant des anémies (saturnismes) ou dégénérescence nerveuse.

1.3.1.2 L'antimoine (Sb) dans l'environnement

L'antimoine est un élément qui n'est ni essentiel ni bénéfique pour les organismes vivants (Alloway, 2013) et dont l'intérêt a augmenté ses dernières années car il est lié à la pollution industrielle. La

valeur moyenne de Sb dans la croûte continentale est de 0.4 mg.kg^{-1} (Rudnick and Gao, 2003). La stibnite (Sb_2S_3) est le principal minerais d'antimoine, qui s'oxyde en valentinite (Sb_2O_4 ; Alloway, 2013). Toutefois, les minéraux porteurs de Sb les plus fréquemment observés dans les zones minéralisées sont la tétraédrite-freibergite-tennantite ($(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$, $(\text{Ag,Cu,Fe})_{12}(\text{Sb,As})_4\text{S}_{13}$, $(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$), et la bournonite (PbCuSbS ; Paktunc, 1999). Dans les sols, les teneurs en Sb sont généralement équivalentes à celles observées dans les roches ; les sols européens présentent une valeur médiane de $0.6 \pm 2 \text{ mg.kg}^{-1}$ (Salminen et al., 2005). Le Canada propose une valeur guide de 20 mg.kg^{-1} Sb pour les sols agricoles, ce qui correspond aux valeurs maximums observées en Europe (30 mg.kg^{-1} ; Salminen et al., 2005). Pour les sédiments de rivière, des teneurs médianes équivalentes sont observées ($0.6 \pm 2 \text{ mg.kg}^{-1}$, max. = 34 mg.kg^{-1} , Salminen et al., 2005). Pour les eaux, l'OMS définit une limite de potabilité de $20 \mu\text{g.L}^{-1}$ (World Health Organization, 2022). L'antimoine est considéré comme un élément peu mobile dans les sols alors que les formes solubles dans l'eau sont considérées relativement mobiles (Resongles et al., 2015; Ettler et al., 2010).

1.3.2 Les différents modes de transfert des ETM dans la zone critique

1.3.2.1 Transport particulaire des ETM

Les particules de déchets miniers et métallurgiques, stockées en surface, sont soumises aux agents de transport, tels que les eaux de ruissellement, le vent ou la gravité, qui sont susceptibles de les déplacer vers les compartiments terrestres et aquatiques (Figure 1.2 et Figure 1.5). L'absence de confinement des déchets miniers historiques provoque leur dispersion le long des rivières, et ce processus peut perdurer sur plusieurs centaines d'années (MacKenzie et Pulford, 2002; Camizuli et al., 2021). Les rivières situées à proximité d'anciens sites miniers et métallurgiques concentrent généralement les ETM sous forme particulaire dans la fraction fine des sédiments ($<53 \mu\text{m}$; Pulford et al., 2009). Ainsi, les sols et les sédiments de rivière sont des proxys idéaux pour étudier la dispersion des particules porteuses d'ETM (Hudson-Edwards, 2003; Macklin et al., 2006).

1.3.2.2 Transport en solution des ETM

Une fois stockés en surface, les déchets porteurs de sulfures s'oxydent au contact de l'oxygène de l'air et des eaux de ruissellement. Cette oxydation libère des ions H^+ dans les eaux de ruissellement et les acidifie (Evangelou and Zhang, 1995). Ce phénomène, appelé *drainage minier acide*, déclenche la mise en solution par lixiviation d'ETM potentiellement toxiques vers les écosystèmes (Akcil and Koldas, 2006). La présence de roches carbonatées peut neutraliser l'acidification des eaux (pH

neutre) ; on parle alors de *drainage minier neutre*, qui est aussi associé à la lixiviation des métaux (INAP, 2009). Par leur nature « artificielle », les scories métallurgiques sont aussi réactives que les roches stériles (Ettler and Johan, 2014; Yin et al., 2017). Les eaux de surface emportées vers le réseau hydrographique sont le principal vecteur de transport des ETM issus de la lixiviation des déchets miniers et métallurgiques solides abandonnés en surface. Les eaux de ruissellement des sols transportent et dispersent des ions métalliques susceptibles de précipiter ou d'être adsorbés au cours de leur transfert (Figure 1.5), sous des changements physico-chimiques appropriés, et peuvent migrer vers les eaux de surface et vers les nappes phréatiques en profondeur (Khaska et al., 2018).

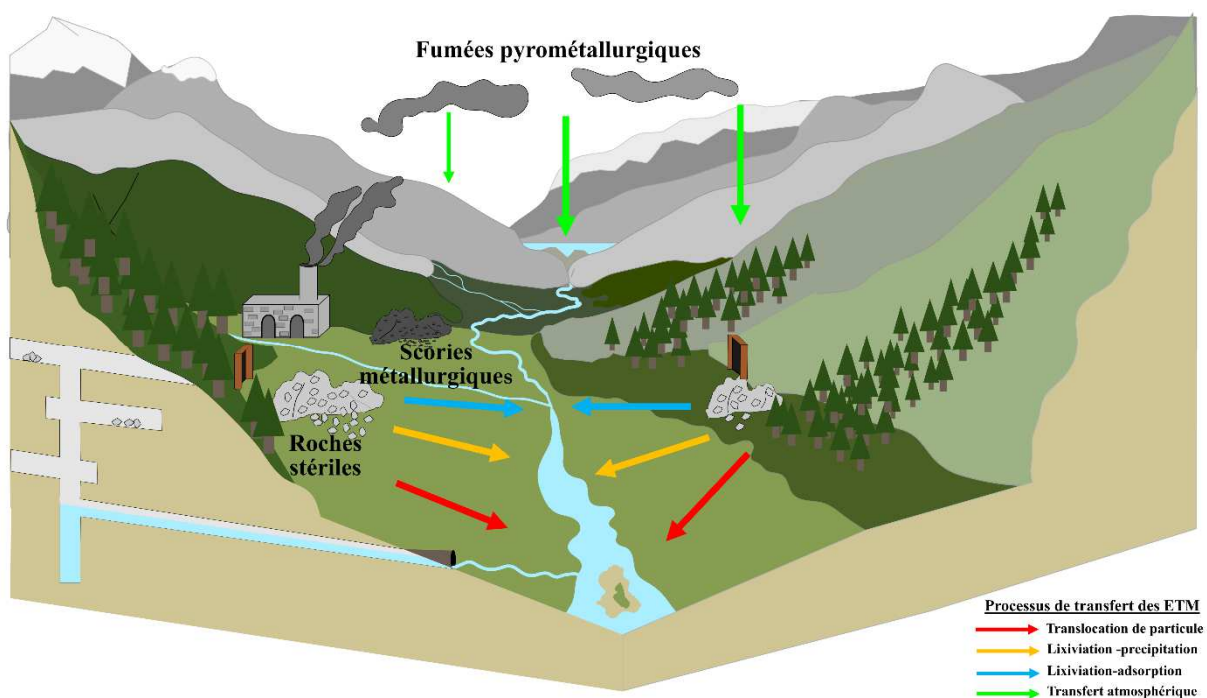


Figure 1.5: Schéma d'un site minier et métallurgique mettant en évidence les sources, les puits et les principaux modes de transferts des ETM dans les différents compartiments de la zone critique.

1.3.2.3 Transport atmosphérique

Dans les environnements arides et/ou désertiques, l'envol de particules fines de déchets miniers est couramment observé, transportant ces poussières sur quelques kilomètres (Csavina et al., 2012; Ettler et al., 2019; Mihaljevič et al., 2019). Lors de la pyrométallurgie, les fumées émises dans l'atmosphère peuvent être transportées sur plusieurs milliers de kilomètres (Hong et al., 1994); la proportion d'ETM diminuant depuis la source d'émission (Cloquet et al., 2006a). Le principal gaz émis lors de la fusion du minerai est le dioxyde de soufre (H_2S) dégagé par l'oxydation des sulfures

et provoquant des pluies acides (Leverington and Schindler, 2018). Ce dégagement s'accompagne de phases micrométriques porteuses de métaux susceptibles d'être transportées sous forme d'aérosols au-delà du site de la fonderie (Figure 1.5, Zdanowicz et al., 2006). Lors de la fusion de minerai plombifère, l'émission de particules très fines ($< 5\mu\text{m}$) de PbO et PbSO_4 a été observée (Sobanska et al., 1999). La mise en place des filtres en sortie des cheminées a réduit significativement la quantité de métaux émis dans l'atmosphère (Shotyk et al., 2016).

1.3.2.4 La remobilisation des ETM dans l'environnement

Outre les transferts d'ETM qui ont lieu pendant les activités minières et métallurgiques et qui sont beaucoup documentés (Mackay et al., 2013), les questions de remobilisation sur le long terme restent moins bien comprises. Des études récentes ont montré la remobilisation de contaminants historiques récents (quelques décennies) dans l'environnement, comme la remobilisation du Pb des essences plombée accentuée par l'urbanisation (Resongles et al., 2021) ou encore de contaminants organiques mis à nu lors des changements d'usage des sols (Sabatier et al., 2014; Mottes et al., 2022). Dans le cas de contaminations métalliques plus anciennes (> 50 ans), notre compréhension reste partielle. Lorsqu'elles existent, ces études se concentrent sur la remobilisation de particules détritiques de déchets lors d'évènement de fortes intensités tels que des crues (Delplace et al., 2022). Cependant la compréhension de la remobilisation des contaminants atmosphériques anciens (> 50 ans) est limitée (Yang et al., 2002b; Bacardit and Camarero, 2010).

Les archives environnementales, comme les carottes de sédiments lacustres ou de tourbe, sont de bons enregistreurs de la contamination ambiante ou historique (Boyle et al., 2015). Les systèmes lacustres enregistrent également les différents processus physico-chimiques à l'échelle du bassin versant, tels que l'augmentation de l'érosion des sols lié à des changements d'usage (Bajard et al., 2018), montrant le potentiel de remobilisation des contaminants sur le long terme (Hansson et al., 2017).

1.3.3 Les contaminations en ETM anthropiques de la zone critique

De nombreuses études portent sur les contaminations métalliques liées aux exploitations minières et à la métallurgie, que cela concerne les mines actuelles ou les mines anciennes. Des teneurs élevées en Pb (jusqu'à 2 wt. %) ont été mesurées dans des sols à proximité d'une fonderie récemment fermée (Křibek et al., 2019); des sédiments de rivières contaminés jusqu'à plusieurs dizaines de km en aval de la mine témoignent de la persistance de Zn, Cu et Pb rémanent (Galán et al., 2003) ; des

eaux enrichies en ETM analysées en sorties d'exhaures contribuent à la contamination (Elbaz-Poulichet et al., 2017) et des sédiments lacustres et tourbes ont enregistré les différentes périodes de contamination par pyrométallurgie en Europe (Shotyk et al., 1998; Brännvall et al., 2001; Martínez Cortizas et al., 2016). Ainsi, dans tous les compartiments de la zone critique², les ETM sont potentiellement transférés vers les organismes vivants terrestres (p ex. chez les vers de terre ou dans les olives, Mariet et al., 2020; Antoniadis et al., 2022) ou aquatiques (Hansson et al., 2019) avec de potentiels effets délétères (Monna et al., 2011; Camizuli et al., 2018). Ainsi c'est l'ensemble de la zone critique qui est contaminée par les ETM issus d'activités minières et métallurgiques passées ou actuelles. Cette fine couche superficielle à l'échelle terrestre, qui est critique pour le vivant (Brantley et al., 2007), peut être perçue comme un *weathering engine* ou *reactor* (Anderson et al., 2007) qui va mettre en mouvement les ETM par différents processus. Pour mesurer l'impact des différents forçages anthropiques exercés sur la zone critique, dont les activités minières et métallurgiques, Brantley et al. (2007) rappellent l'importance d'étudier les processus à différentes échelles spatiales et temporelles.

1.4 Problématiques de la thèse et cadre méthodologique

1.4.1 Problématique

L'impact sociétal et environnemental de l'industrie minière est aujourd'hui beaucoup questionné et remis en question (Forget, 2015; Flexer et al., 2018; Le Berre et Bretesché, 2020). En France notamment, la volonté politique de réouverture de mines se heurte à une très forte contestation qui a abouti à l'abandon de plusieurs projets d'exploration. Cette contestation repose notamment sur une gestion environnementale désastreuse voire inexistante par le passé, qui a été à l'origine de pollutions importantes (Grimaldi et al., 2015; Khaska et al., 2018). L'exploitation potentielle de ressources minérales en France et en Europe sera conditionnée par la prise en compte des impacts sanitaires et environnementaux. Grâce à l'important héritage minier français (Figure 1.4) vieux de 20 à plus de 150 ans, il est possible d'évaluer l'impact environnemental des mines abandonnées sur

² **La Zone Critique** désigne la pellicule la plus externe de la planète Terre, celle qui est le siège d'interactions chimiques entre l'air, l'eau et les roches. C'est un milieu poreux issu de la transformation des minéraux au contact de l'oxygène, du CO₂ et de l'eau à la surface de la Terre. Elle est le siège de la vie et l'habitat de l'espèce humaine. Elle est donc critique au sens physique du terme car c'est une des interfaces de la planète, mais aussi car c'est là que se forme et évolue la ressource en eau et en sol, et que les sociétés humaines cultivent et stockent leurs déchets. Définition de l'Observatoire de la Zone Critique (OZCAR), www.ozcar-ri.org/la-zone-critique.

le long terme (> 100 ans), ce qui apparaît nécessaire pour mieux anticiper et limiter les impacts environnementaux des futures exploitations minières.

En effet, la présence de contaminants métalliques dans l'environnement et leur remobilisation à long terme se pose, même plusieurs siècles après l'arrêt des activités minières et métallurgiques. Outre les retombées atmosphériques liées à la métallurgie, les déchets miniers et métallurgiques sont souvent encore riches en ETM. Ces ETM, qui sont potentiellement toxiques pour les écosystèmes (notamment Pb et Sb) sont susceptibles d'être libérés par l'érosion et l'altération météorique et transférés dans la zone critique, où ils peuvent s'accumuler et être transférés dans les organismes vivants (Hansson et al., 2019; Mariet et al., 2020; Antoniadis et al., 2022). Il est donc crucial d'avoir une meilleure compréhension des modalités de transferts des ETM et de connaître les processus physiques et chimiques entraînant leur remobilisation. Cela permettra (i) d'obtenir l'ordre de grandeur spatial, temporel et « quantitatif » (flux, stock) de leur transfert à long terme ; (ii) d'atténuer leurs effets et leur dispersion actuelle ; et (iii) de mieux anticiper la contamination par les déchets miniers et métallurgiques des futures exploitations.

De très nombreuses études s'attachent à évaluer la contamination par des moyens géochimiques, majoritairement d'un point de vue de la concentration en ETM (p.ex., Ettler, 2016). Bien que cela demeure indispensable, ces méthodes sont limitées pour comprendre la complexité d'une contamination engendrée par des activités minières et métallurgiques. Si la spatialisation de la dispersion des éléments dans l'environnement est une première étape pour comprendre l'étendue de la contamination depuis sa source, elle ne renseigne pas sur les processus dynamiques ayant abouti à cette contamination, ni sur le potentiel de remobilisation des contaminants. Ainsi, malgré de nombreuses études portant sur la caractérisation des contaminations en ETM autour de sites miniers et plus largement sur la caractérisation de l'héritage minier, de nombreuses questions demeurent :

1) Quelle est la part de la contamination naturelle et celle de la contamination anthropique dans la contamination identifiée ? La présence d'une minéralisation induit une anomalie géochimique d'étendue variable. Toutefois, l'excavation de roches minéralisées et leur stockage en surface entraîne une contamination supplémentaire d'origine anthropique, a priori nettement plus importante. L'héritage environnemental de la mine porte donc uniquement sur la contamination anthropique, et non sur la contamination naturelle. **La distinction entre contamination naturelle et anthropique est un point qui est généralement peu discuté dans la littérature, mais qui est important pour la gestion de l'après-mine** : en effet, il n'est pas réaliste de tenter

de décontaminer un site au-delà de sa contamination naturelle. Outre la caractérisation globale de la contamination, déterminer la part de la contamination naturelle revient à caractériser l'état environnemental initial du site.

2) Quelles est la part des différentes sources d'ETM dans la contamination anthropique ?

La contamination anthropique peut avoir plusieurs origines : les déchets d'excavation minière (roches encaissantes plus ou moins minéralisées), les déchets minéralurgiques (souvent évacués par les rivières pour les mines anciennes), les déchets métallurgiques solides (les scories) et les fumées métallurgiques. En fonction des processus de transfert des ETM dominants, la spéciation des ETM et donc leur potentielle remobilisation et biodisponibilité variera. **Une bonne connaissance de la part des différentes sources de contamination permettra une meilleure gestion des déchets de la mine et la mise en place de stratégies adaptées de limitation de la dispersion des ETM.** Or, la distinction entre contamination anthropique issue des roches stériles, des scories ou des fumées métallurgiques reste peu documentée.

3) Quels sont les flux et les stocks de contaminants anthropiques issus des différents modes de transfert des ETM pendant et après les activités minières et métallurgiques ?

La plupart des études portent sur un voire deux compartiments de la zone critique, permettant alors de caractériser un à deux modes de transfert et une seule source de contamination. Peu d'études envisagent la caractérisation de tous les compartiments susceptibles d'être contaminés à différentes échelles spatiales et temporelles. Or, une approche intégrée est nécessaire pour établir des flux et des stocks de contaminants afin de comparer la part des différents processus de transfert mis en jeu. **En particulier, les transferts atmosphériques liés aux émissions métallurgiques restent encore sous quantifiés au-delà de l'attestation d'une contamination.**

4) Quelles sont les relations entre mobilité et biodisponibilité des ETM et la minéralogie des phases porteuses ?

De manière générale, la mobilité et la biodisponibilité des ETM est appréhendée à partir d'essais de lixiviation. Toutefois, ces essais réalisés en laboratoire sont des modèles et permettent de comparer des échantillons entre eux, mais les résultats obtenus sont difficilement transposables au milieu naturel. **L'étude de la spéciation des ETM à partir de la minéralogie des phases porteuses des ETM permet de discuter de leur solubilité et renseigne ainsi sur la mobilité et la biodisponibilité des métaux dans chaque compartiment étudié.** La nature des phases porteuses peut également renseigner sur les processus impliqués dans les transferts des métaux depuis les zones de stockages des déchets vers les compartiments de la

zone critique. Pour cela, l'étude minéralogique des sources de la contamination en amont de celle des compartiments contaminés s'avère nécessaire.

Cette thèse a pour ambition de répondre à l'ensemble de ces questions, à partir de l'**étude de la dispersion à long-terme des ETM dans les différents compartiments de la zone critique**, considérés comme des puits pour les ETM. Elle vise notamment à caractériser et tenter de quantifier (i) les modes de transfert des ETM et leur contribution à la contamination anthropique à différentes échelles spatiales, (ii) leur possible remobilisation et transferts entre compartiments, et (iii) la contribution de chaque type de déchets miniers et/ou métallurgiques à la contamination anthropique. Dans ce but, une **approche multi-compartiments** (sols, sédiments de rivière, sédiment lacustres et eaux) et **multi-échelles spatiales** (du site au bassin versant) a été conduite (Figure 1.5) autour de la mine de Pb-Ag de Peisey-Nancroix (Savoie, XVII^e-XIX^e siècle).

1.4.2 Approche et mise en œuvre

Pour appréhender les trajectoires spatiales et temporelles des ETM générés par des activités minières et métallurgiques, une **approche source-puits** est mise en œuvre intégrant l'ensemble des compartiments de la zone critique (Figure 1.6). Les sources regroupent ici les *roches stériles* (déchets d'extraction), ainsi que les *scories* et les *fumées pyrométallurgiques* (déchets métallurgiques). Les *sols* constituent le compartiment le plus proximal aux sources de contaminations, où les ETM sont susceptibles d'être dispersés par transferts particulaire, en solution et aérien. Ainsi, l'étude des sols de surface et des horizons profonds peut permettre de confronter les trois modes de dispersion des métaux. Les *eaux de rivières* proches du site minier sont susceptibles de contenir des ETM sous forme ionique et les *sédiments de rivière* vont accumuler des particules issues du transport détritique des déchets solides, notamment du minerais. À l'inverse, les *sédiments lacustres* d'un lac situé en amont du site minier représentent l'objet idéal pour tracer uniquement le transfert atmosphérique des ETM sous forme d'aérosols émis par traitement pyrométallurgique du minerais. Une telle **approche multi-compartiments**, induit donc également une dimension **multi-échelles spatiales et temporelles**. L'étude multi-scalaire permettra d'appréhender les différents modes de transferts et l'impact des différentes sources de contamination. La dimension temporelle sera appréhendée à travers la caractérisation des remobilisations et la quantification des flux d'ETM pendant et après les activités minières (notamment pour les émissions atmosphériques).

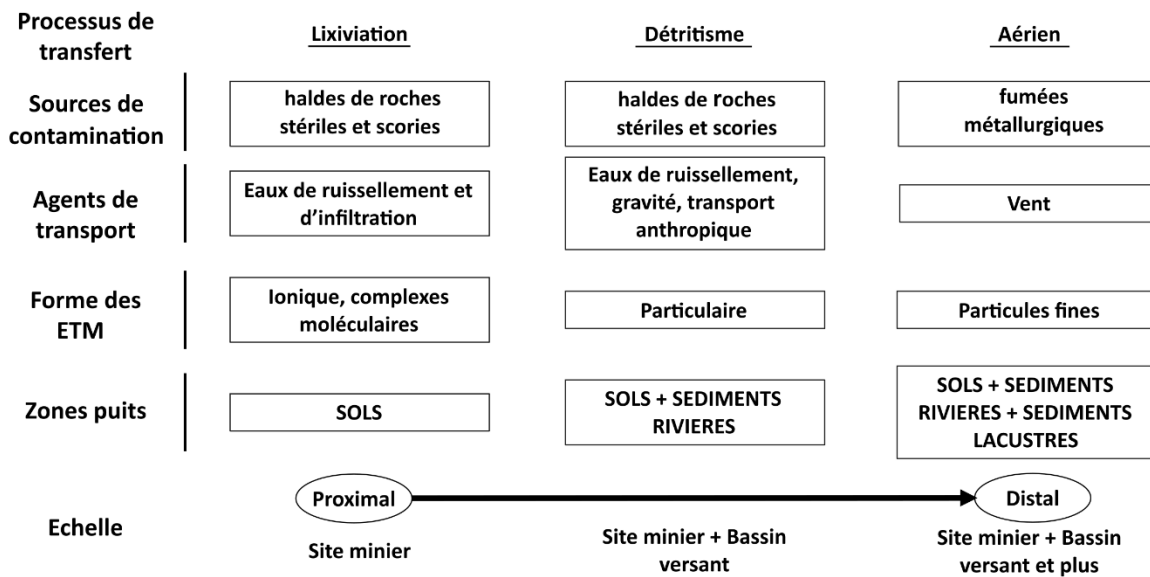


Figure 1.6 : Schéma synthétique de l'approche multi-compartiment et multi-scalaire mise en œuvre dans cette thèse, résumant les principaux modes de transferts des ETM depuis la source de contamination vers les zones puits que sont les différents compartiments de la zone critique.

Pour caractériser les contaminations en ETM, tenter de quantifier la part de contamination naturelle vs anthropique, quantifier les éventuelles remobilisations et dans la mesure du possible la part de chaque source dans la contamination anthropique, des observations et analyses minéralogiques, sédimentologiques, géochimiques et isotopiques (Pb, Sb) ont été conduites sur chaque source de contaminant et chaque puits. Ces données permettront également d'identifier et de pondérer la contribution de chacun des processus de transfert des ETM à l'échelle du bassin versant.

1.5 Organisation du manuscrit

Ce manuscrit se divise en 7 chapitres.

Les deux premiers chapitres de la thèse présentent le contexte général de la thèse. Le **chapitre 1** présente le cycle minier, les déchets miniers et métallurgiques générés qui sont sources de contaminants métalliques, ainsi que les modes de dispersion de ces contaminants. Il détaille la problématique et l'approche méthodologique mise en œuvre dans le cadre de cette thèse. Le **chapitre 2** présente le site minier de Pb-Ag de Peisey-Nancroix (Savoie, XVII^e-XIX^e siècle). Il présente également le contexte géographique, géologique et historique du site minier, et expose comment ce site apparaît comme idéal pour étudier l'héritage environnemental à long terme des exploitations minières.

Les trois chapitres suivants compilent les résultats de la thèse autour d'articles publiés (chapitre 3), soumis (chapitre 4) ou sur le point d'être soumis (chapitre 5), rédigés en anglais. Le **chapitre 3** présente les travaux réalisés sur la dispersion de la contamination en ETM à l'échelle du site minier, à partir de l'étude de sols de surface situés à proximité immédiate et en aval de la zone de stockage des déchets. Le **chapitre 4** vise à caractériser la contamination rémanente liée à l'émission de fumées lors du traitement du minerai par pyrométallurgie et enregistrée dans le lac de La Plagne (situé 7 km en amont du site minier, sous le vent) et dans les sols de son bassin versant. Il discutera également des processus de remobilisation des ETM depuis leur dépôt il y a plus de 200 ans. Enfin le **chapitre 5** utilise le couplage de deux systèmes isotopiques (Pb, Sb) pour déterminer (i) la part de la contamination naturelle vs la contamination anthropique, et (ii) la contribution de chaque source de déchets métallurgiques dans la contamination anthropique, et ce pour chaque compartiment de la zone critique étudié.

Le **chapitre 6** vise à estimer l'inventaire de Pb anthropique des sols de surface du site minier et du bassin versant du Lac de La Plagne, accumulé à l'échelle du bassin versant à partir des fumées atmosphériques (contamination pendant et après la période d'exploitation) et de la remobilisation des déchets miniers (contamination post-mine).

Enfin, le **chapitre 7** fait la synthèse de ce travail de thèse avant d'en présenter les perspectives.

Ce travail de thèse est le fruit d'un travail collaboratif dont les principales collaborations sont présentées en ANNEXE A.

Chapitre 2 |

La mine de Pb-Ag de Peisey-Nancroix (Savoie)

Chapitre 2 | La mine de Pb-Ag de Peisey-Nancroix (Savoie)

Aujourd'hui, l'extraction de métaux est limitée en France métropolitaine; seules deux mines de bauxite (Hérault) et une mine d'étain-tantale-niobium (Allier) sont exploitées sur le territoire. Toutefois, la France fut un pays minier important pendant plus de 2500 ans. Entre le XVII^e et XIX^e siècles, les efforts industriels ont porté sur le plomb et l'argent, car la France n'était pas dotée de ressources en cuivre suffisantes (Garçon, 1995). La relance minière du début du XVIII^e siècle voit apparaître une répartition selon un axe est-ouest des exploitations minières, de la Bretagne jusqu'au Dauphiné, en passant par les Cévennes. Bien qu'alors non rattachée à la France, la Savoie³ voit également un regain de ses activités minières durant cette période.

Dans les six départements des Alpes françaises (Alpes-Maritimes, Alpes de Haute-Provence, Hautes-Alpes, Isère, Savoie et Haute-Savoie), le BRGM a recensé 116 mines et 248 indices et gîtes métallifères, dont 59 mines et 97 gîtes et indices de Pb-Zn-Ag. Les travaux archéologiques indiquent une exploitation du cuivre dès le Néolithique et considèrent que l'argent ait pu être exploité dès la période romaine à la mine de La Plagne (Savoie; Meloux, 1975). La plupart de ces gîtes ont été exploités de manière industrielle à partir du XVIII^e siècle, avant de fermer progressivement à partir de la fin du XIX^e siècle du fait de l'épuisement des ressources et de la baisse de rentabilité face à la découverte de nouveaux types de gisements de classe mondiale plus faciles à exploiter. La mine de Pb-Ag de Mâcot-La Plagne (Savoie) fut la dernière à fermer en 1973, au profit du développement d'une station de sports d'hiver (Rossi et al., 2017).

Ainsi, des centaines de sites miniers abandonnés, depuis 50 ans voire plus de 150 ans, sont dispersés sur l'ensemble du territoire alpin, dont les résidus miniers (minerais abandonnés et déchets métallurgiques) constituent de possibles sources de contaminations métalliques actuelles. Ce travail de thèse se focalise sur l'un des principaux sites miniers des Alpes françaises, la mine de Pb-Ag de Peisey-Nancroix (Savoie; Meloux, 1975).

³ La Savoie a été rattachée une première fois à la France de 1792 à 1815, où elle est rendue à l'état Sarde. Les Etats de Savoie ont ensuite été rattachés à la France le 24 mars 1860 (Traité de Turin).

2.1 Contexte géographique

L'ancienne mine de Peisey-Nancroix est située dans la vallée du Ponturin, dans les Alpes du Nord françaises, à 1550 mètres d'altitude (Figure 2.1A). Localisé à 3 km en amont du village de Peisey-Nancroix, le site minier et métallurgique est facilement accessible par la route départementale qui mène au fond de la vallée (voie sans issue). Le climat est de type montagnard avec une température annuelle de 1.4°C et des précipitations annuelles de 1380 mm. La neige recouvre le site du mois de novembre au mois d'avril. Le site minier est situé en bordure d'une forêt de mélèzes, recouvrant les déchets miniers et les sols environnants d'un épais tapis d'aiguilles. Le site se situe à l'interface entre un écosystème forestier, caractérisé par une densité importante de mélèzes et un système prairial utilisé pour alimenter en foin des exploitations agricoles environnantes. Il est longé au nord-ouest par le ruisseau de l'Arc qui se jette dans le Ponturin, qui lui-même longe le site au nord (Figure 2.1B).

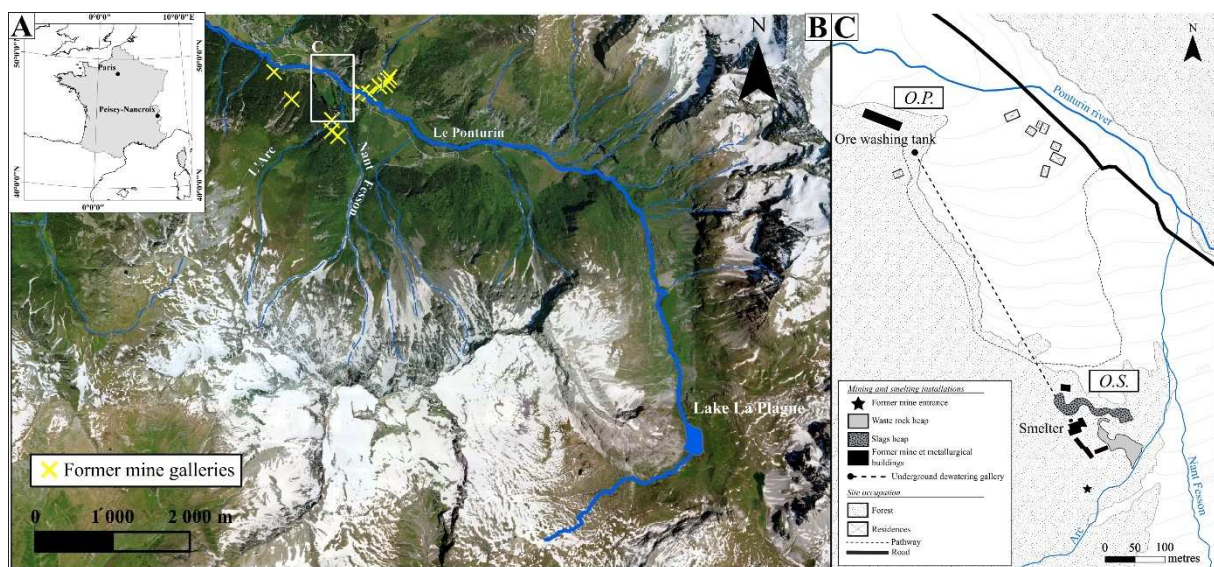


Figure 2.1 : Cartes de localisation de la mine de Pb-Ag de Peisey-Nancroix (Savoie, France). A) Localisation du village de Peisey-Nancroix dans les Alpes françaises. B) Vue photographique partielle du bassin versant de la vallée du Ponturin avec en tête de bassin le lac de la Plagne, et 7 km en contre-bas l'emprise du site minier et métallurgique de la mine de Pb-Ag de Peisey-Nancroix (rectangle blanc). C) Organisation de l'ancien site minier et des infrastructures encore présentes aujourd'hui, réparties entre le site de traitement du minerai (*Ore processing site* - O.P.) au nord et le site de fusion du minerai (*Ore smelting site* - O.S.) au sud-est, où se trouvent les déchets miniers (waste rock heap) et métallurgiques (slag heap).

Les vestiges de l'exploitation de la mine de Peisey-Nancroix sont toujours visibles (Figure 2.2). Les sentiers autrefois utilisés pour l'acheminement du minerai sont toujours utilisés comme chemin de randonnée et sentier de découverte de l'histoire et des techniques de l'exploitation minière



Figure 2.2 : Planche photographique détaillant l'environnement du site minier et métallurgique de Peisey-Nancroix. A) Vue distante sur les anciennes bâtiments de la mine et la zone prairial en contrebas B) Anciennes ruines de la fonderie C) Halde de roches stériles recouvertes par un épais couvert d'épine de résineux. D) Halde de scorie. E) Echantillon de roche stérile toujours richement minéralisé. G) Halde de roche stérile secondaire en rive droite du Ponturin. H) Ancienne galerie d'exploration dont l'entrée est bétonnée avec écoulement d'eau ©. Echantillons de scorie prélevé sur la halde de scorie © Magali Rossi. © Estelle Camizuli © Gaël Monvoisin.

(extraction) et des traitements du minerai (minéralurgie et pyrométallurgie). Les galeries souterraines sont aujourd’hui effondrées ou murées et non accessibles (Figure 2.3). Les vestiges de la fonderie perdurent et témoignent de la présence de plusieurs types de hauts-fourneaux permettant la fusion du minerai. Les tas de déchets d’extraction et de déchets métallurgiques sont reconnaissables dans le paysage et forment deux barrières naturelles entre le flanc de la montagne et la prairie située en contre-bas. Le tas de déchets d’extraction se situe à proximité immédiate du ruisseau de l’Arc. Le tas de scories se situe juste en aval des déchets d’extraction (Figure 2.1C).

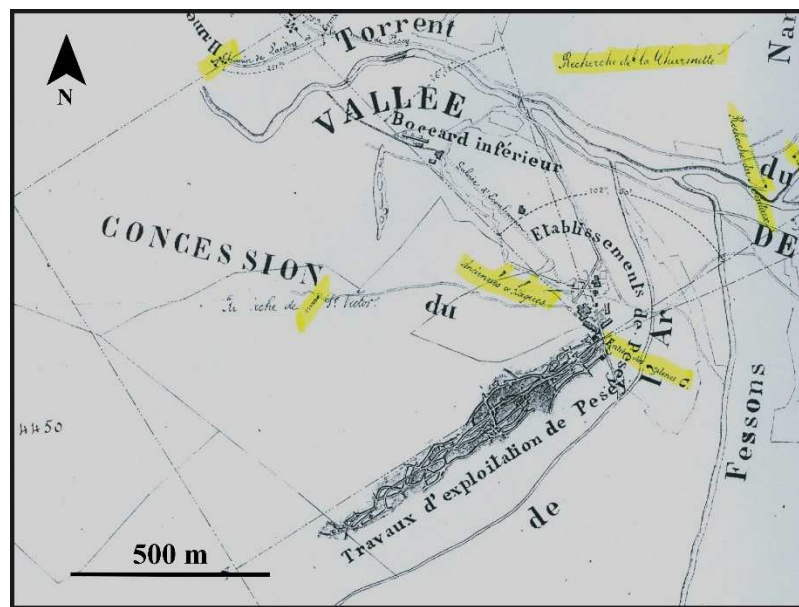


Figure 2.3: Plan général de la mine royale de Peisey en 1864 (Comm. Pers. R. Durand)

2.2 Contexte géologique

La mine de Pb-Ag de Peisey-Nancroix se situe dans les Alpes occidentales internes, le long du Front Briançonnais interne (FIB), qui permet le chevauchement du domaine Briançonnais interne sur le domaine Briançonnais externe (Figure 2.4A). Le socle du Briançonnais externe est recouvert par une couverture sédimentaire permo-triasique représentée par l’empilement de schistes, quartzites, calcaires et dolomies (Figure 2.4B). Il présente un métamorphisme alpin de faible degré, passant du faciès des schistes verts inférieurs au faciès des schistes verts supérieurs (Bertauts et al., 2022). Le FIB se matérialise sur le terrain par la présence d’évaporites du Trias, principalement du gypse et des cargneules. Les cargneules sont des dolomies triasiques qui ont été bréchifiées et partiellement dissoutes au cours de l’orogénèse alpine par des fluides riches en sulfates dérivés du gypse. Le gisement de Pb-Ag de Peisey-Nancroix est encaissé dans la couverture sédimentaire du Briançonnais externe, et en particulier dans des quartzites du Trias, des schistes séricitiques et des

quartzites du Permien situés au mur du FIB (Figure 2.4B). En surface les installations de traitement du minerai et les installations métallurgiques ont été construites en bordure d'un cône de déjection torrentielle qui contient des roches du socle Varisque et des cargneules. Un éboulis de cargneules est intercalé dans ce cône, du côté ouest du site minier (Figure 2.4C).

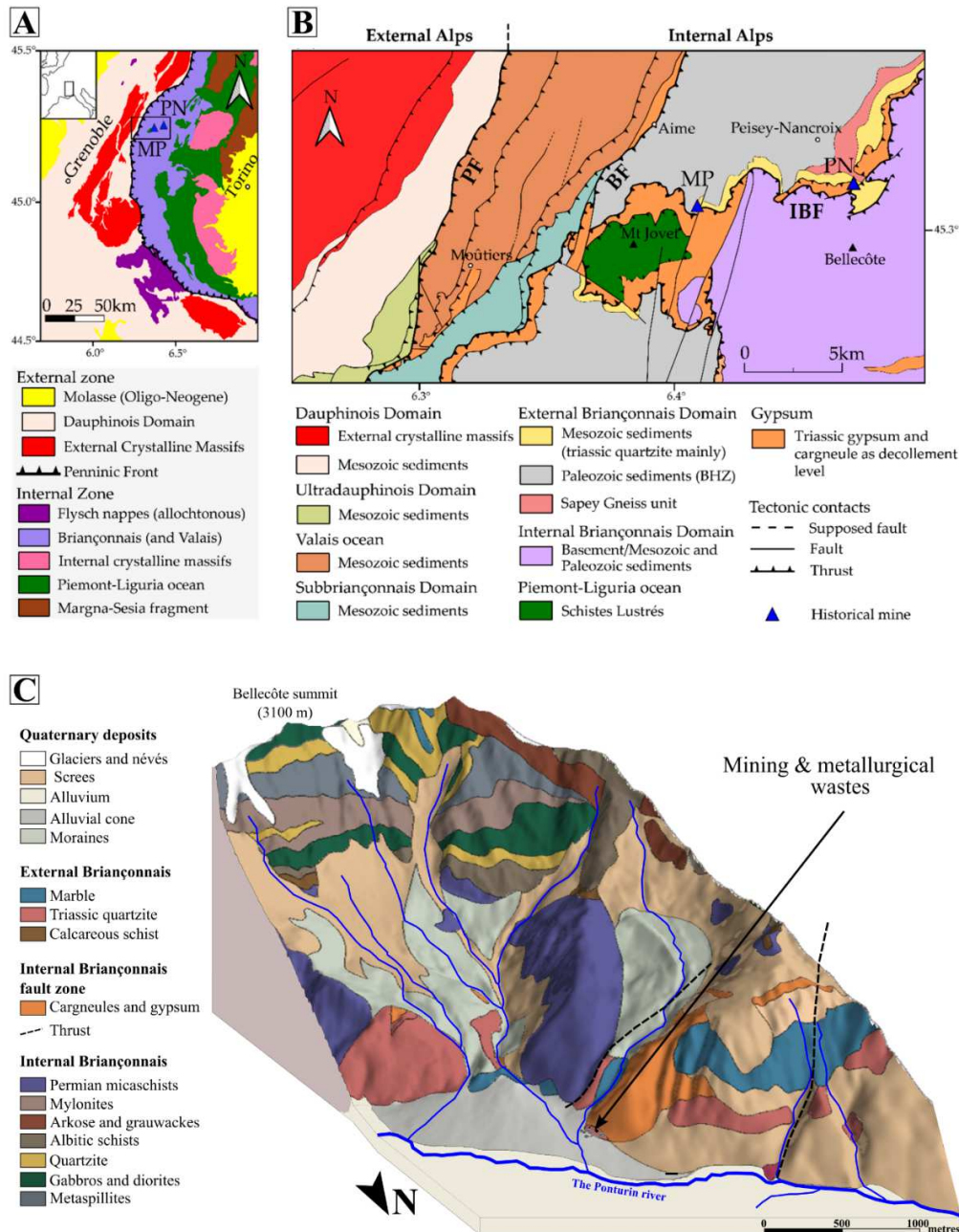


Figure 2.4 : A) Schéma structural des Alpes occidentales avec un carré représentant la localisation de la carte B (d'après Bertauts et al., 2022). B) Carte géologique de la zone Briançonnaise située entre les massifs de la Lauzière et de la Vanoise modifiée d'après la carte géologique de Moutiers (1 :50 000) : MP : Macôt-la Plagne ; PN : Peisey-Nancroix ; PF : Front Pennique ; BF : Front Briançonnais ; IBF : Front du Briançonnais Interne. (d'après Bertauts et al., 2022). C) Carte géologique de la mine de Pb-Ag de Peisey-Nancroix et de ses environs (Guillevic et al., 2023).

Une étude menée par Bertauts et al. (2022) détaille les conditions de P-T-t de mise en place de la minéralisation ainsi que sa paragenèse. La minéralisation s’est formée au cours de l’orogénèse alpine, il y a environ 35 Ma lors du chevauchement du Briançonnais interne sur le Briançonnais externe (Figure 2.4B). Le minerai se caractérise par la présence de galène (PbS) massive et disséminée, considérée comme argentifère, associée à de la tétraédrite ((Cu,Fe)₁₂Sb₄S₁₃) et de la pyrite (FeS), dans une gangue riche en quartz ou en barytine.

La galène (PbS) présente de faibles teneurs en Ag (<540 ppm) et en Sb (<700 ppm). La tétraédrite est présente en intercroissance ou en (micro)inclusions dans la galène. Le contenu en Sb, As et Ag de la tétraédrite montre une solution solide avec la tennantite ((Cu,Fe)₁₂Sb₄S₁₃) et la freibergite ((Ag,Cu,Fe)₁₂(Sb,As)₄S₁₃). La tétraédrite - riche en arsenic – contient jusqu’à 6 wt. % Ag (Bertauts et al., 2022). Des quantités variables de chalcoppyrite (CuFeS), d’arsénopyrite (FeAsS), de sphalérite (ZnS) et de bournonite (PbCuSbS) sont également observées dans la paragenèse principale.

2.3 Contexte historique

Le gisement de Pb-Ag de Peisey-Nancroix a été exploité de manière (pré)industrielle entre 1734 et 1865 (Figure 2.5), bien qu’elle fût exploitée antérieurement de manière artisanale. En effet, des archives rapportent des conflits entre paysans mineurs dès 1644 (Barbier, 1875). C’est pourtant en 1734 que commence l’exploitation préindustrielle du gisement par une succession de compagnies minières.

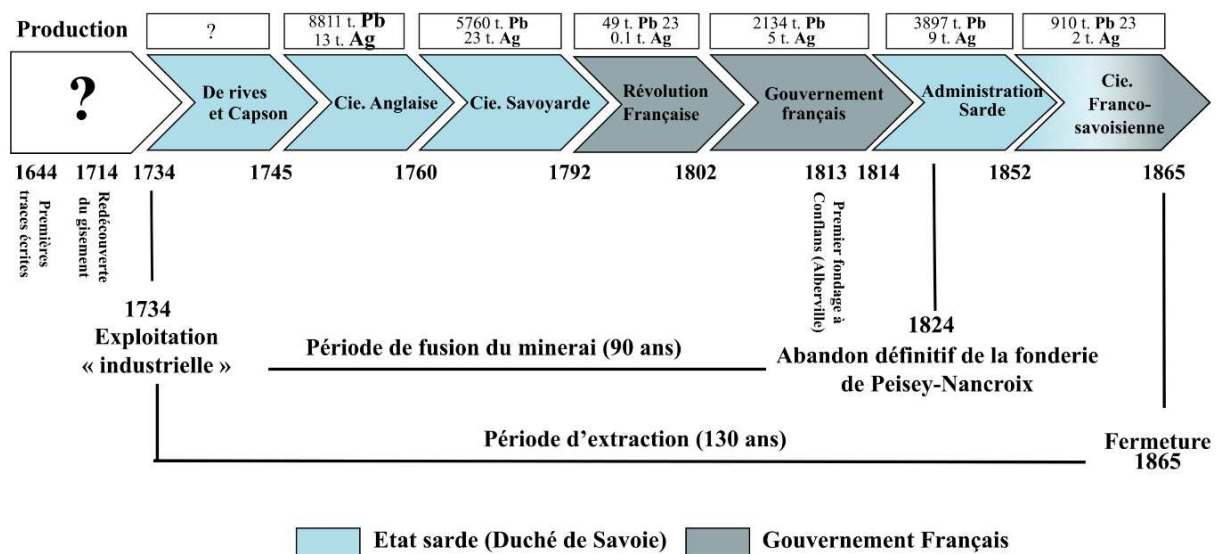


Figure 2.5 : Frise chronologique de l’exploitation de la mine de Peisey-Nancroix entre le XVII^e et le XIX^e siècle, montrant les différents exploitants successifs ainsi que les tonnages extraits.

Cette chronologie reflète bien la chronologie nationale de grande reprise entre 1730 et 1740 décrite par Garçon (1995). La mine de Peisey-Nancroix fait partie de la cinquantaine de mines dite polymétalliques qui étaient en activité sur l'actuel territoire français. Au XVIII^e siècle, la mine de Peisey-Nancroix fait tout de même figure d'exception car peu de mines sont exploitées au-delà de la dizaine d'année par manque de ressource (Garçon, 1995). Le gisement a produit 21 500t Pb et 52 t Ag sur une période d'au moins 130 ans (Figure 2.5; Meloux, 1975). Garçon et al. (1995) rapporte une mise en place de l'exploitation laborieuse, lorsqu'en 1740 deux personnes seulement y travaillent. La première compagnie industrielle d'origine anglaise lance réellement l'exploitation en 1734. La fusion du minerai par la méthode allemande (demi- haut fourneaux) débute et se poursuit jusqu'en 1760, produisant près de 9000 tonnes d'équivalent de Pb et 13 t. d'argent. C'est alors la période la plus productrice à la mine de Peisey-Nancroix. Entre 1760 et 1792, la production reste importante malgré un déclin à partir de 1775, du fait de l'épuisement des réserves (Barbier, 1875). Entre temps, la méthode anglaise remplace la méthode allemande en utilisant le four à réverbère pour faire fondre le minerai (Figure 2.2). Pendant ce premier demi-siècle d'exploitation, des témoignages attestent de la toxicité liée à la présence de la mine et en particulier de la fonderie :

« Elles [les fabriques] forment un brouillard plus épais qui n'altère pas moins la santé que les fruits de la terre »

(Archives du Département de la Savoie - ADS C7, griefs formulés par la commune de Peisey contre la compagnie qui exploita les mines de plomb argentifère 20 juillet 1764).

Parmi les employés de la mine, des fondeurs et des affineurs tombent malades, de même que le directeur en 1763 qui doit se rendre à Genève pour se faire soigner (Clary et al., 1995). Le rejet d'acide sulfureux dans l'atmosphère reste probablement la source de pollution principale et a fait craindre à ce voyageur de respirer :

« l'air infecté par les vapeurs d'arsenic qu'exhalent les fonderies »

(ADS - E. fonds J. Cochon).

La Révolution française stoppe les activités de 1792 et 1802. En 1802, la mine devient propriété nationale de France. L'arrivée de l'ingénieur Schreiber améliore grandement les techniques d'extraction et de fusion du minerai. En raison du manque de bois dans la vallée, la fonderie est progressivement déplacée à Conflans, à proximité d'Albertville, à 60 km en aval en suivant la vallée de l'Isère (30 km à vol d'oiseau) ; la fonderie cessera d'être utilisée en 1824. Le minerai a donc été fondu sur le site minier pendant environ 90 ans. Néanmoins la mine continuera d'extraire du minerai jusqu'en 1865 pour une production inférieure à 1000 t de plomb.

2.4 La mine de Peisey-Nancroix, le site idéal pour une étude multi-compartiments à différentes échelles

Par sa localisation dans un vallée d'altitude reculée dans les Alpes, le site minier de Pb-Ag de Peisey-Nancroix constitue un site atelier unique pour étudier l'héritage environnemental sur le long terme d'une exploitation minière dans un milieu sensible (milieu montagnard).

- i. Toutes les étapes du cycle minier, de l'exploitation au traitement métallurgique, se trouvent sur une zone limitée géographiquement ($< 1 \text{ km}^2$), ce qui permet d'étudier les différents modes de dispersion des ETM.
- ii. Le site est abandonné depuis plus de 150 ans (1865).
- iii. Le site est demeuré en l'état depuis l'arrêt de l'exploitation en 1865. Depuis 150 ans, l'anthropisation y est très limitée : pastoralisme et fauche des prairies situées en aval du site en été, parc accrobranche sur le site de traitement du minerai, et ski de fond en hiver.

Ainsi, le site a été intégralement préservé depuis plus de 150 ans : on trouve encore des hauts-fourneaux et les stocks de déchets miniers (> 150 ans) et métallurgiques (> 200 ans) laissés à l'abandon et non remaniés (Figure 2.2). Par ailleurs, bien que les galeries ne soient plus accessibles, une halde contenant de la minéralisation est présente à l'entrée d'une galerie en rive droite du Ponturin, permettant ainsi d'étudier la minéralisation (Figure 2.2G & H). Trois sorties d'exhaures sont accessibles (2 galeries en rive droite du Ponturin et 1 galerie sortant au niveau du site de lavage du minerai ; O.P sur la Figure 2.1B) qui permettront le prélèvement de sédiments et d'eaux directement issus de la mine.

Deux rivières longent le site minier (l'Arc et le Ponturin Figure 2.1A) ce qui permettra d'étudier le transfert particulière des déchets situés à proximité, alors que la présence du lac de La Plagne, situé en amont et sous le vent permettra d'étudier les seules retombées atmosphériques issues de la pyrométallurgie. Enfin, bien que situé à 1550 m d'altitude, le site est accessible toute l'année car il est situé au départ des pistes de ski de fond (la route est fermée à partir du site minier).

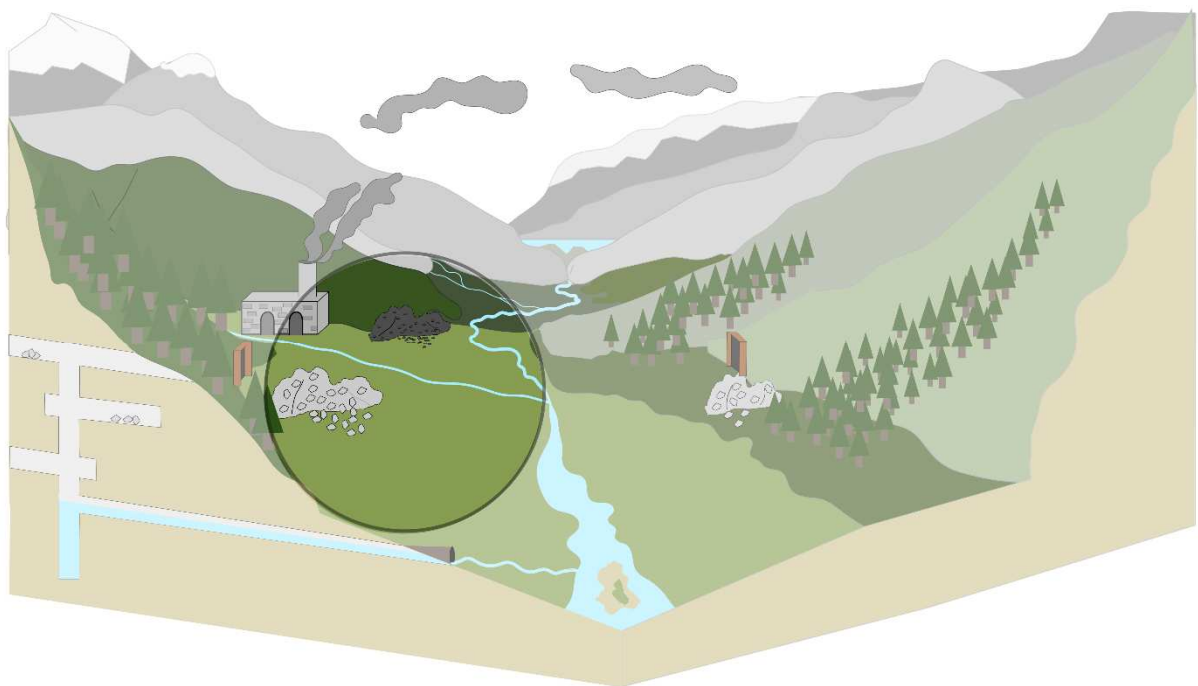
Chapitre 3 |

**Modes de dispersion du Pb dans
les sols miniers**

[Article 1]

Chapitre 3 | Modes de dispersion du Pb dans les sols miniers

Ce chapitre se concentre sur l'étude des sols de surface (0-20 cm) en aval de la zone de stockage des déchets miniers et métallurgiques. Les travaux présentés visent à caractériser les différents modes de dispersion des déchets depuis la zone de stockage vers les sols (transport particulaire et lixiviation uniquement, car il n'est pas possible d'évaluer ici les transferts atmosphériques) et à évaluer la mobilité des phases porteuses en ETM des sols à court terme et sur le long-terme. Les matériels supplémentaires de ce chapitre sont disponibles en fin de chapitre et sont signalés par un S.



ARTICLE 1 | published in APPLIED GEOCHEMISTRY

Vol. 150, March 2023, 105556, doi.org/10.1016/j.apgeochem.2022.105556.

Pb dispersion pathways in mountain soils contaminated by ancient mining and smelting activities.

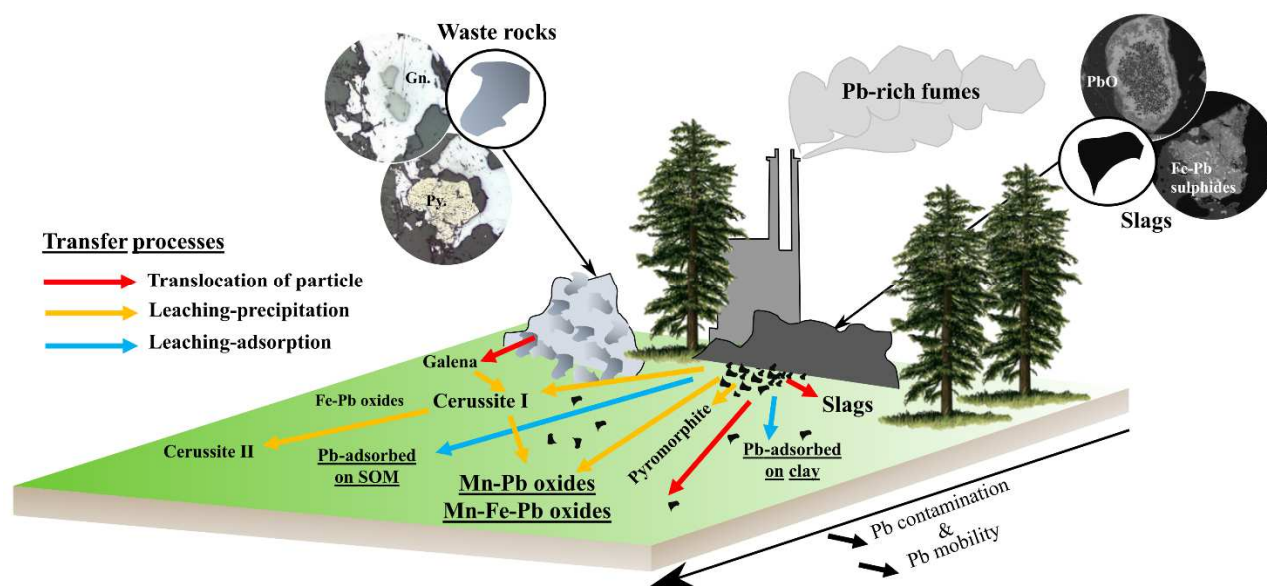
Floriane Guillevic¹, Magali Rossi¹, Anne-Lise Develle¹, Lorenzo Spadini², Jean M.F. Martins²
Fabien Arnaud¹, Jérôme Poulenard¹

¹Université Savoie Mont-Blanc, CNRS, EDYTEM, F-73000, Chambéry, France

²Université Grenoble Alpes, CNRS, G-INP, IRD, IGE, F-38000 Grenoble, France

Keywords: Mining and smelting soils, Pb-bearing phases, Pb-bearing Mn (hydr-)oxides, Pb mobilisation.

Graphical Abstract



Abstract

Over the last millennia, mining and smelting activities have produced large amounts of mine and metallurgical wastes that remain enriched in potentially toxic trace elements (PTE). A spatial distribution of Pb content was coupled to mineralogical observations and single extraction tests to characterise the Pb contamination legacy and Pb dispersion trajectories in an ancient mining and smelting site that has been abandoned for approximately 200 years. In the Peisey-Nancroix Pb-Ag mine (Savoy, France), extreme anthropogenic Pb contamination is located close to the slag heaps and along ore and slag transport paths. The contamination gradient is restricted to a few hundred metres downhill, down to background Pb values. The Pb-bearing phases change along the contamination gradient. The most contaminated soils contain significant amounts of galena and slags that are more or less weathered into pyromorphite and cerussite. Pb-bearing Mn (hydr-)oxides are the most stable and ubiquitous forms of Pb, which proportions increase downgradient. Despite the presence of some stable Pb-bearing phases (pyromorphite, Pb-bearing Mn (hydr-)oxides), extraction tests indicate that a small proportion of Pb may still be mobile over time.

3.1 Introduction

Since the beginning of metallurgy, the exploitation of geological resources has been one of the most significant human activities releasing metals into the environment. Over the last millennia, mining and smelting activities have produced large amounts of mine wastes (waste dumps and tailings) and metallurgical wastes (slags and fumes) that remain enriched in potentially toxic trace elements (PTE; e.g., Pb, Sb, As, Cd, Cu and Zn). These wastes are sources of contamination, from which PTE are dispersed into the environment through different mechanisms. Ore smelting activities produce atmospheric particles carrying PTE over several tens of kilometres (Zdanowicz et al., 2006; Navel et al., 2015) to thousands of kilometres (Hong et al., 1994; Doucet and Carignan, 2001; Cloquet et al., 2006b, 2015). Old mining and metallurgical wastes are usually abandoned on soils without any protection and therefore are subjected to weathering. Particles of wastes can be transported by wind, gravity, runoff water or even by anthropogenic transport. Weathering of mining and metallurgical wastes may induce the transfer of PTE within runoff water and soils as free ions or complexes. Overall, these remobilisation processes lead to the release of PTE to the environment for centuries or even millennia after mining and smelting have ceased (e.g., Galuszka et al., 2015; Hansson et al., 2017; Camizuli et al., 2021), making the metal contamination legacy an environmental issue that requires attention in many places in the world (van der Voet et al., 2013).

Among PTE, lead (Pb) is considered one of the most toxic elements in the environment (Alloway, 2013). Its toxicity depends on its mobility and reactivity between abiotic compartments and biota (bioavailability). The soil is one of the environmental compartments most affected by mining and metallurgical wastes as it is the closest sink to the wastes. Very high metal contents in soils are often measured in the vicinity of former smelters and former mines (Ettler, 2016; Cortada et al., 2018; Křibek et al., 2019). Soil quality guidelines only consider metal content as a contamination criterion (e.g., Canadian Environmental Quality Guidelines - CEQG for soils: Pb = 70 mg.kg⁻¹; United States Environmental Protection Agency - US EPA: Pb = 400 mg.kg⁻¹). However, metal speciation is the key parameter for assessing the mobility of metals and their biological harmfulness (Lejon et al., 2008; Navel et al., 2015; Spadini et al., 2018). Lead speciation is influenced by soil properties that tend to reduce its transfer (Alloway, 2013), therefore, Pb is generally considered immobile.

To better limit the environmental impacts of future mining activities, it appears necessary to understand the long-term behaviour of PTE (dispersion and persistence) in the environment by developing studies on mining sites that have been abandoned for several hundred years.

Thousands of ore deposits have been formed and are located in mountain ranges. In the French Alps, hundreds of small ore deposits and occurrences have been reported by the French Geological Survey (BRGM). Environmental contamination related to past mining activities has already been identified in the French Alps based on records of direct atmospheric fallout deposition from mining exploitation in lake sediments (Arnaud et al., 2006; Elbaz-Poulichet et al., 2020) and remobilisation of abandoned mining and metallurgical wastes in river sediments (Camizuli et al., 2021). While recent studies showed the persistence of PTE contamination in former mining soils in the Vosges Mountains over hundreds of years (Monna et al., 2011; Mariet et al., 2017), this contamination has never been studied in alpine soils.

PTE contamination studies have often relied only on geochemical data such as PTE contents, which are insufficient to encompass their behaviours. Nevertheless, a combination of geochemical, mineralogical and extraction tests has more widely been used in PTE contamination studies (Chopin and Alloway, 2007; Swęd et al., 2022). However, the spatialisation of these data has rarely been undertaken and could help to better characterise the PTE dispersion from the sources of contamination to sinks. This paper aims to characterise the environmental legacy of former mining and smelting activities in the soils of a mountain mining site abandoned for more than 150 years: the Pb-Ag mine of Peisey-Nancroix, Savoy, France. A spatial approach, coupling soil properties,

geochemistry, mineralogical observations, and single extraction tests, allows us to discuss the mobility, transfer mechanisms and remobilisation of lead in soils for more than 150 years.

3.2 The Pb-Ag mine of Peisey-Nancroix (Savoy, France)

The northern French Alps have been mined for millennia (Judet, 2014; Peloux et al., 2015), with the 18th and 19th century being the apex of industrial ore extraction in terms of production and number of sites. Indeed, most of these mines closed between the 19th and 20th centuries (Judet, 2014) leaving hundreds of uncontrolled contamination spots in the environment. Pb, as a by-product of silver mining, was the most extracted nonferrous metal in France (Garçon, 1995), providing large amounts of mining and smelting wastes that were abandoned all over the territory. The Peisey-Nancroix mining site has a former regional importance, and no anthropization has been identified since mine closure. The mining site is located in the northern French Alps at 1500 m a.s.l. on the Vanoise Massif, on the left bank of the Ponturin River (Figure 3.1A). The mean annual temperature at the site is 1.5 °C and snow covers the area from November to May. The prevailing wind direction trends from northeast to southwest flowing up the valley. The ore deposit is located along the Internal Briançonnais Fault (IBF), which allows thrusting of the Internal Briançonnais on the External Briançonnais. The External Briançonnais is essentially composed of Carboniferous schists that extend over a few kilometres downstream from the mine site, overlying the Variscan basement. In the study area, the Internal Briançonnais is composed of various Variscan crystalline rocks (metagabbros, metabasites, micaschists and gneisses) and Permian micaschists. Some marbles of unknown age are also present in the area.

The Pb-Ag deposit of Peisey-Nancroix is hosted in Permian schists and Triassic quartzites of the External Briançonnais unit, which are trapped within the Internal Briançonnais Fault. The IBF is evidenced by the presence of Triassic dolomites that were brecciated and partly dissolved during alpine thrusting, called *cargneules*. The ore consists mainly of galena (PbS) and pyrite (FeS) that are disseminated or concentrated in veinlets. Silver is hosted in As-rich tetrahedrite ($[\text{Cu,Fe}]_{12}\text{Sb}_4\text{S}_{13}$) that occurs as small inclusions within galena. Bertauts et al. (2022) provide a thorough description of the ore mineralogy. Galena and Ag-As-rich tetrahedrite were mined industrially between 1734 and 1866 to produce 22000 t Pb and 52 t Ag (Meloux, 1975). The ore was smelted on site for 90 years (1745-1824, Barbier, 1875). The ore processing and metallurgical facilities were built on the edge of an alluvial cone that contains Variscan basement rocks and

cargneules. A cargneule scree is intercalated in the alluvial cone on the western side of the mine site (Figure 3.1B).

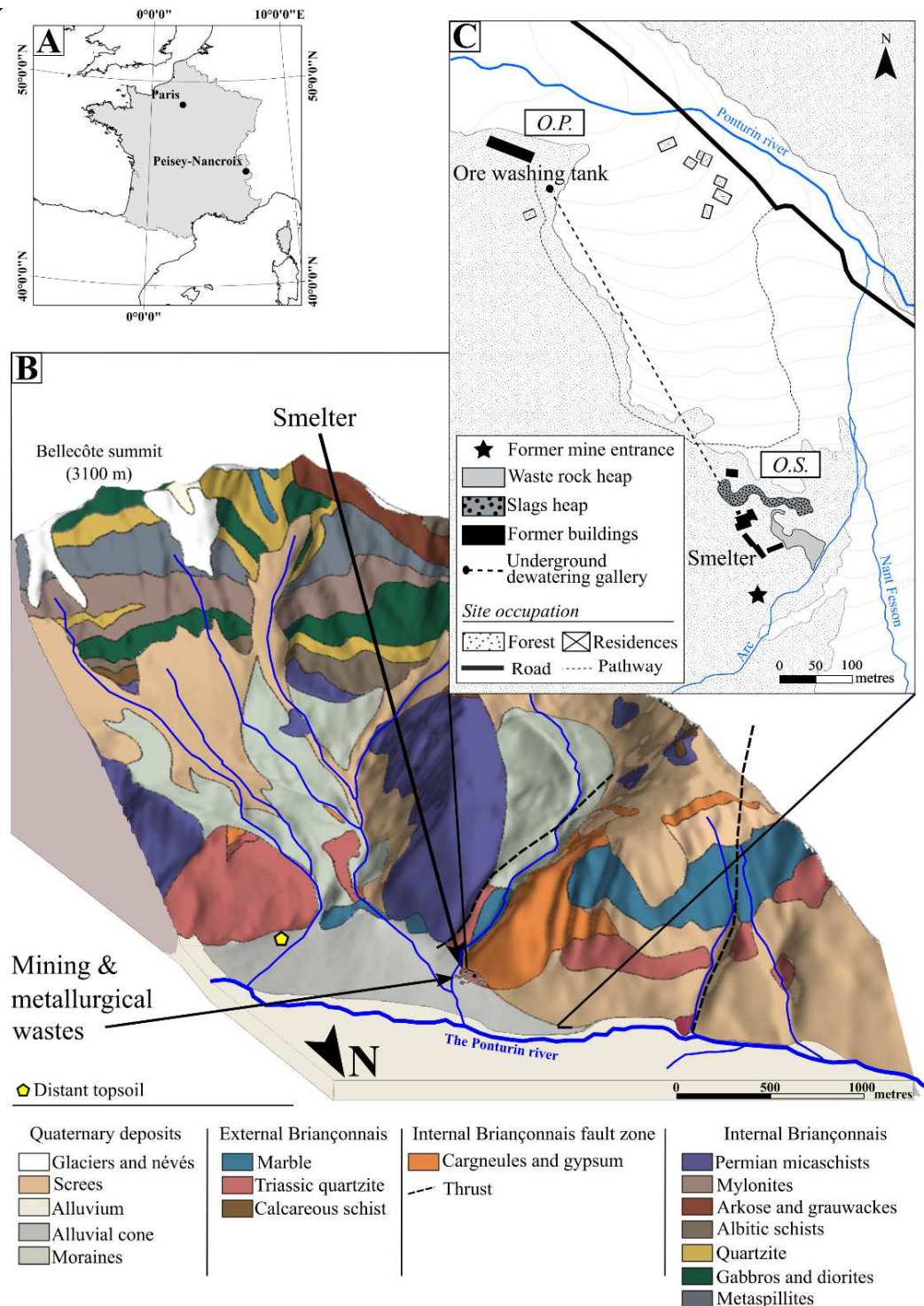


Figure 3.1 : A) Location map of Peisey-Nancroix in the northern French Alps; B) Geological map of the Peisey-Nancroix Pb-Ag mine and its surroundings; C) Organisation of the old mine site, and infrastructures still present today divided between the ore-processing site (O.P.) to the north and the ore-smelting (O.S.) site to the southeast, where waste rock heaps and slag heaps are located.

At the beginning of the exploitation, the ore was crushed, ground, and washed near the metallurgical and ore smelting site (O.S. site), immediately next to the mine entrance and the Arc stream (Figure 3.1C). Soon, ore processing was moved further north to the ore-processing site (O.P. site) to take advantage of greater hydraulic power. A dewatering gallery allowed groundwater evacuation, aeration and ore transport directly to the O.P. site (Barbier, 1875). The crushed ore was then transported from the ore-processing site to the ore-smelting site by a pathway that is still visible on the site. Close to the O.S. site, thousands of tons of abandoned waste rocks and smelting residues (slags) were stored and are still visible (Figure 3.1C).

3.3 Material and methods

3.3.1 Contamination source materials

Slags ($n = 3$) and waste rocks ($n = 3$) were sampled randomly on the heaps. Polished thin sections were made to perform scanning electron microscopy (SEM) observations to identify Pb-bearing phases. Each sample was analysed for major and trace elements by inductively coupled plasma-optical-emission-spectrometry (ICP-OES) and inductively coupled plasma-mass-spectrometry (ICP-MS), respectively, at the Service d'Analyse des Roches et des Minéraux (France, Carignan et al., 2001).

3.3.2 Soil sampling

With the help of a manual auger, 117 topsoils (0-20 cm) were sampled on a 40x40 metre grid from the O.S site to the O.P site (Figure 3.2B) to characterise the spatial distribution of the contamination. These soil samples were air-dried for several days, gently crushed and sieved to 2 mm. The coarse fraction (> 2 mm) was observed under a binocular microscope to study the translocation of ore (e.g., galena) and slag particles. The fine fraction (< 2 mm) was kept for further analysis as Pb-bearing phases tend to concentrate in the fine fraction. In addition, a distant topsoil from waste heaps was sampled 2 km upstream on the same alluvial cone (yellow pentagon on Figure 3.1B).

3.3.3 Physical and chemical characterisation of soils

Soil properties play an important role in the mobility of Pb. Soil organic matter (SOM) and carbonate contents were assessed by loss-on-ignition (LOI) using a furnace for the whole soil

dataset ($n = 117$). Weight loss after a 550 °C-first and 950 °C-second heating step corresponds to the SOM and carbonate (%) fractions, respectively (Heiri et al., 2001). Detailed analyses were performed on 27 soil samples at the French national reference soil laboratory (INRAE, France) including particle size distribution (5 fractions), pH (ISO 10390), cation exchange capacity (CEC), and exchangeable cation content (ISO 23470, cobaltihexamine method). The $\text{SOM}_{550^\circ\text{C}}$ and $\text{Carbonates}_{950^\circ\text{C}}$ fractions were compared to the measured equivalent CaCO_3 total content (CaCO_{3T} , ISO 10693, volumetric method), the C total content (C_T , ISO 10694, dry combustion), and the N total content (N_T , ISO 13878). The total organic carbon (TOC) and organic matter (OM) contents were calculated as follows :

$$(1) \text{TOC} = C_T - (\text{CaCO}_{3T} * 0.12)$$

$$(2) \text{OM} = \text{TOC} * 1.73$$

The calculation of an equivalent CaCO_{3T} content by the volumetric method may be improper when dolomite is predominant (Vuong et al., 2016). However, a comparison of the LOI and dry combustion methods showed a good linear trend between $\text{Carbonates}_{950^\circ\text{C}}$ and CaCO_{3T} ($R^2 = 0.83$) and between $\text{SOM}_{550^\circ\text{C}}$ and OM ($R^2 = 0.95$) assessments (Supplementary Material Table S1). The $\text{Carbonates}_{950^\circ\text{C}}$ and $\text{SOM}_{550^\circ\text{C}}$ content from the LOI measurements were then used in the following results as a good estimator for the whole soil dataset.

3.3.4 Quantitative analysis of soils by WDS-XRF

The total Pb content of the soils was assessed by measuring the chemical content with a Bruker S8 Tiger wavelength dispersive X-ray fluorescence spectrometer (WDS-XRF) equipped with a Rh anode X-ray tube (1 kW, 50 kV, and 170 mA). A mass of 7 g of the fine fraction of soil (< 2 mm) was crushed and pressed with 10 % Licowax C powder into 34-mm diameter pellets with a manual press (at 15 kN.m^{-3}). Aliquot duplicates of 12 soil samples were prepared and added to the sample list (Table S2). A certified standard was introduced at regular interval in the unknown samples list. The WDS-XRF calibration method included 12 standard samples, with 8 certified standards and 4 internal standards for very high Pb content (Pb content $> 1000 \text{ mg.kg}^{-1}$, Table S3). The soil samples were analysed under vacuum conditions. The acquisition time of each spectrum was approximately 30 min for 23 elements. Hereafter, major elements (Na_2O , MgO , Al_2O_3 , SiO_2 , P_2O_5 , K_2O , CaO , TiO_2 , MnO , and Fe_2O_3) are given in weighted percentages (wt. %), and minor and trace elements

(V, Cr, Co, Ni, Cu, Zn, As, Br, Rb, Zr, Ba, Pb, and Sb) in mg.kg^{-1} . Details of the method are available in Table S4.

The Pb Enrichment factor (EF_{Pb}) and Pb geoaccumulation index (I_{geoPb}) helping to discriminate anthropogenic from natural geogenic contamination were calculated (Chester and Stoner, 1973; Reimann and de Caritat, 2005). The EF_{Pb} was calculated considering Ti as an immobile element with a content range close to Pb in contaminated soil (Thiombane et al., 2019):

$$(3) \quad EF = \frac{\left(\frac{M}{Ti}\right)_x}{\left(\frac{M}{Ti}\right)_{bkg}}$$

where M_x and Ti_x are the concentrations of the element and Ti in the soil sample, while M_{bkg} and Ti_{bkg} are their concentrations in the reference soil sample chosen as the local pedo-geochemical background. The enrichment factor was classified into 7 classes (Table S5). A common approach to estimate metal enrichment above background is to calculate the geoaccumulation index (I_{geo}) as proposed by Müller (1979). This index is calculated as follows:

$$(4) \quad I_{\text{geo}} = \log_2((M_x)/(1.5 * M_{bkg}))$$

where M_x is the concentration of the element in enriched samples, and M_{bkg} is the background or pristine concentration of the element considered. The Factor 1.5 is introduced to minimise the effect of possible variations in the background values which may be attributed to lithological variations (Stoffers et al., 1986). Müller (1979) proposed 7 descriptive classes to assess the degree of metal pollution for increasing I_{geo} values (Table S5).

3.3.5 Mineralogical characterisation

Quantitative analysis of minerals from 10 soil samples ($< 2 \text{ mm}$) was performed in the X-ray Diffractometry Laboratory of the Institut des Sciences de la Terre of Grenoble (ISTerre, France). X-Ray Diffraction (XRD) patterns were collected with a Bruker D5000 X-ray diffractometer equipped with a Sol-XE Si (Li) detector operated at 40 kV and 40 mA (Baltic Scientific Instruments). The Rietveld refinements of diffractograms obtained from disoriented powders of the bulk samples, were carried out with Profex software (Doebelin and Kleeberg, 2015). The clay fraction analysis was used to refine the phyllosilicate description, and the diffractograms obtained were fit with Sybilla software (Aplin et al., 2006).

The Pb-bearing phases were identified for 19 soils using scanning electron microscopy (SEM) imaging and semiquantitative analyses at the ISTerre laboratory on an epoxy mounting pad and with free coated powders, with a Vega3 Tescan equipped with a 30 mm² X-Ray SDD detector (EDX). Detailed observations were carried out on a smaller scale (hundreds of nanometres to micrometres) using a SEM-field emission gun (FEG), JEOL IT500HR equipped with an energy dispersive X-ray spectrometer (EDX) at the Consortium des Moyens Technologiques Communs (CMTC Grenoble, France).

3.3.6 Single extraction tests

Single extraction tests are one of the few tools available to determine PTE mobilisation in soils related to metal speciation (Rao et al., 2008). Despite their inherent limitation, they permit us to generally evaluate the potential mobility (long-term) and the mobile fraction of Pb in soils (Gupta et al., 1996; Quevauviller, 1998). Such tests were carried out on 21 samples selected according to their Pb content and soil properties. Three different extractants with increasing extraction power were used: distilled water, humic acid solution and an ethylene-diamine-tetra-acetic acid (EDTA) solution. Humic acids are used to mimic both degraded polymerized organic matter in soils (to which humic acids belong) and dissolved soil organic matter of soil, which are known to have a high density of reactivity sites similar to that of as humic acids (Causse et al., 2013).

A 2 g mass of soil (< 2 mm) mixed with 20 ml of extractant solution (solid : liquid ratio of 10) was agitated on a vibrating plate for 48 hours. Humic acid extraction was performed with a 0.1 g.L⁻¹ humic acid solution (Agros organic 50-60 %) and EDTA extraction was performed with a 10 mmol.L⁻¹ EDTA, 1 M Na-acetate solution yielding a buffering pH of 7 (AFNOR X31-120). Each extraction was duplicated. Extracts were filtered at 0.45 µm and stabilised with 2 % HNO₃ before analysis by ICP-AES (Varian 720ES Atomic Emission Spectrometer, IGE, France). ICP-AES emission at 220,353 nm was used for determination of Pb.

The limit of detection was 0.02 mg.L⁻¹ (L.O.D. = mean of blanks + 3σ) and the limit of quantification was 0.04 mg.L⁻¹ (L.O.Q. mean of blanks + 10σ). The mean of the Pb-extracted values for duplicates was calculated for each sample and used in the results. If a duplicate was below the L.O.Q, half of the L.O.D. was assigned to the sample. Samples were compared based on the percentage of Pb extracted (per extractant) as a function of the total Pb content, calculated for each sample:

$$(5) \text{ Part of extracted Pb (\%)} = (\text{extracted Pb})/(\text{total Pb content}) * 100$$

3.3.7 Analytical data treatment

Data analysis was carried out in R (open-source software, <http://cran.r-project.org>). Despite the constant sum problem of the compositional data of soil, basic statistics (minimum, percentiles, maximum, etc.) were calculated for an easier comparison with guidelines. Clr-transformation was then applied to the geochemical (major, traces and SOM content) dataset to perform statistical analysis of compositional data. Hierarchical classification following a principal component analysis (package FactomineR, Lê et al., 2008) was performed to distinguish the different soil types in the study area. All data (geochemistry, mineralogy, extraction tests, etc.) were reported on a GIS (ArcGIS) to develop a source-to-sink spatial analysis.

3.4 Results

3.4.1 Slags and waste rocks compositions

Table 3-1 provides geochemical compositions of some waste rocks and slags. The analysed waste rocks contain up to 7.1 wt. % for Pb, 125 mg.kg⁻¹ for Zn and 137 mg.kg⁻¹ for Sb. The PTE contents of slags were higher than those of the waste rocks: up to 10.8 wt. % Pb, 5276 mg.kg⁻¹ Zn and 1638 mg.kg⁻¹ Sb. The Pb-bearing phases observed in the waste rocks are those found in the ore (Bertauts et al., 2022): galena is largely dominant, and bournonite is locally observed. Because of weathering of the wastes, galena may slightly be altered into cerussite. In slags, three different Pb-bearing phases embedded in a Si-Fe-Ca-Ba-Al-rich silicate matrix were evidenced by SEM observations: (i) Pb-oxides, with different advancement in weathering processes, which had an ovoid shape of one to several hundred micrometres with a porous rim (Figure 3.2B and Figure 3.2C); (ii) millimetric Fe-sulphide containing lead (Figure 3.2C); and (iii) prills that were micrometric to tens of micrometres (Figure 3.2E). Trace amounts of Pb were also found in the vitreous silicate-rich matrix (Figure 3.2B).

Table 3-1: Major and trace element contents of waste rocks and slags

<i>Unit</i>	Waste Rock 1	Waste Rock 2	Waste Rock 3	Slag 1	Slag 2	Slag 3
SiO ₂	81.10	84.13	83.02	38.72	42.55	40.46
Al ₂ O ₃	5.74	0.54	5.86	5.34	6.19	6.22
Fe ₂ O ₃	1.11	1.10	1.04	18.90	20.60	21.13
MnO	0.08	0.07	0.08	1.15	1.29	0.60
MgO	0.97	0.55	0.98	2.22	2.37	2.57
CaO <i>wt. %</i>	1.42	1.53	1.39	8.43	8.93	8.63
Na ₂ O	0.08	0.06	0.08	0.84	1.01	0.92
K ₂ O	1.94	0.17	1.97	1.71	1.89	1.91
TiO ₂	0.06	< L.D.	0.06	0.31	0.35	0.45
P ₂ O ₅	< L.D.	0.20	< L.D.	0.39	0.40	0.53
CO ₂	3.73	3.77	2.53	-0.64	-0.67	-1.17
As	31	18	37	31	22	22
Cd	3	3	6	0.2	0.1	0.9
Cu	71	2018	87	239	335	143
Ni <i>mg.kg⁻¹</i>	12	46	5	21	24	< L.D.
Pb	29846	71384	18621	108418	75516	22694
Sb	128	112	137	1638	931	452
Zn	125	111	114	3790	3730	5276

Waste rock 1 : PN17-R-07; Waste rock 2 : PN21-R-05; and Waste rock 3 : PN17-R-07.

Slag 1 :PN21-SCO-01; Slag 2: PN21-SCO-03; and Slag 3 : PN17-R-14.

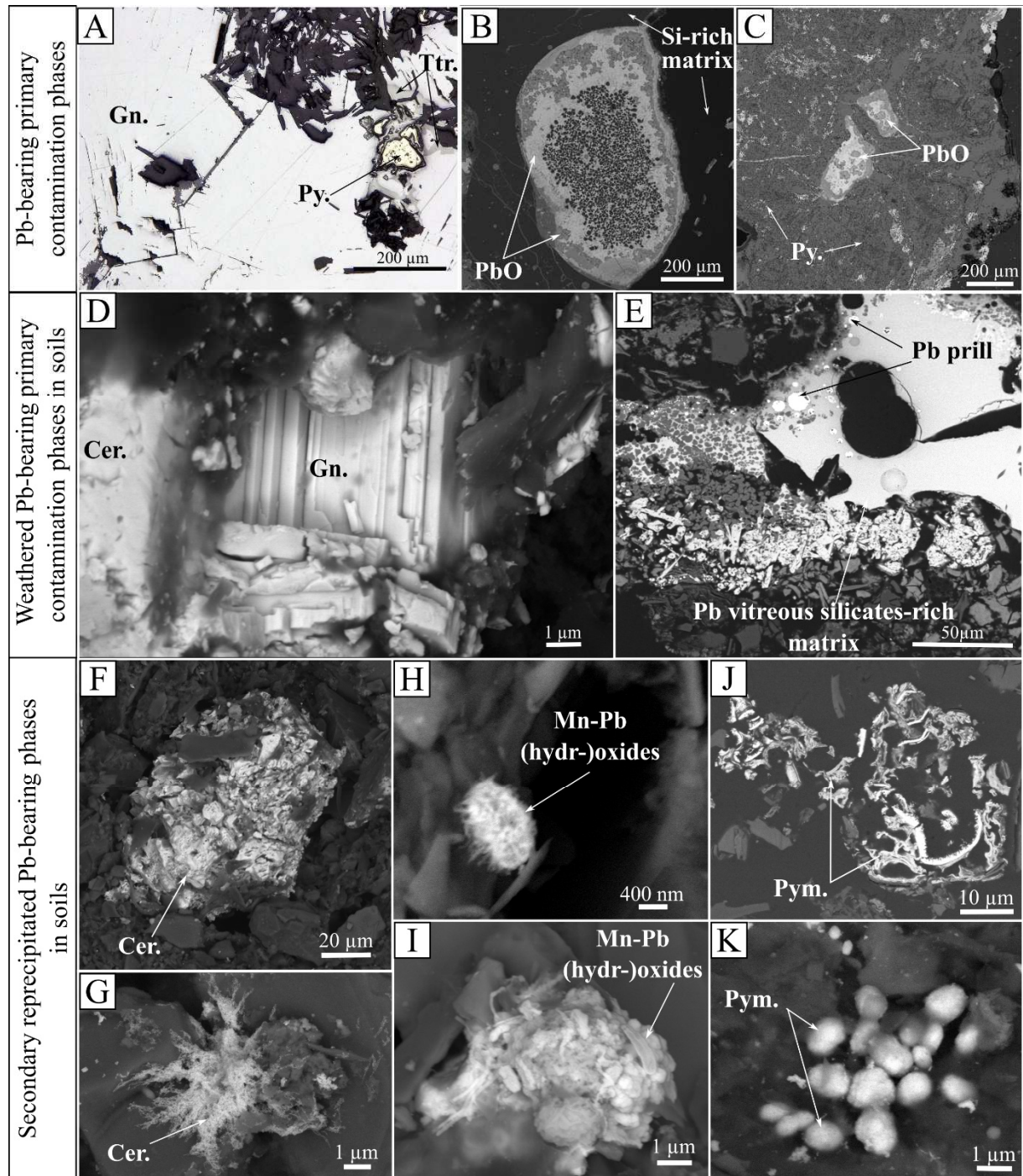


Figure 3.2: Reflected light (A) and SEM images (B-K) of primary and secondary Pb-bearing phases identified in the ore (A), slags (B-C) and soils (D-K). In Pb-bearing primary contamination phases: A) galena (Gn.-), pyrite (Py.), and tetrahedrite (Ttr.) from the ore; B) rounded-shaped PbO with empty holes in the centre observed in slags; C) Fe-sulfides mixed with PbO phases in slags. In weathered Pb-bearing primary contamination phases in soils: D) galena particles altered into cerussite (cerussite I); E) weathered slag particles with micrometric to tens of micrometres-sized Pb prills in a Pb-enriched silicate matrix. In secondary reprecipitated Pb-bearing phases in soils: F) cerussite particles with relict galena (cerussite I); G) reprecipitated cerussite (cerussite II); H) rounded nanometric aggregate of Pb-bearing Mn (hydr)-oxides; I) aggregate of Pb-bearing Mn (hydr)-oxides; J) pyromorphite; K) rounded aggregates of pyromorphite.

3.4.2 Soil properties

3.4.2.1 *Majors elements, carbonates, and soil organic matter content*

Based on a principal component analysis (PCA), hierarchical clustering (Figure S1) on principle components was performed on clr-transformed major element (Na_2O , MgO , Al_2O_3 , SiO_2 , P_2O_5 , K_2O , CaO , TiO_2 , MnO , and Fe_2O_3) and soil organic matter ($\text{SOM}_{550^\circ\text{C}}$) content datasets (Figure 3.3A). Pb was added as an additional illustrative variable to explain the variability. The PCA allowed the identification of 3 clusters: highly Pb-contaminated cambisols (Cluster 1), carbonate-rich less-contaminated cambisols (Cluster 2) and carbonate-poor less-contaminated cambisols (Cluster 3). Basic statistics (minimum, 10th, 25th, 50th, 75th, 90th, IQR, and maximum) for the 3 groups of soils are presented in Table 3-2. This classification reflects the local geology of the study site, leading to contrasting soil bedrocks (Figure 3.3B). Carbonate-poor soils (CPS, cluster 3) were developed on the Nant-Fesson alluvial cone (dark grey in Figure 3.1B) and present a high SiO_2 content (min.-max.: 42-70 wt. %; median: 53 wt. %) and a low CaO content (min.-max.: 0.3-12 wt. %; median: 2 wt. %). Carbonate-rich soils (CRS, cluster 2) were developed on top of cagneule scree and led to a higher CaO content (min.-max.: 11-26 wt. %; median: 17 wt. %). Highly contaminated soils (HCS, cluster 1) were located at the O.P. site (Samples O1 and Q1), the O.S. site (e.g., Samples D1 and B1), along the former ore transport paths (Sample F3), and a potential waste material storage area (Sample H7; Figure 3.3B). Among these samples, sample D1, which was collected on a poorly vegetated slag heap, can be considered as a technosol essentially made of slags. Most of these HCS are chemically close to CRS. Hence, the hayfields exploited downwards from the waste heaps are divided into two chemically different soils: CRS to the west and CPS to the east of the site (Figure 3.3B).

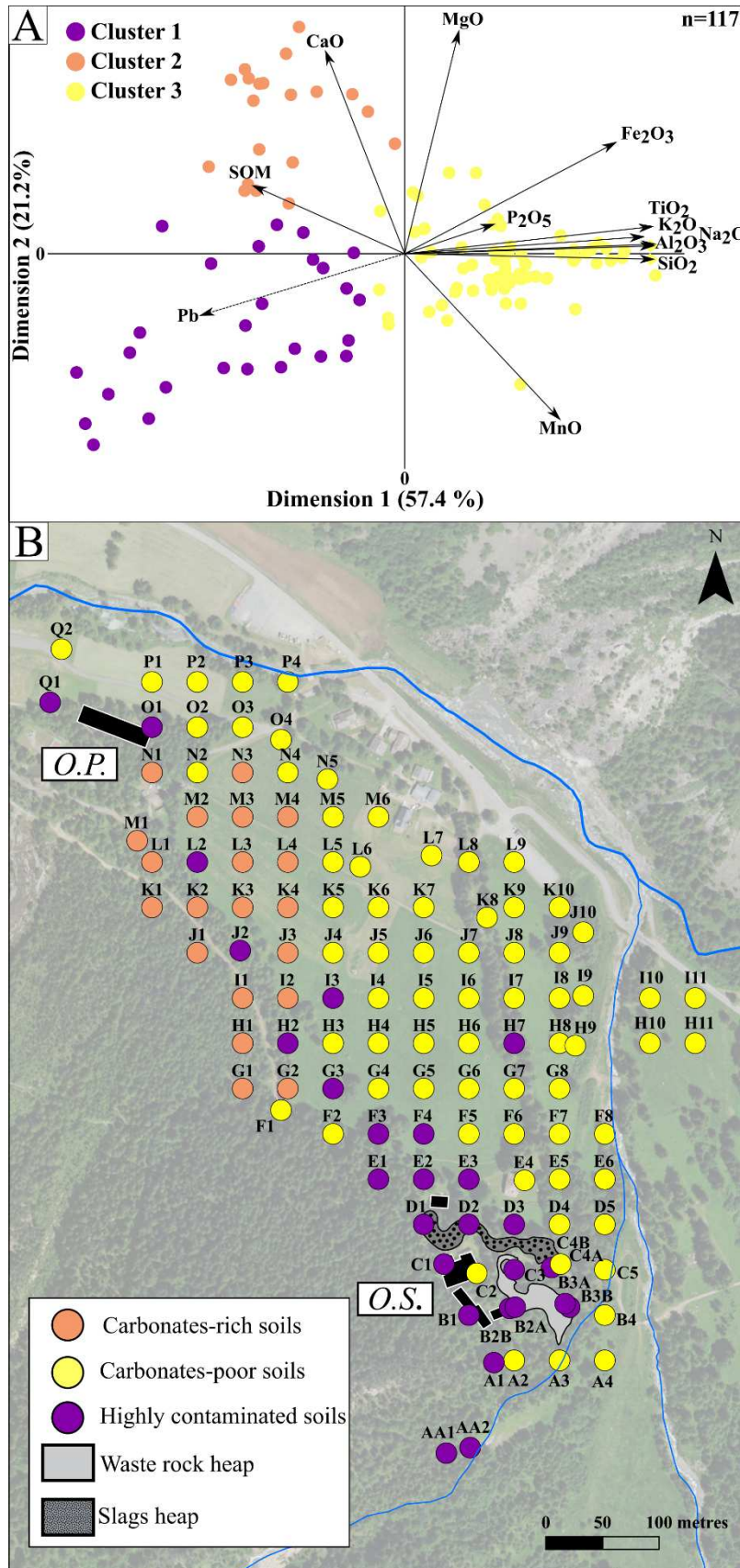


Figure 3.3 : A) Principal component analysis of the 117 samples based on major elements and soil organic matter (SOM) with Pb as an illustrative supplementary variable, allowing the characterisation of three soil types: carbonate-rich cambisols, carbonate-poor cambisols and highly contaminated soils; B) Distribution map of the three soil types.

Irrespective of the type of land-use (hayfields or forest cover), the soil organic matter (SOM_{550°C}) content in the CRS (min.-max.: 4-55 wt. %; median : 17 wt. %, Table 3-2 and Table S1) was twice as high as that in the CPS (min.-max.: 1-19 wt. %; median: 9 wt. %). Detailed analyses were performed on selected soil samples (n = 27, Table S6). A slightly higher pH was observed for the CRS (pH = 7.7) compared to the CPS (pH = 7.0), due to a higher CaCO_{3T} content. The particle size distribution was similar for all soil samples. The clay fraction represented a minor fraction for all types of soils, with a content ranging from 5 to 16 %. The content of exchangeable cations was dominated by Ca and Mg (Ca = 11.3-32.7 cmol⁺.kg⁻¹, Mg = 0.6-6.7 cmol⁺.kg⁻¹).

3.4.2.2 Mineralogy of soils

According to XRD measurements carried out on the fine fraction (n = 10), the CRS was dominated by dolomite while the CPS was dominated by quartz, plagioclase, and clay minerals such as K-micas and expanding phyllosilicates (Table S7 and Figure S2). The only oxide identified was haematite, and its proportion contributed to less than 0.5 % to the total mineral content. With the exception of Sample P2, which was located on the right bank of the Nant Fesson stream, all samples were abundant in amorphous phases ranging from 2 % to 30 % in the soils. This amorphous material most likely corresponds to slag fragments, organic matter, or coal.

3.4.3 Pb contamination of soils

3.4.3.1 Definition of the local pedo-geochemical soil background

To define a reference of Pb in soil, several options were considered: i) an external reference (continental crust content), ii) the average Pb content of the rocks in the watershed (excluding mineralized rocks), iii) a deep-horizon soil (45-60 cm) sampled the farthest away from the O.S. site, near the Ponturin River (sampled between Samples K5 and L6; Figure 3.3B), and iv) a distant soil (0-20 cm) located 2 km upwards on the same alluvial cone, which was sampled near the active torrent in order to have the youngest possible soil to avoid the presence of airborne Pb emitted during smelting. The two soils (deep-horizon soil and distant soil) had a Pb content one order of magnitude larger than that of the middle continental crust and the local lithologies (Table 3-3). The distant soil from the alluvial cone was selected as a reference, considering (i) that the comparison of rocks and soils may not be relevant, and (ii) that a deep-horizon soil near the mine site could be naturally contaminated by the presence of the ore deposit.

Table 3-2: Basic statistics of the 3 groups of soil based on PCA and hierarchical clustering (highly Pb-contaminated soil : highly Pb-cont.; carbonates-rich soil : carb.rich ; and carbonate-poor soil : carb. poor).

Component	Unit	Min.				Q10				Q25				Q50 (median)				Q75			
		All data	highly Pb-cont. ¹	carb. rich	carb. poor	All data	highly Pb-cont.	carb. rich	carb. poor	All data	highly Pb-cont.	carb. rich	carb. poor	All data	highly Pb-cont.	carb. rich	carb. poor	All data	highly Pb-cont.	carb. rich	carb. poor
Na ₂ O		0.50	0.56	0.50	0.99	0.64	0.65	0.54	1.44	0.95	0.71	0.59	1.56	1.51	0.99	0.67	1.71	1.75	1.32	0.86	1.95
MgO		1.17	1.17	5.86	1.29	1.84	1.58	7.26	2.17	2.93	1.96	7.68	3.03	3.58	2.55	9.04	3.50	4.22	3.56	10.15	3.70
Al ₂ O ₃		3.64	3.64	4.22	12.08	7.60	7.10	4.92	13.88	11.14	8.19	6.23	14.73	14.46	12.15	8.00	15.53	15.63	13.47	9.76	15.98
SiO ₂		16.89	24.43	16.89	41.77	28.15	28.95	19.05	48.65	36.91	32.05	21.14	51.14	50.24	43.19	26.59	52.91	53.48	46.72	31.34	55.72
P ₂ O ₅		0.06	0.12	0.06	0.10	0.13	0.15	0.13	0.12	0.15	0.16	0.16	0.14	0.19	0.22	0.21	0.18	0.24	0.28	0.27	0.22
K ₂ O	(wt. %)	0.72	0.72	0.90	2.27	1.44	1.16	1.00	2.44	2.07	1.69	1.26	2.55	2.53	2.09	1.56	2.83	2.98	2.49	1.91	3.09
CaO		0.33	0.80	10.90	0.33	0.83	1.33	12.10	0.79	1.29	2.06	12.94	0.89	2.42	3.24	17.26	1.68	7.29	5.76	19.46	2.48
TiO ₂		0.17	0.23	0.17	0.41	0.35	0.28	0.26	0.62	0.50	0.39	0.31	0.70	0.68	0.56	0.39	0.76	0.78	0.62	0.50	0.80
MnO		0.02	0.07	0.02	0.06	0.06	0.08	0.03	0.07	0.08	0.11	0.03	0.09	0.10	0.12	0.05	0.10	0.11	0.16	0.07	0.11
Fe ₂ O ₃		2.29	3.29	2.29	3.22	4.29	3.93	4.20	4.94	5.54	4.63	4.69	6.19	6.25	5.55	5.87	6.40	6.78	6.22	6.88	6.82
S.O.M. carb.	(LOI, %)	1.10	9.50	4.20	1.10	5	14.06	12.15	4.08	7.9	15.2	13.7	6.42	11.00	18.60	16.70	9.20	15.5	28.3	24.9	10.67
		0.50	0.50	5.40	1.30	1.70	1.66	15.05	1.60	1.90	2.30	16.82	1.80	2.60	3.20	22.30	2.20	7.10	6.85	24.18	3.08
Cu		9	26	9	17	22	42	12	23	27	46	19	27	36	83	25	35	47	99	31	40
Zn		35	91	35	71	82	102	56	90	98	178	68	99	116	256	95	114	160	307	127	125
Pb	(mg.kg-1)	5	1560	141	5	41	3070	488	17	355	5942	752	130	1173	12249	1272	467	4236	18211	3463	1428
Sb		2	4	2	0	2	16	2	2	3	27	2	3	6	67	2	5	20	128	7	10

Component	Unit	Q90				Maximum				IQR				Skewness				Kurtosis			
		All data	highly Pb-cont.	carb. rich	carb. poor	All data	highly Pb-cont.	carb. rich	carb. poor	All data	highly Pb-cont.	carb. rich	carb. poor	All data	highly Pb-cont.	carb. rich	carb. poor	All data	highly Pb-cont.	carb. rich	carb. poor
Na ₂ O		2.10	1.38	0.94	2.32	2.57	1.49	1.08	2.57	0.80	0.61	0.27	0.39	-0.02	-0.01	0.50	0.53	-0.88	-1.62	-1.12	-0.16
MgO		8.75	4.53	10.75	4.02	12.52	5.56	12.52	4.97	1.29	1.60	2.47	0.66	1.56	0.74	0.07	-0.76	1.65	-0.33	-0.79	0.76
Al ₂ O ₃		16.29	14.40	10.32	16.52	19.00	15.55	11.75	19.00	4.49	5.28	3.53	1.25	-0.99	-0.51	-0.05	-0.39	-0.15	-0.87	-1.36	1.09
SiO ₂		56.87	47.75	32.63	57.85	70.40	52.43	36.08	70.40	16.57	14.67	10.20	4.58	-0.71	-0.36	-0.03	0.86	-0.40	-1.38	-1.39	2.18
P ₂ O ₅		0.28	0.35	0.31	0.24	0.56	0.56	0.36	0.29	0.09	0.12	0.10	0.07	1.52	1.41	-0.08	0.21	4.74	1.92	-0.87	-0.95
K ₂ O	(wt. %)	3.18	3.01	2.05	3.22	4.44	3.67	2.26	4.44	0.91	0.79	0.65	0.54	-0.25	0.06	-0.03	1.41	0.13	-0.36	-1.38	2.69
CaO		15.73	10.12	23.34	4.49	25.75	15.40	25.75	11.56	6.00	3.70	6.52	1.59	1.52	1.41	0.41	2.30	1.27	1.14	-0.95	5.11
TiO ₂		0.81	0.70	0.51	0.86	0.99	0.75	0.61	0.99	0.28	0.23	0.18	0.10	-0.58	-0.32	-0.08	-0.61	-0.58	-1.22	-1.02	1.17
MnO		0.14	0.21	0.09	0.12	0.37	0.37	0.09	0.17	0.03	0.06	0.04	0.02	2.40	1.71	0.19	0.39	10.87	2.98	-1.42	1.52
Fe ₂ O ₃		7.32	7.08	7.13	7.30	8.15	7.95	7.67	8.15	1.24	1.39	2.18	0.63	-0.76	0.17	-0.50	-1.18	0.26	-0.74	-0.47	1.81
S.O.M. carb.	(LOI, %)	26.88	41.04	29.6	13.42	55.3	49.5	55.3	19.1	7.6	13.1	11.20	4.25	1.88	1.02	1.49	0.26	3.92	-0.31	2.29	0.09
		20.30	12.30	26.22	4.27	31.50	12.70	31.50	10.90	5.20	4.55	7.35	1.28	1.69	1.02	-0.64	2.46	1.62	-0.46	0.28	5.77
Cu		84	131	45	50	551	551	55	64	20	53	12	13	7.14	3.73	0.54	0.65	62.23	14.67	-0.49	0.20
Zn		262	411	163	148	1202	1202	184	236	63	130	59	26	5.37	2.95	0.45	1.56	38.85	10.12	-1.03	4.29
Pb	(mg.kg-1)	13157	34915	6041	2114	37609	37609	6449	5781	3882	12269	2710	1298	2.78	0.88	0.94	2.08	7.79	-0.41	-0.79	3.92
Sb		75	155	16	23	407	407	17	52	17	102	7	6	4.08	1.97	1.05	2.24	22.29	5.11	-0.68	4.85

¹ highly contaminated soil (n=27); carbonates-rich soil (n=20); carbonates-poor soil (n=70)

3.4.3.2 Total Pb content of soils

Geochemical maps based on PTE content allow the identification of “hot spots” of contamination (Rao et al. 2008). Among the PTE analysed (Table 3-2), Pb had the highest values above the guidelines and references (Table 3-3). The Pb content varied from < 10 mg.kg⁻¹ to 3.8 wt. % (median: 1173 mg.kg⁻¹). The high contents of Cu, Zn and Sb were very localised to the O.S. and O.P. sites. Therefore, the following study focuses on the Pb distribution. The highest Pb content was measured in the soils from the O.S. site and along the edge of the forest and hayfield (Figure 3.4A). Downwards from the hayfield slope, the Pb content decreased down to the local pedo-geochemical background (blue points in Figure 3.4A). The spatial distribution of Pb content in soils indicated a clear gradient of anthropogenic contamination from the mine site downwards. Major element and other trace element contents are available in Supplementary Material Table S8.

Table 3-3: PTE content of site reference soils and rocks and guidelines.

PTE	Site reference (in mg.kg ⁻¹)				Guidelines (in mg.kg ⁻¹)	
	Distant topsoil ¹	Deep-horizon soil ¹	Average watershed rocks ²	Continental crust ³	CCME ⁴	E.U. ⁵
Pb	87	123	17	17	70/140	300
Sb	2	5	2	0.4	20	-
Cu	15	34	17	28	63	140
Zn	126	77	94	67	250	300

¹ n = 2; one soil sampled 2 km upstream of the mining site and one deep horizon soil from the mining site

² n = 34 rocks

³ Rudnick & Gao 2003

⁴ CCME (Canadian Council of Ministers of the Environment) 2007

⁵ EC Directive 86/278/EEC (Agricultural and after sewage sludge application)

3.4.3.3 Enrichment factor & geoaccumulation index

In comparison to the reference soil content, extreme enrichment ($EF_{Pb} \gg 50$ and up to 250) and extreme contamination were observed near the O.S. and O.P. sites, and between the two sites along transport paths (Figure 3.4B). There was a rapid decrease in EF_{Pb} and I_{geoPb} down to a minor to moderate enrichment and contamination, respectively ($EF < 5$ and $I_{geo} < 2$; Figure 3.4B & C). No enrichment and contamination were observed in the samples on the right bank of the Nant Fesson and in the samples the closest to the Ponturin River.

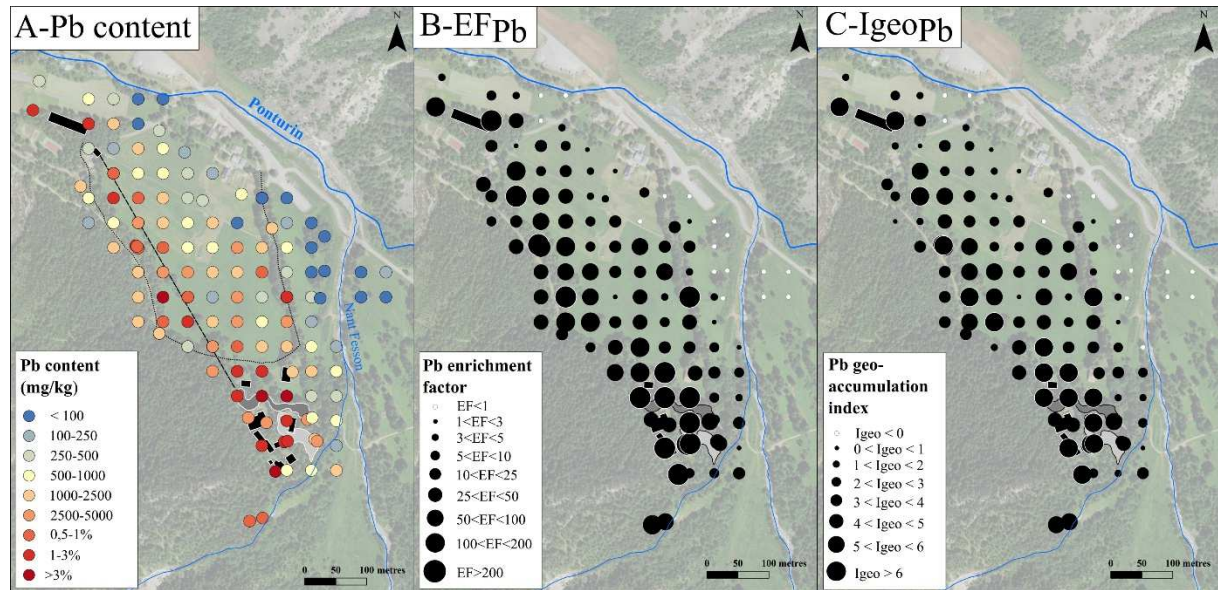


Figure 3.4: A) Spatial distribution of the total Pb content in soils indicating that Pb content decreases down to the local pedo-geochemical background (blue points); B) the Pb enrichment factor and; C) the Pb geoaccumulation index. Represented in A: waste rock heap (light grey), slag heap (dark grey), former mine and metallurgical buildings (black), underground dewatering gallery (wide dotted line) and footpath (small dotted line).

3.4.3.4 Pb association with major elements

Overall, the Pb content of the soil had a medium correlation with MnO ($r^2 = 0.58$, $p < 0.001$; Table 3-4) and P₂O₅ ($r^2 = 0.57$, $p < 0.001$). In detail, carbonate-rich soils (CRS) had a significantly higher correlation between Pb and MnO than highly contaminated and carbonate-poor soils (HCS and CPS, respectively). Nevertheless, the HCS and the CRS had a higher average correlation between Pb and P₂O₅ than CPS. These correlations suggest that Pb in the CRS was mainly associated with Mn first and P then, whereas it was mostly associated with P in the HCS. In CPS, no strong correlation between Pb and any major element was observed. The distribution of Pb correlated well with the distribution of Sb ($r^2 = 0.79$, $p < 0.001$), especially for CRS and CPS, and with SOM ($r^2 = 0.43$, $p < 0.001$).

Table 3-4: Spearman correlations between the Pb total content and major elements and constituents of soil.

	MnO		P ₂ O ₅		Sb		Carbonates _{950°}		SOM _{550°}	
	Group of soil type	Per soil type	All samples	Per soil type	All samples	Per soil type	All samples	Per soil type	All samples	Per soil type
Pb	CPS	0.37		<u>0.27</u>		0.93		-0.03		0.33
	CRS	0.58	0.82	0.57	0.67	0.79	0.91	-0.08	0.43	0.22
	HCS		<u>0.44</u>	0.68		0.61		-0.13		-0.07

Statistically significant correlation at probability levels: $p < 0.05$, $p < 0.01$, and $p < 0.001$

3.4.4 Pb-bearing phases in soils

The mineralogical nature of the Pb-bearing phases was investigated by (i) observation of the coarse fraction using a binocular microscope (> 2 mm, $n = 117$) to qualify the presence of slag or ore mineral particles (e.g., galena) and (ii) detailed observations on 19 fine fraction samples (free powder or pressed pellets) using SEM.

Coarse fraction (> 2 mm)

Qualitative binocular observations on the coarse fraction (small circles in Figure 3.5A) showed the presence of slag particles in the soils in the vicinity of the O.S. site and along the ore transport pathways. This observation was confirmed by the presence of slag particles in the fine fraction (large circles in Figure 3.5A). Fewer slag particles were observed downwards in the coarse fraction, suggesting a lower proportion or the absence of them in the fine fraction.

Fine fraction (< 2 mm)

SEM observations allowed the identification of many phases that were not identified by XRD because they were not abundant enough (< 0.1 %). The Pb-bearing phases observed by SEM and their spatial distribution in the fine fraction of soils are shown in Figure 3.2 and Figure 3.5, respectively. Typical EDS spectra are presented in Figure S3 in the supplementary material.

Galena particles were observed only in the soils sampled in the vicinity of the waste heaps or along the former transport path between the O.S. and O.P. sites (Figure 3.5A). They most likely fell from the heaps by gravity or due to human transport from the O.P. site to the O.S. site for smelting. SEM observations indicated a widespread distribution of Pb-rich slags and a restricted dispersion of galena (Figure 3.5A), in agreement with qualitative observations on the coarse fraction. This result indicates that slag particles were the first primary contamination sources of PTE in soils.

Most of the galena particles in the soils have been weathered to a secondary reprecipitated mineral (Figure 3.2D). The pseudomorphosis of galena to cerussite, called cerussite I, is recognisable by its tens of micrometres size and its preserved shape of vuggy-faced galena (Figure 3.2D & F). Cerussite I was observed in the most Pb-contaminated soils. The vuggy aspect of these large cerussite particles was evidenced by ongoing alteration and dissolution of Pb, which may be partly transported in solution. Cerussite has also been observed in less contaminated samples (Figure 3.5B). This cerussite II was not well crystallised and had a smaller-size and a filamentous structure, suggesting a leaching-reprecipitation mechanism (Figure 3.2G). Cerussite was the only Pb-bearing mineral identified by XRD (< 0.1 %); it was only identified in three samples located at the O.S. site

or along the ore transport pathway between the O.S. and O.P. sites (Table S7). Slag fragments were also often associated with cerussite at their edges.

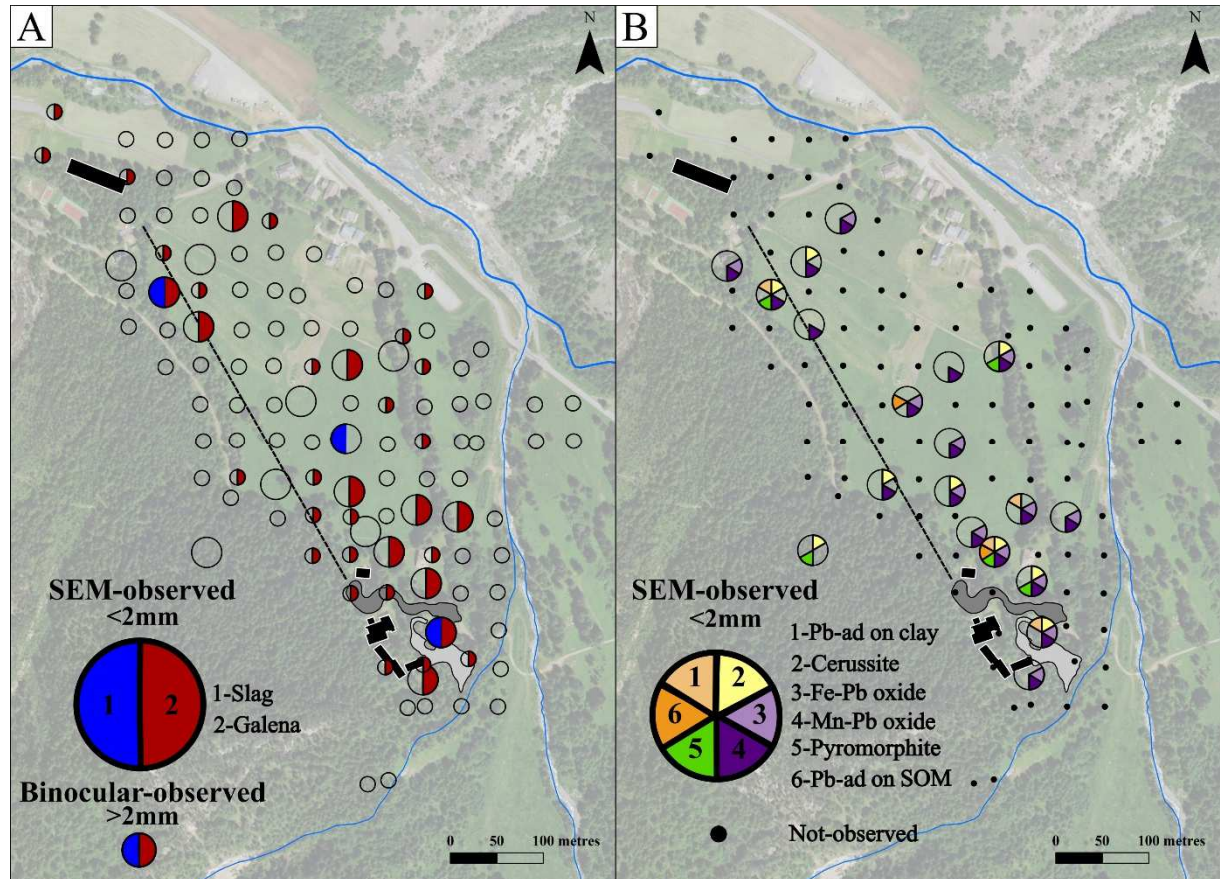


Figure 3.5: Spatial distribution of the Pb-bearing phases based on mineralogical observations: A-primary contamination phases (slags and ore particles) observed in soils based on binocular (> 2 mm, n = 117) and SEM (< 2 mm, n = 19) observations. B- the Pb-bearing secondary phases observed in soils, based on SEM (< 2 mm) observations only (n = 19).

In addition to cerussite II, Ca-rich pyromorphite ($\text{Pb}_5(\text{PO}_4)_3(\text{Cl}, \text{OH}, \text{F})$) was observed at the O.S. site or along the former transport path (Figure 3.5B), either as tens of micrometres-sized fibrous shapes or as micrometric rounded grains (Figure 3.2J & K).

The most ubiquitous Pb-bearing phases were the Pb-bearing Mn (hydr-)oxides (Figure 3.5B). Pb can either be adsorbed at the surface of the Mn (hydr-)oxides or included in the crystal lattice to form Pb-Mn (hydr-)oxides through $\text{Pb}^{2+} \leftrightarrow \text{Mn}^{2+}$ substitution. SEM spectra and semiquantitative analysis (Figure S3) indicated that the Pb stoichiometric part in the total phases is commonly several tens of percents. Such high Pb content suggest the occurrence of $\text{Pb}^{2+} \leftrightarrow \text{Mn}^{2+}$ substitution rather than Pb-adsorption. A significant consistent C peak was associated with Pb-bearing Mn

(hydr-)oxides in EDX analyses, suggesting an association of these (hydr-)oxides with carbonates and/or organic matter. Downwards from the slope, mineralogical observations tended to indicate a higher occurrence of rounded micrometric to tens of micrometres-sized aggregates of Pb-bearing Mn (hydr-)oxides (Figure 3.2H & I) at the expense of Pb-bearing slags and galena particles. A minor proportion of Pb-bearing Fe-Mn (hydr-)oxides and Fe (hydr-)oxides with traces of Pb were also observed. Such Fe-rich phases likely derived from the alteration of pyrite.

Due to SEM-EDX detection limits and the very small amount of Pb adsorbed, it was very difficult to identify sorbed phases using SEM. However, Pb associated with clays and organic matter could occasionally be identified (Figure 3.5B), based on the presence of a fairly small Pb peak observed in the SEM-EDX spectra (Figure S3). Because of its very low content, Pb is likely adsorbed on these phases.

3.4.5 Pb single extraction tests

The amount of Pb extracted by distilled water, humic acid and EDTA versus the total Pb content of the soil measured by WDS-XRF is shown in Figure 6. The total Pb content of soils and Pb-extracted by water, humic acid and EDTA showed a good linear trend (respectively $r^2 = 0.93$, $r^2 = 0.75$, and $r^2 = 0.91$, respectively). The higher the total Pb content of the soil was, the higher the amount of Pb extracted. Samples with a low Pb content extracted less Pb than highly contaminated samples in proportion to the total Pb content. This was visually observable because the three overall slopes established by the amount of Pb extracted from water, humic acid, and EDTA were steeper than the slope established by the total Pb content (Figure 3.6). Therefore, the percentage of extracted Pb relative to the total Pb content (see Equation 5) is presented in Figure 7 to spatially visualise the distribution of extracted Pb fraction. Water-extracted Pb quantities from 5 samples and humic acid-extracted Pb quantities from 3 samples were below the detection limit (Table S9).

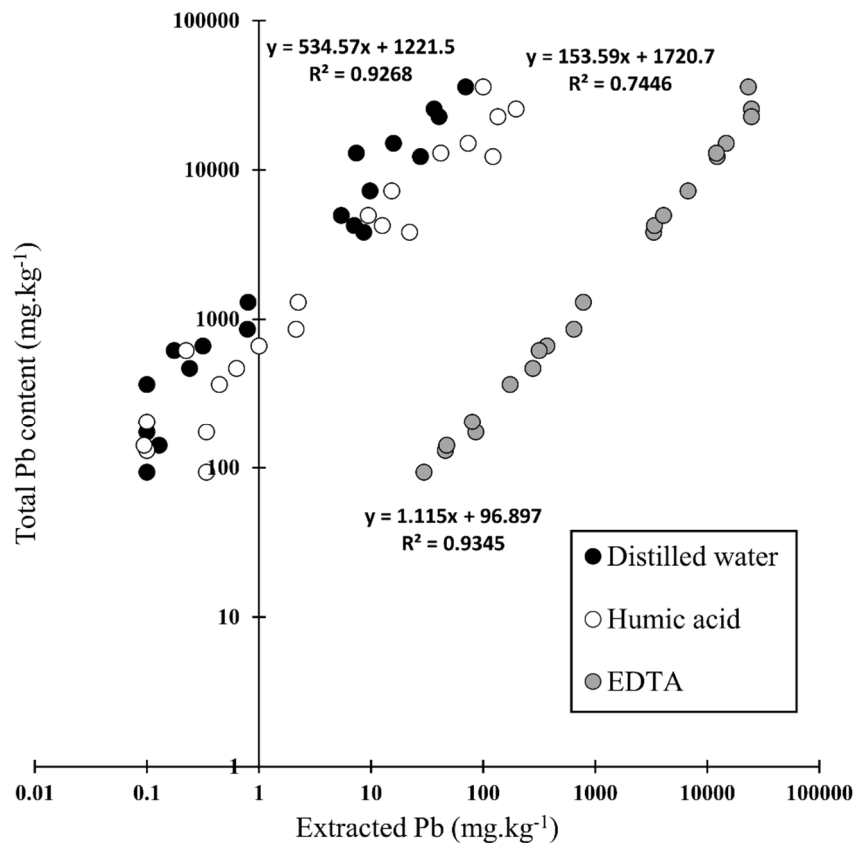


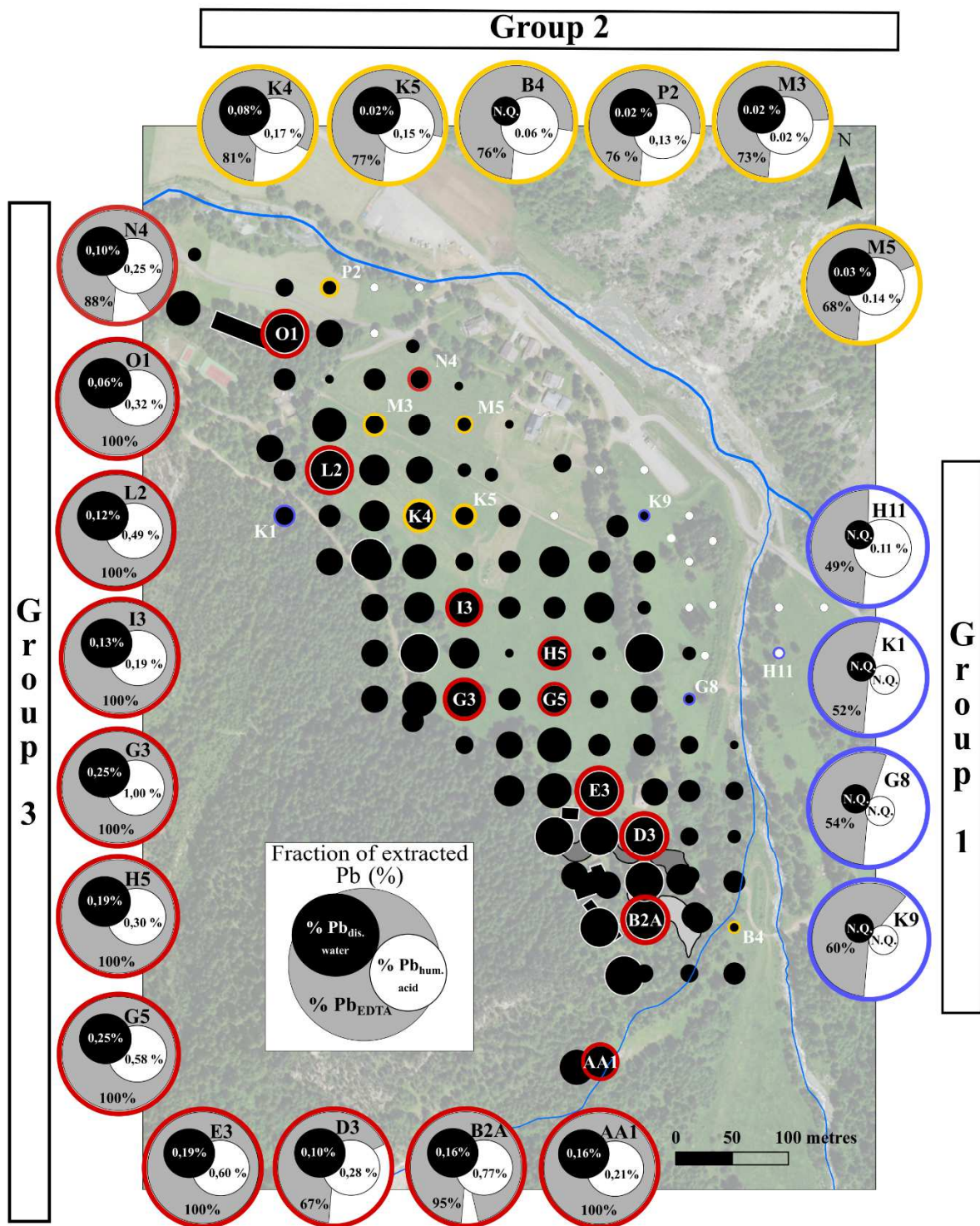
Figure 3.6: Graph of the amount of extracted Pb (mg.kg⁻¹) using 3 extractants (distilled water, humic acid, and EDTA) as a function of the total soil Pb content (mg.kg⁻¹) on a logarithmic scale.

3.4.5.1 Water extraction

The measurable water-extracted Pb quantities varied from 0.1 to 42 mg Pb kg⁻¹. The highly contaminated soil E3 had the highest extracted Pb content, followed by the highly contaminated soils B2A and D3 (downhill slag heap), which also presented very high water soluble Pb contents of 40 and 35 mg Pb kg⁻¹, respectively. The water-extracted Pb represented 0.02 to 0.25 % of the total Pb content of the soil samples (Figure 3.7).

3.4.5.2 Humic acid extraction

The measurable humic acid-extracted Pb quantities varied from 0.1 to 197 mg Pb kg⁻¹. The highly contaminated soil B2A had the highest Pb content of humic acid-extracted Pb. Humic acid-extracted Pb quantities were 2 to 5 times higher than water-extracted Pb quantities (Figure 3.6). Pb extracted by humic acid represented 0.02 to 1 % of the total Pb content of the soil samples (Figure 3.7).



N.Q. (Non Quantifiable) Measured Pb content from the initial solution is under the limit of quantification.

Figure 3.7: Spatial distribution of the fraction of extracted Pb (%) for each extractant: distilled water (in black circles), humic acid (in white circles) and EDTA (in grey circles). The 3 extraction groups were distinguished according to the amount of extracted Pb with distilled water and EDTA, the Pb contamination (EF_{Pb}) and the proximity of the slag heap (see text).

3.4.5.3 EDTA extraction

EDTA-extracted Pb quantities were much higher, varying from 45 to 25 423 mg Pb kg⁻¹. They were equivalent to the total Pb content of most of the highly contaminated samples (Figure 3.6), with the exception of the most contaminated soil D3, which contains the most slag and coal particles and therefore less accessible Pb. Pb extracted by EDTA represented 49 to 120 % of the total Pb content of the soil samples (Table S9). EDTA extractant is known to often leach a higher Pb content than the total Pb content (Sterckeman et al., 1996). These samples were fixed at 100 % in Figure 3.7 (Samples G3, G5, L2 and O1).

3.4.5.4 Data comparison

The soil samples were divided into 3 groups according to the total Pb content, the amount of Pb extracted by water and EDTA and the distance to the slag heaps (Table 3-5). The Group 1 samples had no or low Pb contamination (blue circles in Figure 3.7). They were characterised by a nonquantifiable water extraction of Pb and a low EDTA extraction of Pb (< 60 %). These samples were disconnected from the waste heaps downslope (H11; K9; and G8) or upstream of the ore transport pathway (K1). The Group 2 samples were moderately contaminated with Pb and characterised by low water extraction of Pb and median EDTA extraction of Pb (yellow circle in Figure 3.7). These samples were far away from mining and metallurgical wastes. The Group 3 samples were highly contaminated and characterised by high Pb water extraction and high Pb EDTA extraction (red circle in Figure 3.7). These samples were close to or in the immediate vicinity of mining and metallurgical wastes.

3.5 Discussion

Geochemical analyses provide evidence of extreme Pb contamination in the soils that is restricted to the ancient mining and smelting site of Peisey-Nancroix. The most contaminated soils are localised along anthropogenic features, close to the slag heaps and along the transport pathway and dewatering gallery that connect the O.P. site to the O.S. site. Such a spatial distribution provides evidence of the anthropogenic origin of the contamination there.

3.5.1 Remobilisation and long-term mobility of Pb

3.5.1.1 Mobility of Pb

Water is considered to be a weak acid extractant that allows the determination of the water-soluble metal fraction, considered the most mobile fraction (Rao et al., 2008). No water-extractable Pb fraction was measured in the samples of extraction Group 1 (Figure 3.7), which corresponds to control samples due to their disconnection from the sources of contamination (slag heaps and transport pathways). Such a low Pb mobility suggests the absence of water-soluble phases, which corroborates the presence of only Pb-bearing Mn and Fe (hydr-)oxides in these samples (Figure 3.5B). In contrast, the most contaminated soils in Group 3 samples had a high amount of water-extracted Pb, which still represents a small proportion of the total Pb content (Figure 3.7). Pb water-extracted quantities tended to decrease in soils downgradient and represented a smaller extracted fraction of the total Pb content (Group 2 samples).

Table 3-5: Classification of samples in groups of Pb extraction variability

Slope	Distance from sources	Pb contamination	Pb mobility		Potential mobilisation	Samples
			EF _{Pb}	Distilled water	Humic acid	
Group 1	Off slope	Distal	EF < 4	Non quantifiable	Low (< 60 %)	G8, H11, K1 (EF _{Pb} = 5), K9
Group 2	Downslope	Distal	4 < EF < 40	Non quantifiable to low (< 0.10 %)	Median (60 to 80 %)	B4 (EF _{Pb} = 2), K4, K5, M3, M5, P2
Group 3	Downslope	Proximal	EF > 40	High (> 0.10 %)	High (> 80 %)	AA1, B2A, D3, E3, G3, G5, H5, I3, L2, N4 (EF _{Pb} = 10), O1

The water-soluble fraction was generally defined as easily exchangeable Pb and bound to carbonates and/or organic matter (Sahuquillo et al., 2003). Cerussite was the most abundant Pb-bearing mineral in the highly contaminated samples, with slag particles (by relative proportion and by preferential weathering phase of galena and PbO in slags, Figure 3.5). Cerussite is known to be insoluble in pure water at neutral to alkaline pH (Keim and Markl, 2015). However, one can consider the soil organic matter as a competitive ligand to cerussite conducting to Pb partial

extraction in solution, under in-situ conditions. Water extraction tends also to leach the not easily observable Pb adsorbed phases, which is suggested by the good correlation between TOC and water Pb extracted ($r = 0.63$, $p < 0.05$, Table 3-6). The decrease in Pb mobility is associated with a decrease in Pb contamination in the soils, reflecting a redistribution of the Pb-bearing phases.

Table 3-6: Spearman correlation coefficients between extracted Pb and soil properties ($n = 20$).

	pH	TOC	CEC	CaCO _{3T}	Mn _{ex}	Ca _{ex}	Pb _{total}
Pb _{total}	0.12	0.79	0.7	0.49	0.12	0.62	1
Pb _{distill.water}	-0.08	0.63	0.55	0.33	0.25	0.43	0.93
Pb _{hum.acid}	-0.10	0.61	0.50	0.26	0.20	0.38	0.92
Pb _{EDTA}	0.08	0.74	0.64	0.45	0.11	0.53	0.98

ex. exchangeable cation

Statistically significant correlation at probability levels: $p < 0.05$, $p < 0.01$, and $p < 0.001$

3.5.1.2 Potentially mobilisable Pb

EDTA is a strong complexing agent that acts as a metal extractant. It is often used to estimate the potentially mobilisable pool of metals (Cappuyns, 2012) bound to soil organic matter (SOM) and carbonate complexes. EDTA-extraction tests of Group 1 samples showed the smallest fraction of Pb extracted by EDTA of all samples tested. Group 1 samples were uncontaminated or minimally contaminated, with less than 100 mg.kg^{-1} Pb, which is insignificant in the long-term. In contrast, the samples in Group 3 had an EDTA-extracted Pb content between 80 to 100 % of the total Pb content. This result suggests that the Pb content of the Pb-bearing phases is mobilisable in the long-term and represents a potential source of Pb in soil solution. However, the EDTA-extractable Pb fraction decreased rapidly downgradient indicating a greater proportion of less mobilisable Pb-bearing minerals downgradient (Group 2 Samples M5 and K5; Figure 3.7). Ostergren et al. (1999) showed that EDTA successfully dissolved strongly bound surface Pb complexes and EDTA-soluble phases as carbonates and poorly crystalline Fe (hydr-)oxides. There was an evolution of the chemical form of Pb from waste heaps to downgradient: Pb water soluble forms (weakly bound) disappeared for the benefit of a higher proportion of more stable phases (Pb-bearing Mn (hydr-)oxides), leading to a less mobile Pb down the slope. However, EDTA extraction tests suggest that an important pool of Pb, stocked in the most stable phases, could be mobilised in the long-term.

3.5.2 Pb dispersion processes in soils

Two Pb dispersion processes were identified by combining mineralogical observations, geochemical contents and leaching tests: particulate translocation of the Pb-bearing primary contamination phases and Pb leaching of the primary contamination phases leading to reprecipitated or adsorbed Pb.

3.5.2.1 Translocation of particles

The most contaminated soils provided evidence of the presence of significant amounts of galena and slag particles, which are weathered in soils. A few dropped galena were identified in the fine fraction of highly contaminated soils and in soils along former transport paths. No coarse (> 2 mm) or fine (< 2 mm) galena particles were observed in soils down to the O.S. site. In contrast, slag particles were more widespread in the coarse and fine fractions of soils. Nevertheless, qualitative mineralogical observations indicated their scarcer proportion downwards in both the fine fraction and coarse fractions.

The extensive dispersion of slags can be explained by the natural translocation of small slag particles, by the reuse of slags for roasting the ore and the reuse of slags for construction (path, roads, etc.). Particulate translocation of Pb-bearing slag fragments significantly contributed to the Pb contamination in the soils due to their high Pb content (several wt. %).

3.5.2.2 Leaching processes

3.5.2.2.a. Leaching-reprecipitation processes

The dispersion and weathering of Pb-bearing galena particles or slag phases in soils represents a source of Pb, which can be leached and reprecipitated. These primary Pb-bearing phases were transformed into secondary Pb-bearing reprecipitated phases: cerussite, pyromorphite and Pb-bearing Mn (hydr-)oxides.

Cerussite I was mainly observed in the most contaminated samples, located along the transport path and the dewatering gallery, between the O.S and O.P. sites. Galena particles are directly altered into cerussite (cerussite I) in carbonate-rich alkaline environments (Bao et al., 2021), which is consistent with our observations. Cerussite I has a porous layer on its faces that accelerates galena dissolution and releases Pb^{2+} into the pore waters (Lara et al., 2011). The released Pb^{2+} is likely to be reprecipitated further into cerussite II.

The restricted presence of Ca-rich pyromorphite in highly contaminated soils supports the significant correlation between Pb and P in these soils (Table 3-4). Pyromorphite is commonly

observed in Pb-contaminated soils (Cotter-Howells and Thornton, 1991). It is considered a long-term host for Pb or a mature alteration product of Pb (Davis et al., 1993) and as the most insoluble secondary form of Pb in soils under a wide range of environmental conditions (Nriagu, 1974; Hettiarachchi et al., 2000; Morin et al., 2001). The substitution of Ca^{2+} for Pb^{2+} accentuates the insoluble character of pyromorphite (solid solution, Cotter-Howells et al., 1994). Therefore, the Ca-rich pyromorphite observed at the site is considered to be highly insoluble (Figure S2). The source of P must be very localised within the highly contaminated soils as no pyromorphite was observed in the hayfields despite fertiliser application. The presence of monazite, xenotime and apatite in the ore (Bertauts et al., 2022) may be the main source of phosphorus as well as the P-enriched slags (Table 3-1). It can be assumed that pyromorphite crystallises as long as Pb is leached out and P is available (Buatier et al., 2001).

Pb-bearing Mn (hydr-)oxides, based on mineralogical observations, were the most ubiquitous Pb-bearing phases observed in soils and the dominant Pb-bearing phase observed downgradient. Mineralogical observations tended to show a decrease in cerussite and pyromorphite downgradient in favour of a greater proportion of Pb-bearing Mn (hydr-)oxides. It is widely known that Mn-(hydr-)oxides and Fe-(hydr-)oxides have a high capacity to retain PTE in the environment and are considered also as a mature alteration phase (Davis et al., 1993). The characteristics of the Pb-bearing Mn (hydr-)oxides suggest leaching of the Pb-bearing slag or galena particles, solute transport and reprecipitation.

3.5.2.2.b. Leaching-adsorption processes

Few Pb-adsorbed phases were observed knowing the limits of the SEM to identify such phases with a low to a very low Pb content using backscattered electrons. The observed spatial distribution of Pb-adsorbed on clays and organic matter (Figure 3.5B) is likely not representative of their real distribution because of the high difficulty to identify these phases using SEM. Despite this difficulty, these phases play an important role in the mobility of Pb, as they can represent up to 50 % of the Pb-bearing phases in mining and smelting areas (Brown et al., 1999).

3.5.3 The airborne portion of the Pb contamination

Pb-rich atmospheric fallout was most likely been deposited on site during smelting. However, no Pb enrichment was evidenced among the farthest samples from the O.S. and O.P. sites (Figure 3.4A), suggesting that the part of airborne lead contamination was negligible. Considering that smelter fumes can be transported over several kilometres to thousands of kilometres (Hong et al.,

1994; Doucet and Carignan, 2001; Zdanowicz et al., 2006; Cloquet et al., 2006b, 2015), it is necessary to obtain samples from a few kilometres downwind to characterise airborne Pb contamination. Lake sediment cores were sampled in La Plagne Lake (7 km upstream of the mining site) together with soils from its watershed in order to quantify the contamination contribution of the atmospheric deposition to the total Pb contamination observed at the site in soils (Guillevic et al. submitted).

3.6 Conclusion

This study shows the persistence of a 200 years Pb contamination in the vicinity of the Peisey-Nancroix Pb-Ag mine (Savoy, France). Severe anthropogenic Pb contamination is localised in soils around the former mining and smelting sites: it is restricted to anthropogenic features (slag heaps, former transport path and dewatering gallery) and decreases rapidly, in a few hundreds of metres in soils downwards. Slag particles are most likely the main source of Pb contamination, especially particles dispersed by anthropogenic transport between the O.P and O.S sites.

Coupling mineralogical observations and extraction tests suggests a rearrangement of Pb-bearing phases from labile to more stable phases downgradient. The highest contaminated soils account for a higher proportion of water-soluble and less stable Pb-bearing phases, as Pb-carbonates and Pb-adsorbed phases tend to decrease downgradient for the benefit of a higher proportion of Pb-bearing Mn (hydr-)oxides which are more stable. A form of Pb stabilisation is set up by moving away from the sources of contamination. This study contributes to a better understanding of the long-term dispersion of Pb due to mining activities. Evaluation of the mining legacy in soils and its memory effects should involve mineralogical characterisation in addition to leaching tests, in order to assess the Pb mobility/stability. Such knowledge is necessary to establish mitigation strategies that limit PTE migration in the different environmental compartments.

3.7 Acknowledgement

This work was supported by the French National Program EC2CO (Ecosphère Continentale et Côtière), by the University of Savoie Mont-Blanc and by the IRS Program of the University of Grenoble Alpes. Chemical analysis at the Air-O-Sol facility at IGE was made possible with the funding of some of the equipment by the Labex OSUG@2020 (ANR10 LABX56). We acknowledge the work of C. Voiron (IGE) regarding chemical analysis of extracting solutions and the work of N. Findling (ISTerre) regarding XRD patterns acquisition and treatment. We also thank

the three anonymous reviewers and the editor for valuable comments which significantly help to improve the original version of the manuscript.

A RETENIR

- Une contamination anthropique en Pb extrême de plus de 200 ans, liée à des activités minières et pyrométallurgiques.
- Des changements des phases porteuses de Pb observés dans les sols depuis les sols à proximité immédiate des haldes vers l'aval.
- Transfert détritiques de minerai et de scories & processus de lixiviation-précipitation
- Le Pb associé aux (hydr-)oxydes de Mn constitue la phase la plus stable.
- Des quantités significatives de Pb restent mobilisables à long terme.

3.8 Supplementary material

Table S1. Comparison between carbonates and soil organic matter (n=27).

Table S2. Duplicates of soil samples measured by WDS-XRF.

Table S3. Majors and traces element contents of certified and internal standards used for WDS-XRF calibration method.

Table S4. Comparison between carbonates and soil organic matter (n=20).

Table S5. Classification of the enrichment factor (EF) and the geoaccumulation index (Igeo).

Table S6. Physical and chemical properties of soils (n=27).

Table S7. XRD mineralogical results on soil samples (n=10).

Table S8. Major and trace elements contents of soils by WDS-XRF .

Table S9. Single extraction test results from distilled water, humic acid and EDTA extractions on soil samples (n=21).

Figure S1. Hierarchical clustering on soil samples (n=117) to identify 3 main soil types.

Figure S2. XRD patterns for the three soil types (modified from DRX report Lanson 2020).

Figure S3. SEM-EDX spectra of Pb-bearing phases.

Table S1. Comparison between carbonates and soil organic matter (n=27).

Sample Name	Loss on Ignition		Dry combustion (INRAE)							
	SOM _{550°C}	Carbonates _{950°C}	CaCO _{3T}		C _T		TOC		Organic matter	
	wt. %	wt. %	g/kg	wt. %	g/kg	wt. %	g/kg	wt. %	g/kg	wt. %
PN20-G3	15,2	2,1	3	0,3	61	6,1	60,88	6,1	105	10,5
PN20-K5	11,7	2,5	3	0,3	43,99	4,4	43,63	4,4	75,5	7,6
PN20-P2	7,7	1,7	3	0,3	59,45	5,9	59,09	5,9	102	10,2
PN20-B4	12,4	2	8	0,8	51,15	5,1	50,19	5,0	86,8	8,7
PN20-I3	15,2	2,6	8	0,8	60,97	6,1	60,01	6,0	104	10,4
PN20-E3	15,5	2,3	11	1,1	80,24	8,0	78,92	7,9	137	13,7
PN20-B2A	27,6	3	13	1,3	150,49	15,0	148,93	14,9	258	25,8
PN20-D3	34,9	3,3	13	1,3	172,60	17,3	171,04	17,1	296	29,6
PN20-H11	10,1	3,2	17	1,7	42,32	4,2	40,28	4,0	69,7	7,0
PN20-K9	7,7	2,4	21	2,1	31,65	3,2	29,13	2,9	50,4	5,0
PN20-O1	24	3,2	24	2,4	124,10	12,4	121,22	12,1	210	21,0
PN20-G8	7,4	3,2	33	3,3	30,99	3,1	27,03	2,7	46,8	4,7
PN20-L2	18,9	10,3	75	7,5	100,59	10,1	91,59	9,2	158	15,8
PN20-M3	12,8	16,2	87	8,7	90,59	9,1	80,15	8,0	139	13,9
PN20-AA1	20,3	12,3	249	24,9	107,25	10,7	77,37	7,7	134	13,4
PN20-K1	12,3	31,5	253	25,3	140,51	14,1	110,15	11,0	191	19,1
PN20-G5	10,6	2,4	0.5 ¹	0,05	43,61	4,4	43,61	4,4	75,4	7,5
PN20-H5	11,8	1,8	0.5 ¹	0,05	44,23	4,4	44,23	4,4	76,5	7,7
PN20-M5	11	1,9	0.5 ¹	0,05	36,15	3,6	36,15	3,6	62,5	6,3
PN20-N4	11	1,9	0.5 ¹	0,05	40,50	4,1	40,5	4,1	70,1	7,0
PN20-K3	13,7	20,3	94	9,4	108,37	10,8	97,09	9,7	168	16,8
PN20-K4	14,2	25,5	201	20,1	129,00	12,9	104,88	10,5	181	18,1
PN20-I2	13,7	15,3	78	7,8	93,91	9,4	84,55	8,5	146	14,6
PN20-C4A	15,9	5,7	78	7,8	101,10	10,1	91,74	9,2	159	15,9
PN20-I6	9,3	2	4	0,4	35,54	3,6	35,06	3,5	60,6	6,1
PN20-J6	10	1,6	0.5 ¹	0,05	35,43	3,5	35,40	3,5	61,2	6,1
PN20-K6	9,7	2,4	0.5 ¹	0,05	37,77	3,8	37,77	3,7	65,3	6,5

¹ Limit of detection <1 g/kg replaced by 0.5 g/kg for graphical display

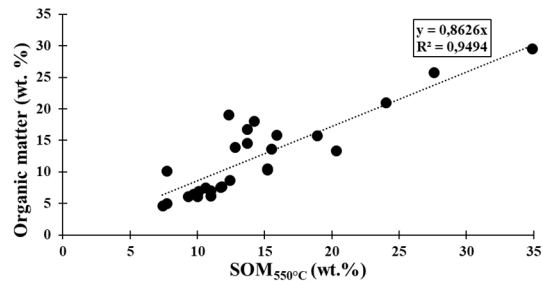
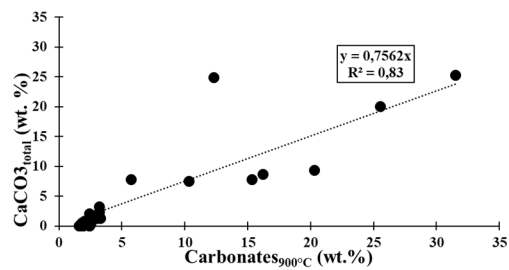


Table S4. Parameters of the WDS-XRF method (Internal calibration name : GEO_PP_34mm_2021).

A- Machine parameters for rays

Element Line	Na K α 1	Mg K α 1	Al K α 1	Si K α 1	P K α 1	K K α 1	Ca K α 1	Ti K α 1	Mn K α 1	Fe K α 1	Pb L β 1	Sb K α 1
Line energy (keV)	1,041	1,253	1,487	1,74	2,014	3,314	3,692	4,511	5,899	6,404	12,61	4,026
X-raytube (kV)	30	30	30	30	30	50	50	50	50	50	50	50
X-ray tube (mA)	33	33	20	20	33	20	10	20	20	10	20	20
Collimator	0,23	0,23	0,23	0,23	0,23	0,46	0,23	0,46	0,23	0,23	0,46	0,23
Detector	FPC	FPC	FPC	FPC	FPC	FPC	FPC	FPC	Sci	Sci	Sci	Sci
Analysing crystal	XS-55	XS-55	PET	PET	XS-Ge-CLIF-200	LIF-200	LIF-200	LIF-200	LIF-200	LIF-200	LIF200	LIF200
Peak (2 θ)	24,647	20,393	144,62	109,01	141	136,55	113,2	86,096	62,937	57,483	28,26	13,419

B- Calibration method parameters

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃
	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
Numbers of standards	12	12	12	12	11	12	12	12	12	11
Min	0,03%	0,08%	0,10%	0,62%	0,01%	0,04%	0,30%	0,01%	100	0,21%
Max	4,05%	21,80%	16,56%	90,36%	0,34%	5,43%	30,02%	7,69%	0,19%	24,75%
Standard deviation	0,28%	0,19%	0,91%	2,62%	0,02%	0,13%	0,47%	0,04%	60	0,41%
r ²	0,932	0,999	0,966	0,986	0,983	0,992	0,997	1,000	0,986	0,996
Limit of detection	48	35	69	124	5	13	19	9	5	25

	V	Cr	Co	Ni	Cu	Zn	As	Br	Rb	Sr	Zr	Ba	Pb	Sb
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Numbers of standards	11	10	11	9	11	11	5	7	11	12	11	12	12	9
Min	2	3	2	17	9	12	9	0	1	27	3	44	4	0
Max	768	94	93	241	112	274	41	60	213	1198	403	4057	1,39%	94
Standard deviation	8	2	2	7	4	7	4	0	3	9	9	66,7	82,6	2
r ²	0,999	0,996	0,996	0,990	0,981	0,991	0,892	1,000	0,998	0,999	0,994	0,997	1,000	0,995
Limit of detection	1	2	1	7	3	3	1	3	2	1	1	13	9	3

Table S5: Classification of the enrichment factor (EF, Chester and Stoner 1973; Reimann and de Caritat 2005) and the geoaccumulation index (I_{geo}, Müller et al. 1979).

EF Classification	Characterisation of the contamination	I _{geo} classification	Characterisation of the contamination
<1	no enrichment	<0	uncontaminated
1<EF<3	minor enrichment	0<I _{geo} <1	uncontaminated to moderately contaminated
3<EF<5	moderate enrichment	1<I _{geo} <2	moderately contaminated
5<EF<10	moderate to severe enrichment	2<I _{geo} <3	moderately to strongly contaminated
10<EF<25	severe enrichment	3<I _{geo} <4	strongly contaminated
25<EF<50	very severe enrichment	4<I _{geo} <5	strongly to extremely contaminated
EF>50	extreme enrichment	I _{geo} >5	extremely contaminated

Table S6: Physical and chemical properties of soils (n=27).

Sample Name	Soil type	pH ¹	Effectif CEC	Particle size distribution (without decarbonation) ²				
				Clays (0 to 0,002 mm)	Fine silt (0,002 to 0,02 mm)	Coarse silt (0,02 to 0,05 mm)	Fine sand (0,05 to 0,2 mm)	Coarse sand (0,2 to 2,0 mm)
<i>Unit</i>		<i>cmol±/kg</i>		<i>g/kg</i>	<i>g/kg</i>	<i>g/kg</i>	<i>g/kg</i>	<i>g/kg</i>
PN-AA1	high-contaminated soil	7,6	28,46	107	215	141	123	414
PN-B2A	high-contaminated soil	6,97	28,76	96	182	149	188	385
PN-B4	carbonates-poor soil	7,43	17,67	68	214	135	135	448
PN-D3	high-contaminated soil	6,63	42,58	97	263	222	170	248
PN-E3	high-contaminated soil	6,45	16,73	91	241	187	234	247
PN-G3	high-contaminated soil	6,5	21,82	140	351	169	129	211
PN-G5	carbonates-poor soil	6,22	16,59	108	348	149	133	262
PN-G8	carbonates-poor soil	7,8	12,92	80	269	136	136	379
PN-H11	carbonates-poor soil	7,45	16,53	125	318	163	146	248
PN-H5	carbonates-poor soil	6,24	16,58	158	365	165	145	167
PN-I3	high-contaminated soil	7,11	25,99	132	324	158	170	216
PN-K1	carbonates-rich soil	7,76	25,78	102	305	228	140	225
PN-K5	carbonates-poor soil	7,07	20,51	138	304	134	123	301
PN-K9	carbonates-poor soil	7,76	13,27	100	250	123	134	393
PN-L2	high-contaminated soil	7,55	31,15	132	328	242	179	119
PN-M3	carbonates-rich soil	7,69	24,50	151	335	209	161	144
PN-M5	carbonates-poor soil	6,15	15,45	165	350	146	107	232
PN-N4	carbonates-poor soil	6,38	16,48	161	347	146	103	243
PN-O1	high-contaminated soil	7,43	19,37	49	201	177	214	359
PN-P2	carbonates-poor soil	7,17	12,53	67	267	160	172	334
PN-K3	carbonates-rich soil	7,65	25,22	126	377	210	128	159
PN-K4	carbonates-rich soil	7,66	26,99	128	348	212	133	179
PN-I2	carbonates-rich soil	7,67	26,33	104	399	242	160	95
PN-C4A	high-contaminated soil	7,79	22,02	78	229	161	174	358
PN-I6	carbonates-poor soil	7,02	14,19	76	288	184	169	283
PN-J6	carbonates-poor soil	6,37	14,87	128	342	153	126	251
PN-K6	carbonates-poor soil	6,36	15,89	149	321	133	123	274

CHAPITRE 3 | Modes de dispersion du Pb dans les sols miniers

Sample Name	Total limestone (CaCO _{3T}), Total Carbone organic (COT), Total Nitrogen (N _T) ³					
	Measured			Calculated		
	Nitrogen total (N _T)	Carbonates total (CaCO _{3T})	Carbone total (C _T)	Total Organic Carbone ⁴ (TOC)	C/N	Organic matter ⁵
Unit	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg
PN-AA1	4,27	249	107,25	77,37	18,10	134
PN-B2A	5,04	13	150,49	148,93	29,60	258
PN-B4	3,76	8	51,15	50,19	13,30	86,8
PN-D3	6,17	13	172,60	171,04	27,70	296
PN-E3	4,39	11	80,24	78,92	18,00	137
PN-G3	5,36	3	61,24	60,88	11,40	105
PN-G5	4,10	<1	43,61	43,61	10,60	75,4
PN-G8	2,66	33	30,99	27,03	10,20	46,8
PN-H11	3,75	17	42,32	40,28	10,70	69,7
PN-H5	4,09	<1	44,23	44,23	10,80	76,5
PN-I3	6,05	8	60,97	60,01	9,91	104
PN-K1	2,74	253	140,51	110,15	40,20	191
PN-K5	4,76	3	43,99	43,63	9,17	75,5
PN-K9	2,91	21	31,65	29,13	10,00	50,4
PN-L2	6,44	75	100,59	91,59	14,20	158
PN-M3	5,45	87	90,59	80,15	14,70	139
PN-M5	3,94	<1	36,15	36,15	9,17	62,5
PN-N4	4,22	<1	40,50	40,50	9,60	70,1
PN-O1	2,52	24	124,10	121,22	48,20	210
PN-P2	2,83	3	59,45	59,09	20,90	102
PN-K3	5,42	94	108,37	97,09	17,90	168
PN-K4	6,29	201	129,00	104,88	16,70	181
PN-I2	5,41	78	93,91	84,55	15,60	146
PN-C4A	2,85	78	101,10	91,74	32,20	159
PN-I6	2,97	4	35,54	35,06	11,80	60,6
PN-J6	3,69	<1	35,43	35,40	9,58	61,2
PN-K6	4,12	<1	37,77	37,77	9,16	65,3

Unit	Exchangeable cobaltihexammine Al, Ca, Fe, Mg, Mn, K, Na (ICP-AES/EAF) ⁶						
	Aluminium (Al)	Calcium (Ca)	Iron (Fe)	Magnesium (Mg)	Manganese (Mn)	Potassium (K)	Sodium (Na)
	cmol+/kg	cmol+/kg	cmol+/kg	cmol+/kg	cmol+/kg	cmol+/kg	cmol+/kg
PN-AA1	0,02	30,31	0,01	0,84	0,01	0,21	0,01
PN-B2A	<0,02	25,39	<0,005	2,25	0,02	0,13	0,01
PN-B4	0,02	15,02	0,01	3,04	0,01	0,23	0,03
PN-D3	0,04	32,62	0,02	6,70	0,07	0,08	<0,0050
PN-E3	<0,02	12,55	0,01	1,96	0,04	0,06	0,01
PN-G3	<0,02	16,94	0,01	3,37	0,03	0,13	0,01
PN-G5	<0,02	13,19	<0,005	2,34	0,04	0,13	0,03
PN-G8	<0,02	13,47	<0,005	0,81	<0,005	0,08	0,02
PN-H11	<0,02	15,94	<0,005	1,15	<0,005	0,26	0,02
PN-H5	0,03	13,60	0,01	1,97	0,07	0,07	0,05
PN-I3	<0,02	21,41	0,01	3,62	0,01	0,15	0,03
PN-K1	<0,02	21,23	<0,005	4,32	<0,005	0,08	0,01
PN-K5	0,02	16,56	0,01	3,47	0,01	0,12	0,04
PN-K9	0,02	13,13	0,01	0,87	<0,005	0,17	0,07
PN-L2	0,03	24,00	0,01	6,40	<0,005	0,11	0,03
PN-M3	<0,02	20,59	0,01	4,63	0,01	0,12	0,04
PN-M5	0,02	12,23	<0,005	3,06	0,05	0,11	0,11
PN-N4	0,03	14,05	0,01	2,42	0,05	0,11	0,07
PN-O1	<0,02	17,28	<0,005	1,84	0,01	0,29	0,01
PN-P2	<0,02	11,29	0,01	1,42	0,01	0,10	0,01
PN-K3	0,06	21,53	0,01	3,53	<0,005	0,12	0,02
PN-K4	<0,02	25,33	<0,005	2,70	<0,005	0,25	0,06
PN-I2	<0,02	22,73	<0,005	3,30	<0,005	0,11	0,02
PN-C4A	<0,02	21,05	<0,005	0,62	<0,005	0,08	0,01
PN-I6	<0,02	11,18	0,01	1,78	0,02	0,08	0,05
PN-J6	<0,02	11,11	<0,005	1,98	0,08	0,12	0,03
PN-K6	<0,02	11,67	<0,005	2,36	0,12	0,38	0,01

¹ NF ISO 10390 (pH)

² NF X 31-107 (Particle size distribution)

³ NF ISO 10693 (CaCO_{3T}), NF ISO 10694 (C_T) and NF ISO 13878 (N_T)

⁴ TOC=C_T-(0.12*CaCO_{3T})

⁵ Organic matter = TOC*1.73

⁶ NF ISO 23470 (Exchangeable cobaltihexammine Al, Ca, Fe, Mg, Mn, K, Na)

Table S7: XRD mineralogical results on soil samples (n=10).

Echantillon	Type_sol	Quartz	Plagioclase	Dolomite	Calcite	Barite	Rutile	Hematite	Amphibole	Cerussite	Chlorite	K-mica	Na-Mica	Talc	Vermiculite	Mica-Exp.	Amorphous	TOTAL	
H5	carbonates-poor soil	20.6	19.3	0.6	-	-	0.9	0.3	-	-	13.7	27.1	Tr.	3.1	0.9	7.6	6	100	
K5	carbonates-poor soil	23.7	16.4	1.3	-	0.1	1	0.1	-	-	12.2	26.6	Tr.	3.4	1.3	6.6	7.5	100	
P2	carbonates-poor soil	26.8	24.4	1.2	-	-	0.6	0.5	0.6	-	13.1	22	Tr.	0.7	0.3	9.8	0	100	
K1	carbonates-rich soil	5.9	3.2	65.5	10.3	-	0.2	0.1	-	-	3.2	9	Tr.	0.2	0.1	-	2.3	100	
M3	carbonates-rich soil	14.1	11.4	31.9	0.5	-	0.8	0.4	-	-	7.6	18.7	Tr.	0.3	0.3	8	5.9	100	
D3	high-contaminated soil	29	10.3	4.3	-	1.7	0.2	0.1	-	-	4.8	8.8	Tr.	0.5	0.1	10.3	30.1	100	
E3	high-contaminated soil	27.6	16.1	3.7	-	1.1	0.7	0.2	-	1.1	9.8	21.2	Tr.	1.8	0.3	8.3	8.1	100	
I3	high-contaminated soil	22.9	16.5	1.7	0.7	0.2	1.2	0.1	-	-	12.4	29.2	Tr.	4.5	0.5	-	10.2	100	
L2	high-contaminated soil	18.4	12.4	19.6	-	0.2	0.5	0.3	-	0.4	7.3	20.2	Tr.	0.5	0.2	10	10.1	100	
O1	high-contaminated soil	22.7	11.3	4.6	1.2	0.6	0.8	0.4	-	0.8	7	17.7	Tr.	1.5	0.1	-	31.3	100	
slag heap	technosol	28.2	-	-	-	1.8	-	-	-	-	-	9.3	-	-	-	-	-	60.2	100

The uncertainty on the relative proportions of the different phases is in the order of $\pm 1-2\%$ (5% for the amorphous contribution).

CHAPITRE 3 | Modes de dispersion du Pb dans les sols miniers

ID	SampleName	NORTH	EAST	Group of soil	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃
61	PN20-I3	45.526691	6.7828366	high-contaminated topsoil	1.33	4.04	14.46	47.66	0.29	3.05	1.84	0.71	0.13	6.25
62	PN20-I4	45.526703	6.78334713	carbonates-poor soil	1.56	3.38	16.07	53.11	0.22	3.18	0.89	0.73	0.10	5.77
63	PN20-I5	45.526668	6.7838645	carbonates-poor soil	1.59	3.60	15.78	51.09	0.25	2.90	0.89	0.79	0.11	6.42
64	PN20-I6	45.526668	6.78431273	carbonates-poor soil	1.79	3.47	15.17	53.58	0.19	2.75	1.03	0.71	0.11	5.84
65	PN20-I7	45.526661	6.7849226	carbonates-poor soil	1.63	3.80	15.99	52.85	0.15	3.10	0.86	0.80	0.11	6.19
66	PN20-I8	45.526596	6.78534222	carbonates-poor soil	2.29	3.14	15.28	56.14	0.14	2.51	2.11	0.81	0.10	6.66
67	PN20-I9	45.526615	6.78567362	carbonates-poor soil	2.38	3.08	14.79	55.43	0.14	2.27	3.92	0.79	0.10	7.35
68	PN20-J1	45.527145	6.78125238	carbonates-rich soil	0.60	9.63	6.45	21.14	0.17	1.31	18.43	0.34	0.04	4.99
69	PN20-J10	45.527123	6.78571081	carbonates-poor soil	2.24	2.78	14.88	56.69	0.12	2.45	1.49	0.78	0.10	6.24
70	PN20-K10	45.527309	6.78542233	high-contaminated topsoil	2.39	3.13	15.54	57.43	0.13	2.48	2.38	0.81	0.10	6.89
71	PN20-J2C	45.527107	6.78182507	carbonates-rich soil	0.63	5.25	7.55	24.43	0.22	1.51	11.31	0.41	0.10	5.72
72	PN20-J3	45.527092	6.7823267	carbonates-poor soil	0.91	7.49	9.98	31.78	0.34	1.92	13.00	0.51	0.08	6.87
73	PN20-J4	45.527042	6.78286505	carbonates-poor soil	1.67	3.75	16.33	52.64	0.22	2.98	0.83	0.79	0.10	6.40
74	PN20-J5	45.52705	6.7835333	carbonates-poor soil	1.71	3.54	16.20	53.57	0.20	2.89	0.97	0.78	0.10	6.18
75	PN20-J6	45.527058	6.78385067	carbonates-poor soil	1.55	3.40	15.64	51.59	0.24	2.83	0.74	0.76	0.13	6.12
76	PN20-J7	45.526993	6.78440046	carbonates-poor soil	1.69	3.73	17.02	53.84	0.16	3.04	0.60	0.84	0.12	6.49
77	PN20-J8	45.527008	6.78492212	carbonates-poor soil	1.94	3.11	14.71	51.70	0.23	2.53	1.68	0.76	0.09	6.34
78	PN20-J9	45.52697	6.78540707	carbonates-rich soil	2.34	2.77	14.82	56.41	0.14	2.34	1.48	0.80	0.10	6.28
79	PN20-K1	45.527634	6.780828	carbonates-poor soil	0.54	12.52	4.75	16.89	0.08	0.90	25.61	0.24	0.02	3.78
80	PN20-K2	45.527462	6.7813502	carbonates-rich soil	0.64	11.37	4.94	21.11	0.13	1.00	23.09	0.27	0.03	4.24
81	PN20-K3	45.527466	6.78191948	carbonates-rich soil	0.85	8.71	10.01	31.19	0.25	1.90	14.49	0.49	0.07	6.90
82	PN20-K4	45.527481	6.78239441	carbonates-rich soil	0.70	10.37	7.63	24.75	0.29	1.49	19.28	0.37	0.04	5.61
83	PN20-K5	45.527378	6.78281927	carbonates-poor soil	1.44	4.32	15.43	50.86	0.24	3.24	1.26	0.75	0.11	6.22
84	PN20-K6	45.527431	6.78340912	carbonates-poor soil	1.54	3.69	15.78	52.57	0.24	3.18	0.79	0.76	0.11	6.12
85	PN20-K7	45.527363	6.7838769	carbonates-poor soil	1.95	1.82	14.05	65.02	0.14	3.21	2.42	0.58	0.07	4.29
86	PN20-K8	45.527275	6.78461981	carbonates-poor soil	1.71	3.44	15.02	51.14	0.16	2.84	3.14	0.72	0.09	6.54
87	PN20-K9	45.527321	6.78501034	carbonates-poor soil	1.92	3.48	15.63	54.00	0.17	2.79	1.92	0.77	0.08	6.42
88	PN20-L1	45.527813	6.78081989	carbonates-rich soil	0.57	9.79	5.22	19.06	0.16	1.11	19.41	0.29	0.03	4.30
89	PN20-L2	45.527805	6.78138351	high-contaminated topsoil	1.04	5.40	11.14	36.91	0.22	2.01	7.58	0.58	0.11	6.78
90	PN20-L3	45.527763	6.78182983	carbonates-rich soil	0.83	7.88	10.21	32.33	0.36	2.05	12.52	0.50	0.09	6.91
91	PN20-L4	45.527752	6.78237534	carbonates-rich soil	0.74	10.68	8.12	27.23	0.27	1.62	17.77	0.40	0.05	5.95
92	PN20-L5	45.527752	6.7828579	carbonates-poor soil	1.76	4.00	15.82	55.27	0.18	3.11	1.08	0.74	0.09	6.19
93	PN20-L6	45.527725	6.78322744	carbonates-poor soil	1.62	3.92	16.69	53.47	0.20	3.15	0.71	0.81	0.10	6.27
94	PN20-L7	45.527794	6.78403759	carbonates-poor soil	1.72	3.51	15.97	52.14	0.29	3.04	0.87	0.79	0.10	6.27
95	PN20-L8	45.527687	6.78439188	carbonates-poor soil	2.06	1.73	14.20	67.83	0.12	3.37	1.94	0.58	0.06	4.17
96	PN20-L9	45.527695	6.78498125	carbonates-poor soil	2.51	3.06	15.20	56.65	0.17	2.47	2.16	0.92	0.10	7.16
97	PN20-M1	45.528023	6.78072071	carbonates-rich soil	0.60	8.80	6.78	21.52	0.18	1.38	16.74	0.36	0.04	5.25
98	PN20-M2	45.528126	6.78135824	carbonates-rich soil	0.87	7.45	9.49	32.30	0.31	1.80	12.75	0.50	0.08	6.73
99	PN20-M3	45.528126	6.78187466	carbonates-rich soil	1.08	7.75	11.32	35.36	0.24	2.07	12.15	0.61	0.07	7.67
100	PN20-M4	45.528141	6.78240013	carbonates-rich soil	0.75	10.07	7.88	25.49	0.26	1.49	19.01	0.39	0.05	6.00
101	PN20-M5	45.528198	6.78288889	carbonates-poor soil	1.56	3.80	16.36	51.45	0.21	3.14	0.78	0.81	0.11	6.52
102	PN20-M6	45.528111	6.78342104	carbonates-poor soil	1.64	1.91	15.84	60.47	0.25	3.66	1.78	0.57	0.08	4.49
103	PN20-N1	45.528568	6.78099394	carbonates-rich soil	0.50	8.92	4.22	29.29	0.06	1.01	25.75	0.17	0.02	2.29
104	PN20-N2	45.528549	6.78141499	carbonates-poor soil	1.30	3.08	16.96	57.25	0.16	4.06	1.57	0.64	0.11	5.16
105	PN20-N3	45.528542	6.78188038	carbonates-rich soil	0.94	9.94	9.45	30.46	0.21	1.65	16.23	0.50	0.06	7.07
106	PN20-N4	45.528496	6.78241921	carbonates-poor soil	1.60	3.59	16.32	50.80	0.24	2.88	0.83	0.80	0.11	6.63
107	PN20-N5	45.528442	6.78289986	carbonates-poor soil	1.89	3.44	16.02	57.73	0.14	3.09	2.17	0.71	0.10	6.07
108	PN20-O1	45.528938	6.78106165	high-contaminated topsoil	1.32	2.55	12.28	47.05	0.17	2.28	3.24	0.54	0.12	5.55
109	PN20-O2	45.528901	6.7814483	carbonates-poor soil	1.39	2.50	16.64	55.82	0.13	3.86	1.92	0.70	0.10	4.94
110	PN20-O3	45.528767	6.78195667	carbonates-poor soil	1.66	1.37	12.08	70.40	0.22	2.85	1.13	0.47	0.09	3.22
111	PN20-O4	45.528778	6.78239012	carbonates-poor soil	1.74	4.53	14.18	50.08	0.15	2.41	6.46	0.73	0.08	7.75
112	PN20-P1	45.529469	6.780996	carbonates-poor soil	2.08	3.03	15.11	52.63	0.21	2.53	1.68	0.88	0.11	6.93
113	PN20-P2	45.529423	6.781454	carbonates-poor soil	2.15	2.99	15.36	53.55	0.20	2.54	1.53	0.86	0.12	6.77
114	PN20-P3	45.529232	6.781889	carbonates-poor soil	2.49	3.11	15.63	58.96	0.12	2.47	2.46	0.82	0.10	6.90
115	PN20-P4	45.528667	6.782272	carbonates-poor soil	2.57	3.01	14.72	57.16	0.14	2.36	2.54	0.90	0.11	7.17
116	PN20-Q1	45.529221	6.77973843	high-contaminated topsoil	1.22	5.56	10.91	43.88	0.16	2.08	9.32	0.52	0.08	5.91
117	PN20-Q2	45.529537	6.77989626	carbonates-poor soil	2.32	2.88	15.13	54.15	0.22	2.46	1.69	0.95	0.11	6.80

CHAPITRE 3 | Modes de dispersion du Pb dans les sols miniers

ID	SampleName	V	Cr	Co	Ni	Cu	Zn	As	Br	Rb	Sr	Zr	Ba	Pb	Sb	SOM	Carbonates	TOTAL	EF _{Pb}	EF _{Pb} (Td)	Igeo _{Pb}
61	PN20-I3	105	71	16	48	47	171	205	12	105	84	163	1615	4942	33	15	3	98	39	61	5
62	PN20-I4	106	76	15	47	41	109	0	6	107	59	181	1143	1572	15	11	2	98	12	19	4
63	PN20-I5	116	80	16	60	51	135	24	5	97	62	175	837	1587	13	12	2	97	14	18	4
64	PN20-I6	106	70	15	54	57	165	0	6	84	102	162	2311	5760	52	9	2	97	57	71	5
65	PN20-I7	119	79	16	54	37	111	13	5	98	59	175	776	413	6	10	2	98	4	5	2
66	PN20-I8	112	65	19	42	26	99	17	0	74	83	182	533	8	0	6	2	97	0	0	-4
67	PN20-I9	103	61	22	37	26	97	18	0	65	123	177	554	24	2	5	3	98	0	0	-2
68	PN20-J1	37	31	16	0	19	69	320	12	62	305	77	332	1102	0	24	23	111	15	29	3
69	PN20-J10	108	70	18	43	23	91	19	1	73	84	194	514	0	3	7	2	96	0	0	<LD
70	PN20-K10	112	69	20	42	26	99	18	1	74	102	186	538	0	2	4	3	98	0	0	0
71	PN20-J2C	56	46	15	7	44	256	2171	25	80	276	101	3994	8649	26	38	13	110	91	183	6
72	PN20-J3	60	39	20	21	47	161	1218	17	82	277	115	1599	6449	14	55	5	135	66	111	6
73	PN20-J4	116	79	16	55	41	118	12	4	96	59	170	684	611	4	10	2	97	5	7	2
74	PN20-J5	115	78	16	53	39	116	0	5	94	61	171	800	997	8	9	2	97	9	11	3
75	PN20-J6	114	85	16	56	51	155	5	8	96	67	164	1442	4720	32	10	2	95	41	55	5
76	PN20-J7	126	83	17	58	43	130	0	2	100	61	182	1287	1904	20	7	2	96	16	20	4
77	PN20-J8	106	71	17	49	42	124	17	5	81	78	181	687	867	10	10	2	96	9	10	3
78	PN20-J9	111	72	17	42	20	95	17	2	72	86	187	526	42	1	7	2	96	0	0	-2
79	PN20-K1	23	20	16	0	9	35	66	4	39	381	58	200	141	0	12	32	109	3	5	0
80	PN20-K2	26	20	14	0	12	51	156	6	41	353	66	311	503	0	15	27	110	10	16	2
81	PN20-K3	58	38	22	11	34	149	616	16	78	247	104	1436	3126	6	14	20	109	34	57	5
82	PN20-K4	40	31	18	0	26	88	331	17	66	320	82	542	1296	0	14	26	111	17	31	3
83	PN20-K5	112	79	16	62	36	114	25	5	107	60	169	658	661	7	12	3	98	5	8	2
84	PN20-K6	113	78	16	51	37	116	0	5	106	57	165	842	1696	12	10	2	97	13	20	4
85	PN20-K7	68	45	10	11	18	77	11	0	104	89	198	494	31	2	3	2	99	0	0	-2
86	PN20-K8	98	72	19	48	42	123	23	5	85	90	158	1334	1539	16	10	3	99	15	19	4
87	PN20-K9	109	80	17	46	35	105	14	3	84	68	166	584	203	5	8	2	97	2	2	1
88	PN20-L1	33	33	14	0	19	56	205	12	53	312	71	260	654	0	28	23	111	10	20	2
89	PN20-L2	77	51	20	38	95	267	2145	27	89	211	129	2378	15037	51	19	10	103	141	229	7
90	PN20-L3	63	45	21	15	40	182	919	22	88	246	106	2149	5021	16	19	17	110	48	89	5
91	PN20-L4	45	29	18	0	28	115	423	14	70	296	88	913	1810	1	15	24	112	22	40	4
92	PN20-L5	112	74	17	51	33	108	2	6	100	58	165	608	381	6	9	2	100	3	5	2
93	PN20-L6	120	83	17	59	42	115	11	1	100	56	183	675	357	6	8	2	97	3	4	1
94	PN20-L7	117	80	17	54	40	120	15	3	98	58	173	741	609	4	11	2	98	5	7	2
95	PN20-L8	69	44	10	18	19	76	12	1	106	69	202	462	13	3	1	2	99	0	0	-3
96	PN20-L9	124	64	21	33	27	114	18	0	74	100	194	543	10	4	4	2	97	0	0	-4
97	PN20-M1	44	38	16	0	23	84	353	14	65	271	82	357	1249	0	29	20	111	16	30	3
98	PN20-M2	62	43	21	13	55	184	1099	20	79	236	117	1291	6003	16	18	16	108	64	105	6
99	PN20-M3	72	42	23	10	29	109	121	9	80	206	137	679	615	1	13	16	108	6	9	2
100	PN20-M4	42	32	20	0	21	77	215	9	65	318	84	538	785	0	15	24	111	10	18	3
101	PN20-M5	122	82	17	57	39	119	21	4	108	56	176	718	365	8	11	2	98	3	4	1
102	PN20-M6	72	51	10	24	26	100	4	0	130	78	185	656	131	5	8	2	101	1	2	0
103	PN20-N1	16	14	9	0	9	95	94	12	37	749	81	750	355	0	4	26	103	8	18	1
104	PN20-N2	83	56	13	24	28	136	8	2	153	58	190	718	147	4	6	3	99	1	2	0
105	PN20-N3	56	36	22	1	25	96	250	8	67	249	107	795	1151	0	11	22	109	14	20	3
106	PN20-N4	121	88	17	60	52	125	26	1	98	61	169	751	855	7	11	2	97	7	9	3
107	PN20-N5	101	69	17	48	34	95	0	0	93	81	161	668	227	4	5	3	99	2	3	1
108	PN20-O1	78	61	14	41	84	354	576	17	94	212	139	2736	12950	60	24	3	104	116	212	7
109	PN20-O2	91	67	13	24	23	236	0	3	141	83	231	1216	2064	26	10	3	101	12	26	4
110	PN20-O3	57	69	7	13	22	96	5	3	107	55	177	479	40	4	5	1	100	0	1	-2
111	PN20-O4	93	57	23	31	35	106	26	3	75	112	158	682	313	4	6	8	102	3	4	1
112	PN20-P1	123	74	20	38	35	136	12	6	79	89	203	683	626	6	8	2	95	7	6	2
113	PN20-P2	121	71	19	38	31	125	9	2	78	88	199	701	468	5	8	2	96	5	5	2
114	PN20-P3	112	67	20	42	23	93	15	0	70	98	185	560	13	2	2	3	98	0	0	-3
115	PN20-P4	119	61	20	25	22	102	15	1	66	104	190	531	60	1	3	2	96	1	1	-1
116	PN20-Q1	64	44	18	22	62	283	880	14	80	243	126	2509	11525	48	10	13	103	121	196	6
117	PN20-Q2	129	67	18	34	30	124	9	0	77	93	213	626	356	5	15	1	103	4	3	1

Table S9 : Single extraction test results from distilled water, humic acid and EDTA extractions on soil samples (n=21).

SampleName	Total Pb _{tot}	Measured Pb _{water}	Extracted Pb _{water}	Part_Extracted Pb _{water}	Measured Pb _{humic}	Extracted Pb _{humic}	Part_Extracted Pb _{humic}	Measured Pb _{EDTA}	Extracted Pb _{EDTA}	Part_Extracted Pb _{EDTA}
PN20_AA1	7211	1.04	11.44	0.16	1.53	15.35	0.21	1.61	7247.71	100.51
PN20_B2A	25584	3.62	39.81	0.16	1.89	197.11	0.77	1.55	24237.41	94.74
PN20_B4	173	<LD ¹	N.Q.	N.Q.	0.01 ²	0.10	0.06	0.59	131.73	76.14
PN20_D3	35808	6.29	34.57	0.10	0.98	100.31	0.28	1.42	24127.17	67.38
PN20_E3	22667	3.84	42.21	0.19	1.28	135.55	0.60	1.46	25423.26	112.16
PN20_G3	12249	2.74	30.19	0.25	12.24	122.36	1.00	0.79	14650.99	119.61
PN20_G5	3808	0.88	9.70	0.25	2.20	22.05	0.58	0.94	4198.48	110.25
PN20_G8	130	<LD ¹	N.Q.	N.Q.	<LD ¹	N.Q.	N.Q.	0.32	70.41	54.16
PN20_H11	93	<LD ¹	N.Q.	N.Q.	0.01 ²	0.10	0.11	0.20	45.45	48.87
PN20_H5	4236	0.73	7.98	0.19	1.26	12.58	0.30	0.96	4252.03	100.38
PN20_I3	4942	0.56	6.18	0.13	0.95	9.48	0.19	1.12	4970.45	100.58
PN20_K1	141	<LD ¹	N.Q.	N.Q.	<LD ¹	N.Q.	N.Q.	0.33	73.83	52.36
PN20_K4	1296	0.09	0.98	0.08	0.22	2.24	0.17	0.24	1048.02	80.87
PN20_K5	661	0.01 ²	0.11	0.02	0.10	1.00	0.15	1.14	508.94	76.99
PN20_K9	203	<LD ¹	N.Q.	N.Q.	<LD ¹	N.Q.	N.Q.	0.52	122.33	60.26
PN20_L2	15037	1.68	18.47	0.12	7.36	73.59	0.49	0.97	17043.55	113.34
PN20_M3	615	0.01 ²	0.11	0.02	0.01 ²	0.10	0.02	1.01	450.56	73.26
PN20_M5	364	0.01 ²	0.11	0.03	0.04	0.44	0.14	1.14	248.33	68.22
PN20_N4	855	0.86	0.86	0.10	0.21	2.14	0.25	1.77	750.29	87.75
PN20_O1	12950	0.74	8.12	0.06	4.20	42.03	0.32	0.83	14516.15	112.09
PN20_P2	468	0.01 ²	0.11	0.02	0.06	0.63	0.13	1.57	356.63	76.20

Figure S1 : Hierarchical clustering on soil samples (n=117) to identify 3 main soil types : A) Hierarchical tree; B) Inertia; C) Representation of the clusters.

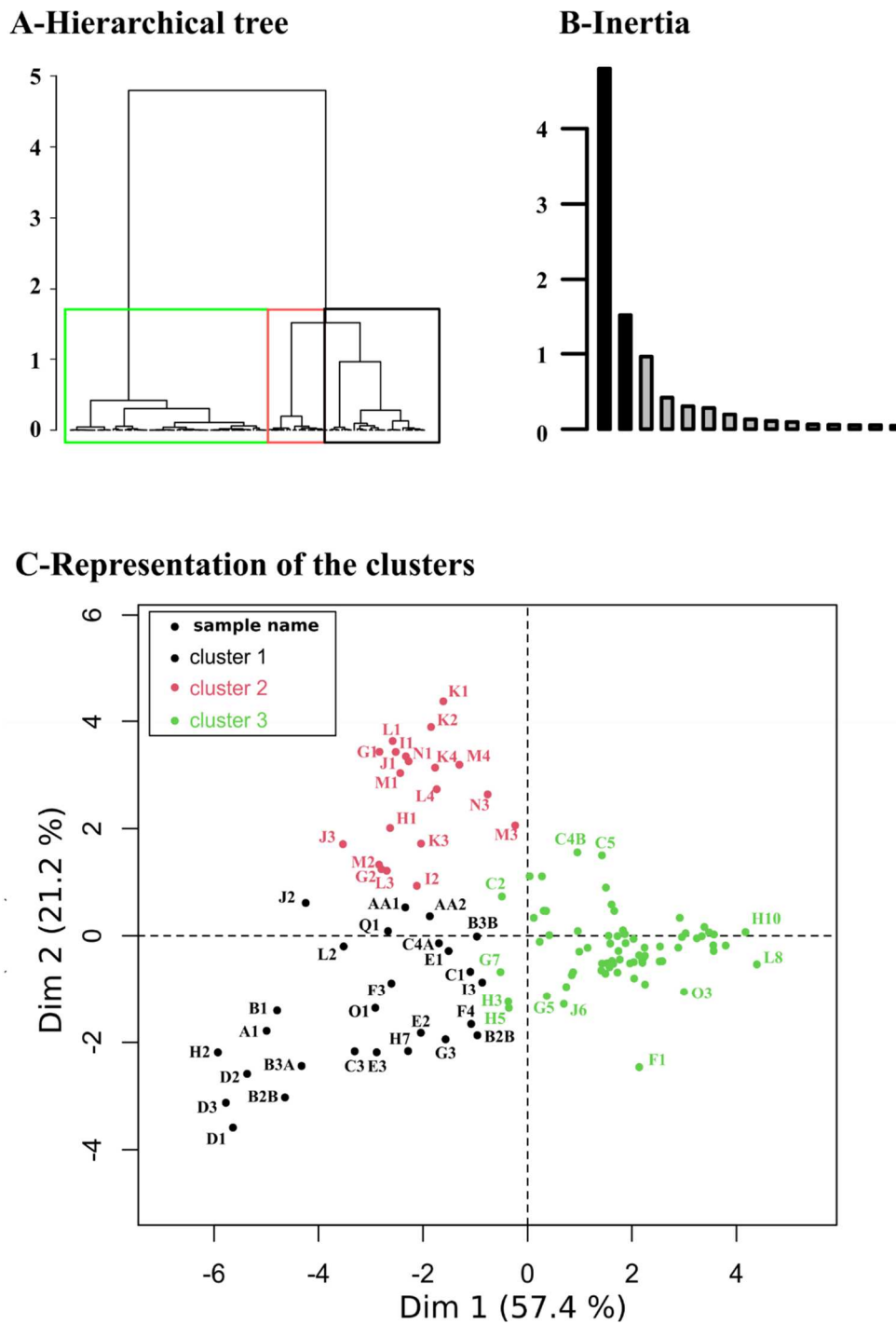


Figure S2 : XRD patterns for the three soil types.

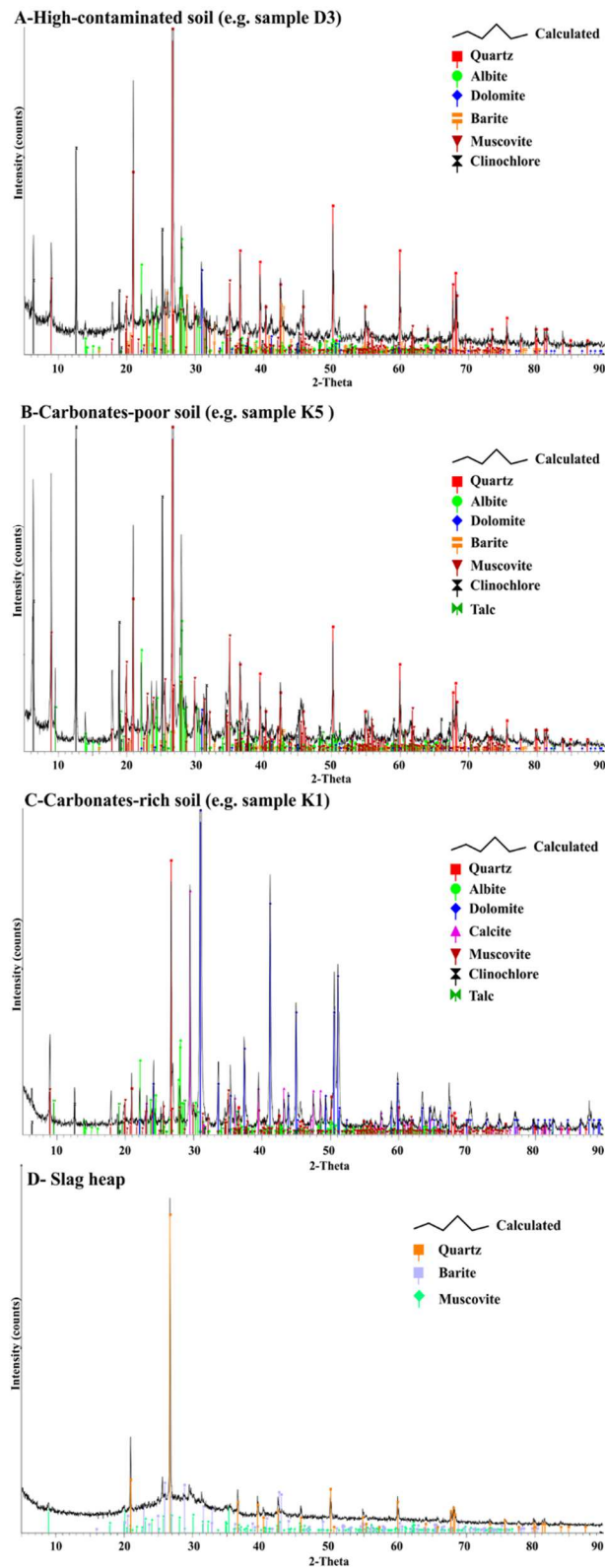
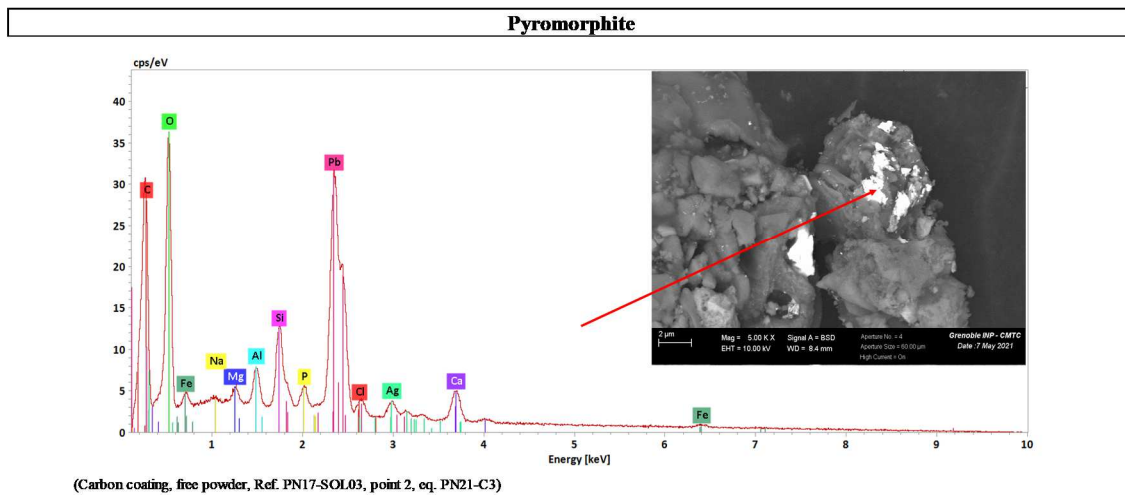
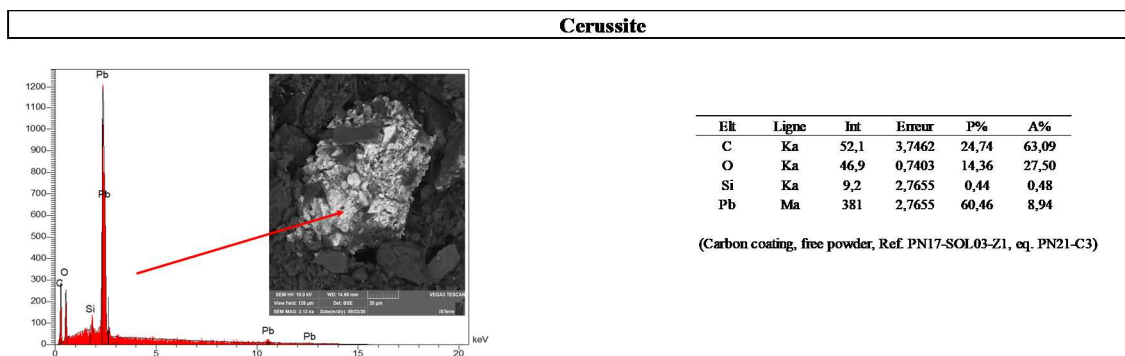
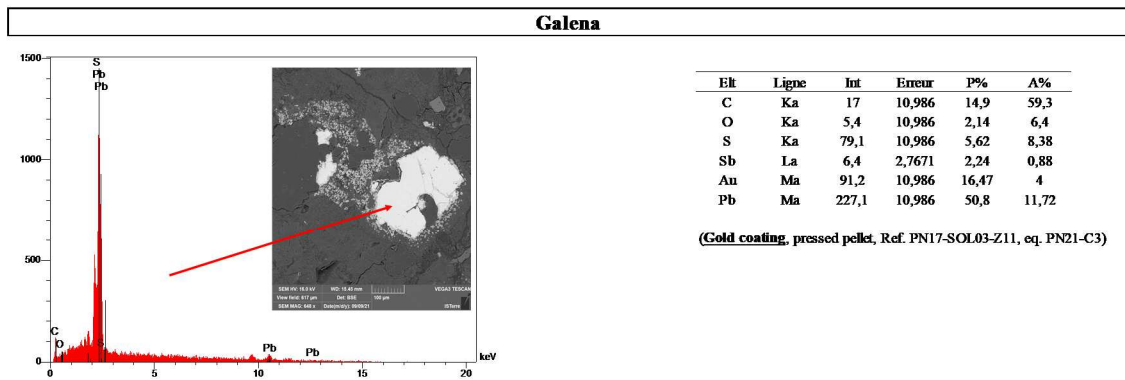
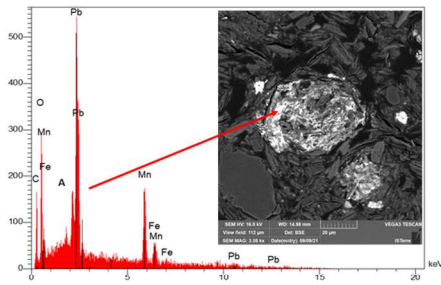


Figure S2 : SEM-EDX spectra of Pb-bearing phases.

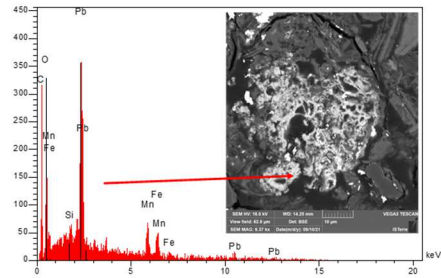


Mn-Fe-Pb (hydr-)oxides



Elt	Ligne	Int	Erreur	P%	A%
C	Ka	20.2	8,7234	17,45	44,7
O	Ka	43.8	8,7234	17,38	33,41
Mn	Ka	47.7	2,0119	14,83	8,3
Fe	Ka	10.2	2,0119	3,76	2,07
Pb	Ma	105	8,7234	30,09	4,47

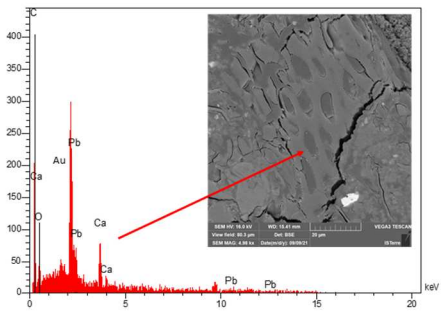
(Gold coating, pressed pellet, Ref. PN20-G3-Z3-1)



Elt	Ligne	Int	Erreur	P%	A%
C	Ka	43.4	4,9773	31,27	55,83
O	Ka	59.1	4,9773	24,67	33,06
Mn	Ka	22.9	0,7105	6,92	2,7
Fe	Ka	12.2	0,7105	4,38	1,68
Pb	Ma	106.3	7,8294	26,86	2,78

(Carbon coating, pressed pellet, Ref. PN20-L2-Z7-3)

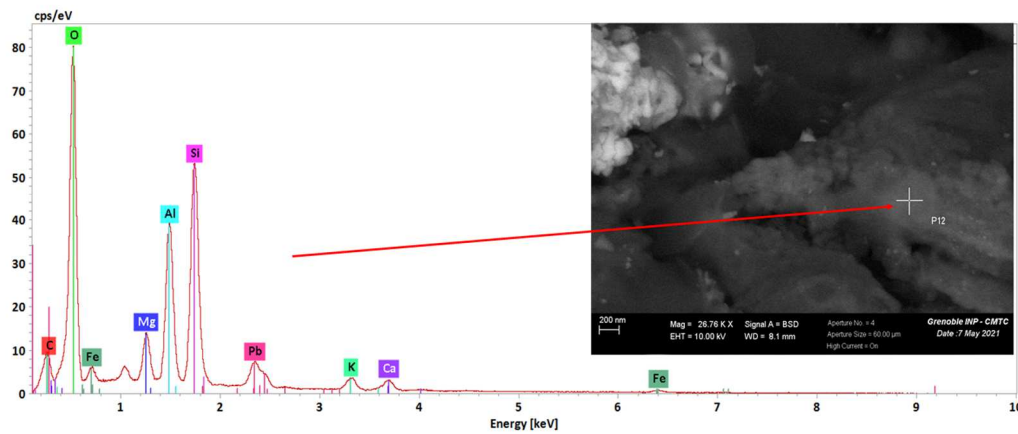
Pb adsorbed on coal



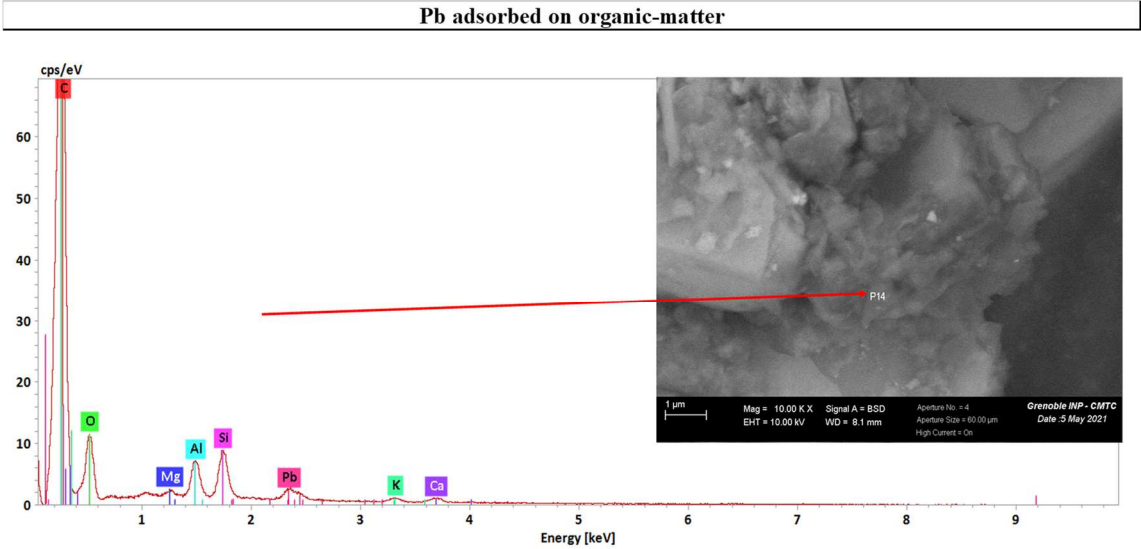
Elt	Ligne	Int	Erreur	P%	A%
C	Ka	54.4	5,0582	51,61	79,72
O	Ka	13.2	5,0582	11,6	13,45
Ca	Ka	19.5	1,0195	4,21	1,95
Au	Ma	61.2	5,0582	21,14	1,99
Pb	Ma	13	5,0582	5,92	0,53

(Gold coating, pressed pellet, Ref. PN17-SOL03-Z6-4)

Pb adsorbed on clay



(carbon coating, pressed pellet, Ref. PN21-L2-12)

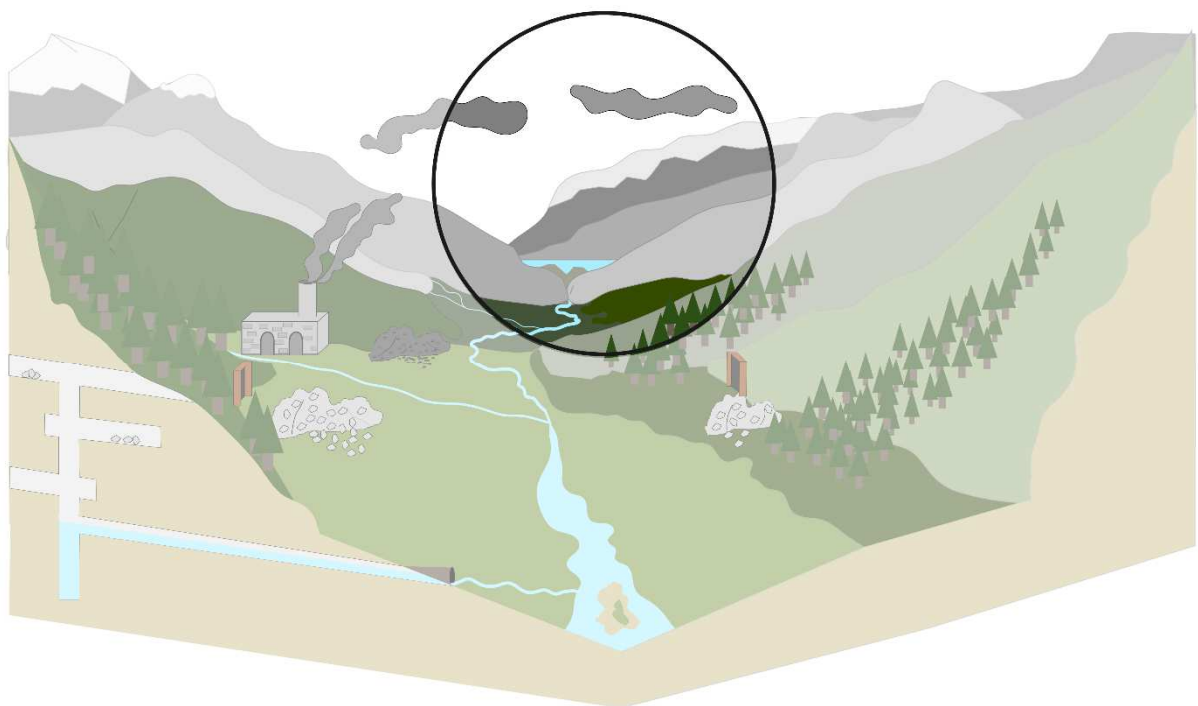


(Carbon coating, free powder, Ref. PN19-SOL06-14)

Chapitre 4 |
Héritage à long-terme
des fumées pyrométallurgiques
[Article 2]

Chapitre 4 | Héritage à long-terme des fumées pyrométallurgiques

Ce chapitre se concentre sur l'étude des sédiments lacustres du lac de le La Plagne, situé 7 km en amont du site minier, et sur les sols de son bassin versant. Les travaux présentés visent à caractériser l'héritage métallurgique laissé par les fumées pyrométallurgiques lors du traitement du minerai de la mine de Pb-Ag de Piesey-Nancroix. Les matériels supplémentaires de ce chapitre sont disponibles en fin de chapitre et sont signalés par un S.



ARTICLE 2 | Submitted to SCIENCE OF THE TOTAL ENVIRONMENT

Submitted online on the 8th of March 2023, under review.

**The Legacy of Metallurgical Atmospheric Contamination in a Mountainous Catchment :
A Delayed Response of Pb Contamination**

Floriane Guillevic¹, Magali Rossi¹, Jérôme Poulenard¹, Pierre Sabatier¹, Anne-Lise Develle¹, Cécile Quantin², Gaël Monvoisin², Fabien Arnaud¹

¹Université Savoie Mont-Blanc, CNRS, EDYTEM, F-73000, Chambéry, France

²Université Paris-Saclay, CNRS, GEOPS, F-91405, Orsay, France

Keywords: Pb contamination, ore smelting, soil remobilisation, contaminant legacy

Abstract

The mining and smelting of ores have led to global contamination, with ancient metal contamination evidenced by environmental archives recording fallout deposited on lake and terrestrial surfaces. Even after anthropogenic activities stop, soil continues to scavenge metal-bearing fallout, contributing to persistent metal contamination in a catchment. To assess the delayed response of contamination in a mountainous catchment, lake sediments and soils were collected 7 km upward a 200-year-old historic mine. The Pb-Ag mine of Peisey-Nancroix was operated between the 17th and 19th with documented smelting period of 90 years. Pb contamination was identified during the smelting period using dating techniques on lake sediments, and Pb isotopes confirmed the Pb local ore origin ($^{206}\text{Pb}/^{207}\text{Pb} = 1.173$; $^{208}\text{Pb}/^{206}\text{Pb} = 2.094$) as well as the ongoing remobilization of anthropogenic lead in the environment. Despite metallurgical Pb transfer decreases over time in La Plagne lake sediment, the catchment soils still contain significant stocks of anthropogenic Pb (54-89 %). Small topographic sinks revealed contamination disparities in superficial soils. Measurements showed the contamination of 80 years of Pb smelting emissions affecting different compartments of the environment and their lagged response to the contamination.

4.1 Introduction

The mining industry associated with ore smelting is one of these industries that threatens Earth's ecosystems (Thienpont et al., 2016; Mariet et al., 2017; Camizuli et al., 2018; Hansson et al., 2019) through the dispersion of metal-bearing particles into all compartments of the environment (Nriagu and Pacyna, 1988; Hong et al., 1994; Renberg et al., 1994). Numerous studies have investigated the soil contamination in close vicinity of smelting waste storage areas (e.g., Křibek et al., 2016). However, a substantial amount of particles is also emitted toward the atmosphere during smelting operations. While most of this atmospheric contamination falls out in the vicinity of the smelters (Doucet and Carignan, 2001; Cloquet et al., 2006b) an important part of it may spread much further (Hong et al., 1994; Brännvall et al., 1997). One way to track both the spatial distribution and the timing of past pollution is the use of sedimentary archives, such as lake sediments (Arnaud et al., 2004; Sabatier et al., 2014), peatbogs (Shotyk et al., 1998; Martínez-Cortizas et al., 1999; De Vleeschouwer et al., 2007) or ice cores (Rosman et al., 2000). Environmental archives have been widely used for decades to evidence such a contamination from a regional to a global scale within a long-term perspective (e.g., Mariet et al., 2018). It has been hence shown that global lead contamination occurred as early as during the Antiquity period, (Shotyk et al., 1998; Brännvall et al., 2001) while the oldest evidence of metals contamination was dated 4 500 years ago (Leblanc et al., 2000). During the historic period, the Middle Age was also a period of widespread metal contamination in Europe, and the earliest evidence was found to originate from Germany (Brännvall et al., 1999). It was hence possible to establish a worldwide history of metal contamination (Shotyk et al., 1998; Renberg et al., 2001).

However, this wide picture does not provide any information about the present-day dispersion and remobilisation within the environment of ancient metal contaminations. Mining legacy is of great concern hundreds to thousands of years after activities stop (Hansson et al., 2017; Le Roux et al., 2020; Corella et al., 2021) and remains harmful to biota (Monna et al., 2011; Camizuli et al., 2018).

Lake sediments may integrate both direct fall-outs and catchment-derived fluxes of contaminating metals. However, even when the primary flux has ceased, contaminants stocked in soils can be remobilised by physical erosion and/or runoff waters, and thus enter the recording system (i.e., the lake). Although soil represents the largest reservoir of airborne contaminants (e.g., Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2001), very little is known about the remobilisation of metals after they originally fell out on soils. The storage of trace elements within soil has the potential to act as a delayed and persistent source of contamination. (Yang et al., 2002a; Bacardit and Camarero,

2010; Rose et al., 2012; Hansson et al., 2017, 2019). At the scale of a catchment area, this should induce a lag between metal fall-outs into a catchment and their downstream transfer to a lake basin where they could be stored.

In this paper we aim to test the hypothesis that metal release continues to occur upstream of a historic mining area even nearly 200 years after the cessation of any metallurgical activity. The lack of data on the duration of mining activities (e.g., Gabrieli and Barbante, 2014 in Roman times) makes it difficult to assess the potential time-lag between metal emission, deposition, remobilisation and finally storage in a given lake catchment area. To do so, we attempted to determine the timing of contaminant remobilisation in the context of a well-known historical mining activity that took place in a small valley in the French Alps, between the 17th and 19th centuries. Moreover, the long-term environmental legacy of ancient mining activities is still poorly documented (Camizuli et al., 2014, 2018; Wiklund et al., 2020) and remote areas such as high mountain catchments are favourable for studying activities far from any urban centre and from other sources of anthropogenic contaminants (Monna et al., 2011; Hansson et al., 2019). To contribute at filling that gap, here we identified Pb contamination sources using Pb isotopes, quantified Pb contamination over time, compared it to the regional signal, and finally connected recent post-smelting Pb fluxes from soils to lake sediments, which is rarely undertaken.

4.2 Study area

The Peisey-Nancroix Pb-Ag mine is located at 1 500 m a.s.l. in the Ponturin Valley, in the northern French Alps (Savoy; Figure 4.1). The first written evidence of ore extraction at the Peisey-Nancroix mine and subsequent smelting on site was dated back to the mid-17th century (1644 CE; Barbier, 1875). However, industrial installations were implemented in the mid-18th century (1734 CE), and the mine was operated until 1866. During this industrial period, 21 500 t Pb and 53 t Ag were extracted. For at least 80 years (1745-1824), galena (PbS) and Ag-rich tetrahedrite ((Cu, Fe)₁₂(Sb,As,Ag)₄S₁₃) ore was smelted on site with great variability in ore production over decades (Table S1). All supplementary tables, text and figures are referenced with an S. For pre-industrial (17th century) and industrial (18th and 19th centuries) times, historical archives, written by mining engineers, are available. They provide information on the amount of ore extracted and smelted, on the smelting techniques used, and on the spatial distribution of the mining and smelting infrastructures. Ore smelting began to decline in 1813 CE when smelting facilities were relocated in the city of Albertville (Figure 4.1B), 35 km as the crow flies, from Peisey-Nancroix village (65

km down valley) and was then definitively abandoned in 1824 CE. Local contamination of the surrounding hayfields has been engendered by 200-hundred years of mining and smelting waste storage on the surface (Guillevic et al., 2023).

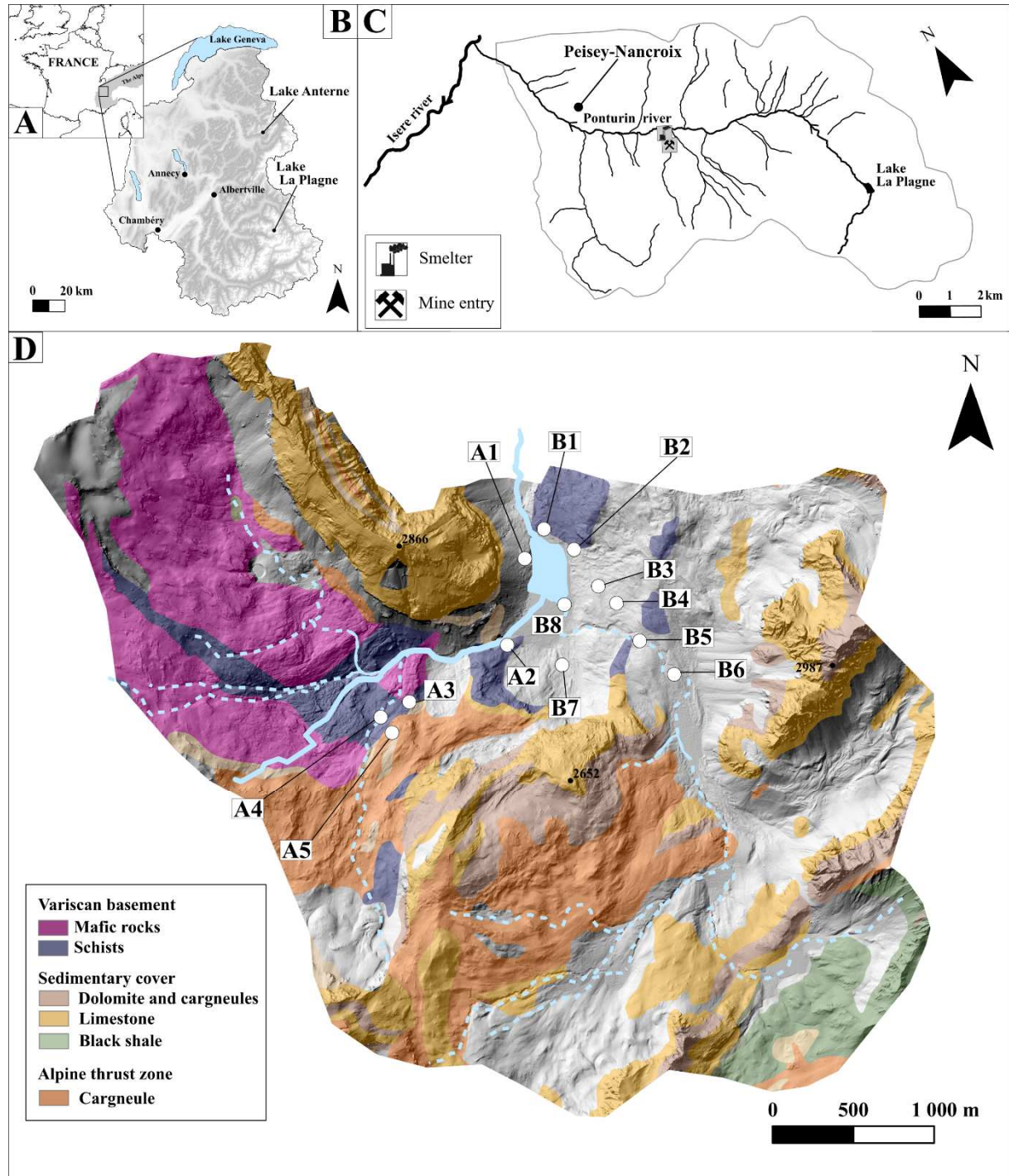


Figure 4.1 : Location maps of the study area. A) Map of France indicating the study area; B) Location of the lakes of La Plagne and Anterne in the northern French Alps, 56 km apart; C) Location of the Peisey-Nancroix mining and smelting areas and of Lake La Plagne along the Ponturin catchment; D) Geological map of the Lake La Plagne catchment, showing the location of the soil samples.

To study atmospheric contaminant emissions during smelting and their subsequent deposition and transfers, Lake La Plagne and its catchment were selected because the lake is located in the upper valley of the Ponturin River, 7 km downwind and upwards of the former Pb-Ag mining and smelting site (Figure 4.1C). Lake La Plagne, located at 2100 m a.s.l. in the Vanoise massif corresponds to a catchment of 1742 ha with a maximum altitude of 3100 m (Figure 4.1D). The upper valley is only accessible by foot, and only pastoral activities are known in the area. The bedrock of the catchment consists of metamorphic rocks of the Variscan basement (intermediate to mafic compositions) and carbonate rocks (marble, dolomite and alpine dedolomitised breccia called “cargneules”) from the Mesozoic sedimentary cover (Figure 4.1D). A large part of the area is covered by screes and tills. The alpine meadows are covered with *Rumex alpina*, *Nardus stricta*, *Vaccinium vitis-idea*, *Achillea millefolium* and *Sempervivum montanum*. The waterways upstream of the 19 m-deep Lake La Plagne cross basement rocks into a peaty-like delta system. The Ponturin River runs from the outlet of the lake northwards before bordering the ancient Pb-Ag mining and smelting site of Peisey-Nancroix, 7 km downstream.

4.3 Materials

4.3.1 Lake sediments

With the help of a UWITEC gravity corer hammering from a small boat, 5 sediment cores, PLG-01 (IGSN: TOAE0000000343; 1.52 m), PLG-02 (IGSN: TOAE0000000344; 2.25 m), PLG-03 (IGSN: TOAE0000000345; 1.06 m), PLG-04 (IGSN: TOAE0000000347; 0.95 cm), and PLG-05 (IGSN: TOAE0000000349; 2.14 cm), were collected in the centre of Lake La Plagne (N 45°29'2.709"; E 6°50'29.667", Figure 4.1D) in July 2019. Detailed fieldwork information can be found at <https://www.cybercarotheque.fr/index.php?mission=PLAGNE>. At the laboratory, each core was split into two halves, one of them was used for the following analyses.

4.3.2 Surface and subsurface soil samples

A total of 13 surface soil samples were collected with a manual auger at a depth of 0-20 cm along two altitudinal transects in the lake catchment (Figure 4.1D). Transect A (n=5) follows a southwestern direction from the west of the lake: samples A1 (2170 m), A2 (2177 m), A3 (2330 m), A4 (2402 m), and A5 (2447 m). Transect B (n=6) points towards the southeast from the northern side of the lake: samples B1 (2153 m), B2 (2170 m), B3 (2227 m), B4 (2264 m), B5 (2314 m), and B6 (2336 m). Sample B7 (2190 m) was collected between these two transects, and sample

B8 (2149 m) was collected in the lake delta. Additionally, two soil profiles were dug at the top of each transect (A5 and B6) to retrieve samples from different soil horizons. Soil samples were air-dried for a few days and sieved to 2 mm before analyses.

4.4 Methods

4.4.1 High-resolution elemental EDS-XRF analyses

After visual logging and photographing, the relative major (Al, Si, K, Ca, Mg, Ti, Mn, Fe) and trace (Zn, Pb, As, Rb, Sr, Zr) element contents were measured along the lake sediment core by energy dispersive spectrometer-X-ray fluorescence (EDS-XRF) using the AVAATECH Core scanner at the EDYTEM laboratory. A continuous 1-mm step measurement was performed on a PLG-03 one-half core with multiple runs at 10 kV and 0.2 mA during 15 s, allowing the detection of lightweight elements, and a second run at 30 kV at 0.15 mA during 20 s to detect heavy elements. In order to discriminate As and Pb, which suffer from peak overlap, peak intensities were calculated using only Pb_{Lβ} and As_{Kα}. Argon was also analysed and used as an element control for the homogeneity of the core. Hierarchical clustering on principal component analysis (PCA) of major elements was applied to compare visual logging to geochemical units of lake sediment using the multivariate analysis package FactoMineR (Lê et al., 2008) in R statistical software (R Core Team, 2022).

4.4.2 Carbonates and organic matter content

The determination of the organic matter and carbonate contents of the lake sediments was performed by loss on ignition (LOI) on discrete samples from PLG-03 following the method by Heiri et al. (2001). The weight loss was measured after a first heating step at 550°C (LOI₅₅₀), providing an assessment of the organic matter content within lake sediments, and after a second heating step at 950°C (LOI₉₅₀), used as a proxy of the carbonate content.

The carbon total content (inorganic and organic fraction, C_T) of the fine fraction of soils was measured by dry combustion (ISO 10694), and the CaCO₃ total content (CaCO₃, ISO 10693) was measured by the volumetric method at the French national reference soil laboratory (INRAE, France). Based on the C_T and CaCO₃ contents, the total organic carbon (TOC, TOC = C_T – CaCO₃ *0.12) and the soil organic matter (OM, OM = TOC*1.7) were calculated. The pH of the soil samples was also measured.

4.4.3 Major and trace element contents, and enrichment factor (EF)

Following the routine analysis of Carignan et al. (2001), soils (< 2 mm; n= 13) and lake sediment samples (n=66) were analysed for 54 elements after lithium tetraborate fusion using ICP–OES iCap6500 (major elements) and ICP–MS iCapQ (trace elements) at the Service d’Analyse de Roches et Minéraux (SARM-CNRS, Nancy, France). Total concentration uncertainties were about 1% for major elements and between 5% and 10% for trace elements, depending on concentration levels. Reference materials and blanks were prepared along with the samples. Lake sediment sampling along the core was performed approximatively at each cm according to facies changes for a total of 66 samples for a 106 cm core (PLG-03). Sampling was spaced to avoid thick instantaneous events identified during logging, such as event deposits that were considered instantaneous deposits and non-representative of continuous sedimentation (Arnaud et al., 2002; Sabatier et al., 2022). In this paper, major and trace element contents are presented as the median \pm standard deviation.

For both soil and lake sediments, the enrichment factor (EF) of potentially toxic trace elements (PTEs) was calculated to quantify the PTE contamination in comparison to a reference background:

$$EF_{M_1} = \frac{\left(\frac{M_1}{M_2}\right)_{SAMPLE}}{\left(\frac{M_1}{M_2}\right)_{BKG}} \quad \text{equation (1)}$$

where M_1 is the Pb or As content of the sample and of the reference background (BKG), and M_2 is the content of a selected “conservative” element in soil and lake sediments that has exclusively a lithogenic origin (Reimann and de Caritat, 2000) and has a content on the same order of magnitude as the studied PTE. Both Rb and Th were tested as conservative lithogenic elements for the calculus of the EF. The classification of EF is presented in Table S2.

4.4.4 Pb isotopes

A selection of lake sediment (n = 9) and all soil samples (surface and subsurface horizons, n = 20) were analysed for Pb isotopic composition (^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb) using a Thermo Fischer Multicollector (MC-ICP–MS) Neptune Plus at the SARM-CNRS laboratory. After digestion, the samples are placed on an ion exchange resin to chemically separate the mineral matrix. Lake sediment samples were chosen before the sampling of the continuous 66 discrete samples based on the Pb and As peaks identified on the EDS-XRF profiles. Two samples (85-86 cm and 103-

104 cm) presenting the lowest Pb and As abundances were chosen to define the local background isotopic composition.

In-situ Pb isotope measurements were performed on 10 to 20 individual galena crystals of two ore-bearing samples collected on the waste heaps to determine the local ore signature. Measurements were performed at the CRPG-CNRS (Nancy, France) using the 1270 ion microprobe in monocollection mode to a mass resolution of 4000, following Deloule et al. (1986).

4.4.5 Short-lived radionuclides (^{210}Pb , ^{137}Cs , ^{230}Am)

The activities of natural short-lived radionuclides ^{210}Pb , ^{226}Ra and ^7Be and artificial radionuclides ^{241}Am and ^{137}Cs in lake sediment samples were measured at the Laboratoire Souterrain de Modane (LSM, France) on EDYTEM-operated low background SAGe well detectors (Reyss et al., 1995). For each sample, the excess ^{210}Pb ($^{210}\text{Pb}_{\text{ex}}$) activities were calculated as the difference between the total ^{210}Pb and ^{226}Ra activities. The first 30 cm of lake sediments from the PLG-03 core were sampled according to lithological variations. Using a small cylinder (3 cm^3), the dry bulk density (DBD) was determined by measuring the dry weight for a constant volume of sediment before analysis. Short-lived radionuclide data were computed with the serac package (Bruel and Sabatier, 2020) in R software (R Core Team, 2022) build an age-depth model for the recent sediments.

4.4.6 ^{14}C dating

Organic macroremains were sampled for ^{14}C (radiocarbon) dating from cores PLG-01, PLG-03, PLG-04 and PLG-05, which were correlated thanks to XRF analyses (Figure S1). Despite difficulties in providing a proper quantity of macroremains, 13 samples were dried at 60°C and sent to the accelerator mass spectrometer (AMS) of the Poznan Radiocarbon laboratory (Poland) to measure ^{14}C . The radiocarbon ages were calibrated with the Intcal20 calibration curve (Reimer, 2020) using the clam package (Blaauw, 2010) in R software (R Core Team, 2022) to construct a single age-depth model correlated with short-lived radionuclide measurements (^{210}Pb , ^{137}Cs , ^{231}Am).

4.4.7 Anthropogenic Pb (Pb_{ANTH}) and accumulation rate ($\text{AR}_{\text{Pb_ANTH}}$)

Two methods were used to measure the anthropogenic Pb (Pb_{ANTH}) of lake sediment (and soils): elemental and isotopic methods. First, we considered the total Pb content of one sample as the sum between the lithogenic background Pb and the anthropogenic Pb contents: $\text{Pb}_{\text{TOTAL}} = \text{Pb}_{\text{BKG}} + \text{Pb}_{\text{ANTH}}$; which allowed us to calculate :

$$Pb_{ANTH} = Pb_{TOTAL} - \left(Rb_{TOTAL} * \left(\frac{Pb_{BKG}}{Rb_{BKG}} \right) \right) \text{ equation (3)}$$

Second, the calculation of Pb_{ANTH} was also isotopically determined using a two end-member mixing model, where the mean of the two deepest lake sediments represents the lithogenic background end-member (85-86 cm and 103-104 cm):

$$Pb_{ANTH} = Pb_{TOTAL} * \frac{\left(\frac{Pb^{206}}{Pb^{207}} \right)_{sample} - \left(\frac{Pb^{206}}{Pb^{207}} \right)_{BKG.}}{\left(\frac{Pb^{206}}{Pb^{207}} \right)_{local_ore} - \left(\frac{Pb^{206}}{Pb^{207}} \right)_{BKG}} \text{ equation(4)}$$

The accumulation rate of anthropogenic Pb (AR_{Pb_ANTH}) represents the annual flux of anthropogenic Pb per m^2 . It was calculated in lake sediments to evaluate (i) changes in metal accumulation along the sediment core, and (ii) to compare the Lake La Plagne accumulation rate to regional fluxes that were estimated at Lake Anterne (Figure 4.1B) during the same time period. The AR_{Pb_ANTH} (in $mg \cdot m^{-2} \cdot y^{-1}$) was calculated according to equation (2):

$$AR_{Pb_ANTH} = SR * DBD * Pb_{ANTH} \text{ equation (2)}$$

where SR is the sedimentation rate (or accumulation rate, in $mm \cdot y^{-1}$) obtained from the age-depth model, DBD is the dry bulk density (in $g \cdot cm^{-3}$) and Pb_{ANTH} corresponds to the anthropogenic Pb content (in $mg \cdot kg^{-1}$). Details on the DBD calculation of lake sediments and the fine fraction of soil (< 2 mm) are presented in Text S1.

4.4.8 Inventory calculations

4.4.8.1 Inventories of anthropogenic Pb ($g \cdot m^{-2}$)

The inventory of anthropogenic Pb (Inv_{Pb}) represents the quantity of anthropogenic Pb stored per area unit in soils or in lake sediments (in $g \cdot m^{-2}$). For lake sediments, it is possible to calculate the total amount of metal accumulated for a given surface area (here, the area of the sediment core, $Inv_{Pb_lake_sed}$) following equation (5):

$$Inv_{Pb_lake_sed} = \sum_{i=1}^n SR * DBD * Pb_{ANTH} = \sum_{i=1}^n AR_{Pb_ANTH} \text{ equation (5)}$$

where n is the thickness of the accumulated sediment, which represents a time period using the age-depth model.

For soils, the inventory ($Inv.pb_{soil}$) is calculated following equation (6), with T being the thickness of the soil to integrate:

$$Inv.pb_{soil} = T * DBD * Pb_{ANTH} \text{ equation (6)}$$

4.4.8.2 Inventories of $^{210}Pb_{ex}$ ($Bq.m^{-2}$)

The larger the catchment area is, the larger the quantity of sediment is, and therefore the larger the anthropogenic contaminant is supposed to be remobilised (assuming uniform fall-outs). A focus factor (FF) is calculated to compare inventories of $^{210}Pb_{ex}$ (fine sediment proxy) among lakes:

$$FF = \frac{Inv.Pb_{ex}^{210} PLG}{Inv.Pb_{ex}^{210} ANT} \text{ equation (7)}$$

where $Inv.Pb_{ex}^{210} PLG$ is the inventory of $^{210}Pb_{ex}$ in Lake La Plagne (PLG), and $Inv.Pb_{ex}^{210} ANT$ the inventory of $^{210}Pb_{ex}$ in Lake Anterne (ANT). An $FF > 1$ is indicative of net accumulation of sediment. The FF will help to calculate the difference in anthropogenic Pb accumulated over a given period of time and calculate the local surplus of anthropogenic Pb ($Surplus_{pb}$ in $g.m^{-2}$) potentially engendered by smelting activities, following equation (8).

$$Surplus_{pb} = Inv.pb_{PLG} - FF * Inv.pb_{ANT} \text{ equation (8)}$$

Lake La Plagne was compared to Lake Anterne (Figure 4.1B) as (i) its relatively small catchment area (256 ha) makes it a good atmospheric recorder, and (ii) there was no important metallurgical activity in the 18th and 19th centuries nearby, so that it only recorded the regional atmospheric signal.

4.5 Results

4.5.1 Sedimentology of Lake La Plagne

Pictures of the sediment texture are visible in Figure S1. As it is often the case in alpine lakes, we identified many event layers interbedded with the continuous sedimentation in PLG-03 sediment core. These layers show a coarser grain size at the base (normal grading) associated with few millimetres size organic debris. They present a beige or brown yellowish colour contrasting with the dark brown facies characterising the continuous sedimentation. A list of the event depths is reported in Table S3 for each studied core.

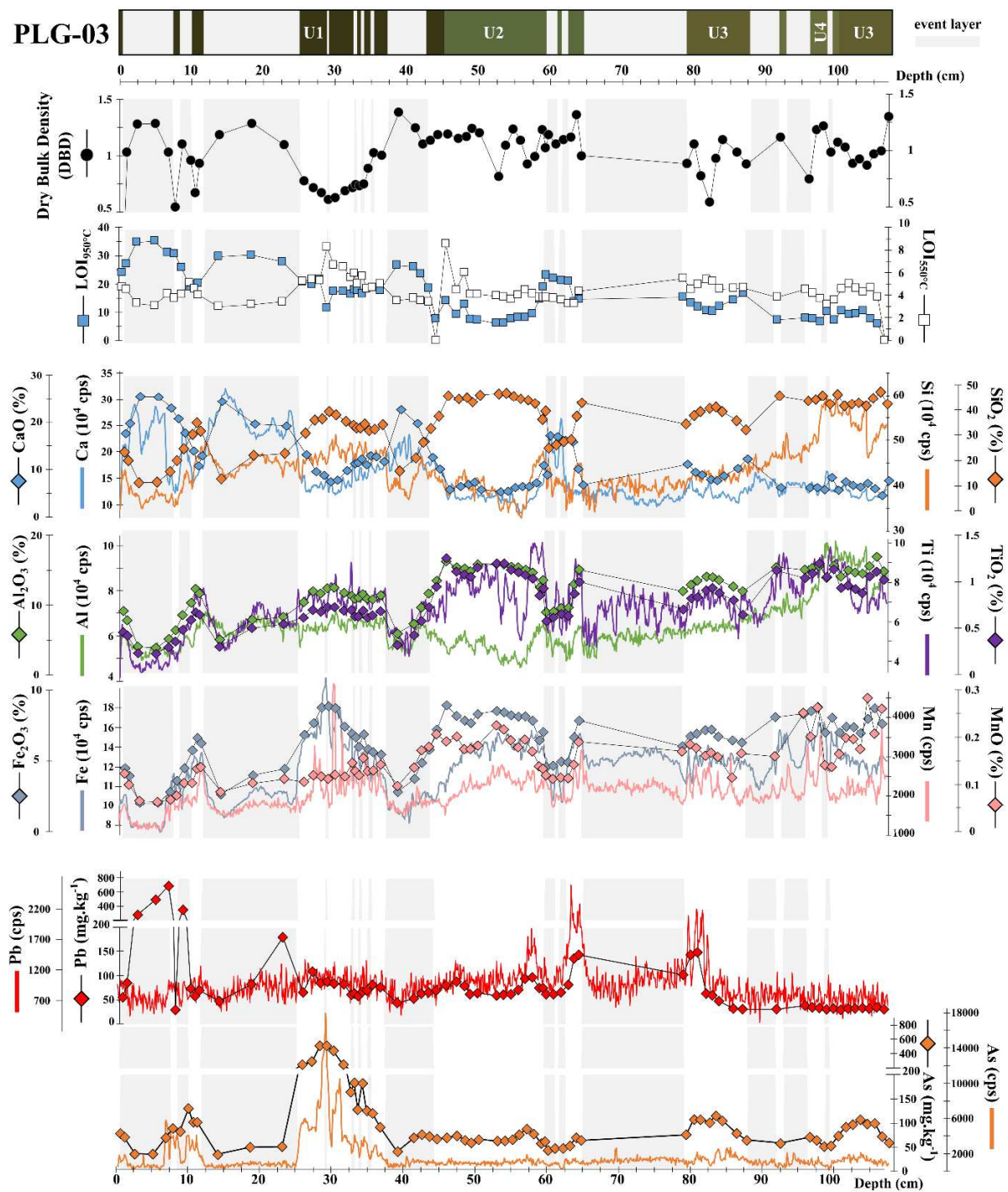


Figure 4.2: Dry bulk density (DBD) and LOI_{550°C} and LOI_{950°C} for discrete samples (units %) along the PLG-03 core as well as major and trace element content profiles measured by EDS-XRF with a 1-mm step (continuous line, in counts per second); and ICP-OES and ICP-MS contents (diamond, in % or mg.kg⁻¹). Transparent grey rectangles represent the Ca-rich events and events identified during logging by a higher particle size at the base and by a different colour.

The continuous sedimentation presents slight changes over the studied sequence and was thus divided into 4 units based on XRF logging, LOI₅₅₀ and LOI₉₅₀ data. Unit 1 (6-11 cm; 25- 45 cm, Figure 4.2) consists of a dark brown silt with LOI₅₅₀ up to 8 wt. % (5.1 ± 1.9 wt. %), which is slightly higher than the other units. The carbonate content estimate based on LOI₉₅₀ is also the highest among continuous sedimentation units (18.0 ± 4.6 wt. %). This induces a lower DBD (0.8 ± 0.2 g.cm⁻³) than for the more silicate-rich units found at depth (Figure 4.2). Only sediment colour allows us to distinguish Unit 2 (45-64 cm) and Unit 3 (78-87 cm; 99.5-107 cm) as their LOI₅₅₀ and LOI₉₅₀ are similar (4.3-4.7 and 9.3-10.6 wt. %, respectively). The slightly lower organic content of Unit 2 (4.3 ± 1.3 wt. %) may be responsible for its greener colour in comparison to the brown-dark colour of Unit 3 (4.7 ± 1.3 wt. %). Unit 4 (87-99.5 cm) corresponds to laminated mixing between Unit 2 and Unit 3.

4.5.2 Major elements

4.5.2.1 Lake sediments

Hierarchical clustering on principal components was performed on major elements measured by EDS-XRF (Si, Al, K, Mg, P, Ca, Ti, Fe, Mn, in cps), which allowed us to identify 3 clusters (Figure S2). The first dimension (50.73 %) and the second dimension (29.18 %) of the PCA distinguish carbonate-rich top event layers (cluster 1) and terrigenous continuous sedimentation (clusters 2 and 3). This classification corroborates the total major element contents (Figure 4.2) showing a lower SiO₂ content (22.3 ± 9.3 wt. %, $n = 16$) and a higher CaO content (19.4 ± 4.1 wt. %) in the carbonate-rich events compared to continuous sedimentation (SiO₂: 39.3 ± 6.4 wt. %; CaO: 7.9 ± 3.3 wt. %, $n = 53$).

The continuous sedimentation represented by cluster 2 and cluster 3 encompassed the 4 units identified during logging as well as the deep event layers (64-78 cm; 87-91 cm; 93-95 cm and 98-99 cm). These deep events, which have a geochemical signature similar to continuous sedimentation (Figure S2), are identified based on their brown-yellowish colour and sandy texture. Unit 2, Unit 3 and Unit 4 present similar major element contents whereas Unit 1 presents higher carbonate content, thus diluting the silicate signal.

4.5.2.2 Soils

Most soils from the Lake La Plagne catchment are developed on basement rocks and/or till with minor proportions of carbonate fragments which are abundant in screes (Figure 4.1D). These soils can be classified as rankosols with the exception of sample B8, which is a saturated fluvisoil with the highest $\text{CaCO}_{3\text{T}}$ content (5 wt. %, Table 4-1). The other surface soils are silty-sandy soils with no carbonates ($< 1\%$ $\text{CaCO}_{3\text{T}}$). The total organic carbon (TOC) content varies from 6 to 12 wt. %. Superficial soils collected on basement rocks and tills (A2, A4, B1, B3, B4, B5 and B6) presented a higher SiO_2 content (52.4 ± 4.5 wt. %) and a lower CaO and MgO contents (0.7 ± 0.5 wt. %; and 2.3 ± 0.4 wt. %; respectively) than the soils overlying the cargneules and the carbonate-rich screes (SiO_2 : 43.9 ± 3.5 wt. %; CaO: 1.6 ± 2.4 wt. %; MgO: 3.8 ± 1.5 wt. %; A1, A3, A5, B2, B7, B8). Surface soils have heterogeneous pH values ranging between 4.5 and 7.6 (Table 4-1). The most alkaline soils (pH > 7 ; samples A1, B2, B7 and B8) are located down the slope or along the slopes with downhill carbonate rock outcrops. The most acidic soils (pH < 5 ; samples A2, A4, B4 and B5) are developed on basement rocks of the catchment. Soil samples A3, A5, B1, B3, and B6 present an intermediate pH.

Table 4-1: Principal soil properties, trace elements and major contents for superficial soil in the surrounding of Lake La Plagne, divided in two subgroup types according to underlying lithologies

Sample_Name	Lithology	Soil properties				Potentially toxic trace elements						Majors elements				
		pH	TOC	CaCO ₃	CEC	As	Cd	Cu	Pb	Sb	Zn	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
			%	%		mg.kg ⁻¹						wt. %				
A2	basement rocks	4,8	6	0,05	8	27,9	0,33	15,3	133	2,36	154	53,2	13,4	5,7	2,5	1,3
A4	basement rocks	4,9	8	0,05	7	26,5	0,25	23,9	39,1	1,63	78,6	51,6	12,6	6,4	2,1	0,6
B1	basement rocks	5,1	9	0,05	14	12,2	0,29	14,3	76,3	1,84	134	49,0	11,9	5,4	2,0	1,2
B3	basement rocks	5,8	9	0,05	21	21,7	0,28	17,5	75,1	6,92	101	50,2	11,9	5,6	2,5	0,8
B4	basement rocks	4,5	6	0,20	7	17,5	0,12	17,7	96,2	4,89	107	58,3	12,2	5,9	2,4	0,1
B5	basement rocks	4,7	7	0,05	8	5,74	0,09	12,9	66,1	1,32	39,2	67,6	8,7	1,7	1,0	0,1
B6	till	5,3	7	0,05	14	6,53	0,26	23,3	102	1,29	102	60,0	10,8	5,1	1,4	0,4
A1	carbonates scree	7,3	12	0,05	31	23,8	0,43	41,2	121	3,26	103	40,9	12,5	4,9	3,2	2,5
A3	carbonates scree	6,6	11	0,05	24	37,5	0,71	20,6	51,3	1,96	99,9	44,7	12,9	3,5	4,4	1,2
B2	carbonates scree	7,2	10	0,05	31	42,6	0,39	25,6	103	3,96	151	48,1	11,3	4,6	2,6	1,5
B7	carbonates scree	7,7	6	0,90	23	22,6	0,72	15,1	101	5,58	169	49,9	13,6	6,0	4,1	1,7
B8	carbonates scree	7,5	7	5,00	18	35,6	0,33	21,9	66,9	1,99	112	42,5	10,8	4,4	6,9	7,3
A5	cargneules	5,6	10	0,05	22	16,0	1,38	19,1	116	2,08	176	43,1	12,0	5,4	3,6	0,7

4.5.3 Trace elements and enrichment factor

4.5.3.1 Lake sediments

Among the elements of metallurgic interest, Pb and As show clear variations according to XRF scanning. In contrast, Zn, Cu and Ni display weak and noisy signals. No signal was recorded for Sb despite the presence of Sb-bearing minerals in the ore. The Pb profile shows three peaks (56.5-58.3 cm, 82.5-79.5 cm, and 62.5-64.5 cm) interspersed with event layers (in red, Figure 4.2). The As profile shows 2 peaks (30-31 cm and 27.9-29.3 cm) also interspersed with an event layer.

The total trace element contents in discrete samples confirmed that apart from Pb and As, the other potentially toxic trace elements (PTE; Ni, Cu, Sb and Zn) do not display any positive anomaly. The Ni content varied between 12 and 37 mg.kg⁻¹ (26.7 ± 4.5 mg.kg⁻¹), the Cu content varies between 16 and 51 mg.kg⁻¹ (39.3 ± 5.3 mg.kg⁻¹), the Zn content varied between 69 and 235 mg.kg⁻¹ (182.6 ± 28.5 mg.kg⁻¹) and the Sb content varied between 1.8 and 4.1 mg.kg⁻¹ (3.0 ± 0.4 mg.kg⁻¹). The total arsenic content confirmed the EDS-XRF data, with the As content varying from 34.7 to 505 mg.kg⁻¹ (87.8 ± 109.0 mg.kg⁻¹). Simultaneously, for the As peaks, an increase in the organic matter was measured with LOI_{550°C} (between 6 and 8 wt. %, Figure 4.2).

The total Pb content varies from 29 to 148 mg.kg⁻¹ for the continuous sedimentation samples (61.5 ± 30.4 mg.kg⁻¹, n = 54). The deepest lake sediment samples (85 to 106 cm) present a low Pb content, which varies between 29 and 38 mg.kg⁻¹. The highest Pb content was measured between 54 and 85 cm (from 47 to 148 mg.kg⁻¹). This confirmed the 3 Pb peaks identified from the EDS-XRF profile (Figure 4.2). From the top of the core to 54 cm, the total Pb content varies between 29 and 87 mg.kg⁻¹. Noticeably, the total Pb content of one of the top events was very high reaching a total content of 690 mg.kg⁻¹ between 6 and 7 cm (Figure 4.2). This result is very surprising as no major Pb peak was identified by EDS-XRF at this depth in any core, as it would have been expected for such a Pb content (Figure S3).

The EF_{Pb} was calculated for each lake sediment discrete sample using for reference background the mean Pb/Rb ratio of the discrete samples collected between 85 and 106 cm (Pb/Rb: 0.32 ± 0.02 , n=15), which are considered to represent the local geological background. Element Rb was chosen over Th as conservative element because the standard error of the mean background ratio was lower and because Rb was identified with terrigenous fraction (Figure S2). The enrichment was considered significant for EF_{Pb} > 2. Table S4 presents EF_{Pb} values in depth along the sediment core. From 0 to 55 cm, the EF_{Pb} increases from 2 to 4. From 55 to 62 cm, the EF_{Pb} is equal to 3, showing a minor enrichment. From 62 to 81 cm, the EF_{Pb} shows a moderate enrichment up to 5.

As the deeper sediments are used for background and reference values, EF_{Pb} is close to 1 between 85 and 106 cm.

4.5.3.2 Soils

The Pb content in superficial soil samples varies from 39 to 132 $mg.kg^{-1}$ ($96.2 \pm 28.2 mg.kg^{-1}$), with a high variability depending on the sample location, but no relationships with the underlying lithologies (Table 4-1 and Figure 4.3). The deepest soil horizons of profiles A5 (overlying cagneule and dolomite) and B6 (developed on basement-rich tills lying over cagneule and dolomitic rocks) present equivalent Pb/Th ratios. Despite lithological differences, these deepest horizons are used as background references to calculate enrichment factors in soils as Pb/Th ratio is equivalent ($Pb/Th \sim 2.7$). EF_{Pb} in soils varies between 2 and 9 (Figure 4.3). Despite Pb enrichment, the PTE contents (Ni, Cu, As, Sb) of surface soil samples are very low and therefore show no significant enrichment (Table 4-1). The depth transfer of Pb is limited; only the first two horizons of profiles A5 and B6 show moderate to severe Pb enrichment whereas the deeper horizons display no enrichment (Table S5).

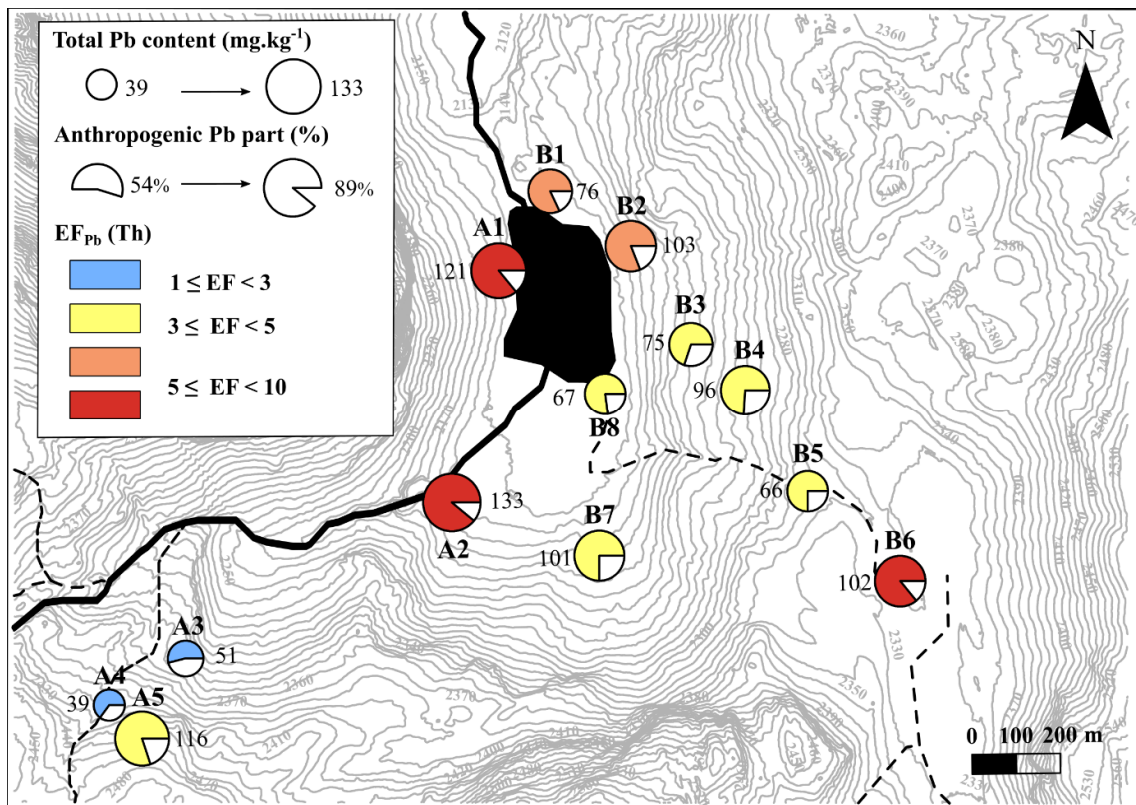


Figure 4.3: Distribution map of surface soil around Lake La Plagne indicating EF_{Pb} , the total Pb content (in $mg.kg^{-1}$) and the anthropogenic Pb content (Pb_{ANTH} in $mg.kg^{-1}$). See text for the calculation of Pb_{ANTH} .

4.5.4 Pb stable isotopes

4.5.4.1 Local ore

The local galena displays $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.172 ± 0.002 and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 2.095 ± 0.005 ($n=29$, Table S6) that will be named Pb local ore in the following.

4.5.4.2 Lake sediments

The two deepest samples of the lake sediment core present a $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic ratio of 1.209 and a $^{208}\text{Pb}/^{206}\text{Pb}$ isotopic ratio between 2.041 and 2.042 (Table 4-2, Figure 4.4), falling within the range of the Variscan continental crust (Monna et al., 2000). Hence, these samples may be considered an uncontaminated local background.

The lake sediment Pb isotopic signatures provide evidence of binary mixing between the local background and the local Pb ore end-members on a $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$ diagram (Figure 4.4). The proportion of anthropogenic Pb calculated from $^{206}\text{Pb}/^{207}\text{Pb}$ (Pb_{ANTH} , equation 4) decreased from 79-84% at 80 cm depth down to 20-25% at the top of the core (Table S7). The anthropogenic Pb in the deeper samples at 52 cm, 57.5 cm, 63.5 cm, and 80 cm represents more than 50 % of the total Pb content (59 %, 66%, 79% and 84%, respectively). Such high proportions of Pb_{ANTH} are related to the highest Pb contents (e.g., at 80 cm, $\text{Pb} = 148 \text{ mg.kg}^{-1}$). Even though the shallowest samples (7.3 cm, 10 cm and 30.5 cm) only displayed minor enrichment from the EF_{Pb} calculation, their Pb isotope ratios display significant proportions of anthropic Pb, of 24%, 43% and 50%, respectively.

4.5.4.3 Soils

The Pb isotope signature of the soil samples (Table 4-2) indicates a binary mixing between the local Pb-ore and the geochemical background end-members (Figure 4.4), suggesting the persistent presence of anthropogenic Pb derived from local metallurgy. Samples A3, A5, B3 and B7 have isotopic signatures close to or in the range of the local background end-member (between 1.195 and 1.209 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.038 and 2.059 for $^{208}\text{Pb}/^{206}\text{Pb}$). Samples A2, A1, B6 and B1 present isotopic signatures close to the local galena (between 1.177 and 1.180 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.085 and 2.089 for $^{208}\text{Pb}/^{206}\text{Pb}$). Samples A4, B8, B4 and B2 have an intermediate isotopic signature between the local Pb ore and the geochemical background end-members (between 1.185 and 1.189 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.069 and 2.078 for $^{208}\text{Pb}/^{206}\text{Pb}$). Sample B5 has an isotopic signature similar to the

Pb local ore. The subsurface soil samples of profile A5 and the deepest soil horizon of B6 show a more radiogenic signature ($^{206}\text{Pb}/^{207}\text{Pb}$ ranging from 1.24-1.29). than the local geochemical background (Figure 4.4). Such heterogeneity in geogenic signatures made it difficult to calculate the proportion of anthropogenic Pb in soils from the Pb isotope ratios . However, we attempt to calculate the anthropogenic Pb part (%) of soil samples using part of equation 4. The fraction of anthropogenic Pb was calculated according to the different lithologies and compared in the following with the fraction of anthropogenic Pb calculated from the elemental method (Table S7).

 Table 4-2: Pb isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb) of lake sediments, superficial and subsurface soils

	Sample	$^{206}\text{Pb}/^{204}\text{Pb}$ b	err (2σ)	$^{207}\text{Pb}/^{204}\text{Pb}$ b	err (2σ)	$^{208}\text{Pb}/^{204}\text{Pb}$ b	err (2σ)	$^{206}\text{Pb}/^{207}\text{Pb}$ b	err (2σ)	$^{208}\text{Pb}/^{206}\text{Pb}$ b	err (2σ)
Lake sediments	7.3-8.2 cm	18,819	0,001	15,678	0,001	38,617	0,004	1,200	0,00002	2,052	0,00008
	10-11 cm	18,699	0,000	15,667	0,001	38,606	0,002	1,193	0,00001	2,065	0,00006
	30.5-31.5 cm	18,651	0,001	15,657	0,001	38,545	0,002	1,190	0,00001	2,067	0,00007
	52-53 cm	18,608	0,001	15,663	0,001	38,575	0,002	1,187	0,00001	2,073	0,00006
	57.5-58.5 cm	18,562	0,001	15,657	0,001	38,544	0,003	1,185	0,00001	2,077	0,00007
	63.5-64.5 cm	18,443	0,001	15,648	0,001	38,478	0,002	1,178	0,00001	2,086	0,00007
	80-81 cm	18,472	0,001	15,651	0,001	38,496	0,003	1,180	0,00002	2,084	0,00005
	85-86 cm	18,965	0,001	15,692	0,001	38,714	0,003	1,209	0,00002	2,041	0,00009
	103-104 cm	18,972	0,001	15,688	0,001	38,748	0,003	1,209	0,00001	2,042	0,00007
Superficia l soils	A1	18,443	0,002	15,654	0,002	38,481	0,005	1,178	0,00002	2,086	0,00010
	A2	18,420	0,001	15,651	0,001	38,473	0,003	1,177	0,00002	2,089	0,00008
	A3	18,721	0,001	15,665	0,001	38,544	0,003	1,195	0,00002	2,059	0,00007
	A4	18,554	0,001	15,662	0,001	38,556	0,004	1,185	0,00002	2,078	0,00009
	A5	18,731	0,001	15,662	0,001	38,518	0,004	1,196	0,00002	2,056	0,00009
	B1	18,473	0,001	15,656	0,002	38,514	0,004	1,180	0,00003	2,085	0,00010
	B2	18,619	0,001	15,661	0,001	38,516	0,003	1,189	0,00002	2,069	0,00008
	B3	18,760	0,002	15,669	0,001	38,589	0,004	1,197	0,00003	2,057	0,00010
B4	18,611	0,001	15,661	0,001	38,565	0,004	1,188	0,00003	2,072	0,00010	
B5	18,360	0,001	15,645	0,001	38,428	0,004	1,174	0,00003	2,093	0,00010	
B6	18,472	0,001	15,653	0,001	38,511	0,004	1,180	0,00003	2,085	0,00008	
B7	18,955	0,001	15,680	0,001	38,628	0,004	1,209	0,00002	2,038	0,00010	
B8	18,564	0,001	15,660	0,001	38,520	0,004	1,186	0,00003	2,075	0,00009	
Soil profiles	A5-H1	18,550	0,002	15,655	0,002	38,478	0,005	1,185	0,00002	2,074	0,00008
	A5-H2	19,463	0,002	15,697	0,002	38,684	0,005	1,240	0,00003	1,988	0,00010
	A5-H3	19,762	0,002	15,711	0,002	38,730	0,005	1,258	0,00003	1,960	0,00009
	B6-H1	18,421	0,001	15,651	0,001	38,467	0,003	1,177	0,00002	2,088	0,00006
	B6-H2	18,724	0,002	15,668	0,002	38,690	0,006	1,195	0,00003	2,066	0,00010
	B6-H3	18,966	0,001	15,681	0,001	38,852	0,004	1,209	0,00002	2,049	0,00009
	B6-H4	20,338	0,001	15,742	0,001	38,700	0,003	1,292	0,00002	1,903	0,00008

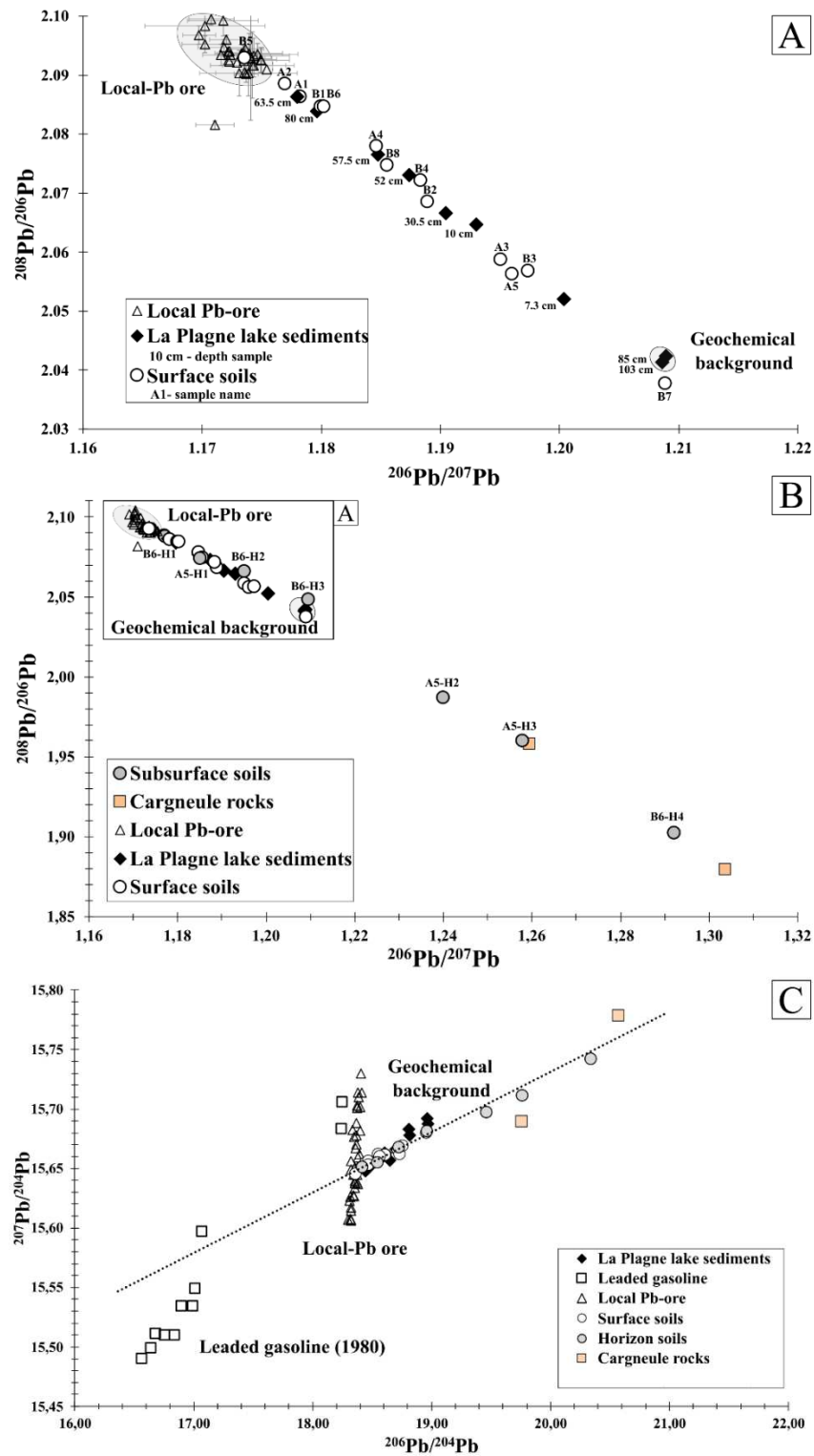


Figure 4.4: Pb isotope ratios of soils (surface and subsurface soils) and lake sediments compared to the Pb local ore. A) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratios; B) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratios with subsurface soils in comparison with more radiogenic cargneule rocks; C) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of soil and lake sediment far from leaded gasoline end-members. The deepest lake sediments are considered representative of the local isotopic background (see text). Error bars are not larger than point size for the environmental samples.

4.5.5 Age-depth model of lake sediments

Applying a constant flux-constant sedimentation rate (CFCS) model to an event-free sedimentary sequence (Bruel and Sabatier, 2020), the $^{210}\text{Pb}_{\text{ex}}$ activity profile indicates two distinct periods of constant accumulation rate (AR; Figure 5): i) $\text{AR} = 0.99 \pm 0.3 \text{ mm}\cdot\text{y}^{-1}$ between 0 and 245 mm, and ii) $\text{AR} = 1.25 \pm 0.2 \text{ mm}\cdot\text{y}^{-1}$ between 245 and 335 mm. According to the computed age-depth model, the change in sedimentation rate occurred in $1982 \pm 10 \text{ y}$. The downcore ^{137}Cs activity profile shows a first small peak at a depth of $104 \pm 10 \text{ mm}$ and a second peak at $290 \pm 10 \text{ mm}$, which are associated with a peak in ^{241}Am activity. The uppermost peak is attributed to the Chernobyl accident in 1986 CE and is in relatively good agreement with $^{210}\text{Pb}_{\text{ex}}$ derived ages (Figure 4.5 on the right, Appleby et al., 1991). However, the $^{210}\text{Pb}_{\text{ex}}$ derived ages are poorly equivalent to the deepest to the maximum nuclear test fallout in 1963 CE identified from both ^{137}Cs and ^{241}Am activity peaks. Therefore, ^{137}Cs and ^{241}Am peaks were used as privileged time-markers for the age-depth model combining ^{14}C dates (Smith, 2001).

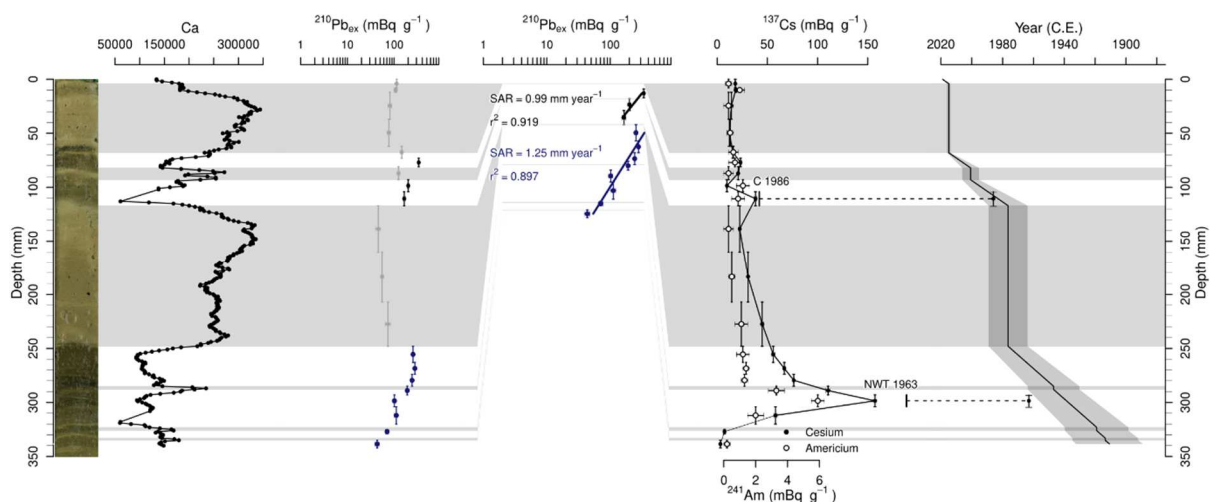


Figure 4.5: Age-depth model on the continuous sedimentation removed from events based on (from left to right) $^{210}\text{Pb}_{\text{ex}}$ activity ($\text{mBq}\cdot\text{g}^{-1}$), ^{137}Cs activity ($\text{mBq}\cdot\text{g}^{-1}$), ^{241}Am activity ($\text{mBq}\cdot\text{g}^{-1}$) and the age model calculated from $^{210}\text{Pb}_{\text{ex}}$ on the real depth. The light grey lines represent the Ca-rich events removed from the age-depth modelling, C: Chernobyl, NWT: Nuclear Weapon Test

Among the 13 organic macroremains analysed for ^{14}C (Table 4-3), 4 dates were removed from the age model calculation because they were sampled at the base of event deposits and yielded ages older than the general trend (Figure S4): Poz-121305; Poz-121306; Poz-120585 and Poz-133271 (see position in Figure S2). The Poz-133277 and Poz-144680 dates, which were the shallowest samples of the core, were also removed from the age model as they provided the oldest calibrated ages among the dated samples (Table 4-3). Finally, only 4 dates were kept for age-depth modelling, because Poz120584, Poz133273, and Poz121164 were also too old to fit the general trend of ^{14}C ages and probably correspond to reworked materials. The core depths of the Poz-144609, Poz-

133272, Poz-133275 and Poz-133276 dates were computed on the master core depth (216 cm) using the correlation between cores (Figure S2).

Table 4-3: The ^{14}C dates collected in Lake La Plagne cores (PLG) with depth reported on a unique master core depth (MCD). Only 4 dates were kept for the age-depth modelling.

	Sample Name	Core	MCD depth	^{14}C Ages	95% (BC/AD)	Status
1	Poz-133277	PLG-05	53,5	2665 ± 35 BP	(-897/-791)	rejected
2	Poz-144680	PLG-04	56,5	1110 ± 110 BP	678-1157	rejected
3	Poz-121305 ¹	PLG-03	76	510 ± 30 BP	1329-1447	rejected
4	Poz-133271 ¹	PLG-05	76	595 ± 30 BP	1302-1408	rejected
5	Poz-120584	PLG-03	85,5	330 ± 30 BP	1482-1639	rejected
6	Poz-121306 ¹	PLG-03	94	405 ± 30 BP	1436-1621	rejected
7	Poz-120585 ¹	PLG-04	94	175 ± 30 BP	1659-1950	rejected
8	Poz-144609	PLG-04	96,3	275 ± 30 BP	1509-1795	kept
9	Poz-133272	PLG-05	147,7	685 ± 30 BP	1271-1387	kept
10	Poz-133273	PLG-05	150,5	1090 ± 70 BP	775-1150	rejected
11	Poz-121164	PLG-01	176,3	1870 ± 30 BP	85-237	rejected
12	Poz-133275	PLG-05	178,5	740 ± 60 BP	1177-1392	kept
13	Poz-133276	PLG-05	211,5	1430 ± 30 BP	585-656	kept

¹ at the base of event

To produce an age-depth model with radionuclides and radiocarbon ages, a smooth spline model (smoothing = 0.45, Figure 4.6) was used in the clam package on event-free master core depth (155 cm) (Sabatier et al., 2022). The event spacing of the master core is reported in Table S3. According to the age-depth model (Figure 4.6), the bottom of the PLG-03 core is dated at 1581 yr cal CE at 106.8 cm (2σ : 1514-1640). The uncertainties (2σ) of the age-depth model do not allow to properly constraint the period of Pb peaks (between 56.5 and 82.5 cm, Figure 2). To improve the model accuracy around the period of interest (Figure 4.6, dashed gray line), an additional historical date was implemented in the general model, which corresponds to the beginning of smelting at the Peisey-Nancroix mining site (1745 ± 1 yr cal CE, at 82 cm). These changes are visible in purple in Figure 4.6 to produce a second model (in blue). According to the age-depth model, the sediment accumulation rate (SR) was relatively constant between 0 and 100 cm varying from 1.15 to 1.45 mm.y^{-1} . Then, it increases in depth until 150 cm to reach 2.08 mm.y^{-1} .

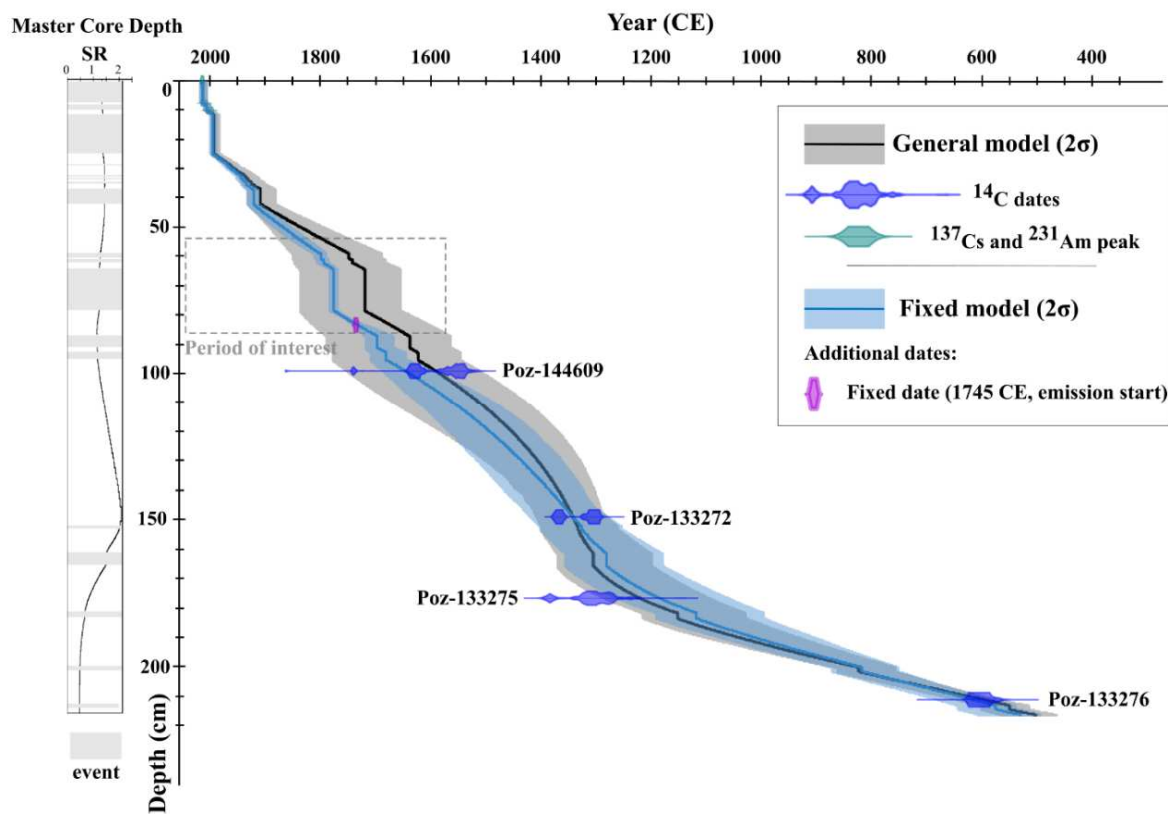


Figure 4.6: Age-depth model of the master core combining ^{137}Cs and ^{231}Am peaks with ^{14}C dates. A first general model was built with measured data with dark grey showing the confidence interval (2σ) around the best calibration date (black line). The second model was built with an additional date indicating the historical beginning of smelting at the Peisey-Nancroix mining site (1745 ± 1 yr cal CE, at 82 cm).

4.5.6 Anthropogenic Pb inventories

4.5.6.1 Lake sediment anthropogenic Pb inventories

The accumulation rate of anthropogenic Pb ($\text{AR}_{\text{Pb_ANTH}}$) was calculated using both the elemental method and the isotopic method, based on equation (2) on nine selected samples. Both methods yielded similar results (Figure 4.7B), which shows the accuracy of the element-based method. We will thus use element-based ARs in further development of this paper, in order to reconstruct it at the highest resolution.

From 1593 to 1713 yr cal CE, $\text{AR}_{\text{Pb_ANTH}}$ is non-significant. The oldest significant rise in $\text{AR}_{\text{Pb_ANTH}}$ is dated 1731 CE ± 10 yr. It then peaked between 1750 and 1790, i.e. during the oldest activity period of Peisey-Nancroix metallurgical site (Figure 4.7C). The most recent samples present $\text{AR}_{\text{Pb_ANTH}}$ very close to pre-industrial values, however, several peaks in ARs are observed along the decreasing trend which followed the closing of Peisey-Nancroix metallurgical site in 1824.

The two peaks of contamination evidenced both by the core scanner XRF data and computed ARs seem to mirror the ore production data from the local smelting site characterised by two phases of activity separated by an industrial pause between 1792 and 1804 (Figure 4.7C). However, one must remember the age-depth model presents large uncertainties and such an interpretation must be discussed cautiously.

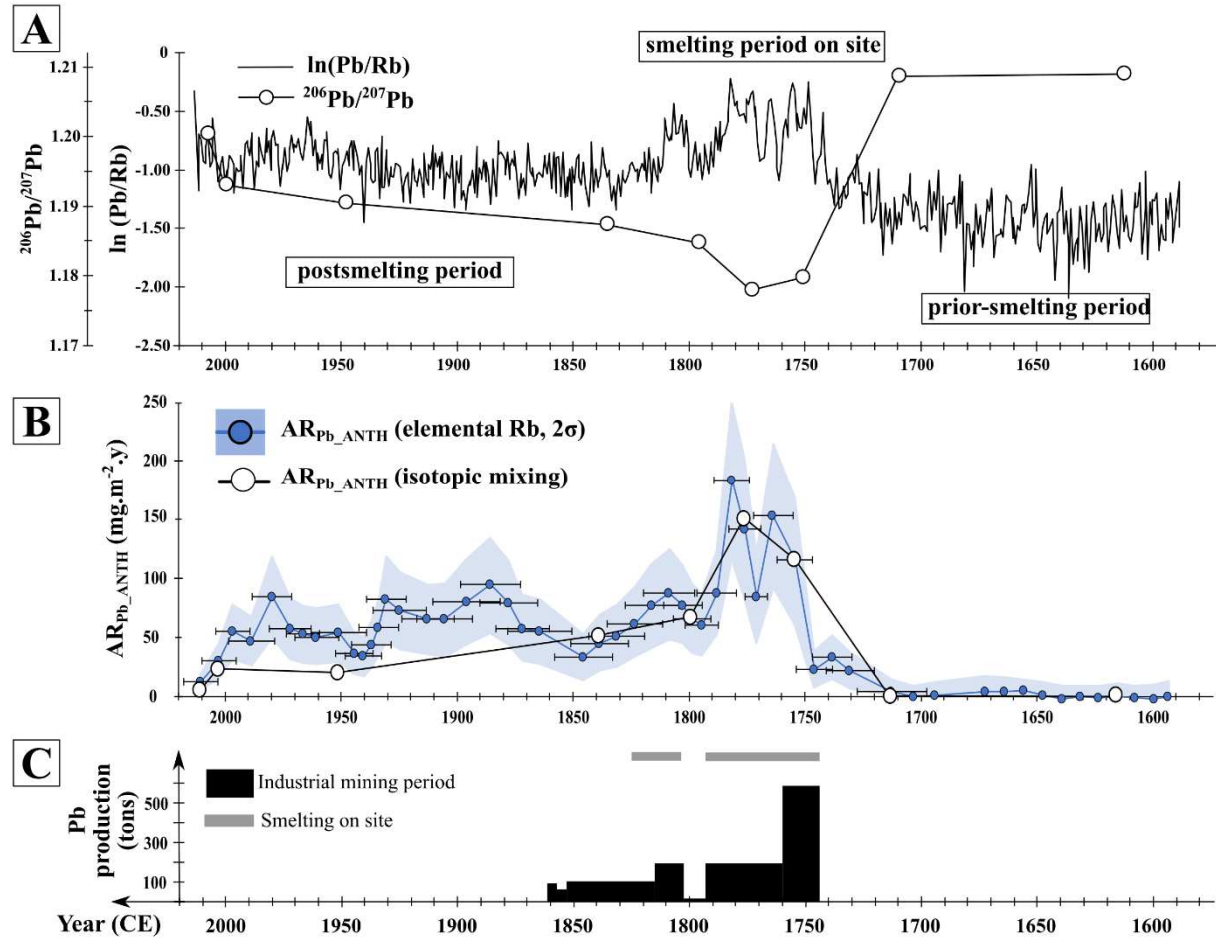


Figure 4.7: A) The ratio $\ln(\text{Pb}/\text{Rb})$ from XRF-EDS data according to time (age CE) divided into 3 periods : pre-smelting, smelting and post-smelting periods with $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 9 samples along PLG-03; B) Accumulation rate of anthropogenic Pb ($\text{AR}_{\text{Pb_ANTH}}$) calculated using both the elemental ratio (Rb) and Pb isotopes (equations 3 and 4); C) Historical timeline of the ore production from 1745 to 1865 yr cal CE.

In order to mitigate the effect of age-model uncertainties, we computed contaminating Pb inventories over large time periods. Indeed, from equation 5, we computed the total inventory of anthropogenic Pb as well as the inventory during the smelting period ($\text{Inv}_{\text{Pb}}^{\text{smelting}}$ during 1745-1824 yr cal CE; i.e. 79 years) and after the smelting period ($\text{Inv}_{\text{Pb}}^{\text{post-smelting}}$; 1824-2019 yr cal CE; i.e. 195 years), respectively. A total of $19.3 \text{ g}\cdot\text{m}^{-2}$ of Pb due to anthropogenic activities has been cumulated in PLG-03 core from 1593 to 2019 yr cal CE; with less than 0.1% accumulated prior to the period of local smelting activity (1593-1745 yr cal CE).

During the 79 years of the smelting period ($Inv_{Pb\ smelting}$) a total of 7.8 g of Pb has been accumulated per m^2 , at the bottom of the lake, which represents a mean accumulation rate of ca. $98\ mg\cdot m^{-2}\cdot y^{-1}$. This is comparable to the post-smelting period in terms of inventory ($10.7\ g\cdot m^{-2}$) although the mean accumulation rate was slightly lower during this latest period (ca. $55\ mg\cdot m^{-2}\cdot y^{-1}$). These inventories account for 40% and 54% of the total inventory of the core, respectively.

4.5.6.2 *Soil anthropogenic Pb inventories*

The anthropogenic Pb (Pb_{ANTH}) was determined using the elemental method, using Th as the immobile element. This approach is appropriate because the ratio of Pb/Th remains constant in the deepest soil horizons whatever their lithology. The anthropogenic contribution of Pb in soils ranges from 54% to 89% (Figure 4.4). The highest percentages were found in the vicinity of the (A1; 86%) or within relatively flat areas higher in the catchment area (A2; 89% and B6; 86%), i.e. in zones of potential accumulation. By contrast the lowest percentages were observed in A3 (54%), A4 (65%), and B3 (70%), all located in steep areas, thus more exposed to erosion processes. Based on equation (6), the inventories of anthropogenic Pb accumulated within a soil thickness of 20 cm were calculated for each superficial soil sample (Inv_{Pb_soil}). The Inv_{Pb_soil} of superficial soils varies from 1.6 to $9.0\ g\cdot m^{-2}$ (4.9 ± 2.5 , Table 4-4).

4.6 Discussion

4.6.1 Recording of local ore smelting activities

In order to test the validity of a local origin for this pollution period, we compared it with similar data acquired from the sediment of Lake Anterne, which is located in the Aiguilles Rouges massif, 56 km as the crow flies (Massif des Aiguilles Rouges, France, Figure 4.1B). Arnaud et al. (2004) estimated anthropogenic Pb fluxes since 1725 CE in Lake Anterne sediments. The absence of significant Pb contamination in Lake Anterne prior at the end of the 19th century, permits to exclude a regional phase of contamination between 1745 and 1824 and thus reinforce both the proposed age-model hypothesis and the attribution of the Pb excess to a local contamination.

The focus factor (equation 7) estimated from the $^{210}Pb_{ex}$ inventories of Lake La Plagne and the Lake Anterne allows us to calculate a surplus of $7.3\ g\cdot m^{-2}$ of anthropogenic Pb (equation 8) for Lake La Plagne (Table 4-4). Such a value means that Lake La Plagne is enriched 30 times compared to the regional signal recorded in Lake Anterne during the smelting period at Peisey-Nancroix mine

site (1745-1824). This confirms that the anthropogenic Pb recorded in Lake La Plagne results from atmospheric fallouts during smelting rather than from a more regional signal.

Table 4-4: Inventories of anthropogenic Pb and $^{210}\text{Pb}_{\text{ex}}$

	Inv. Pb_{ANTH} ($\text{g}\cdot\text{m}^{-2}$)				Inv. $^{210}\text{Pb}_{\text{ex}}$ Bq $\cdot\text{m}^{-2}$
	Smelting	Post-smelting	Recent	Total	
Lake La Plagne sed.	7.8	8.5	1.8	19.3	17280
Lake Anterne sed.	0.3	1.9	0.4	2.5	8170
Surplus (FF=2.12)	7.3	4.5	0.8	-	
La Plagne soils	4.88 \pm 2.5 (1.64-9)				

Indeed, during the period of maximum ore production in Peisey-Nancroix, the anthropogenic Pb accumulation rate (i.e., anthropogenic flux, $\text{AR}_{\text{Pb}_{\text{ANTH}}}$) reached $183 \pm 67 \text{ mg}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$. During that period, the variations in anthropogenic Pb fluxes are consistent with the evolution of the ore production, from an average $\text{AR}_{\text{Pb}_{\text{ANTH}}}$ of $113 \text{ mg}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ between 1745 and 1792 yr cal CE ($n=7$) to an $\text{AR}_{\text{Pb}_{\text{ANTH}}}$ of $74 \text{ mg}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ between 1804-1824 yr cal CE ($n=5$, Figure 4.7).

Anthropogenic Pb fluxes recorded at Lake La Plagne during smelting activities are high and no such $\text{AR}_{\text{Pb}_{\text{ANTH}}}$ were recorded during the Roman, Medieval or recent times in the western Alps (Arnaud et al., 2004; Guyard et al., 2007; Thevenon et al., 2011b, 2011a; Giguët-Covex et al., 2011; Simonneau et al., 2014; Guédron et al., 2016; Elbaz-Poulichet et al., 2020). The only equivalent comparison was described by Mihaljevič et al. (2006) at Příbram, Czech Republic, (19th-20th centuries), which reached a total Pb flux of $\sim 120 \text{ mg}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ in a peat bog, corresponding to a mass of 5000 t Pb produced from Pb-ore.

The total amount of anthropogenic Pb accumulated in the Lake La Plagne sediment core ($\text{Inv}\cdot\text{Pb}_{\text{anth}}$) corresponds to a total of $19.3 \text{ g}\cdot\text{m}^{-2}$, exceeding the Pb inventories estimated from various archives sampled near Pb-Ag mining districts (Yang et al., 2002a; Yang and Rose, 2005; Bacardit et al., 2012). For example, the Etang de la Gruère (Switzerland, Shotyk et al., 1998) or the Etang Mort (Spain, Hansson et al., 2017) accumulated less than $9 \text{ g}\cdot\text{m}^{-2}$ of anthropogenic Pb during Roman and Medieval times in peat bog. Local industrial contamination may hence contribute to a much higher Pb load in the environment than both global Roman and medieval contaminations. Remote mountain areas have the potential to store global, regional, and local contaminations. It has been shown that mountain soils have an isotopic signature between anthropogenic sources

driven by industrial emissions and the uncontaminated background (Hernandez et al., 2003; Lahd Geagea et al., 2008). Present-day remobilisation of past deposited leaded gasoline has also been identified as a lake contaminant (Bacardit and Camarero, 2010; Hansson et al., 2017).

In this study, the Pb isotopic compositions of lake sediments and catchment soils do not show any contribution from leaded gasoline or any anthropogenic sources of Pb other than local metallurgy (Figure 4.4C). In lake sediments, a small Pb peak similar to the one recorded in Lake Anterne was identified in Lake La Plagne between 1965 and 1975 CE, but no Pb isotope data can confirm the presence of gasoline Pb. Lake Redò (Central Pyrenees, Spain), which is located between two mining districts (~20 km apart) operated during the last century, has evidenced no trace of gasoline Pb. However, in areas previously contaminated by smelting of nearby Pb-ore mines, the signal of Pb contamination may have been weakened due to the dilution caused by the presence of inherited Pb for several hundred years. The same seems to have occurred in Lake La Plagne. We could also hypothesize that very distant mountain catchment areas may thus have been preserved from Pb fluxes, showing no or minor contribution (Lake La Plagne, this study; Lake Redò, Camarero et al. 1998) in contrast to lakes located closer to urban centres (Lake Anterne, Arnaud et al. 2004, Giguet-Covex et al. 2011; Lake Lucerne, Thevenon et al. 2011; Lake Robert, Elbaz-Poulichet et al., 2020).

4.6.2 Long persistence of anthropogenic Pb in lake sediments

Unlike other archives, such as ombrotrophic peats that record direct atmospheric deposition, the accumulation of anthropogenic contaminants in sediments is the sum of the atmospheric deposition over the lake itself and a fraction of the deposition over the entire catchment area, which have been remobilized by erosion (Bacardit and Camarero, 2010; Rose et al., 2012). Consequently, the larger the catchment and the more connected it is to the lake, the higher the contaminant inventory will be for a similar atmospheric flux.

During the post-smelting period, Inv_{Pb} of Lake La Plagne is 5 times higher than that of Inv_{Pb} in Lake Anterne (10.5 and 2.2 $g \cdot m^{-2}$, respectively, Table 4-4). A surplus of 5.9 $g \cdot m^{-2}$ of anthropogenic Pb (+56 % compared to the regional signal) is hence recorded in Lake La Plagne during the post-smelting period (1824-1999 yr cal CE). However, the difference in AR_{Pb_ANTH} between Lake La Plagne and Lake Anterne tends to decrease (Figure 4.8A) over the most recent period (1970-1999 yr cal CE) with a local surplus of anthropogenic Pb of 0.8 $g \cdot m^{-2}$. These Pb inventories hence indicate a significant anthropogenic Pb surplus in Lake La Plagne since the smelter was shut down (Figure 4.8B). As no other source of anthropogenic Pb was identified apart from metallurgic

emissions, these results suggest the presence of a pervasive source of metallurgical Pb in the catchment area due to the remobilisation of lead fallouts that accumulated in soils during the 76 years of metallurgical activities.

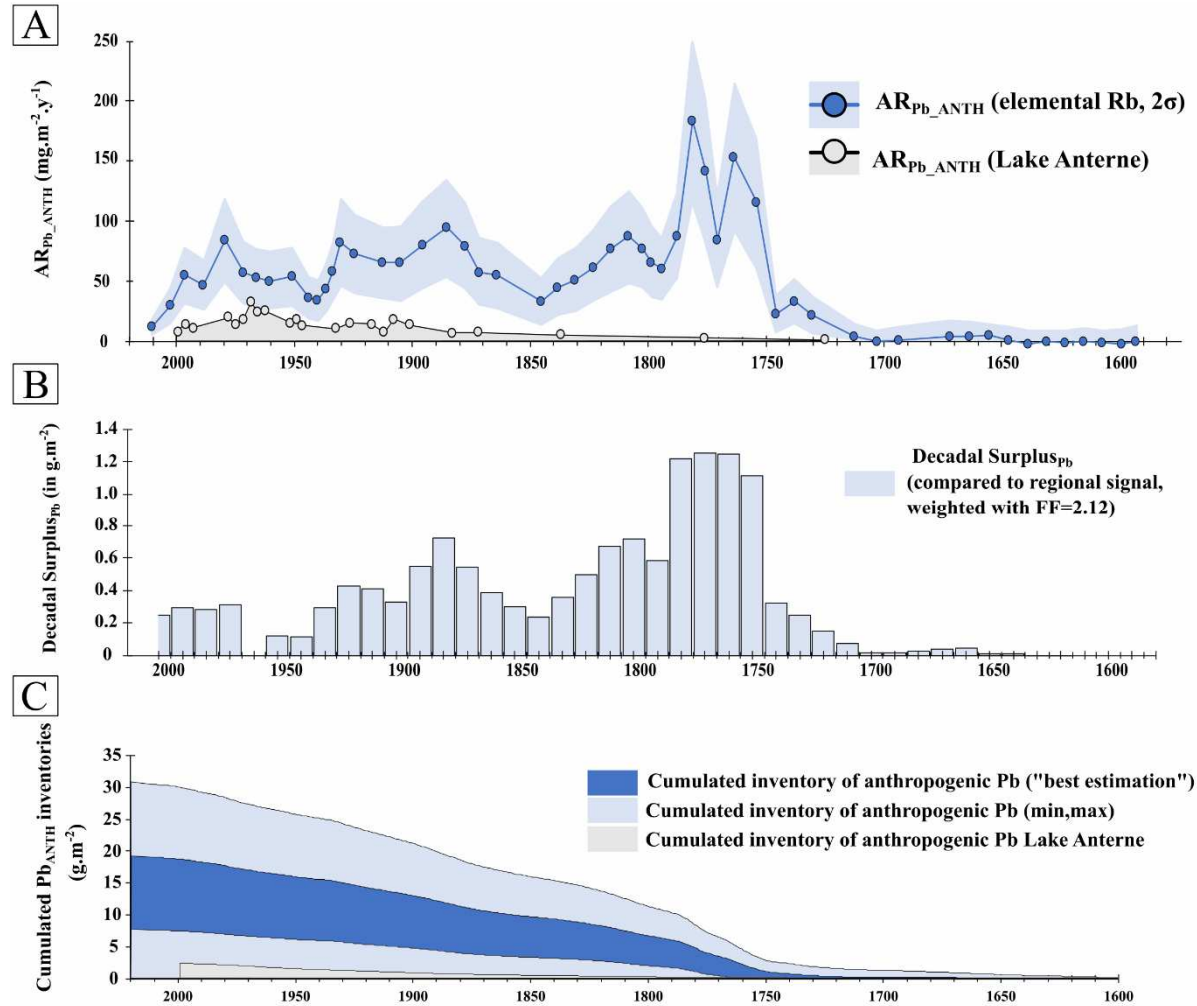


Figure 4.8: Comparison between Lake La Plagne and Lake Anterne. A) Comparison between ARPb_ANTH of Lake Anterne and of Lake Plagne; B) Local surplus of PbANTH per m² calculated from ARPb_ANTH subtracted from the regional signal (2.12*Lake Anterne); C) Cumulated Pb_ANTH through time in both lakes corresponding which in turn correspond to the total inventory recorded in lakes at the sampling date.

This is confirmed by the Pb isotopic compositions of shallowest sediments, which show a mixing between the local isotopic background and the local ore, with a remaining contribution of the anthropogenic lead around 20 to 25% of the total. A small proportion of the Pb emitted during smelting processes is hence still being eroded from the catchment soils nowadays and transferred to the lake. Therefore, soils within Lake La Plagne catchment area could be considered as a long-term, slowly emptying, source of anthropogenic Pb contamination. Such a process has been suggested by several studies.

4.6.3 Long-lasting remobilisation of legacy Pb from soil

We evidenced a decreasing trend in anthropogenic Pb fluxes from local inherited smelting contamination in the sediments of Lake La Plagne which now tends to be negligible ($\sim 20 \text{ mg}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$, Figure 4.8A). This suggests that less and less anthropogenic Pb have been washed out from the catchment over time (Figure 4.8B). However, superficial soils from the catchment are not yet free of local anthropogenic Pb (Figure 4.4). These combined observations suggest that the most mobile Pb has already been washed out into the lake and that the remaining Pb might be relatively stable. Further investigations, including mineral phases analyses, should be led to confirm this hypothesis. The current inventories of anthropogenic Pb in soils seems greatly influenced by the catchment topography (Figure 4.4). Indeed, we showed the most contaminated soils are located at the footstep of the catchment area and/or on the flattest parts of it, where the matter eroded upstream can accumulate. By contrast, soil samples collected uphill and/or on the steepest slopes present the lowest Pb-inventories. This confirms our hypothesis of a progressive washing out of past lead fallout since the end of metallurgical activities, through physical erosion processes.

4.7 Conclusion

This study highlights the importance of a multi-compartment approach to investigate the long-term persistence and remobilisation of anthropogenic contaminants in the critical zone. In the Lake La Plagne catchment (northern French Alps), the Pb emitted during smelting in Peisey-Nancroix (1745-1824) fell out on the lake surface and the surrounding soils. The lake sediments have recorded this primary anthropogenic contamination, reaching $180 \text{ mg}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ during the maximum production of Pb-ore. Pb isotope ratios and estimated fluxes of anthropogenic Pb in more recent sediments provide evidence of anthropogenic Pb transfer from the catchment to the lake for almost the last 200 years. If such transfer decreases over time, the catchment soils still contain significant stocks of Pb (54-89 %) that is considered as a secondary source of Pb to the environment. This study illustrates that such legacy contamination stored in soil and then remobilized through soil erosion have to be considered in contaminant mitigation strategies. Therefore, smelting that occurred 200 years ago has contributed to increasing the stock of Pb in both soils and lake sediments in the long-term (several centuries).

4.8 Acknowledgement

This work was supported by the French National Program EC2CO (Ecosphère Continentale et Côtière) and by the MITI Program (Mission pour les initiatives transverses et interdisciplinaire) of CNRS. We acknowledge the work of L. Marchal (EDYTEM) regarding field work and soil density measurements.

A RETENIR

- Une contamination anthropique en Pb vieille de 170 ans dans le bassin versant du lac de La Plagne.
- La persistance des retombées atmosphériques des anciennes fonderies de Pb, dominant largement les apports plus récents des essences plombées.
- La remobilisation de la contamination ancienne au plomb par l'érosion des sols depuis 200 ans

4.9 Supplementary Material

Table S1. Lead and silver production of the Peisey-Nancroix mine during the industrial period (1745-1866) described by Barbier (1875).

Table S2. Classification of enrichment factor (EF).

Figure S1. Cores correlation based on visual logging between PLG-03, PLG-01, PLG-04, PLG-05 and PLG-02.

Text S1. Procedure for dry bulk density (DBD) measurement in lake sediments and in soils.

Table S3. Event depth intervals of the 5 collected cores in Lake La Plagne. Events less than 5 mm were not reported.

Figure S2. Classification of lake sediments based on EDS-XRF core scanner data.

Figure S3. The Pb/Rb ratio from EDS-XRF core scanner data for the 5 lake sediment cores from La Plagne Lake.

Table S4. Major and trace element and enrichment factor (EF) of discrete lake sediments samples.

Table S5. Major and trace element of deep horizon soil from profile A5 et profile B6.

Table S6. The Pb isotopic composition of galena minerals (Pb-local ore).

Table S7. Fraction of anthropogenic Pb determined through both isotopic and elemental methods.

Figure S4. ¹⁴C dates collected in Lake La Plagne cores.

Table S8. ¹⁴C dates and Cs and Am to clam package.

Figure S5. Isotopic composition of Pb contaminant in lake sediments.

Table S1. Lead and silver production of the Peisey-Nancroix mine during the industrial period (1745-1866) described by Barbier (1875).

Period (CE)	1734 1745	1745 1760	1760 1792	1792 1802⁽¹⁾	1802 1814	1814 1824	1824 1852	1852 1856	1856 1861⁽²⁾	TOTAL
Exploitation owner	unknown	English company	Savoyard company	French Government	French Government	Sardinian administration	Sardinian administration	French-Sardinian company	French-Sardinian company	
Lead (t)	unknown	8 811	5 760	49	2 134	unknown	3879	550	360	21 543
Lead (t.y ⁻¹)	unknown	587	178	6	178	unknown	102	69	90	1 211
Silver (kg)	unknown	13 702	23 112	117	4 926	unknown	9 109	1 290	650	52 906

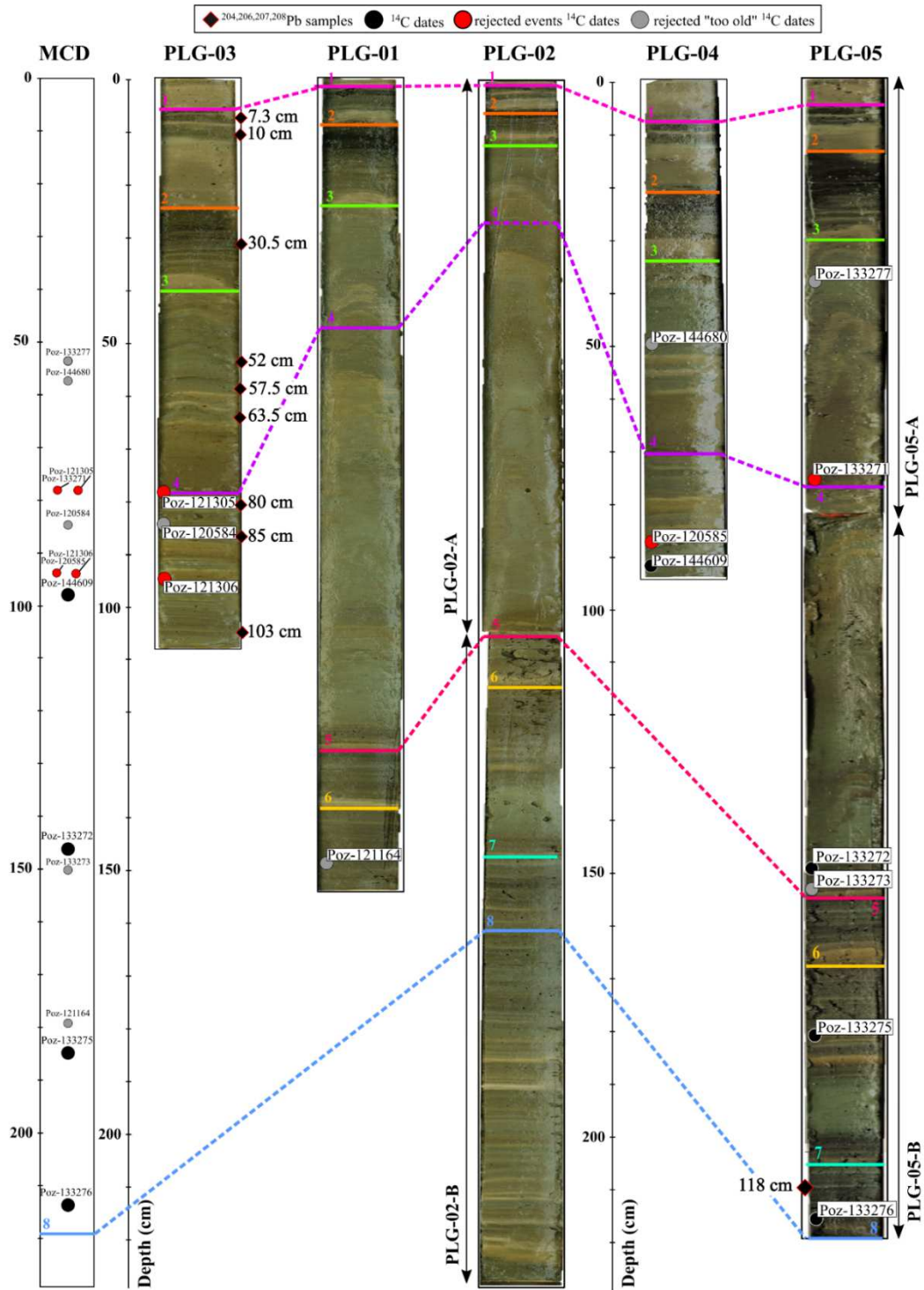
⁽¹⁾ Low production due to the French Revolution.

⁽²⁾ Smelting essentially moved to Albertville; occasional smelting on site (Barbier 1875)

Table S2. Classification of enrichment factor (EF)

EF Classification	Characterisation of the contamination
<1	no enrichment
1<EF<3	minor enrichment
3<EF<5	moderate enrichment
5<EF<10	moderate to severe enrichment
10<EF<25	severe enrichment
25<EF<50	very severe enrichment
EF>50	extreme enrichment

Figure S1. Cores correlation based on visual logging between PLG-03, PLG-01, PLG-04, PLG-05 and PLG-02. Colours lines indicate sediment correlation points. Collected samples for ^{14}C and Pb isotopes are also reported (black, red and grey circles for ^{14}C dates; black diamonds for Pb isotopes). The master core (MC) represents the master depth of core used to correlate dates on one single core.



Text S1. Procedure for dry bulk density (DBD) measurement in lake sediments and in soils.

The dry bulk density (D.B.D., in $\text{g}\cdot\text{cm}^{-3}$) is computed as the weight of the soil or lake sediment sample divided by the volume sample. Two methods were used to calculate the volume of the lake sediments sampled, depending on the depth.

For the first 50 cm of the lake sediment core, a constant cylinder volume of 3 cm^3 ($V = \pi \cdot 0.8 \cdot 0.8 \cdot 1.5$, in cm^3) was sampled during short-lived radionuclide sampling. For deeper samples (50 to 107 cm), a sediment layer (thickness measured) was sampled on all the half-core; the sampled volume (in cm^3) is thus $V = 0.5 \cdot \pi \cdot R^2 \cdot h$, with h the sample thickness and R the core radius ($R=2.85\text{cm}$).

The soil was sampled in the field for DBD measurement, using a 5 cm-diameter and 7 cm-long cylinder ($V = \pi \cdot 2.5 \cdot 2.5 \cdot 7$, in cm^3). The weight of the dry fine fraction ($< 2 \text{ mm}$) was computed in DBD measurements.

Table S3. Event depth intervals of the 5 collected cores in Lake La Plagne. Events less than 5 mm were not reported.

ID	PLG19-03		PLG19-04		PLG19-01		PLG19-02		PLG19-05	
	From_mm	To_mm	From_mm	To_mm	From_mm	To_mm	From_mm	To_mm	From_mm	To_mm
1	4	73	0	88	0	18	0	12	0	59
2	83	98	96	104	-	-	24	28	69	74
3	116	248	124	216	65	92	41	59	96	142
4	371	420	301	388	211	247	103	119	299	327
5	591	605	520	546	388	394	206	225	470	525
6	612	620	551	564	411	420	206	225	470	525
7	644	784	589	713	434	464	235	248	575	799
8	873	911	798	832	550	582	-	-	884	908
9	929	952	852	886	610	635	-	-	930	940
10	-	-	-	-	1021	1044	770	802	1299	1317
11	-	-	-	-	1244	1255	1055	1069	1500	1509
12	-	-	-	-	1346	1368	1139	1160	1591	1631
13	-	-	-	-	-	-	1301	1313	1793	1811
14	-	-	-	-	-	-	1449	1470	1979	1992
15	-	-	-	-	-	-	1560	1565	2107	2119
16	-	-	-	-	-	-	1821	1836	-	-
17	-	-	-	-	-	-	1868	1886	-	-
18	-	-	-	-	-	-	2041	2050	-	-
19	-	-	-	-	-	-	2065	2083	-	-
20	-	-	-	-	-	-	2116	2128	-	-
21	-	-	-	-	-	-	2144	2200	-	-

Figure S2. Classification of lake sediments based on EDS-XRF core scanner data. A) PCA graph of variables. B) factor map. C) inertia gain. D) hierarchical clustering. E) visualisation of classification along depth, based on geochemical EDS-XRF data (top) and visual logging (bottom).

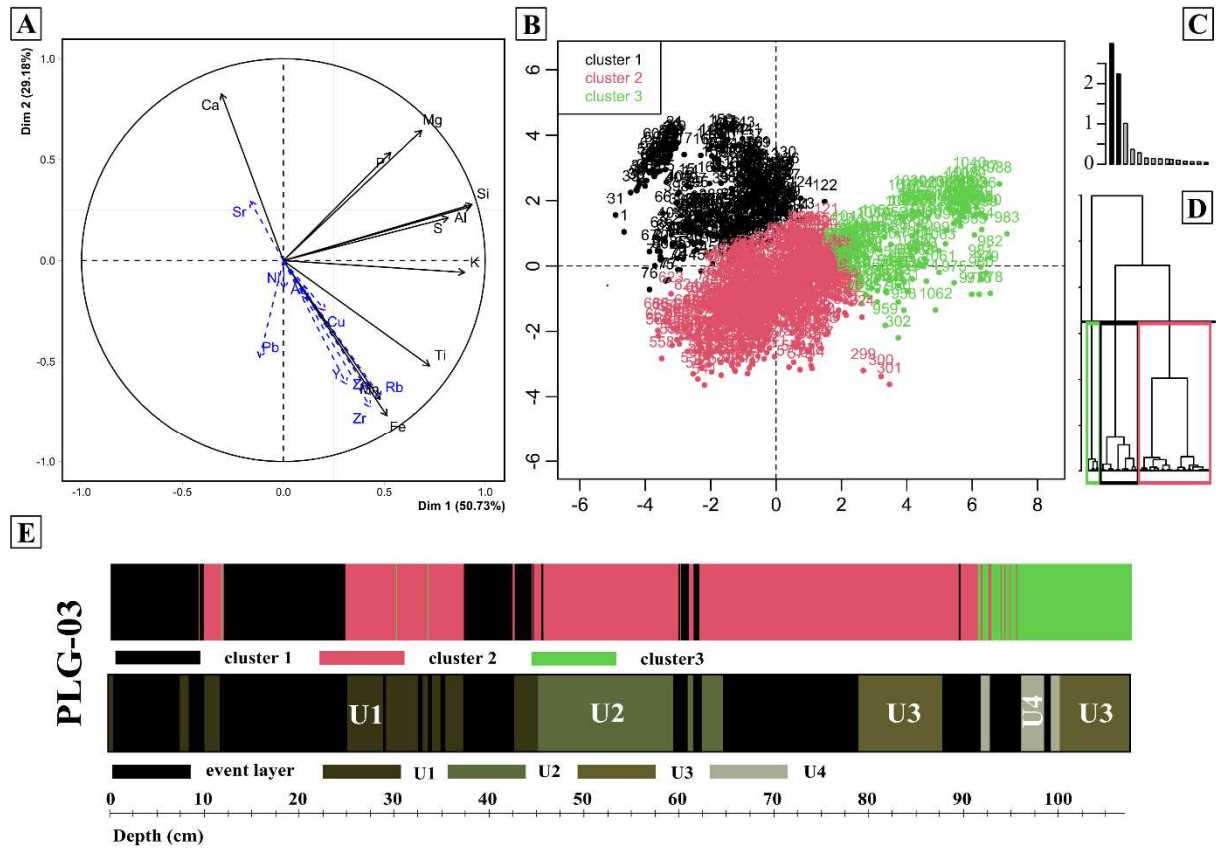


Figure S3. The Pb/Rb ratio from EDS-XRF core scanner data for the 5 lake sediment cores from La Plagne Lake. The 5 cores indicate a significant Pb peak around the violet line. Colour lines indicate correlation point between core matching Figure S1.

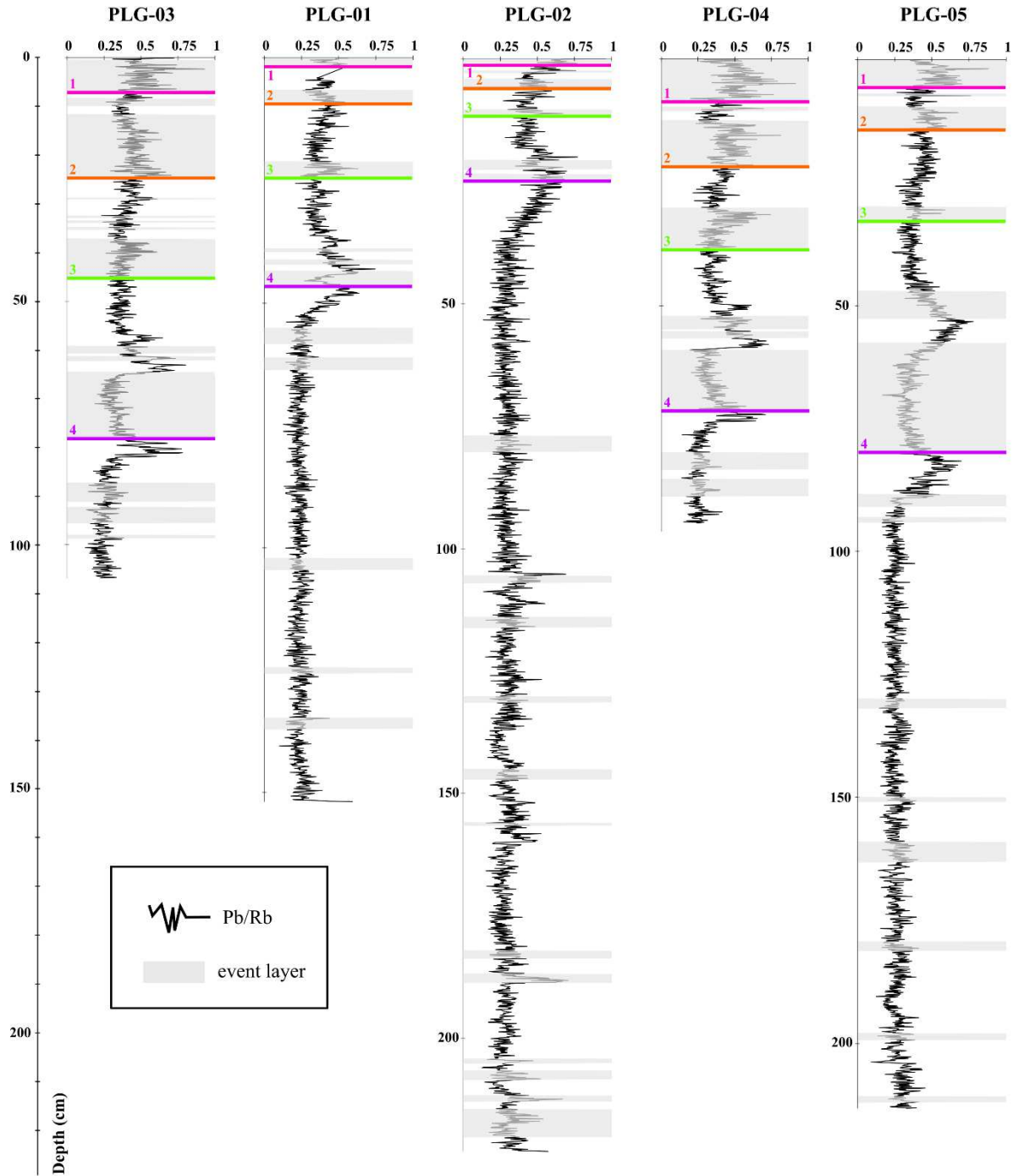


Table S5 : Major and trace element of deep horizon soil from profile A5 et profile B6.

Sample_Name	Lithology	Potentially toxic trace elements						Majors elements				
		As	Cd	Cu	Pb	Sb	Zn	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
		mg.kg ⁻¹						wt. %				
A5-H1 (0-8 cm)	Cargneule rocks	11,1	0,90	16,0	120	1,67	120	37,45	10,52	4,18	3,07	1,32
A5-H2 (8-17 cm)	Cargneule rocks	21,4	0,60	23,6	57,6	2,30	176	50,21	13,94	7,10	4,68	0,61
A5-H3 (17-24 cm)	Cargneule rocks	17,7	0,68	26,6	35,5	2,30	106	50,15	13,49	5,69	5,75	2,66
B6-H1 (0-10 cm)	Till	5,52	0,36	15,5	124	1,20	121	52,38	9,63	4,41	1,53	0,56
B6-H2 (10-20 cm)	Till	8,03	0,17	35,6	44,5	1,64	89,0	64,57	11,54	6,37	1,64	0,16
B6-H3 (20-40 cm)	Till	8,17	0,20	63,2	25,5	1,42	110	66,85	12,16	6,52	2,12	0,21
B6-H4 (40-60 cm)	Cargneule rocks	8,12	0,27	25,1	19,7	1,51	58,2	33,15	9,16	3,10	14,63	12,46

Table S6. In situ Pb isotopic compositions of galena minerals (local Pb ore).

Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	error	$^{207}\text{Pb}/^{204}\text{Pb}$	error	$^{208}\text{Pb}/^{204}\text{Pb}$	error	$^{207}\text{Pb}/^{206}\text{Pb}$	error	$^{208}\text{Pb}/^{206}\text{Pb}$	error	$^{206}\text{Pb}/^{207}\text{Pb}$	error
R05a-1	18.334	0.015	15.682	0.028	38.566	0.027	0.854	0.001	2.102	0.002	1.169	0.003
R05a-2	18.350	0.021	15.677	0.029	38.471	0.094	0.856	0.001	2.104	0.003	1.171	0.003
R05a-3	18.381	0.025	15.714	0.016	38.558	0.055	0.854	0.001	2.097	0.002	1.170	0.002
R05a-4	18.321	0.008	15.607	0.014	38.322	0.049	0.852	0.001	2.090	0.002	1.174	0.001
R05a-5	18.315	0.028	15.607	0.029	38.240	0.094	0.852	0.000	2.092	0.002	1.173	0.003
R05a-6	18.321	0.012	15.617	0.013	38.316	0.041	0.852	0.000	2.090	0.001	1.173	0.001
R05a-7	18.359	0.025	15.667	0.034	38.448	0.130	0.853	0.001	2.095	0.006	1.172	0.004
R05a-8	18.410	0.021	15.714	0.027	38.534	0.087	0.854	0.001	2.093	0.003	1.172	0.003
R05a-9	18.326	0.013	15.649	0.016	38.544	0.181	0.854	0.001	2.082	0.010	1.171	0.002
R05a-10	18.325	0.012	15.656	0.016	38.494	0.057	0.854	0.001	2.101	0.002	1.170	0.002
R05a-11	18.367	0.010	15.688	0.013	38.573	0.042	0.854	0.000	2.100	0.001	1.171	0.001
R05a-12	18.370	0.012	15.678	0.013	38.491	0.052	0.854	0.000	2.099	0.002	1.172	0.001
R05a-13	18.403	0.011	15.701	0.012	38.601	0.048	0.853	0.000	2.096	0.002	1.172	0.001
R05a-14	18.342	0.028	15.627	0.040	38.337	0.118	0.852	0.001	2.090	0.004	1.174	0.004
R05a-15	18.376	0.012	15.703	0.015	38.526	0.042	0.853	0.000	2.095	0.002	1.170	0.002
R05a-16	18.402	0.017	15.682	0.017	38.507	0.084	0.852	0.000	2.094	0.004	1.173	0.002
R05a-17	18.385	0.017	15.710	0.020	38.630	0.054	0.855	0.000	2.103	0.001	1.170	0.002
R05a-18	18.408	0.011	15.730	0.015	38.658	0.049	0.854	0.000	2.098	0.002	1.170	0.002
R05a-19	18.376	0.014	15.701	0.013	38.587	0.042	0.855	0.000	2.102	0.001	1.170	0.002
R11-1	18.369	0.024	15.670	0.024	38.495	0.093	0.852	0.000	2.093	0.001	1.172	0.003
R11-2	18.312	0.015	15.623	0.017	38.342	0.048	0.853	0.000	2.094	0.001	1.172	0.002
R11-3	18.380	0.022	15.637	0.028	38.267	0.141	0.852	0.001	2.091	0.003	1.175	0.003
R11-4	18.340	0.012	15.645	0.012	38.394	0.029	0.854	0.000	2.094	0.001	1.172	0.001
R11-5	18.319	0.008	15.626	0.009	38.341	0.031	0.853	0.000	2.092	0.001	1.172	0.001
R11-6	18.297	0.016	15.607	0.016	38.334	0.048	0.853	0.000	2.094	0.001	1.172	0.002
R11-7	18.323	0.009	15.606	0.009	38.310	0.032	0.853	0.000	2.093	0.001	1.174	0.001
R11-8	18.356	0.011	15.645	0.013	38.420	0.023	0.852	0.000	2.094	0.001	1.173	0.001
R11-9	18.325	0.038	15.615	0.046	38.269	0.151	0.853	0.001	2.090	0.003	1.174	0.005
R11-10	18.358	0.009	15.651	0.007	38.411	0.034	0.853	0.000	2.092	0.001	1.173	0.001
Mean	18.353	0.017	15.660	0.019	38.448	0.068	0.853	0.001	2.095	0.002	1.172	0.002
Std. Dev.	0.032	0.007	0.038	0.010	0.121	0.042	0.001	0.000	0.005	0.002	0.002	0.001
Median	18.356	0.014	15.656	0.016	38.471	0.049	0.853	0.000	2.094	0.002	1.172	0.002

Table S7. Fraction of anthropogenic Pb determined through both isotopic and elemental methods. In bold text, the use of these methods on soils is consistent based on one lithological source. When soils are a mixture of two lithological sources, accurately calculating the fraction of anthropogenic Pb using isotopic methods becomes challenging.

Sample Name	Type of sample	Fraction of Pb-local ore compared to deep lake sediment (basement)	Fraction of Pb-local ore compared to cagneule	Fraction of anthropogenic Pb
		$^{206}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	elemental
7.3 cm	lake sediments	0,24	-	0,55
10 cm	lake sediments	0,43	-	0,56
30.5 cm	lake sediments	0,5	-	0,59
52 cm	lake sediments	0,59	-	0,52
57.5 cm	lake sediments	0,66	-	0,66
63.5 cm	lake sediments	0,84	-	0,81
80 cm	lake sediments	0,79	-	0,80
A2	soil on basement rocks	0,88	0,96	0,89
A4	soil on basement rocks	0,67	0,89	0,65
B1	soil on basement rocks	0,80	0,93	0,82
B3	soil on basement rocks	<u>0,31</u>	<u>0,77</u>	<u>0,70</u>
B4	soil on basement rocks	<u>0,56</u>	<u>0,86</u>	<u>0,74</u>
B5	soil on basement rocks	0,97	0,99	0,75
B6	soil on till	<u>0,79</u>	<u>0,93</u>	<u>0,86</u>
A1	soil on carbonates scree	<u>0,84</u>	<u>0,95</u>	<u>0,86</u>
A3	soil on carbonates scree	<u>0,38</u>	<u>0,79</u>	<u>0,54</u>
A5	soil on cagneule	0,35	0,79	0,80
B2	soil on carbonates scree	0,55	0,85	0,81
B7	soil on carbonates scree	-0,01	0,67	0,75
B8	fluviosoil	<u>0,64</u>	<u>0,88</u>	<u>0,77</u>

Figure S4. ^{14}C dates collected in Lake La Plagne cores.

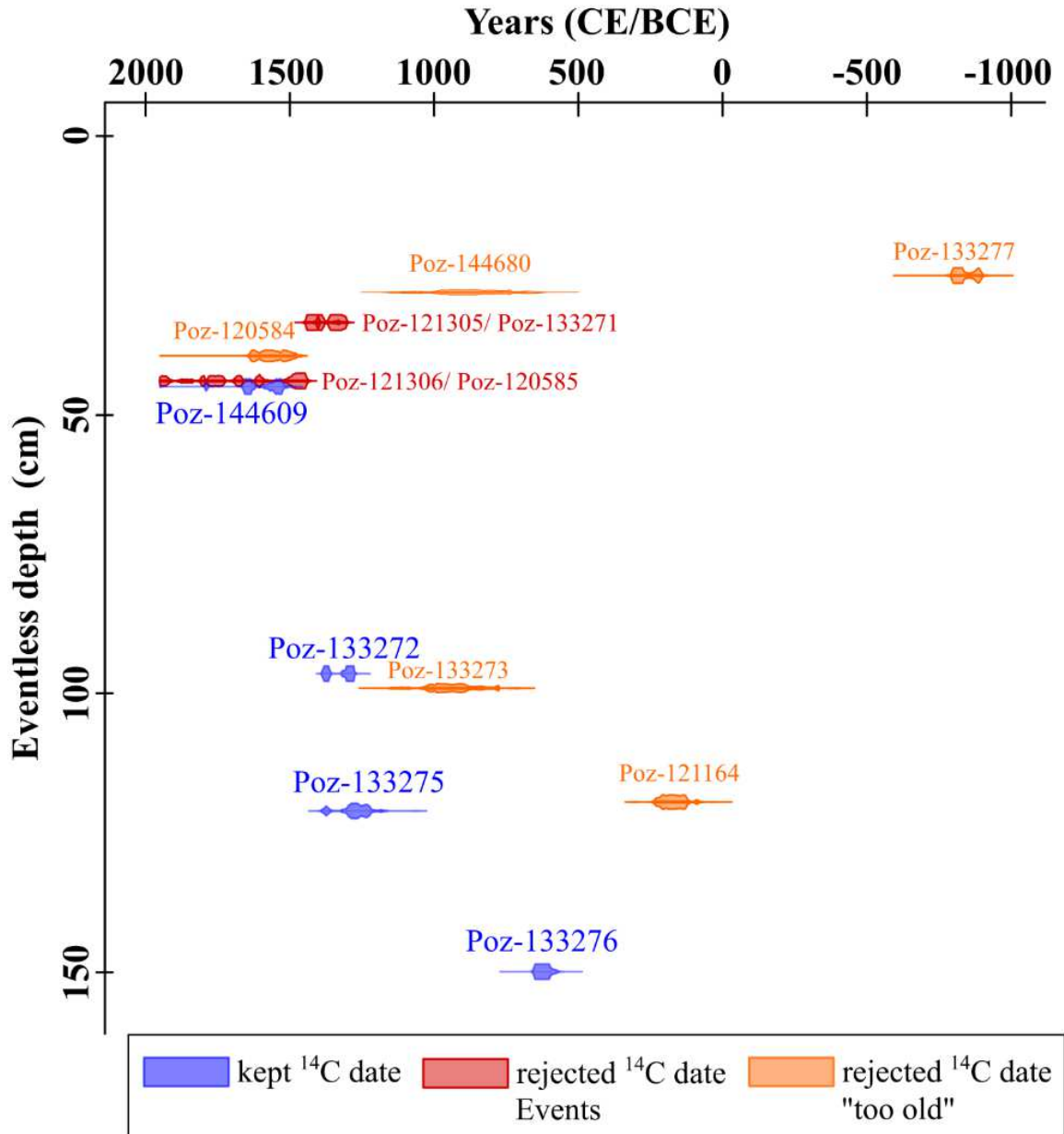
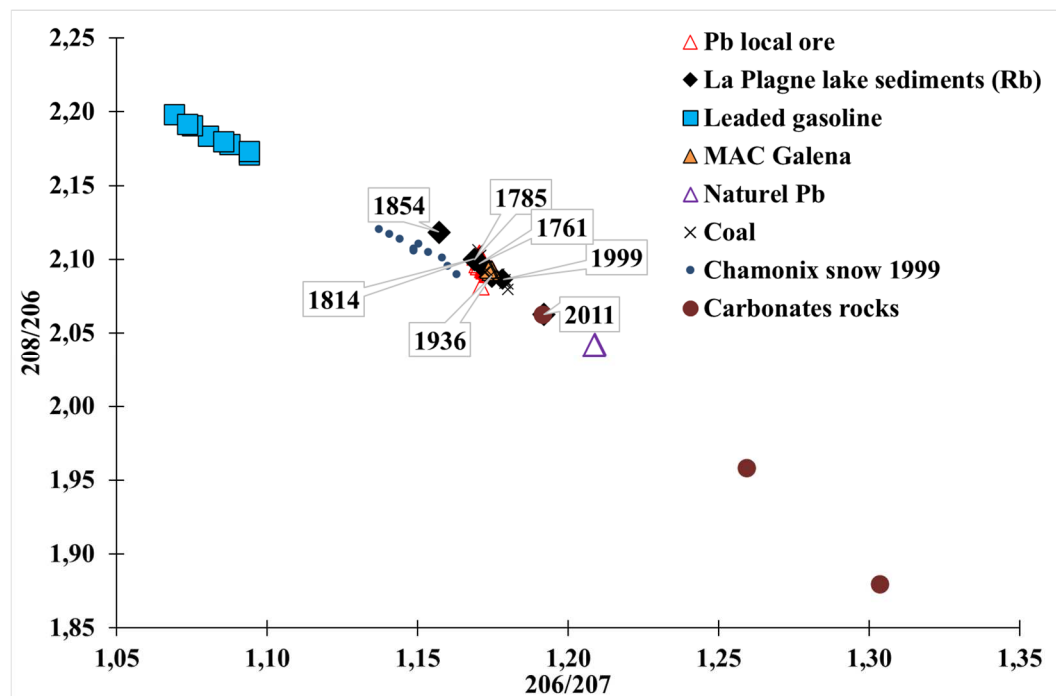


Table S8. Clam input from ^{14}C dates and ^{137}Cs data (1 rejected dates; 2 additional dates to the fixed model).

ID	^{14}C age (yr)	cal_BP (yr)	Error (yr)	Depth (mm)
Pb0	NA	2019	1	0
Pb105	NA	1986	5	19
Pb298	NA	1963	5	76
Poz133277 ¹	2665	NA	35	250
Poz144680 ¹	1110	NA	110	280
Poz121305 ¹	510	NA	30	334
Poz133271 ¹	595	NA	30	334
Hist ²	NA	1745	1	371
Poz120584 ¹	330	NA	30	394
Poz121306 ¹	405	NA	30	439
Poz120585 ¹	175	NA	30	439
Poz144609	275	NA	30	449
Poz133272	685	NA	30	965
Poz133273 ¹	1090	NA	70	991
Poz121164 ¹	1870	NA	30	1195
Poz133275	740	NA	60	1211
Poz133276	1430	NA	30	1499

Figure S5. Isotopic compositions of Pb contaminant.



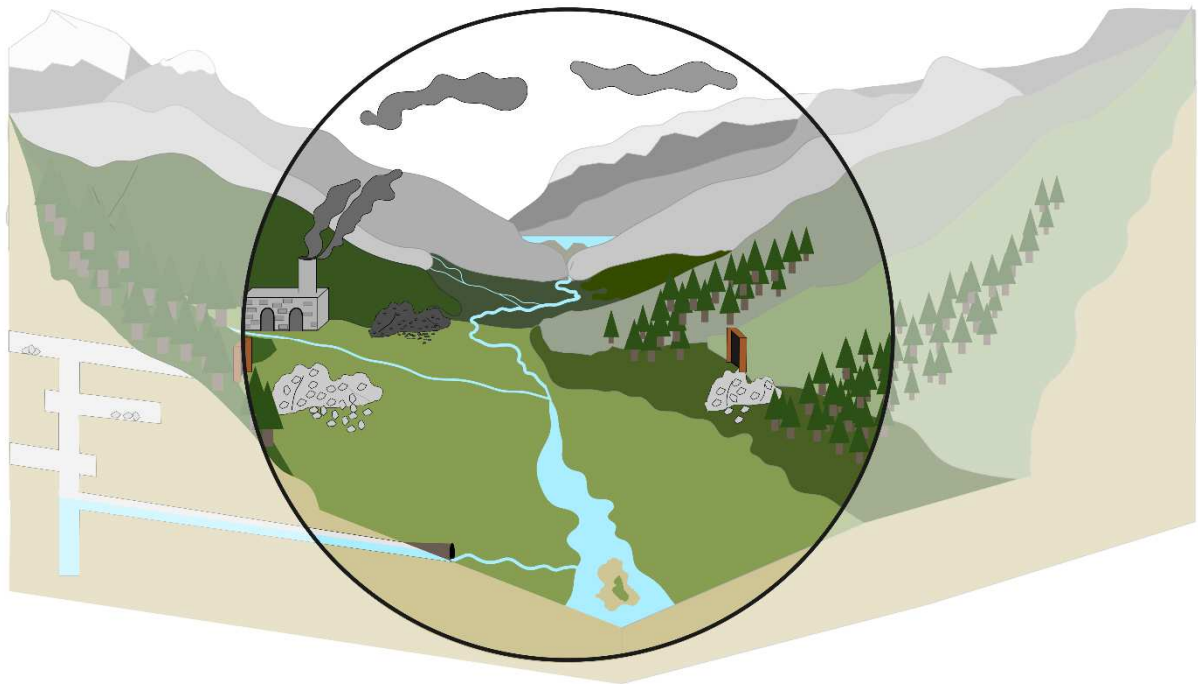
Chapitre 5 |

**Couplage isotopique Pb-Sb sur
sols, sédiments et eaux de rivières**

[Article 3]

Chapitre 5 | Couplage isotopique Pb-Sb sur sols, sédiments et eaux de rivières

Ce chapitre se concentre sur les différents compartiments de l'environnement potentiellement impactés par la présence d'activités minières et métallurgiques anciennes. La contribution des différentes sources (déchets miniers plus ou moins minéralisés et scories) à la contamination des sols de surface et en profondeur, des eaux et des sédiments de rivières sera évaluée. Les matériels supplémentaires de ce chapitre sont disponibles en fin de chapitre et sont signalés par un S.



ARTICLE 3 | In preparation for **CHEMICAL GEOLOGY**

In prep.

Multi-isotope (Pb, Sb) approach to trace metallic contaminant sources at a historical mining and metallurgical site.

Floriane Guillevic¹, Magali Rossi¹, Eléonore Resongles², Rémi Freydier², Colin Ferrari², Cécile Quantin³, Gaël Monvoisin³, Jérôme Poulenard¹, Fabien Arnaud¹

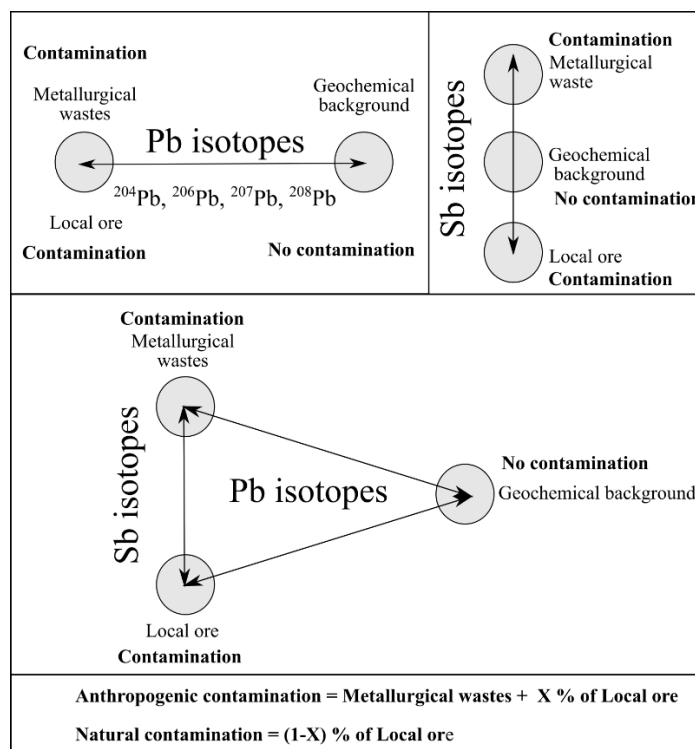
¹Université Savoie Mont-Blanc, CNRS, EDYTEM, F-73000, Chambéry, France

²HydroSciences Montpellier, Univ. Montpellier, CNRS, IRD, Montpellier, France

³Université Paris-Saclay, CNRS, GEOPS, F-91405, Orsay, France

Keywords antimony isotopes, lead isotopes, multi-isotope approach, source tracing, soil contamination, historical metallurgy, mountain critical zone

Graphical abstract



Abstract

In mining and smelting sites, where diverse PTE-rich wastes (e.g., waste rocks and slags) are stored over a mineralized background, difficulties arise to decipher the multiple sources in the contaminated environmental compartments. The former Pb-Ag mine of Peisey-Nancroix has been abandoned 160 years ago, leaving behind mining and metallurgical wastes. Based on their element content and spatial distribution, Pb and Sb isotopes were measured on a selection of ore-bearing rocks (n=4), slags (n=2) and stack residues samples (n=2), dewatering sediments (n=3), river sediments (n=3) and horizon soils (n=31) to decipher the sources of the anthropogenic contamination at the scale of the watershed (waste rocks, slags, pyrometallurgical fumes). The contamination sources, the soils and some sediments display similar $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (1.173 ± 0.003), but distinct Sb isotope ratios. Indeed, slags and stack residues have similar $\delta^{123}\text{Sb}$ signature between 0.62 and 0.78 ‰, whereas the ore-bearing rocks display $\delta^{123}\text{Sb}$ signatures between -0.28 and 0.10 ‰. Therefore, Sb isotopes allow deciphering the part of contamination of metallurgical wastes from that of ore-bearing rocks. By coupling Pb and Sb isotopic systems, we can distinguish first the degree of contamination (Pb isotopes) and then the part of local ore vs slags (Sb isotopes) from the most contaminated samples, as well as differentiate slag/ local-ore from the non-mineralized geochemical background. This approach provides an added advantage of isolating the sources of contamination more accurately.

5.1 Introduction

The extraction and processing of mineral resources are among the most harmful anthropogenic activities mostly due to the production of large volumes of wastes enriched in potentially toxic elements (PTE), such as Pb, Sb, As, Cd, etc. (Pacyna and Pacyna, 2001; Hudson-Edwards et al., 2011; Hudson-Edwards, 2016). Since the beginning of mining activity and subsequent ore smelting, the detrital translocation and weathering of the stocked mine wastes result in PTE dispersal in both terrestrial and aquatic ecosystems, which has had a negative impact on the environment (Monna et al., 2011; Mariet et al., 2017; Camizuli et al., 2018; Asare and Afriyie, 2021). If abandoned mining and metallurgical sites often represent a threat for the environment, they can also be seen as an opportunity for scientists to study the dispersal processes and persistence of PTE in the environment in order to anticipate future impacts of present-day and future mining and smelting activities (Byrne et al., 2012; Asare and Afriyie, 2021).

Therefore, there is tremendous need to develop geochemical tools to better trace the origin of PTE and their transfer pathways in the critical zone. The (bio)-geochemical processes implying mobility of PTEs, such as Cd, Zn or Cu have been enlightened by the study of their isotopic signature but this requires prior knowledge of the isotopic fractionation factors generated by these processes (Chrastný et al., 2015; Desautly and Petelet-Giraud, 2020). Metal(oid) stable isotope systems help to discriminate among different material sources and to follow the fate of PTE (Wiederhold, 2015; Komárek et al., 2021; Wang et al., 2021). If recent studies used the coupling of isotopic systems to decipher multi-contamination in the environment, such a coupling is still poorly documented in a mining and metallurgical context. Combining Cu and Zn isotopes measurements in soils and metallurgical waste allowed distinguishing smelter-Zn from background-Zn in soils using Zn isotopes only; Cu isotopes didn't allow identification of the sources (Bigalke et al., 2010). Cloquet et al. (2006b) have coupled Pb and Cd in polluted topsoils surrounding a Pb–Zn refinery plant, providing evidence of Cd fractionation, which allowed identification of three main Cd origins (industrial dust, slags, agriculture). However such coupling should not allow distinguishing ore-bearing rocks from metallurgical wastes (Wen et al., 2015). Coupling of Pb and Tl isotopic systems (Vaněk et al., 2021; in peatlands), and coupling of Pb and Cd (Baieta et al., 2021; in tree-rings) in smelting areas allowed identifying the anthropogenic contamination. Considering Tl fractionation during pyrometallurgy (Vaněk et al., 2011, 2018), coupling of Pb and Tl isotopic systems could allow deciphering contamination from ore-bearing rocks from metallurgical wastes. In this study, the traditional Pb isotope system was coupled to the less studied Sb isotope system, to better characterized the contamination sources and soil transfer processes of PTE in the setting of an abandoned 18th-19th century Pb-Ag mine (Peisey-Nacroix, French Alps).

Lead is a common co-product of different ores, which constitutes a powerful and commonly used tracer of contamination sources (e.g., Komárek et al., 2008). Commonly measured in different environmental compartments, Pb radiogenic isotopes help to distinguish a mining or/and smelting contamination from the geochemical background, even in the case of a low contamination (Komárek et al., 2008; Brugam et al., 2012; Mihaljevič et al., 2019). However, Pb is a heavy element so the mass-dependent fractionation of its isotopes during geochemical and pyrometallurgical processing is very small and negligible compared to the radiogenic variations. Therefore, on a mining site, it is not possible to isotopically distinguish the anthropogenic contamination (from excavated waste rocks and slags) from the naturally contaminated background (occurrence of nearby underground mineralisation) using Pb isotopes (Baron et al., 2006; Shiel et al., 2010; Cui and Wu, 2011). Lead is often associated with a suite of metal(oids) favourable to consider a multi-

isotope approach that may contribute to the understanding of the waste dispersion. Among them, Sb is a metalloid of interest as it is found in many Pb-Ag ores (Petruk, 2000).

If Sb isotopes have been recently used to trace anthropogenic contamination in the environments (Wen et al., 2018 and references therein), they have never been studied in a metallurgical context. In the recent years, large efforts have been made to understand the yet poorly studied Sb isotopic system (Resongles et al., 2015; Zhai et al., 2021; Ferrari et al., 2021, 2022). Unlike Pb radiogenic isotopes, Sb stable isotopes are likely subjected to significant isotope fractionation during pyrometallurgy and (bio-)geochemical processes that occur in the environment (Rouxel et al., 2003; Ferrari et al., 2022). Based on the pioneer study of Rouxel et al. (2003), describing Sb isotope composition variations within natural matrices (sediments, soils, rocks, ores), archaeologists were among the first to use Sb isotopes as a tool to indicate the origin of ancient Sb-bearing artefacts, such as bronze artefacts, glass, and ceramic objects (Lobo et al., 2013, 2014; Reguera-Galan et al., 2019; Degryse et al., 2020). Metallogenic studies attempted to apply Sb isotopes to improve the understanding of Sb ore formation (Wang et al., 2021; Zhai et al., 2021). Antimony isotopes were also used to investigate the origin and fate of Sb in mine-impacted waters (Resongles et al., 2015; Wen et al., 2022) and in waters impacted by road run-off in an urban area (Philippe et al., 2022). Bio-geochemical processes such as adsorption, redox changes can be responsible for Sb isotope fractionation (Rouxel et al., 2003; Zhou et al., 2022; Ferrari et al., 2022), however, isotope fractionation factors associated to these processes remain largely unknown. While isotopic fractionation of a number of metals including Cd, Zn and Ni (+Hg) during high-temperature evaporation-condensation (e.g. pyrometallurgy) has been documented (Sivry et al., 2008; Shiel et al., 2010; Ratié et al., 2016; Wang et al., 2021), Sb isotopic signature has never been determined in a metallurgical context.

In this study, and for the first time, we couple Pb and Sb isotopes to investigate metal dispersion resulting from a historic Pb-Ag mine in the different compartments (soils, sediments, and water) of a mountainous watershed (Peisey-Nancroix, French Alps). The study tracked metal(oid)s contamination from the sources (ore-bearing rocks and slags) to the environmental samples (soils, river sediments, and water). The specific objectives were to discriminate the influence of different contamination sources, to quantify their contribution and to test if Sb isotopes allow to track metallurgical impacts.

5.2 Material and methods

5.2.1 The Peisey-Nancroix mining site

The Pb-Ag mine of Peisey-Nancroix is located in the north-western French Alps, at 1550 m a.s.l. It was operated from the early 18th century until the mid-19th century (1734-1866). During that period, it produced 21 500 t of Pb and 52 t of Ag and was one of the most Pb and Ag productive French mine at that time (Rossi et al., 2017; Meloux, 1975). Silver, which was the metal with the main economic interest, was considered to be associated to Ag-rich galena. Recent investigations showed limited $2\text{Ag}^+ \leftrightarrow \text{Pb}^{2+}$ substitution in galena, but high Ag-content in minerals from the tetrahedrite group $((\text{Cu,Fe})_{12}(\text{Sb,As,Ag})_4\text{S}_{13})$, which occur as (micro)inclusions in galena in the Peisey-Nancroix ore (Bertauts et al., 2022). Considering that the cut-off grade in the 18th and 19th centuries were higher than today, the mine wastes remain enriched in Pb and Sb (up to 7.1 wt. % for Pb and 137 mg.kg⁻¹ for Sb; Guillevic et al., 2023). In addition to ore extraction and processing, ore roasting and smelting occurred on site for at least 80 years (1745-1824) and generated enriched Pb-Sb glassy slags (up to 10.8 wt. % for Pb and 1638 mg.kg⁻¹ Sb) and fumes (Guillevic et al., 2023). The presence of these metal-rich mine wastes and metallurgical slags has resulted in a local anthropogenic soil contamination that is restricted to the hayfields between the ore processing and the ore smelting sites (O.P. and O.S. sites respectively; Figure 5.1B; Guillevic et al., 2023).

The Peisey-Nancroix Pb-Ag ore formed during alpine thrusting of the Internal Briançonnais over the External Briançonnais (Bertauts et al., 2022). The study site is located near the main underground gallery network, on quaternary sediments overlying the Variscan basement and the alpine thrust associated to the mineralisation. More specifically, the mining site is partly developed on the western side of a large alluvial fan (silicate-rich sediments), on a carbonate-rich scree and on the alluvial terrace of the Ponturin river (Figure 5.1C; Guillevic et al., 2023). The mining site is bordered by the Arc stream to the East and by the Ponturin River to the North. The Arc stream flows along the waste heaps, and water from dewatering mine galleries flows into the Ponturin river (Figure 5.1A).

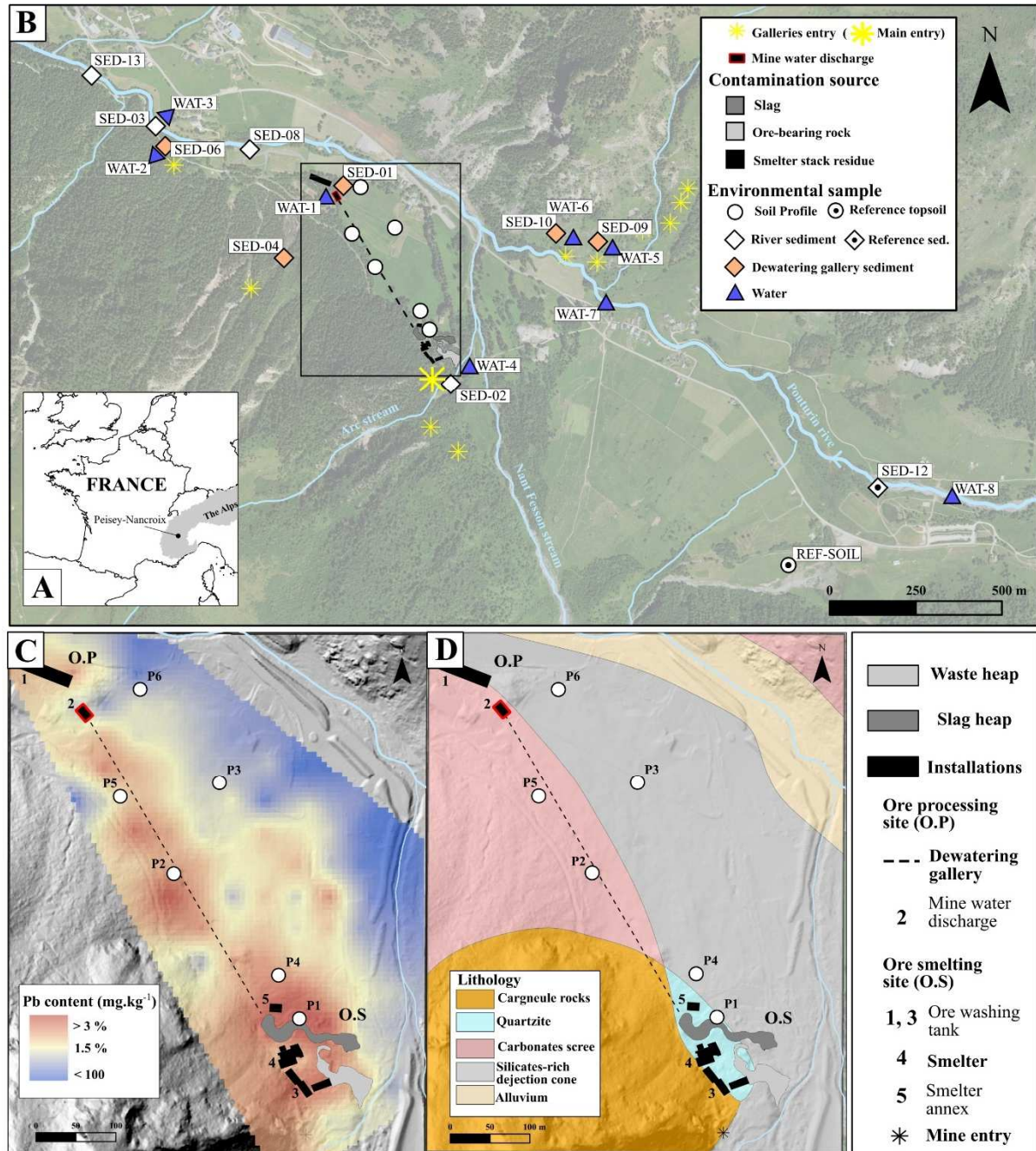


Figure 5.1: A) Location map of the Pb-Ag Peisey-Nancroix mine in the French northern Alps; B) Location map of the collected samples along the Ponturin river and the Arc stream; C) Map of interpolated Pb content of topsoils (package Autokrige; R Core team 2022) of the mining site showing the position of the soil profiles; D) Geological map of the mining site with positions of the soil profiles.

5.2.2 Sampling and sample preparation

5.2.2.1 Sources of potentially toxic elements: ore-bearing waste rocks, stack residues and slags

In order to assess the potential isotope fractionation of Sb during smelting, samples were collected in the ore-bearing waste rocks ($n = 4$), in stack residues from the smelter inner walls ($n = 2$) and in slags from the slag heap ($n = 2$; Figure 5.1). Thin sections were cut through selected samples for mineralogical observation and analysis (optical microscopy and SEM-EDX; see Supplementary Material Figure S1). A detailed analyse of the ore-bearing mineral is presented in Bertauts et al. (2022). Then, the samples were finely crushed into powder and homogenised for geochemical and isotopic analyses.

5.2.2.2 Soil profiles

Guillevic et al (2023) have shown that Pb and Sb distributions were correlated in topsoils. Therefore, the location of six soil profiles was determined based on the distribution of Pb in the hayfields downhill the slags and waste rocks heap, and according to the type of soils (Dystric Cambisols, Calcaric Cambisols and Technosols; Figure 5.1C). Soil profiles 1 (P1), 3 (P3) and 4 (P4) were dug in the Dystric cambisols developed on top of the alluvial cone (basement silicate-rich rocks), whereas soil profiles P2, P5 and P6 were dug in the Calcaric cambisols developed on top of a carbonate scree that covers the alluvial fan (Figure 5.1C). This superposition of materials is clearly demonstrated for P5 and P6, which present a bilithic character with surface horizons developed on carbonate (cargneule) scree materials (actual soil) overlying buried soil(s) from the alluvial fan. P1 is the closest profile from the slags and the waste rocks heaps (~3 m distance, Figure 5.1), and P5 is the closest profile from the former ore transportation pathway between the O.P and the O.S. sites. Among the 6 profiles, a total of 31 soil horizons were sampled: 6 horizons in P1 (0 to -75 cm); 5 horizons in P2 (0 to -55 cm); 4 horizons in P3 (0 to -60 cm); 4 horizons in P4 (0 to -60 cm); 6 horizons in P5 (0 to -70 cm), and 6 horizons in P6 (0 to -80 cm). A detailed field description and photographs of the six profiles are available in Supp. Mat. Fig S2 and Text S1.

In addition to the soil profiles, a reference topsoil (REF-TOPSOIL; 0-20 cm; Figure 5.1B) was sampled 2 km uphill the mining site on the same alluvial cone (i.e., similar main catchment) to avoid direct mining influence. In order to avoid the presence of airborne Pb emitted during smelting, this reference topsoil was collected close to the active Nant Fesson stream. Each soil

sample was air-dried for several days, sieved to 2 mm, homogenised, and then finely crushed before processing and analysis.

5.2.2.3 *Stream sediments and water samples*

Stream sediments were sampled at the exit of dewatering galleries (n=5; SED-01, SED-04, SED-06, SED-09 and SED-10) and along the Ponturin river and its affluents (n=5; SED-02, SED-03, SED-08, SED-12, SED-13) to evaluate the spatial extent of the stream contamination and the effect of dilution in a torrential context (Figure 5.1A) from upstream to downstream the mine site: SED-12 was collected 1.5 km upstream the mining site and is thus considered as a reference sediment; SED-01 was sampled at the exit of the main dewatering gallery, on the O.P. site; SED-09 and SED-10 were sampled at the exit of two exploratory galleries on the right bank of the Ponturin river; SED-02 was collected upstream the waste rock heap in the Arc stream; SED-04 and SED-06 were collected at the exit of two exploratory galleries on the left side of the Ponturin; SED-08, and SED-03 were collected downstream the mining site at the junction of the Ponturin and the dewatering waters related to SED-01 and SED-06 respectively; and SED-13 was sampled ~1 km downstream from the mining site in the Ponturin River. Each sediment sample was air-dried for several days, sieved to 2 mm, and then crushed and homogenised before analysis.

Water samples (n=8) were also collected at the same locations as the sediments (Figure 5.1B). Physico-chemical parameters (pH, conductivity, temperature; Table S2) were measured on-site using a calibrated multimeter (HQ40d, Hach Company). Water samples were filtered through a 0.22 µm PVDF filter (Millipore™) fitted on a polysulfone filter unit (Nalgene™). Filtered samples were collected in acid-cleaned HDPE bottles, acidified to 1 % v/v with HNO₃ (14.5 M, Suprapur Merck) and stored at 4 °C until analysis.

5.2.3 **Sample analysis**

5.2.3.1 *Major and trace elements*

5.2.3.1.a. *Analytical procedures*

A total of 49 samples, including soil horizons and the reference soil (n=32), stream sediments (n=6) and dewatering galleries sediments (n=4), waste ore-bearing rocks (n=4), slags (n=2) and stack residues (n=2), were sent for major and trace elements analysis at the SARM laboratory (Service d'Analyses Roches et Minéraux, CNRS National facility, Nancy, France). After a lithium tetraborate

fusion of each sample, the solutions were analysed by ICP-AES for major elements (SiO₂, Al₂O₃, K₂O, CaO, MgO, P₂O₅, TiO₂, Fe₂O₃ and MnO) and by ICP-MS for trace elements (including As, Cd, Co, Cr, Cu, Ni, Pb, Rb, Sb, Zn, Zr) according to the established protocols of Carignan et al. (2001). The reference topsoil, the two slag samples and two ore-bearing rocks were already analysed by Guillevic et al. (2023) using the same procedure.

Major cations and trace elements were analysed in water samples by ICP-MS (iCAP TQ, Thermo Scientific®) at the AETE-ISO platform, OSU-OREME/Université de Montpellier) as described in Ferrari et al. (2021). Even though this paper focuses on Pb and Sb only, the full geochemical dataset is available in Supp. Mat. Table S3.

5.2.3.1.b. *Enrichment factors*

Lead and Sb enrichment factors (EF_m) were calculated using Equation 1.

$$EF_m = \frac{\left(\frac{M}{Rb}\right)_{sample}}{\left(\frac{M}{Rb}\right)_{ref}} \text{ equation (1)}$$

with (M/Rb)_{sample}, the Pb/Rb or Sb/Rb ratios of the samples, and (M/Rb)_{ref} the Pb/Rb or Sb/Rb ratios of a reference sample (i.e., local geochemical background). For this multi-compartment study, the authors have decided to select reference samples according to the matrix analysed. Therefore, the assumed uncontaminated upstream sediment sample SED-12 (Pb/Rb = 0.16 , Sb/Rb = 0.03) was used for reference for all the stream and dewatering gallery sediments. As two main soil types have been identified in the mining area (Figure 5.1C), the deepest horizon of the least contaminated profiles was selected for each type of soil: the deepest horizon of P3 was used as reference (Pb/Rb = 1.53, Sb/Rb = 0.04) for the Dystric Cambisols P1, P4 and P3, whereas the deepest horizon of P6 was used as reference (Pb/Rb = 0.19, Sb/Rb = 0.01) for the Calcaric Cambisols P2, P5 and P6. EF_{Pb} and EF_{Sb} are reported in Supp. Mat. S3. Marrugo-Negrete et al. (2017) consider 7 classes of enrichment depending on EF_m: EF_m<1 correspond to no enrichment, 1 < EF_m<3 to minor enrichment, 3 < EF_m<5 to moderate enrichment, 5 < EF_m<10 to moderately severe enrichment, 10 < EF_m<25 to severe enrichment; 25 < EF_m<50 to very severe enrichment, and EF_m>50 to extremely severe enrichment.

5.2.3.2 *Soil properties*

A detailed characterisation of each soil horizon was performed at the French national reference soil laboratory (INRAE, France). The size distribution, pH, cation exchange capacity (CEC), exchangeable cation content, equivalent CaCO_3 total content, C_{total} content, N_{total} content, and total organic carbon (TOC) were assessed for the fraction of soil <2 mm. The analytical procedure is described in Guillevic et al. (2023). Supp. Mat. Table S3 presents the results for the six soil profiles.

5.2.3.3 *Determination of Pb and Sb isotopic signature*

Lead and Sb isotopes were measured on a selection of samples: 3 soil profiles with various soil types and Pb-Sb enrichment (P1, P3, P5), the reference topsoil, the 2 slags, the 2 stack residues, 3 river sediments (from upstream to downstream; SED-12, SED-03, SED-13), 3 dewatering sediments (SED-01, SED-09, SED-10). Sample preparation was carried out in a class 10000 cleanroom at the laboratory HydroSciences Montpellier - HSM (sample digestion and Sb isotopes) and at the laboratory Géosciences Paris-Saclay - GEOPS (Pb isotopes) and at the laboratory Services d'Analyse des Roches et des Minéraux - SARM-CNRS (Pb isotopes). All reagents were of Suprapur® quality (Merck) or tri-distilled acids and ultrapure water was used (Milli-Q®, Millipore). All consumables (pipette tips, tubes, PTFE vial, etc.) were acid-cleaned before use.

5.2.3.4 *Digestion of solid samples*

Fifty mg of solid samples (soils, sediments, rocks, slags and stack residues) were digested with an acid mixture (4.5 mL of 14.5 M HNO_3 , 1.5 mL of 22.6 M HF and 1.5 mL of 9.5M HCl) using a microwave (UltraWAVE, Milestone®). Samples were heated to 200 °C in 25 min and held at 200 °C for a further 10 min. After cooling down, digest solutions were transferred in PTFE vials, evaporated at 80 °C to avoid Sb volatilisation. Dry-residues were then re-dissolved in 30 mL of 1.5 HNO_3 , closed vials were ultrasonicated for 1 h and then heated at 80 °C overnight to ensure a complete dissolution of the residue. Digest solutions were filtered using acid-cleaned disposable 0.22 μm PVDF filters and polypropylene syringes. Procedural blanks and certified reference material (NIST 2711a) were processed as samples.

Lead and Sb concentrations were analysed by ICP-MS at the AETE-ISO platform. These digest solutions were used for Sb and Pb purification prior to isotopic analysis at HSM and GEOPS laboratories, respectively.

5.2.3.4.a. *Sample preparation and analysis of Sb isotopic signature*

Antimony separation

Antimony was separated from the sample matrix following the protocol described in Ferrari et al. (2021). Briefly, an aliquot of digest solutions containing 30, 50 or 100 ng was evaporated and re-dissolved in 10 mL of 0.5 M HCl with 0.5 % w/v potassium iodine (KI) and ascorbic acid (AA) to reduce Sb(V) to Sb(III). After at least 3 h, samples were passed through cartridges filled with 0.2 g of TSP (thiol-functionalized silica powder) and rinsed successively with 5 mL of 0.5 M HCl and 6 mL of 2.5 M HCl, then Sb was eluted with 6 mL of 6 M HCl (Sb elution). Finally, samples were diluted to 1 µg/L of Sb in 10 mL of 3 M HCl with 0.5 % w/v KI/AA for Sb isotopic analysis.

Antimony isotope analysis by HG-MC-ICP-MS

Antimony stable isotopes (^{121}Sb and ^{123}Sb) were measured with a MC-ICP-MS (MultiCollector Inductively Coupled Plasma Mass Spectrometer, Neptune+, Thermo Fisher Scientific®) coupled with a hydride generation (HG) system (MP2 hydride ICP, Elemental Scientific®) at the AETE-ISO platform, OSU-OREME/Université de Montpellier. Analytical configuration and instrument tuning parameters are detailed in Ferrari et al. (2021). Each sample was analysed three times using a sample-bracketing method and an in-house isotopic standard solution “SPEX” (SPEX Sb 1000 mg/mL in 20 % w/w HCl, batch number 24-175SBX). ^{126}Te was measured in addition to ^{121}Sb and ^{123}Sb to check that no isobaric interference of ^{123}Te over ^{123}Sb occurred.

Isotopic signatures of Sb are expressed as $\delta^{123}\text{Sb}$ (‰), which represents the deviation between the $^{123}\text{Sb}/^{121}\text{Sb}$ ratio of the sample and the average ratio of the isotopic standards SPEX measured before and after the sample (Equation 2).

$$\delta^{123}\text{Sb} = \frac{\left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}}\right)_{\text{sample}} - \left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}}\right)_{\text{avg SPEX}}}{\left(\frac{^{123}\text{Sb}}{^{121}\text{Sb}}\right)_{\text{avg SPEX}}} \times 1000 \quad (\text{Equation 2})$$

The recovery of Sb after purification was determined based on the initial theoretical mass of purified Sb (30, 50 or 100 ng) and the final mass of Sb recovered in purified samples calculated from the intensity measured by HG-MC-ICP-MS. On average, 100 ± 7 % of Sb was recovered after the purification step. Procedural blanks (including digestion and purification steps) represented less than 1 % of Sb measured in samples. The certified reference material of soil NIST2711a was measured at 0.05 ± 0.02 ‰, which matches with the published value (0.06 ± 0.02 ‰, Ferrari et al., 2021).

5.2.3.4.b. *Sample preparation and analysis of Pb isotopic signature*

Lead isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb) were analysed in solutions of mineralized samples either at GEOPS laboratory or at SARM-CNRS (Table 5-1). Solutions of mineralized samples ($n=21$) were analyzed by High-Resolution ICP-MS (Thermo Scientific®, Element XR, USA, at Laboratoire GEOPS, Université. Paris-Saclay). All solutions were diluted at 500 ppt. Measurement settings were a dwell time of 10 ms, 420 sweeps, and 5 replicates per sample. Mass bias and drift of the isotope ratios were corrected based on repeated measurements of the Pb reference material NIST SRM-981 that was analyzed between every three samples ($^{206}\text{Pb}/^{207}\text{Pb} = 1.0934 \pm 0.0060$, $^{208}/^{206}\text{Pb} = 2.1668 \pm 0.0128$; $n = 27$). Repeated measurements of IAEA-SL-1 reference material over different analytical sessions give values for $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.2207 ± 0.0043 and for $^{208}\text{Pb}/^{206}\text{Pb}$ of 2.0324 ± 0.0048 ($n = 54$), which is in agreement with previous SL1 measurements reported by Froger et al. (2018) et Kobayashi et al. (2023).

Additional solutions of mineralized samples ($n=10$) were analysed using a Thermo Fischer Multicollector (MC-ICP-MS) Neptune Plus at the SARM-CNRS laboratory. Purification with anionic resin (AG1X8) details are described in Manhès et al. (1980). Mass bias and drift of the isotope ratios were corrected based on repeated measurements of the Pb reference material NIST SRM-981. Repeated measurements of NIST SRM-981 reference material give values for less than 0.2 ‰ for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ (Cloquet et al., 2006b).

5.3 Results and interpretation

5.3.1 The potential sources of contamination

5.3.1.1 PTE contents

The PTE contents of Pb and Sb-bearing waste rocks and slags were detailed in Guillevic et al. (2023) and are presented in Table S3. The ore-bearing waste rocks contain 2.9 to 7.9 wt.% of Pb and 54 to 561 mg.kg^{-1} of Sb. The metallurgical wastes display higher Pb and Sb contents than the ore-bearing rocks: the slags contain 7.5 and 10.8 wt.% of Pb and 931 to 1638 mg.kg^{-1} of Sb, whereas the stack residues contain 34 to 46 wt.% Pb and 1098 and 2187 mg.kg^{-1} Sb.

5.3.1.2 *Pb isotopes*

The Pb isotopic signature of the ore-bearing rocks (n=4) is very homogeneous, with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.17 ± 0.002 and a $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of 2.10 ± 0.001 (Guillevic et al. submitted, Table 5-1, Figure 5.2). The Pb isotopic signature of the slags (n=2) varies between 1.171 and 1.173 for $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and between 2.094 and 2.096 for $^{208}\text{Pb}/^{206}\text{Pb}$ ratio. The Pb isotopic signature of the stack residues (n=2) varies between 1.1713 and 1.1714 for $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and between 2.0960 and 2.0962 for $^{208}\text{Pb}/^{206}\text{Pb}$ ratio. The metallurgical wastes (slags and stack residues) display rather similar $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, in the range 1.172-1.177 and 2.094-2.096 respectively (Table 5-1).

5.3.1.3 *Antimony isotopic signature*

Opposite to Pb isotopes, the $\delta^{123}\text{Sb}$ values of the metallurgical wastes differ significantly from those of the ore-bearing rocks. The ore-bearing rocks display quite heterogeneous $\delta^{123}\text{Sb}$ values in the range -0.28 ‰ to 0.10 ‰, whereas slags and stack residues display similar and homogeneous $\delta^{123}\text{Sb}$ values in the range 0.62-0.78 (0.72 ± 0.07 ‰; Table 5-1). These results suggest that pyrometallurgical processes (smelting) of galena-tetrahedrite ores generated an apparent fractionation between the initial ore and the residual metallurgical products of + 0.62 to +1.01 ‰ with a relative enrichment in heavy ^{123}Sb isotope in slags and stack residues. Antimony isotopes could thus allow deciphering the contribution of the metallurgical wastes versus the contribution of the ore in contaminated environmental samples.

5.3.2 Soil, sediment samples and water

5.3.2.1 *PTE contents*

5.3.2.1.a. *River and mine galleries sediments*

The stream sediment collected upstream the mine (SED-12) presents a Pb content of 12 mg.kg^{-1} and a Sb content of 2 mg.kg^{-1} (Table 5-1). The stream sediments downstream the mining site (n=3) indicate a Pb content of in the range $15\text{-}35 \text{ mg.kg}^{-1}$ and a Sb content of $1\text{-}3 \text{ mg.kg}^{-1}$ (Table 5-1). Using SED-12 as reference, the Pb and Sb enrichments of downstream river sediments are very low (no to minor enrichment): $EF_{\text{Pb}} = 3.1$ and $EF_{\text{Sb}} = 1.0$ in SED-08, $EF_{\text{Pb}} = 2.1$ and $EF_{\text{Sb}} = 1.3$ in SED-03, and $EF_{\text{Pb}} = 2.3$ and $EF_{\text{Sb}} = 1.0$ in SED-13 (Table S3). Sample SED-02, which was

sampled in the Arc stream, near the main gallery and the waste rocks if slightly more enriched: it contains 96 mg.kg^{-1} of Pb ($EF_{\text{Pb}} = 7.9$) and 2 mg.kg^{-1} of Sb ($EF_{\text{Sb}} = 0.9$).

Table 5-1: Concentrations and isotopic signatures of Pb and Sb in soils and sediments samples and in potential contamination sources (slags, ore-bearing rocks, stack residues). Measurements performed at SARM are marked with this symbol *.

Sample Name	Pb	Sb	$\delta^{123}\text{Sb}$	2sd	$^{206}\text{Pb}/^{207}\text{Pb}$	error	$^{208}\text{Pb}/^{206}\text{Pb}$	error
	(mg.kg^{-1})	(mg.kg^{-1})	(‰)	(‰)				
Reference topsoil								
REF-TOPSOIL	83	2	0.24	0.02	1.176	0.004	2.088	0.005
Soil horizons								
P1-A	19746	147	0.47	0.03	1.172	0.004	2.099	0.005
P1-Bu1	56140	528	0.51	0.04	1.173	0.004	2.094	0.005
P1-Bu2	18096	145	0.50	0.02	1.169	0.004	2.104	0.005
P1-Bw1	18797	158	0.55	0.04	1.171	0.004	2.097	0.005
P1-Bw2	1531	24	0.64	0.03	1.174	0.004	2.099	0.005
P1-C	1078	21	0.64	0.06	1.171	0.004	2.103	0.005
P3-A	646	6	0.37	0.06	1.171	0.004	2.099	0.005
P3-A/B	647	6	0.40	0.04	1.170	0.004	2.101	0.005
P3-Bw	375	5	0.37	0.02	1.172	0.004	2.094	0.005
P3-C	156	4	0.30	0.02	1.175	0.004	2.092	0.005
P5-A	3439	17	0.45	0.02	1.170	0.004	2.099	0.005
P5-Bw*	1575	7	0.43	0.05	1.171	< 0.001	2.096	< 0.001
P5-C#	174	2	0.45	0.04	1.167	0.016	2.103	0.08
P5-2Bw*	86	2	0.50	0.02	1.175	< 0.001	2.089	< 0.001
P5-2C*	31	1	0.46	0.04	1.180	< 0.001	2.081	< 0.001
P5-3Bw	443	11	0.46	0.01	1.172	0.004	2.095	0.005
Waste ore-bearing rocks								
ORE-1	29846	128	0.10	0.01	1.172	0.004	2.095	0.005
ORE-2	71384	112	-0.21	0.02	1.172	0.004	2.095	0.005
ORE-3*	44077	54	-0.28	0.06	1.173	< 0.001	2.093	< 0.001
ORE-4*	78872	561	-0.06	0.07	1.173	< 0.001	2.094	< 0.001
Metallurgical wastes								
STK-1	345525	2187	0.62	0.06	1.171	0.004	2.096	0.005
STK-2	460992	1098	0.77	0.04	1.171	0.004	2.096	0.005
SLAG-1*	108418	1638	0.78	0.03	1.171	< 0.001	2.094	< 0.001
SLAG-2*	75516	931	0.73	0.05	1.172	< 0.001	2.096	< 0.001
River sediments								
SED-12	12	2	0.23	0.04	1.208	0.004	2.051	0.005
SED-02	96	2	-	-	-	-	-	-
SED-08	35	2	-	-	-	-	-	-
SED-03	22	3	0.18	0.03	1.189	0.004	2.068	0.005
SED-13*	15	1	0.25	0.06	1.187	< 0.001	2.076	< 0.001
Dewatering gallery								
SED-01	4345	19	0.28	0.06	1.172	0.004	2.096	0.005
SED-04	320	4	-	-	-	-	-	-
SED-06	136	2	-	-	-	-	-	-
SED-09	2327	9	0.07	0.02	1.174	0.004	2.089	0.005
SED-10*	102	1	-0.03	0.01	1.175	< 0.001	2.090	< 0.001

Sediments from the dewatering galleries (n=5) present much higher Pb and Sb contents than the Ponturin river sediments. SED-01, which was collected at the exit of the dewatering gallery located on the O.P. site, is the most enriched in PTE : it is extremely enriched in Pb (4345 mg.kg⁻¹ of Pb; EF_{Pb} = 521) and moderately enriched in Sb (19 mg.kg⁻¹ of Sb; EF_{Sb} = 13). The Pb and Sb contents of sediments collected at the exit of the exploratory galleries on the right bank of the Ponturin river (SED-09 and SED-10) contain up to 2327 mg.kg⁻¹ of Pb and 9 mg.kg⁻¹ of Sb (EF_{Pb}=149 and EF_{Sb}=3). These dewatering galleries are thus extremely to very severely enriched in Pb, whereas they only show a minor to a moderate enrichment in Sb. Opposite, sediments collected in sources considered to be related to dewatering (SED-04 and SED-06) are much less enriched; they contain up to 101 mg.kg⁻¹ of Pb and 1 mg.kg⁻¹ of Sb (EF_{Pb}=14 and EF_{Sb}=1).

5.3.2.1.b. *River water*

The dissolved Pb content of the eight water samples varied between < 0.006 and 7.27 µg.L⁻¹. Samples WAT-8 and WAT-7, which were collected between 0.5 and 1.5 km upstream the mining site, display the lowest Pb (<0.006 and 0.30 µg.L⁻¹ respectively, Table 5-2). WAT-4 sample, collected in the Arc stream below the ore-bearing waste rocks heap, present a similar content of 0.40 µg.L⁻¹ Pb than upstream mine site sediments. The highest Pb content is observed at the exit of the main dewatering gallery (WAT-1: Pb = 7.27 µg.L⁻¹, O.P. site), followed by the two secondary dewatering galleries on the right bank of the Ponturin river (WAT-5 = 1.45 µg.L⁻¹ ~ SED-09; WAT-6 = 1.49 µg.L⁻¹ ~ SED-10) and a little further of a former exploratory gallery exit (WAT-2 = 1.42 µg.L⁻¹ ~ SED-6, Figure 5.1A).

The dissolved Sb content of water samples was low and varied between <0.11 and 1.59 µg.L⁻¹. Sample WAT-8 and WAT-7 displays the lowest Sb content (<0.11 and 0.19 µg.L⁻¹ respectively), whereas the highest Sb content is observed at the exit of the main dewatering gallery (WAT-1= 1.59 µg.L⁻¹, O.P. site). The Sb content of WAT-4 is similar to the upstream waters (Sb= 0.21 µg.L⁻¹). Water collected at the exit of the dewatering galleries contain slightly higher Sb concentration than the Ponturin river, with a Sb content of 0.53 µg.L⁻¹ for WAT-5 (~ SED-09) and 0.95 µg.L⁻¹ for WAT-6 (~ SED-10). The water sample WAT-2 presents a similar content of 0.73 µg.L⁻¹. A decreasing gradient is measured in Sb content from water flowing out from the dewatering gallery located downstream (Sb = 0.48 µg.L⁻¹, WAT-3, Table 5-2).

Table 5-2 : Water properties and Pb and Sb content of water samples.

Echantillon eau ($<0.22 \mu\text{m}$)	pH	Conductivity ($\mu\text{S.cm}^{-1}$)	Temperature ($^{\circ}\text{C}$)	Pb ($\mu\text{g.L}^{-1}$)	Sb ($\mu\text{g.L}^{-1}$)
WAT-1*	7.8	2013	6.3	7.27	1.59
WAT-2*	7.9	1741	5.9	1.42	0.73
WAT-3	7.9	1153	6.7	0.40	0.48
WAT-4	8.7	255	6.9	0.09	0.21
WAT-5*	8.7	794	7.6	1.45	0.53
WAT-6*	8.6	728	7.5	1.19	0.95
WAT-7	8.6	662	8.8	0.3	0.19
WAT-8	8.7	165,1	9.1	< 0.006	0.11

* Represents dewatering waters

5.3.2.1.c. Soil profiles

The PTEs contents of the soil profiles and the reference topsoil are available in Table S2. The reference topsoil (0-20 cm) presented a Pb content of 83 mg.kg^{-1} (Pb/Rb = 1.2) and a Sb content of 3 mg.kg^{-1} . The 6 soil profiles display higher Pb and Sb contents than the reference topsoil. The two first horizons ($\sim 0\text{-}30 \text{ cm}$) are the most enriched in Pb and Sb. Then, Pb and Sb rapidly decrease to reach values close to those of the reference topsoil.

P1, which is the closest to the slag heap, has the highest Pb and Sb contents, with Pb in the range $1078\text{-}56140 \text{ mg.kg}^{-1}$ and Sb ranging between 21 and 528 mg.kg^{-1} . P1 can thus be considered as a technosol (Text S1).

Of the two dystric cambisols (P3 and P4), P4 is the most contaminated, with Pb in the range $194\text{-}2019 \text{ mg.kg}^{-1}$ and Sb in the range $2\text{-}16 \text{ mg.kg}^{-1}$. The Pb content of the less contaminated P3, ranges from 156 mg.kg^{-1} in the deepest horizon to 647 mg.kg^{-1} in the shallowest horizon. Therefore, the P3-C horizon has been selected as the reference horizon for the EF calculation in the dystric cambisols profiles ($\text{Pb/Rb}_{\text{P3-C}} = 1.5$, which is close to $\text{Pb/Rb}_{\text{(ref.topsoil)}} = 1.2$). Then, P4-A/B horizon reaches a maximum enrichment, with $\text{EF}_{\text{Pb}}=16$ and $\text{EF}_{\text{Sb}}=4$ (Figure 5.2).

Among the three calcareous cambisols (P2, P5 and P6), P2 is the most contaminated with a Pb content ranging between 54 and 4330 mg.kg^{-1} and a Sb content in the range $1\text{-}21 \text{ mg.kg}^{-1}$. Horizon P2-Bw1 shows the maximum enrichment ($\text{EF}_{\text{Pb}}=248$, $\text{EF}_{\text{Sb}}=2.1$; Figure 5.2). P6, which is the furthest profile from the waste heaps, presents low Pb and Sb contents in comparison with P2 and P5, ranging from $12\text{-}278$ for Pb and from $1\text{-}2$ for Sb. Therefore, horizon P6-3Bw ($\text{Pb/Rb}_{\text{(P6-3Bw)}} = 0.3$) was chosen as the reference horizon for EF calculation for calcareous cambisols. Even though P2 and

P5 are located farther from the slags heap, they show equivalent enrichment profiles, up to extremely severe Pb enrichment ($EF_{Pb} = 4$ to 250) and severe Sb enrichment ($EF_{Sb} = 2$ to 21) in the uppermost horizons. P5, which has intercalated layers of alluvial sediments and calcareous-scree, displays uncommon profile, with (i) horizon P5-A the most enriched with 3439 mg.kg^{-1} of Pb ($EF_{Pb} = 237$) and 17 mg.kg^{-1} of Sb ($EF_{Sb} = 20$), and (ii) an enriched P5-3Bw deeper horizon compared to the above horizons, with 443 mg.kg^{-1} of Pb and 11 mg.kg^{-1} of Pb (second most enriched horizon of the profile; Figure 5.2).

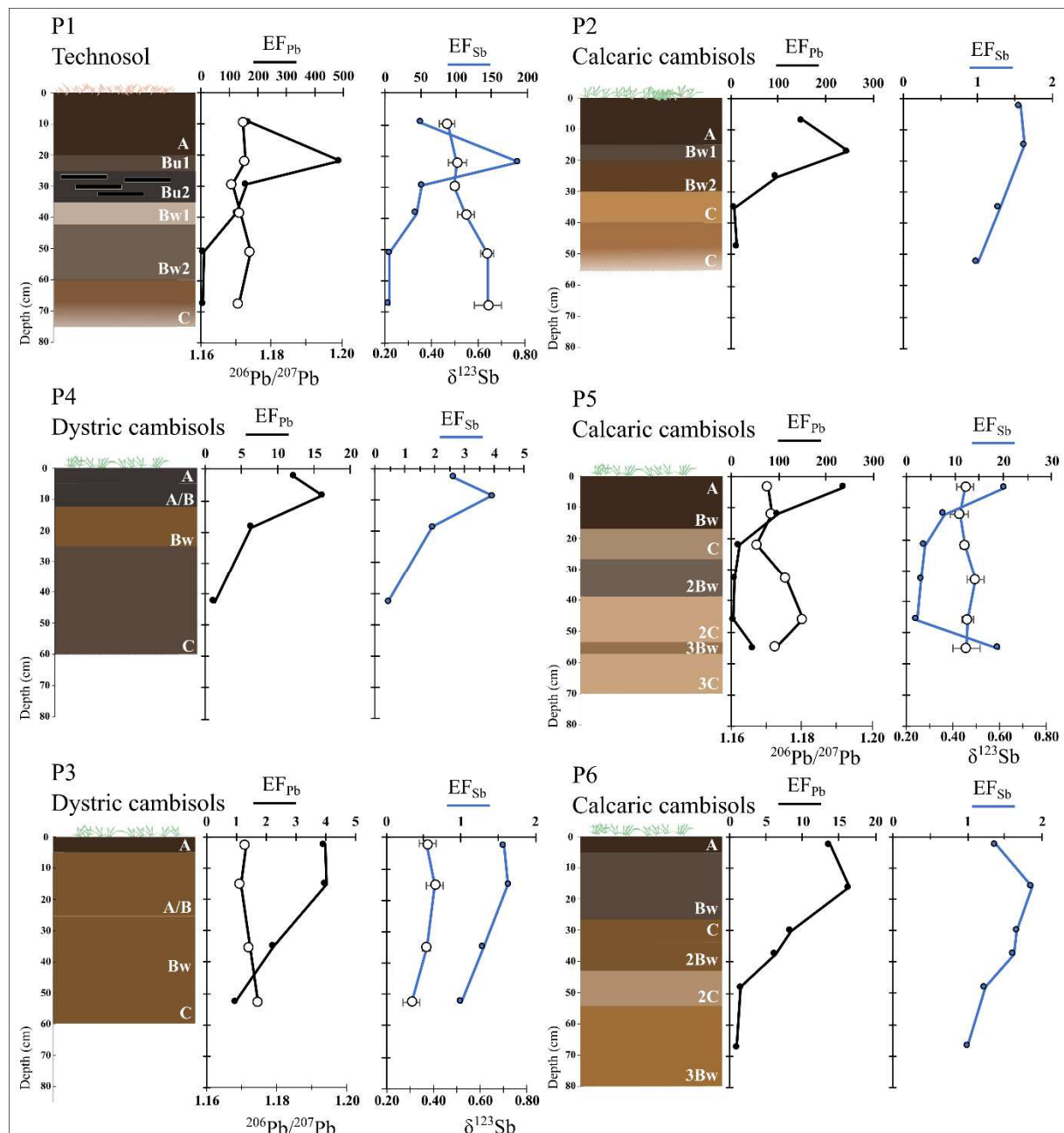


Figure 5.2: Distribution of Pb and Sb enrichment factors with depth (empty circles), and evolution of the $^{206}\text{Pb}/^{207}\text{Pb}$ and $\delta^{123}\text{Sb}$ isotopes for the P1, P3 and P5 soil profiles (grey circles).

5.3.2.2 Lead isotopes signature

Lead isotopes data are reported in Table 5-1 and Figure 5.3. The lead isotopic ratios measured in the different types of samples varied between 1.167 ± 0.004 and 1.208 ± 0.004 for $^{206}\text{Pb}/^{207}\text{Pb}$, and from 2.051 ± 0.005 to 2.104 ± 0.005 for $^{208}\text{Pb}/^{206}\text{Pb}$. Lead isotopic signatures plotted along a single line in the three-isotope space diagram (Figure 5.3). The upstream reference sediment (SED-12), which is not affected by mining and smelting activities, presents a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.208 ± 0.004 and a $^{208}\text{Pb}/^{206}\text{Pb}$ ratio of 2.052 ± 0.005 . The dewatering gallery sediments (SED-01, SED-10 and SED-09) present Pb signatures in the range of the local Pb ore, suggesting particulate remobilisation of the ore, which is consistent with their respective high Pb content and their origin. The downstream river sediments (SED-03 and SED-13) display homogeneous $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of $1.1187\text{-}1.1889 \pm 0.004$ and $2.068\text{-}2.076 \pm 0.005$ (Table 5-1). Such ratios are ranging between those of the uncontaminated river sediment SED-12 and the local ore/metallurgical wastes, suggesting remobilization of ore particles and/or of metallurgical wastes.

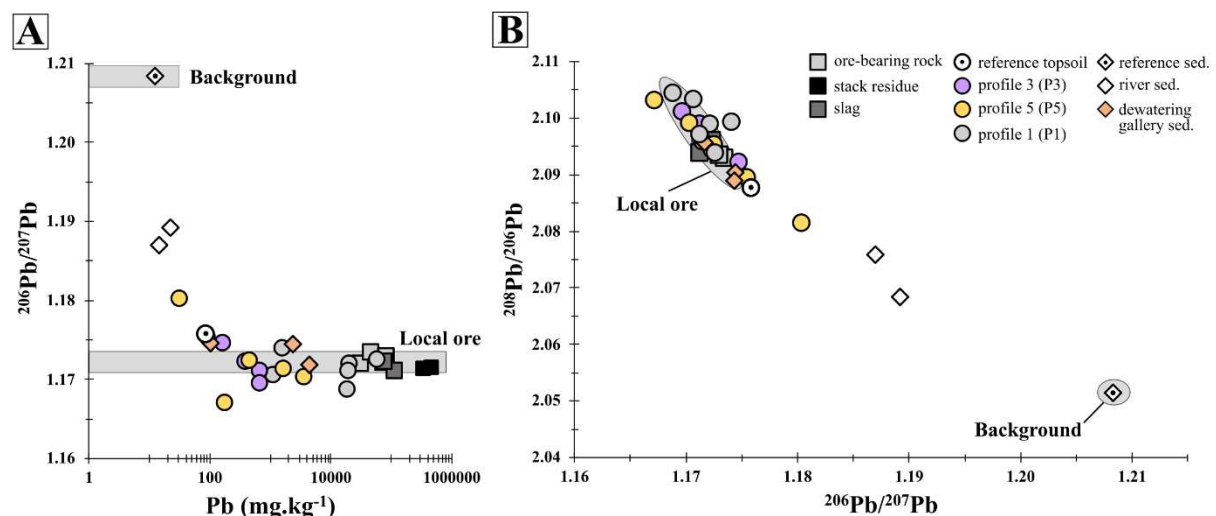


Figure 5.3 : Diagrams showing the Pb isotopic compositions of the contamination sources (squares), the soil horizons (circles) and sediments (diamonds). A) $^{206}\text{Pb}/^{207}\text{Pb}$ ratios versus the total Pb content. B) $^{206}\text{Pb}/^{207}\text{Pb}$ ratios versus $^{208}\text{Pb}/^{206}\text{Pb}$ ratios.

The Pb isotope ratios of the reference topsoil is $^{206}\text{Pb}/^{207}\text{Pb} = 1.176 \pm 0.004$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.088 \pm 0.005$, showing a slightly more radiogenic signature than the ore-bearing rocks and the metallurgical wastes (Figure 5.3A and Table 5-1). With the exception of the two deepest horizons of P5, all soil horizons present a Pb isotopic signature in the range of the local Pb-ore and the metallurgical wastes (Table 5-1).

5.3.2.3 Antimony isotopic signature

The antimony isotopic signature ($\delta^{123}\text{Sb}$) measured in the different types of samples varies between -0.28 ± 0.06 and 0.78 ± 0.03 (Table 5-1; Figure 5.4). The upstream sediment (SED-12) shows $\delta^{123}\text{Sb}$ of 0.23 ‰, which lies between those of the ore-bearing rocks and those of the metallurgical wastes. Sample SED-03 shows a slightly lighter $\delta^{123}\text{Sb}$ signature of 0.18 ‰ that could evidence a minor contamination from the Pb-Sb local ore in sediments. Dewatering gallery sediments SED-09 and SED-10 present significantly lighter $\delta^{123}\text{Sb}$ values than the river sediments, in the range of the local Pb-ore signature, with $\delta^{123}\text{Sb}$ values of -0.03 ‰ and 0.07 ‰, respectively. The Sb-enriched SED-01 sample shows a heavier Sb isotopic signature ($\delta^{123}\text{Sb} = 0.28$ ‰) suggesting a contamination by metallurgical wastes (slags).

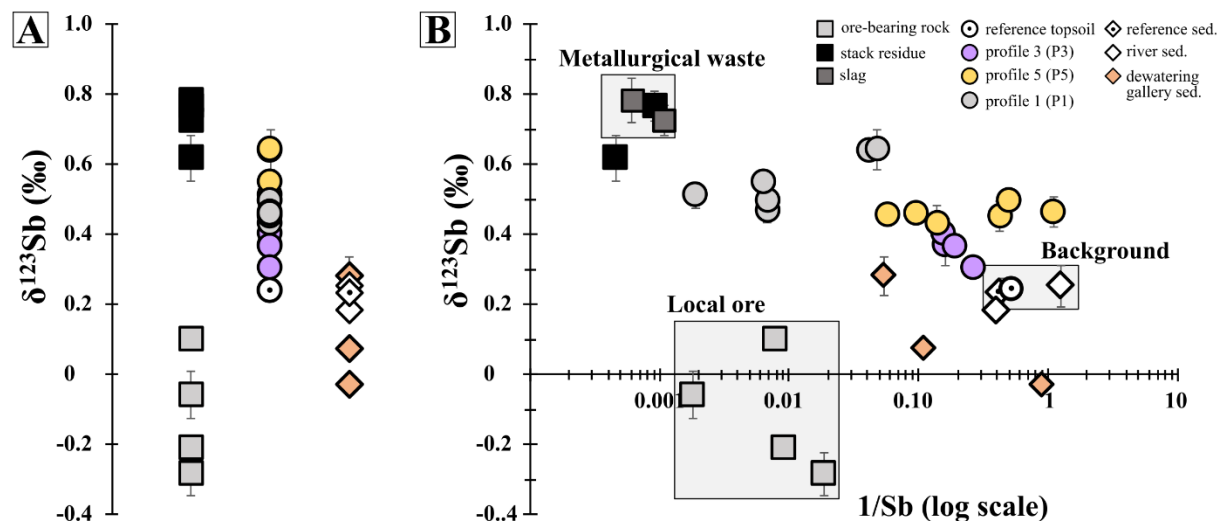


Figure 5.4 : Isotopic signatures of Sb (A) and $\delta^{123}\text{Sb}$ values versus $1/\text{Sb}$ (logarithmic scale, B) for potential contamination sources (squares), soil samples (circles) and sediments samples (diamonds).

The reference topsoil has a $\delta^{123}\text{Sb}$ of 0.24 ‰, which is similar to the value of the uncontaminated sediment SED-12. The Sb isotopic signature of the soil horizons varies from 0.30 to 0.64 ‰ (Figure 5.4). The soil horizons of P1 have a $\delta^{123}\text{Sb}$ between 0.47 to 0.64 ‰. The soil horizons of P5 have a $\delta^{123}\text{Sb}$ between 0.43 and 0.50 ‰ and the soil horizons of P3 have a $\delta^{123}\text{Sb}$ between 0.30 and 0.40 ‰. The deep horizon P1-C (60-75 cm) and horizon P1-Bw2 (43-60 cm) present a $\delta^{123}\text{Sb}$ closer to the metallurgical wastes than the shallowest soil horizon of the profile (e.g., horizon A and horizon Bu1) despite a higher Pb and Sb content. The deep P3-C horizon of (45-60 cm) is similar to the reference topsoil by its Sb content and isotopic signature. Despite a decrease in Sb content with depth, the soil horizons of profile P5 show a constant Sb isotopic signature of $\delta^{123}\text{Sb} = 0.46 \pm 0.02$ ‰ (n=5). These data suggest three types of binary mixing for the various soil and sediment samples:

(i) mixing between slags and ore-bearing rocks, (ii) mixing between slags and the geochemical background, and (iii) mixing between the ore-bearing rocks and the geochemical background.

5.4 Discussion

5.4.1 Spatial characterization of the Pb and Sb contamination

The metallurgical slags display higher concentrations of Pb and Sb than the ore-bearing waste rocks. Therefore, they may be the primary source of contamination on site (Guillevic et al., 2023).

All soil profiles located in the hayfields downward the waste heaps display higher Pb and Sb content than the reference topsoil, with technosol P1 showing the highest contents. However, there is a decreasing trend in Pb and Sb contents in the superficial horizons as the distance from the slags and the ore-bearing waste rocks increases. This observation is consistent with the Pb gradient and spatial distribution observed in 117 topsoil samples from Guillevic et al. (2023), with Pb ranging from 3.7% near the waste heaps to 100 mg.kg^{-1} for the least contaminated samples located about 500 m downslope. The soil profiles clearly show that the Pb and Sb contamination essentially affects the first two soil horizons, before decreasing rapidly in depth to reach values close to the reference values (Figure 5.2). Such profiles suggest that the vertical distribution of Pb and Sb results from inputs of Pb and Sb from the surface rather than from the underlying Pb and Sb-rich rocks. Therefore, one can state that the contamination results from Pb and Sb dispersion and remobilization from the mine and metallurgical wastes stored at the surface (i.e., anthropogenic contamination) rather than from the nearby underground mineralization (i.e., natural contamination). As the Pb and Sb contents of both the dystric and the calcaric cambisols are close to the reference topsoil, one could consider that the natural contamination from the underlying mineralized rocks is negligible in the soil profiles. The fact that only the first 30 cm of all profiles (except Technosol P1) are the most enriched in Pb and Sb can be easily explained by the neutral (Dystric cambisols) to alkaline pH (Calcaric Cambisols), which tends to immobilize Pb and Sb (Text S1 and Table S3).

The upstream sediment (SED-12) and water (WAT-8) collected 1.5 km upstream the mine show the lowest Pb and Sb contents (Table 5-1). These samples are thus good references for uncontaminated sediments and waters. Except for the downstream water (WAT-3, see discussion below), the Ponturin waters show no Pb or Sb contamination (Table 5-2); they fall within the range of the European waters ($0.22 \pm 0.59 \text{ }\mu\text{g.L}^{-1}$ of Pb and $0.19 \pm 0.18 \text{ }\mu\text{g.L}^{-1}$ of Sb; Salminen et al.,

2005). The dewatering waters and sediments are more contaminated in Pb and Sb than the Ponturin River. The dewatering sediments is 8 to 350 times more contaminated in Pb and up to 8 times more contaminated in Sb than the upstream sediment. The dewatering waters are 200 to 1200 times more contaminated in Pb and 4 to 14 times more contaminated in Sb than the upstream water. These results suggest the occurrence of present-days lixiviation of the mineralisation (Pb and Sb in waters) as well as particle translocation of ore minerals (Pb and Sb in sediments) in dewatering waters. Both dewatering waters and sediments are being rapidly diluted as they reach the Ponturin River. Indeed, downstream the mine, if the Ponturin water (WAT-3) is 66 times enriched in Pb and 4 times enriched in Sb, the Ponturin sediment (SED-13) shows no more Pb or Sb contamination. Such a difference among sediments and waters suggest that the contamination of surficial waters is more widespread than the contamination of the sediments. One possible explanation relies on the transfer processes involved: water contributes to the dispersal of dissolved Pb and Sb whatever the water flux, whereas particles of sediments will only be transferred if the water flux is high enough to move them. Due to the torrential regime of the Ponturin River, the particles of ore transferred to the river by the dewatering waters (lower fluxes) will be washed away by the river (much higher flux), so that few particles will be deposited nearby the mine.

5.4.2 Antimony isotope fractionation during pyrometallurgy

The isotopic signature of Sb in the slags produced by smelting of Pb-Ag ore from the Peisey-Nancroix mine ($\delta^{123}\text{Sb}_{\text{slag}} = 0.75 \pm 0.07 \text{ ‰}$) is heavier than the ore isotopic signature ($\delta^{123}\text{Sb}_{\text{ore}} = -0.11 \pm 0.17 \text{ ‰}$). This induces an apparent isotopic fractionation ($\Delta^{123}\text{Sb}_{\text{slag-ore}}$) of +0.62 to +1.01 ‰ between the local ore and the metallurgical wastes. These results provide the first evidence of antimony isotopic fractionation during high-temperature processes such as pyrometallurgy. Such a fractionation between ores and slags has been reported for other elements like Cd (+0.36 ‰, Cloquet et al. 2006), Zn (+0.05-0.13 ‰, Shiel et al., 2010) and Tl (+1.10 ‰; Vaněk et al., 2018; 2021). Thanks to their fractionation during pyrometallurgy, Sb isotopes, as well as Cd, Zn or Tl, can help distinguishing the contamination related to the metallurgical wastes from the contamination related to the Pb-Sb-bearing rocks (ore-bearing waste rocks and/or local mineralized background).

5.4.3 Coupling of Pb and Sb isotopes

Pb isotopes are widely used as a potent indicator of anthropogenic contamination over the geogenic background in mining/smelting areas (Ettler, 2016; Komárek et al., 2008). However, they cannot be used to decipher the source of contamination (ore-bearing rocks vs metallurgical wastes) as Pb doesn't fractionate during pyrometallurgy (Baron et al., 2006; Cui and Wu, 2011; Shiel et al., 2010). The benefit of combining Pb isotopes with another system that fractionates during pyrometallurgy (Sb, Cd, Zn or Tl) is to differentiate the sources of contamination from the geochemical background. Such a knowledge will be important to propose remediation plans of former mining/smelting sites. In Peisey-Nancroix, Pb and Sb-bearing phases are closely associated within the ore (Figure S1; Bertauts et al. 2022), and Pb and Sb are strongly correlated in topsoils (Guillevic et al., 2023). Therefore, coupling Pb and Sb isotopes provides a powerful tool to characterize the sources of contamination.

Figure 5.5 presents the coupling of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios with $\delta^{123}\text{Sb}$ values, for all the samples analysed for this study. Such a coupling allows distinguishing three end-members: (i) the metallurgical wastes (slags and stack residues), (ii) the local Pb-Sb-bearing ore, and (iii) the uncontaminated materials (not-mineralized geochemical background) represented by the upstream sediment (SED-12), which displays similar $^{206}\text{Pb}/^{207}\text{Pb}$ ratios than sediments deposited 7 km upstream the mine in Lake La Plagne prior mining ($^{206}\text{Pb}/^{207}\text{Pb} = 1.209$; Guillevic et al., submitted). Therefore, coupling Pb and Sb isotopes will allow not only identifying the anthropogenic contamination, but also deciphering the importance of the local-ore vs the metallurgical wastes in this anthropogenic Pb-Sb contamination. However, one limitation resides in distinguishing the natural contamination that is related to the underlying mineralization from the part of the anthropogenic contamination related to the ore-bearing waste rocks, as they have the same Pb and Sb isotopic signatures.

The reference topsoil displays a Pb isotopic signature similar to the local ore and the metallurgical wastes, and a $\delta^{123}\text{Sb}$ value similar to the uncontaminated background, suggesting that this sample is contaminated in Pb but apparently not in Sb. Several hypotheses could explain the Pb contamination. First, it could result from airborne deposition of TMM-rich fumes during smelting, as the reference topsoil is located downwind the mining site. However, this hypothesis is rather unlikely as this sample was collected very close to the active Nant Fesson stream in order to avoid such a contamination. Second, the Pb contamination could be part of the natural contamination halo related to the nearby underground Pb-Ag mineralization. Indeed, the exploration of ore deposits aims at identifying these natural contamination haloes by using geophysical and

geochemical tools, in order to locate the mineralization at the regional and local scale (Morin et al., 2001; Galán et al., 2008). However, such hypothesis is rather unlikely here, as the reference soil is young and formed on an active alluvial fan. Finally, considering the reference topsoil developed on a recent alluvial deposit, it could have trapped remobilized anthropogenic Pb emitted during smelting, deposited on surrounding soils, and eroded from the Nant Fesson watershed, as observed in Lake La Plagne watershed (Guillevic et al., submitted). If this last hypothesis may explain the Pb contamination, it fails to explain the apparent lack of Sb contamination. For this study, Sb isotopic data on the metallurgical fumes are lacking. However, as Sb fractionates during pyrometallurgy, the fumes are likely to display lighter $\delta^{123}\text{Sb}$ values than the slags, and even lighter values than the ore-bearing-rocks. Therefore, the $\delta^{123}\text{Sb}$ value of the reference soil could be close to the fumes signature. This needs to be further investigated.

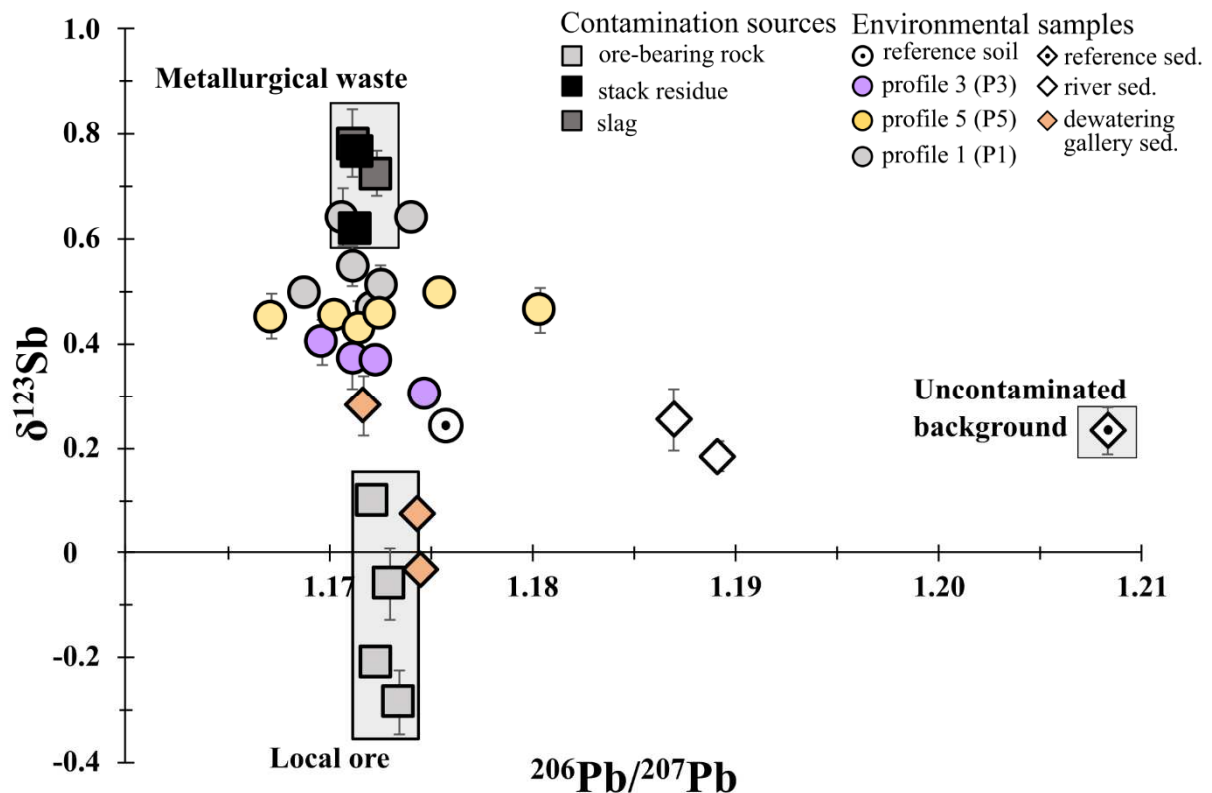


Figure 5.5: Coupling of Pb and Sb isotopes

All horizons of the soil profiles display Pb isotopic signatures similar to the local ore and to the metallurgical wastes. In the Pb-Sb isotopic system, the deep horizon P3-C trends towards the reference soil whereas the upper horizons indicate mixing between the metallurgical wastes and local ore end-members (Figure 5.5). The horizon P5-2Bw and P5-2C have more radiogenic Pb due to their rather high abundance of cagneule ($^{206}\text{Pb}/^{207}\text{Pb} = 1.282$, Guillevic et al., submitted).

Therefore, the deeper horizons of the soil profiles P3 and P5 are very likely naturally contaminated by the nearby underground ore, whereas the topsoils are more likely contaminated by the mine wastes stored at the surface (Guillevic et al., 2023). Profile P1, which is the closest to the slags heap, displays $\delta^{123}\text{Sb}$ values the closest to those of the metallurgical wastes. There, the deeper horizon has the heavier $\delta^{123}\text{Sb}$ values, despite limited Sb enrichment, suggesting vertical remobilization of slag-derived Sb.

In the Pb-Sb isotopic system, the dewatering sediments have signatures similar to the local ore (SED-09, SED-10), with a minor contribution of slags for SED-01. As already evidenced from the Pb and Sb content, this contamination is rapidly diluted downstream, as the Ponturin sediments Pb-Sb isotopic signatures provide evidence of mixing between the mine wastes and the uncontaminated background.

5.4.4 Quantification of the anthropogenic contamination

Coupling Pb and Sb isotopic systems has been shown to be a good tool to distinguish contamination related to Pb-Sb bearing ore, to contamination related to Pb-Sb-bearing metallurgical wastes. Pb-Sb signatures could be used to quantify the importance of each end-member. However, as the $\delta^{123}\text{Sb}$ values of contaminated samples range between those of the Pb-Sb-bearing ore and the metallurgical wastes, it is not possible to quantify the part of local ore and metallurgical wastes for samples that are not extremely contaminated. However, in highly contaminated samples, the part of the uncontaminated background may be considered negligible, so that $\delta^{123}\text{Sb}$ values can be used to decipher the part of the local ore vs the metallurgical wastes using binary mixing.

For the soil horizons, two mixing models were considered (i) binary mixing between the metallurgical wastes and the local ore (minimum and maximum values due to their heterogeneity), assuming no contribution from the uncontaminated background, and (ii) binary mixing between the slags and the uncontaminated background, as slags are assumed to be the main source of topsoil contamination (Guillevic et al., 2023). Binary mixing between the ore and the uncontaminated sediment (SED-12) was applied to the 3 dewatering sediments. For SED-01, binary mixing between the slags and the uncontaminated sediment (SED-12) was also applied. All results are reported in Table 5-3.

As shown in Table 5-3, slags account for a minimum of 44-78% in P1, 12-31% in P3 and 36 to 41% in P5. The dewatering sediments located at the exit of the dewatering galleries on the right

bank of the Ponturin River (no slag heap), contain at least 32 % (SED-09) and 55 % (SED-10) of ore-derived Pb and Sb. SED-01 may contain 8 to 51% of slags and up to xx% of ore-derived Pb and Sb. Such proportions may help to quantify and compare the part of each source among the samples; they help quantifying the proportion of the metallurgical wastes in the anthropic contamination. However, it is not possible to determine for soil samples whether the local-ore contribution refers to the underlying mineralized rocks (i.e., natural contamination) or to the remobilisation ore-bearing waste rocks (i.e., anthropogenic contamination). There is no direct way to decipher and estimate the natural contamination (initial environmental state, prior mining), however, by combining the vertical distribution of Pb and Sb contents with Pb-Sb isotopes, it is possible to approximate its importance. If the natural contamination seems to be negligible in Peisey-Nancroix compared to the anthropogenic contamination related to metallurgical wastes, it may be otherwise in other mining/smelting sites.

Table 5-3: Fractions of the contamination sources to horizons soil and dewatering sediments using $\delta^{123}\text{Sb}$ (in percents)

Sample Name	Fraction of slag (min. to ore)	Fraction of slag (max. to ore)	Fraction of slag (to reference topsoil)	Fraction of ore (min. to reference background)	Fraction of ore (max. to reference background)
1-A	72	56	44	-	-
1-Bu1	76	62	52	-	-
1-Bu2	75	60	50	-	-
1-Bw1	80	68	59	-	-
1-Bw2	89	82	77	-	-
1-C	89	82	78	-	-
3-A	63	41	25	-	-
3-A/B	66	46	31	-	-
3-Bw	63	41	24	-	-
3-C	56	31	12	-	-
5-A	71	54	41	-	-
5-Bw	68	50	36	-	-
5-C	71	53	41	-	-
5-2Bw	75	60	50	-	-
5-2C	72	55	43	-	-
5-3Bw	71	54	42	-	-
SED-12	-	-	-	0	0
SED-03	-	-	-	0.11	0.41
SED-13	-	-	-	0	0
SED-01	51	27	08	-	-
SED-09	-	-	-	32	100
SED-10	-	-	-	52	100

5.5 Conclusion

This study has provided novel insights into the fractionation of Sb isotopes during pyrometallurgy ($\Delta^{123}\text{Sb}_{\text{slag-ore}}$ in the range +0.62 to + 1.01 ‰). Due to Sb fractionation, coupling of Pb and Sb isotopes provide a powerful tool to track the contamination in mining/smelting sites. Indeed, if Pb isotopes allow identification of the contamination, Sb isotopes allow discussing the sources of the (ore-bearing rocks vs metallurgical wastes). In order to decipher the part of the anthropogenic contamination (ore-bearing waste rocks and metallurgical wastes) from the natural contamination associated to the nearby mineralization, vertical soil profiles and a good knowledge of the site organization is required.

In the former Pb-Ag mining/smelting site of Peisey-Nancroix, coupling Pb and Sb have showed that the soils surface horizons are the most contaminated (with the exception of a technosol): these horizons are essentially contaminated by slags, whereas the deep soil is naturally contaminated by the nearby underground mineralization. Mine dewatering waters remobilize Pb and Sb from the ore (lixiviation and particle translocation). However, the torrential regime of the Ponturin River induces a rapid dilution downstream.

5.6 Acknowledgment

This work was supported by the MITI Program (Mission pour les initiatives transverses et interdisciplinaire) of CNRS.

A RETENIR

- Les sols sont localement affectés par une contamination extrême en Pb et modérée en Sb.
- La contamination anthropique des sols est limitée aux horizons de surface (dispersion vertical limitée).
- La contamination des sédiments de rivière est rapidement diluée par l'apport de sédiments non contaminés.
- Les isotopes de Sb fractionnent durant les processus métallurgiques, permettant de distinguer les sources anthropiques de Pb (roches riches en minerai vs déchets métallurgiques)
- Les isotopes de Sb confirment que les déchets métallurgiques sont la principale source de contamination du sol.
- Le couplage isotopique Pb-Sb est un outil puissant pour distinguer les sources anthropogéniques du fond géochimique.

5.7 Supplementary material

Figure S1 SEM and reflected light photographs of the contamination source (stack residues, slags, and ore samples).

Figure S2 Photographs of the six profiles.

Text S1 Field data description of each profile.

Table S1 Manuscript sample and original sample name equivalence.

Table S2 Total content of major and trace element and calculated EF values.

Table S3 Physico-chemical properties of soil horizons.

Figure S1. Reflected light (A,C and E) and SEM images (B, D and F) of ore-bearing waste rocks, slags, and stack smelting residues. In the ore-bearing waste rocks (A and B), galena (Gal.) is associated with tennantite-tetrahedrite (Ten.-Tet.). In the slags (C and D, © Photographs of Estelle Camizuli), various Sb and Pb-bearing phases are associated with Ag, Cu and Fe-bearing phases. For more photographs of slags, see Guillevic et al. (2023). In stack smelting residues (E, F), two principal phases were observed with Zn-Fe-S (small rounded shape) included in Pb-S phase.

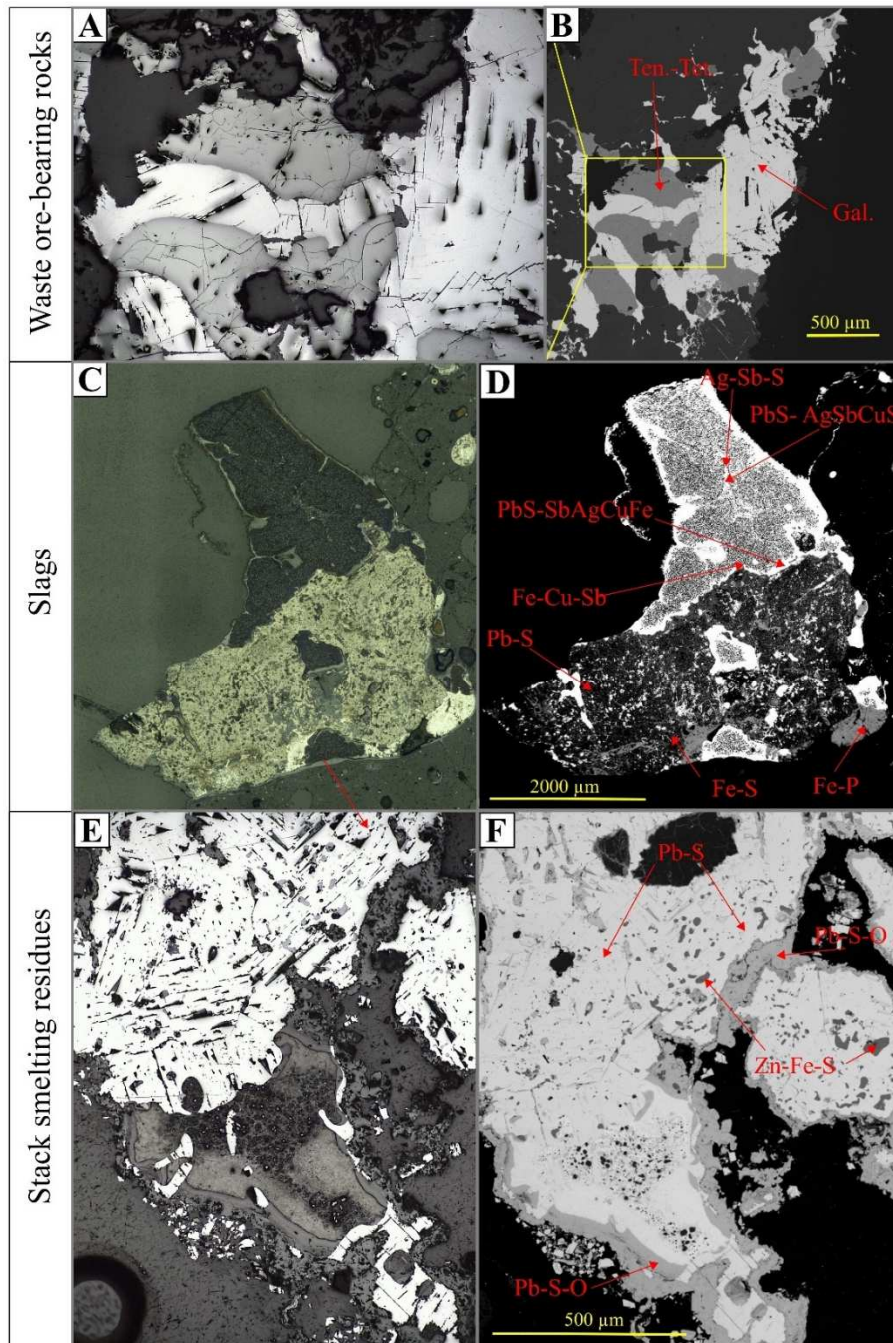


Figure S2. Photographs of the six soil profiles: P1 (Technosol), P3 and P4 (Dystric Cambisols) and P2, P5 and P6 (Calcaric Cambisols).



Text S1. Description of the six soil profiles.

Soil profile 1 (P1; 0-75 cm) is located at a short distance from the slag heap (~3 m). It comprises six soil horizons: P1-A (0-20 cm), P1-Bu1 (20-25 cm), P1-Bu2 (25-35 cm), P1-Bw1 (35-43 cm), P1-Bw2 (43-60 cm), P1-C (60-75 cm). This is a bi-lithic profile that consists of unconsolidated sedimentary rocks of alluvial origin (alluvial fan). At a depth of 40 cm, there is a layer of *cargneule* (former Triassic dolomites that has been brecciated during the alpine orogeny). The six horizons have a silty texture and do not produce any fizzing with HCl. The humus is categorized as Moder type. The coarse elements are a mixture of gravels composed of schistose rocks, quartzite, and *cargneule*. P1-Bu1 and P1-Bu2 are identified as Urbic horizons due to the presence of more than 20% of artefact composed of slags and coal particles. It is likely that this coal was used for ore roasting and smelting. This profile is classified as a **Technosol**.

Soil profile 2 (P2; 0-55 cm) is located on the axis of an underground dewatering gallery, between the O.S and O.P sites, at the forest edge. It comprises 5 soil horizons: P2-A (0-14 cm), P2-Bw1 (14-20 cm), P2-Bw2 (20-30 cm), P2-C (30-40 cm), P2-C (40-55 cm). This is a bi-lithic profile of unconsolidated sedimentary rocks of alluvial origin (alluvial fan). The humus is of the Moder type. The 5 horizons have a loamy to sandy-loamy texture at depth. The matrix effervesces with HCl for P2-Bw2 and P2-C and is reduced to coarse elements for P2-C at the deepest point. Indeed, the second material appears at a depth of 40 cm, consisting of schist and quartzite blocks mixed with *cargneule* pebbles. This profile is classified as a **Calcaric Cambisol**.

Soil profile 3 (P3; 0-60 cm) is situated downward the slag heap (~400 m) in the hayfields and is built on an alluvial cone. This is a monolithic profile of coherent sedimentary rocks of alluvial origin (alluvial fan). The humus in this profile is classified as Mull type. The profile consists of 4 horizons: P3-A (0-5 cm), P3-A/B (5-25 cm), P3-Bw (25-45 cm), and P3-C (45-60 cm), which have a texture ranging from silty-clay to clay-silt at greater depths. There is no effervescence with HCl, except for some *cargneules* pebbles found in P3-C. The major coarse elements present in this profile include schist and quartzite blocks, pebbles, and gravels. This profile is classified as a **Dystric Cambisol**.

Soil profile 4 (P4; 0-60 cm) is located upward Profile 3 in the hayfields and approximately 100 meters from the slag heap. P3 lies on an alluvial cone formed by torrential activity of the Arc and the Nant Fesson streams. This is a monolithic profile of coherent sedimentary rocks of alluvial origin (alluvial fan). The humus in this profile is classified as Mull type. The profile consists of four horizons, namely P4-A (0-5 cm), P4-A/B (5-12 cm), P4-Bw (12-25 cm), and P4-C (25-60 cm), which have a texture ranging from silty-clay to clay-silt at greater depths. There is no reaction to HCl. The coarse elements present in this profile include blocks, pebbles, and gravels of schist and quartzite. This profile is also classified as a **Dystric Cambisol**.

Soil profile 5 (P5; 0-70 cm) is situated on the forest's edge, between the axis of the underground water flow gallery and a footpath. This is a bi-lithic profile of unconsolidated sedimentary rock with a colluvial origin, (carbonate scree). The humus is of Mull type. The seven horizons, namely P5-A (0-7 cm), P5-Bw (7-17 cm), P5-C (17-27 cm), P5-2Bw (27-39 cm), P5-2C (39-53 cm), P5-3Bw (53-57 cm), and P5-3C (57-70 cm), show a silty to silty-sandy texture at depth. The matrix of the C horizons strongly effervesces to HCl, while P5-3Bw shows moderate effervescence. For P5-Bw and P5-2Bw, the effervescence is limited to the coarse elements of the *cargneule* rocks. From 53 cm onwards, a second material appears, resulting in the presence of coarse and blocky quartzite elements in P5-3C. Charcoal particles are also visible at the base of horizons P5-2Bw and P5-3Bw. This profile is classified as a **Calcaric Cambisol**.

Soil profile 6 (P6; 0-80 cm) is located at the interface between the alluvial fan and the carbonate scree, downhill on the hayfields. This is a bi-lithic profile of unconsolidated sedimentary rocks with a dominating colluvial origin. The humus is of Mull type. The six horizons, P6-A (0-5 cm), P6-Bw (5-27 cm), P6-C (27-33 cm), P6-2Bw (33-42 cm), P6-2C (42-54 cm), and P6-3Bw (54-80 cm), exhibit a silty to silty-sandy texture at depth. The matrix of the C horizons and P6-3Bw weakly effervesces to HCl, while for the other horizons, effervescence is limited to the coarse elements of the *cargneule* rocks, which constitute the majority of these. From 55 cm onwards, a second material appears, which is reflected in the presence of coarse elements and quartzite blocks in P6-3Bw. This profile is also classified as a **Calcaric Cambisol**.

Table S1. Manuscript sample and original sample name equivalence.

Sample Name	Sample Type	Manuscript Name	N	E	Sample Name	Sample Type	Manuscript Name	N	E
PN21-SOL02	Reference soil	REF-SOIL	45.5183	6.7972	PN17-R-07	Ore rock	ORE-1	45.5263	6.7908
P1	Profile	P1	45.5249	6.7843	PN21-R-05	Ore rock	ORE-2	45.5263	6.7908
PN21-1-H1	Horizon soil	P1-A	45.5249	6.7843	PN21-R-05-1	Ore rock	ORE-3	45.5263	6.7908
PN21-1-H2	Horizon soil	P1-Bu1	45.5249	6.7843	PN21-R-05-4	Ore rock	ORE-4	45.5263	6.7908
PN21-1-H3	Horizon soil	P1-Bu2	45.5249	6.7843	PN21-SCO-01	Slag	SLAG-1	45.5245	6.7852
PN21-1-H4	Horizon soil	P1-Bw1	45.5249	6.7843	PN21-SCO-03	Slag	SLAG-2	45.5247	6.7850
PN21-1-H5	Horizon soil	P1-Bw2	45.5249	6.7843	PN21-R-01	Stack residue	STK-1	45.5245	6.7841
PN21-1-H6	Horizon soil	P1-C	45.5249	6.7843	PN21-R-02	Stack residue	STK-2	45.5245	6.7841
P2	Profile	P2	45.5266	6.7824	PN17-SED-12	River sediment - upstream	SED-12	45.5202	6.8007
PN21-2-H1	Horizon soil	P2-A	45.5266	6.7824	PN21-SED-03	River sediment - downstream	SED-03	45.5305	6.7744
PN21-2-H2	Horizon soil	P2-Bw1	45.5266	6.7824	PN17-SED-13	River sediment - downstream	SED-13	45.5320	6.7723
PN21-2-H3	Horizon soil	P2-Bw2	45.5266	6.7824	PN17-SED-02	River sediment - upstream	SED-02	45.5236	6.7849
PN21-2-H4	Horizon soil	P2-C	45.5266	6.7824	PN17-SED-06	River sediment - downstream	SED-06	45.5302	6.7747
PN21-2-H5	Horizon soil	P2-C	45.5266	6.7824	PN17-SED-08	River sediment - downstream	SED-08	45.5299	6.7779
P3	Profile	P3	45.5276	6.7832	PN17-SED-09	River sediment - dewatering gallery	SED-09	45.5265	6.7906
PN21-3-H1	Horizon soil	P3-A	45.5276	6.7832	PN17-SED-10	River sediment - dewatering gallery	SED-10	45.5265	6.7894
PN21-3-H2	Horizon soil	P3-A/B	45.5276	6.7832	PN21-SED-01	River sediment - dewatering gallery	SED-01	45.5285	6.7810
PN21-3-H3	Horizon soil	P3-Bw	45.5276	6.7832	PN17-SED-04	River sediment - dewatering gallery	SED-04	45.5269	6.7790
PN21-3-H4	Horizon soil	P3-C	45.5276	6.7832	PN21-EAU-01	stream water	WAT-1	45.5285	6.7810
P4	Profile	P4	45.5254	6.7840	PN21-EAU-02	stream water	WAT-2	45.5301	6.7747
PN21-4-H1	Horizon soil	P4-A	45.5254	6.7840	PN21-EAU-03	stream water	WAT-3	45.5305	6.7744
PN21-4-H2	Horizon soil	P4-A/B	45.5254	6.7840	PN21-EAU-04	stream water	WAT-4	45.5240	6.7855
PN21-4-H3	Horizon soil	P4-Bw	45.5254	6.7840	PN21-EAU-05	stream water	WAT-5	45.5264	6.7907
PN21-4-H4	Horizon soil	P4-C	45.5254	6.7840	PN21-EAU-06	stream water	WAT-6	45.5266	6.7896
P5	Profile	P5	45.5275	6.7816	PN21-EAU-07	stream water	WAT-7	45.5257	6.7906
PN21-5-H1	Horizon soil	P5-A	45.5275	6.7816	PN21-EAU-08	stream water	WAT-8	45.5199	6.8034
PN21-5-H2	Horizon soil	P5-Bw	45.5275	6.7816					
PN21-5-H3	Horizon soil	P5-C	45.5275	6.7816					
PN21-5-H4	Horizon soil	P5-2Bw	45.5275	6.7816					
PN21-5-H5	Horizon soil	P5-2C	45.5275	6.7816					
PN21-5-H6	Horizon soil	P5-3Bw	45.5275	6.7816					
P6	Profile	P6	45.5287	6.7820					
PN21-6-H1	Horizon soil	P6-A	45.5287	6.7820					
PN21-6-H2	Horizon soil	P6-Bw	45.5287	6.7820					
PN21-6-H3	Horizon soil	P6-C	45.5287	6.7820					
PN21-6-H4	Horizon soil	P6-2Bw	45.5287	6.7820					
PN21-6-H5	Horizon soil	P6-2C	45.5287	6.7820					
PN21-6-H6	Horizon soil	P6-3Bw	45.5287	6.7820					

Table S2. Total content of major and trace elements and calculated EF values.

Sample_Name	Sample_Type	SiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	PF	Total	Org
PN21-SOL02	reference soil	54,64	15,71	8,55	0,13	2,65	1,86	3,26	1,78	1,30	0,14	10,20	100,21	1,46
PN21-1-H1	Horizon soil	39,56	10,08	4,98	0,15	2,22	1,93	1,44	1,95	0,49	0,23	32,15	95,18	11,82
PN21-1-H2	Horizon soil	44,49	9,93	6,21	0,23	2,64	2,75	1,40	2,01	0,48	0,23	20,21	90,57	6,73
PN21-1-H3	Horizon soil	40,64	10,28	4,91	0,18	2,28	2,72	1,53	1,96	0,51	0,20	31,31	96,51	14,50
PN21-1-H4	Horizon soil	52,70	13,38	6,14	0,18	3,10	1,78	1,99	2,56	0,66	0,21	14,59	97,29	4,59
PN21-1-H5	Horizon soil	59,59	16,87	7,05	0,11	3,60	0,55	2,45	3,13	0,84	0,10	5,70	99,98	0,48
PN21-1-H6	Horizon soil	59,44	16,86	6,78	0,11	3,98	0,95	2,20	3,15	0,79	0,14	6,69	101,07	0,74
PN21-2-H1	Horizon soil	28,23	9,01	3,77	0,10	8,13	10,61	0,83	2,18	0,43	0,29	34,94	98,52	5,73
PN21-2-H2	Horizon soil	34,79	10,70	4,74	0,14	7,67	8,91	1,01	2,47	0,51	0,19	27,15	98,26	3,46
PN21-2-H3	Horizon soil	24,50	8,31	3,48	0,078	10,63	16,95	0,69	2,04	0,39	0,14	32,59	99,78	2,17
PN21-2-H4	Horizon soil	9,18	3,48	1,36	0,019	12,22	30,76	0,22	0,99	0,16	< L.D.	39,51	97,90	0,32
PN21-2-H5	Horizon soil	14,42	4,84	1,89	0,035	14,96	22,99	0,36	1,33	0,23	< L.D.	37,46	98,51	0,59
PN21-3-H1	Horizon soil	52,72	15,91	6,44	0,089	3,67	0,79	1,64	3,03	0,74	0,27	15,07	100,36	3,22
PN21-3-H2	Horizon soil	54,60	16,21	6,71	0,090	3,67	0,64	2,20	3,02	0,79	0,14	11,28	99,34	1,83
PN21-3-H3	Horizon soil	57,70	17,41	7,15	0,10	3,86	0,49	2,23	3,09	0,82	0,12	7,31	100,27	0,69
PN21-3-H4	Horizon soil	58,51	17,19	7,05	0,10	3,83	0,47	2,16	3,08	0,83	0,10	6,02	99,34	0,45
PN21-4-H1	Horizon soil	50,14	14,80	6,09	0,11	3,10	0,98	1,95	2,86	0,73	0,28	17,98	99,01	4,65
PN21-4-H2	Horizon soil	52,29	15,49	6,39	0,12	3,19	0,97	2,05	2,92	0,76	0,22	14,81	99,21	3,40
PN21-4-H3	Horizon soil	55,61	16,60	6,87	0,11	3,44	0,78	2,22	3,10	0,81	0,15	9,59	99,28	1,49
PN21-4-H4	Horizon soil	59,02	16,67	6,83	0,099	3,52	0,87	2,71	2,80	0,81	0,14	5,76	99,23	0,50
PN21-5-H1	Horizon soil	24,30	8,06	3,24	0,072	10,66	14,36	0,65	2,08	0,38	0,15	34,74	98,69	3,57
PN21-5-H2	Horizon soil	25,78	8,60	3,50	0,081	10,66	13,77	0,71	2,21	0,41	0,16	32,69	98,56	
PN21-5-H3	Horizon soil	16,43	5,58	2,12	0,035	13,47	21,86	0,40	1,58	0,25	< L.D.	36,62	98,35	
PN21-5-H4	Horizon soil	15,70	5,65	2,20	0,038	14,84	20,68	0,36	1,57	0,25	< L.D.	37,42	98,71	
PN21-5-H5	Horizon soil	11,91	3,82	1,42	0,018	14,92	26,13	0,25	1,15	0,17	< L.D.	38,76	98,55	
PN21-5-H6	Horizon soil	17,31	5,32	2,19	0,033	14,18	22,01	< L.D.	1,46	0,24	< L.D.	35,95	98,69	0,99
PN21-6-H1	P6-A	30,30	10,03	4,07	0,074	8,85	10,75	1,14	2,17	0,50	0,22	31,09	99,21	4,02
PN21-6-H2	P6-Bw	32,78	10,94	4,44	0,076	9,05	10,65	1,26	2,30	0,55	0,18	27,31	99,52	2,42
PN21-6-H3	P6-C	29,28	10,25	4,19	0,069	10,66	13,73	1,05	2,25	0,50	0,13	27,29	99,37	1,29
PN21-6-H4	P6-2Bw	29,47	10,56	4,32	0,072	10,75	13,30	1,05	2,30	0,51	0,13	26,78	99,23	1,15
PN21-6-H5	P6-2C	19,38	6,86	2,76	0,044	13,63	20,48	0,58	1,72	0,32	< L.D.	33,14	98,90	0,47
PN21-6-H6	P6-3Bw	17,37	6,64	2,64	0,042	14,65	20,86	0,50	1,69	0,31	< L.D.	34,32	99,03	0,33
PN17-R-07	Ore rock	81,10	5,74	1,11	0,077	0,97	1,42	0,08	1,94	0,057	< L.D.	3,73	96,22	0,01
PN21-R-05	Ore rock	84,13	0,54	1,10	0,072	0,55	1,53	0,06	0,17	< L.D.	0,20	3,77	92,12	<0,01
PN21-R-05-1	Ore rock	82,78	0,26	0,67	< L.D.	0,08	0,38	0,05	0,07	< L.D.	0,15	3,36	87,81	
PN21-R-05-4	Ore rock													
PN21-SCO-01	Slag	38,72	5,34	18,90	1,15	2,22	8,43	0,84	1,71	0,31	0,39	-0,64	77,36	0,03
PN21-SCO-03	Slag	42,55	6,19	20,60	1,29	2,37	8,93	1,01	1,89	0,35	0,40	-0,67	84,89	0,20
PN21-R-01	Stack residue	16,96	2,36	8,92	0,36	1,03	3,38	0,28	0,67	0,18	0,12	-0,920	33,34	<0,01
PN21-R-02	Stack residue	2,35	0,33	1,27	0,021	0,15	0,49	0,04	0,12	0,024	< L.D.	39,76	44,54	0,18
PN17-SED-12	River sediment - upstream	63,95	14,91	6,18	0,09	2,24	2,16	3,65	2,30	0,95	0,18	3,12	99,73	0,09
PN21-SED-03	River sediment - downstream	64,11	14,03	6,55	0,09	2,51	3,12	2,85	1,96	0,89	0,18	3,85	100,15	0,03
PN17-SED-13	River sediment - downstream	60,74	14,3	6,545	0,0971	2,682	3,358	3,156	2,066	1,002	0,2	4,81	98,95	
PN17-SED-02	River sediment - downstream	55,02	13,217	4,731	0,0527	4,065	7,487	2,023	2,843	0,668	< L.D.	9,9	100,0067	
PN17-SED-06	River sediment - downstream	63,98	14,15	5,869	0,0701	2,774	2,265	3,089	2,191	0,889	< L.D.	4,38	99,6571	
PN17-SED-08	River sediment - downstream	63,47	13,997	6,281	0,092	2,608	2,997	3,041	2,025	1,026	< L.D.	4,55	100,087	
PN17-SED-10	River sediment - dewatering gallery	7,66	4,366	1,017	< L.D.	1,229	4,673	0,295	1,75	0,201	< L.D.	5,04	95,17098	
PN21-SED-01	River sediment - dewatering gallery	44,84	6,89	3,08	0,11	7,08	13,17	0,54	1,50	0,32	< L.D.	21,93	99,45	1,64
PN17-SED-09	River sediment - dewatering gallery	72,57	9,16	3,95	0,07	1,00	2,79	1,27	2,48	0,35	< L.D.	5,87	99,50	0,77
PN17-SED-04	River sediment - dewatering gallery	21,95	11,04	3,37	0,04	9,81	16,74	0,46	3,05	0,38	< L.D.	33,33	100,15	

Sample_Name	As	Ba	Be	Bi	Cd	Co	Cr	Cs	Cu	Ga	Ge	Hf	In	Mo	Nb	Ni	Pb	Rb	Sb	Sc	Sr	Ta	Th	U	V	W	Y	Zn	Zr	EF_Pb	EF_Sb		
PN21-SO1.02	13.4	479	1.97	0.28	0.21	18.2	58.9	3.06	17.2	23.0	2.04	6.44	0.10	1.67	7.81	18.3	83.2	69.8	2.46	25.67	3.11	96.6	0.70	6.17	2.95	154	1.33	42.9	132	237			
PN21-1-H1	16.6	5876	1.56	<L.D.	0.09	15.9	64.5	5.05	98.1	14.4	1.37	3.21	0.15	4.91	6.73	31.2	19746	767	147	1079	4.47	171	0.63	6.28	4.00	73.2	1.83	18.9	384	117	168	51	
PN21-1-H2	25.3	13094	1.61	0.15	0.55	24.0	63.5	5.22	589	14.1	1.54	3.53	0.52	5.75	6.60	46.4	56140	748	528	10.11	9.07	309	0.63	7.21	6.44	71.2	1.84	21.0	971	131	488	188	
PN21-1-H3	12.3	5819	1.51	0.05	0.14	14.0	58.1	5.03	99.4	14.1	1.27	3.13	0.13	3.37	6.84	32.6	18096	739	145	11.24	2.92	189	0.67	6.15	3.77	73.2	1.38	19.7	306	113	159	52	
PN21-1-H4	26.7	5241	2.03	0.18	0.53	17.4	73.7	6.41	97.1	19.0	1.86	3.83	0.15	3.78	9.15	38.4	18797	96.9	158	14.48	3.55	146	0.84	8.18	4.54	97.6	1.79	25.1	365	144	126	44	
PN21-1-H5	42.2	833	2.30	0.30	0.51	18.9	94.4	6.47	41.5	22.1	1.81	4.90	0.07	2.46	10.3	45.9	1531	106	24.4	18.63	2.80	57.9	0.97	9.05	3.77	118	1.70	28.1	155	189	9	6	
PN21-1-H6	41.0	790	2.30	0.32	0.29	19.0	96.3	6.30	49.0	21.5	1.89	4.60	0.07	2.71	10.2	45.4	1078	103	20.8	18.66	3.43	60.2	0.96	8.73	3.42	113	1.66	26.5	121	169	7	5	
PN21-2-H1	7.63	1945	0.54	0.09	0.19	11.0	55.1	2.12	22.9	13.0	0.37	2.47	<L.D.	1.03	5.95	21.8	2388	84.2	9.26	10.83	0.63	181	0.57	2.17	1.17	70.9	<L.D.	15.3	211	98.2	152	10	
PN21-2-H2	12.0	3232	0.61	0.09	0.24	13.8	63.1	2.45	33.1	15.5	0.53	2.80	0.05	1.20	7.06	29.9	4330	94.4	21.0	12.13	1.08	178	0.77	2.55	1.38	80.2	<L.D.	18.9	280	109	248	21	
PN21-2-H3	9.59	1270	0.50	0.07	0.16	10.4	40.7	1.93	21.3	12.0	0.35	2.19	<L.D.	0.89	5.45	23.3	1389	77.1	8.63	9.42	0.78	290	0.53	1.98	0.99	66.1	<L.D.	13.2	135	85.0	97	10	
PN21-2-H4	3.61	186	0.23	<L.D.	<L.D.	3.95	22.9	0.94	7.9	5.12	0.16	0.96	<L.D.	6.07	2.36	11.0	54.4	36.6	1.17	4.32	3.72	652	0.23	0.94	0.62	30.3	<L.D.	4.99	46.1	35.4	8	3	
PN21-2-H5	4.59	346	0.29	<L.D.	<L.D.	5.34	30.5	1.33	9.9	7.07	0.21	1.42	<L.D.	0.82	3.46	15.9	130	50.9	1.89	5.47	0.41	293	0.34	1.30	0.75	42.0	<L.D.	7.47	55.3	54.0	14	3	
PN21-3-H1	43.9	582	2.19	0.47	0.32	17.9	97.8	6.34	40.6	21.2	1.92	4.57	0.07	3.26	9.93	41.8	646	106	6.25	17.28	3.20	51.9	0.93	8.27	3.38	110	1.75	27.6	121	170	4	2	
PN21-3-H2	44.0	580	2.25	0.61	0.25	18.1	92.3	6.35	38.4	21.4	1.97	4.35	0.07	3.08	10.1	39.8	647	105	6.44	18.17	3.12	51.0	0.92	8.37	3.32	111	1.67	27.8	114	168	4	2	
PN21-3-H3	51.6	596	2.24	0.41	0.19	20.6	92.1	6.59	47.3	23.4	2.04	5.14	0.08	3.09	11.4	43.4	378	108	5.25	19.28	3.10	50.9	1.08	9.31	3.51	124	1.84	30.5	125	201	2	1	
PN21-3-H4	51.5	526	2.30	0.34	0.19	19.9	91.4	6.04	44.2	22.2	1.87	5.01	0.07	2.72	10.5	42.8	156	102	3.81	19.37	2.85	51.5	0.97	8.59	3.10	116	1.69	29.0	101	193	1	1	
PN21-4-H1	11.7	1113	0.76	0.11	0.17	17.4	86.6	2.31	34.8	20.7	0.57	4.23	<L.D.	1.28	9.89	34.9	2019	107	10.5	16.89	0.89	66.3	0.92	3.22	1.35	108	<L.D.	25.4	182	158	12	3	
PN21-4-H2	14.2	1357	0.77	0.13	0.18	18.5	90.6	2.39	41.2	21.5	0.63	4.43	0.03	1.33	10.0	38.5	2714	109	16.0	16.87	1.06	65.4	0.96	3.39	1.43	113	<L.D.	26.3	196	170	16	4	
PN21-4-H3	17.4	965	0.82	0.12	0.11	20.2	96.2	2.49	42.1	23.2	0.69	4.81	<L.D.	1.31	11.1	45.3	1143	118	8.49	18.53	1.16	63.1	1.04	3.61	1.36	128	<L.D.	27.6	139	182	6	2	
PN21-4-H4	12.8	582	0.69	0.08	0.03	18.9	91.0	1.65	38.3	22.5	0.61	5.03	<L.D.	0.80	10.2	44.8	194	96.2	1.65	18.47	0.97	64.2	0.92	2.94	1.07	124	<L.D.	26.6	110	189	1	0.5	
PN21-5-H1	18.5	837	1.51	0.23	0.47	8.93	52.5	5.63	23.0	11.2	0.92	2.06	0.06	2.45	5.65	22.8	3439	78.4	17.3	9.15	1.88	178	0.51	5.14	3.01	61.9	1.04	12.7	139	79.7	237	20	
PN21-5-H2	7.0	1080	0.54	0.08	0.14	9.84	52.1	2.19	19.2	12.4	0.33	2.48	<L.D.	1.00	5.86	22.8	1575	85.5	7.2	9.72	0.86	184	0.59	2.16	0.98	66.5	<L.D.	13.4	149	93.7	100	8	
PN21-5-H3	4.7	355	0.36	<L.D.	0.03	6.25	33.4	1.43	11.5	8.0	0.22	1.42	<L.D.	0.77	3.85	16.2	174	57.5	2.3	5.89	0.47	270	0.37	1.50	0.66	45.4	<L.D.	9.5	55	52.4	16	4	
PN21-5-H4	4.7	365	0.38	0.05	0.02	6.47	34.8	1.51	9.7	8.5	0.20	1.51	<L.D.	0.83	4.03	15.8	86	61.1	2.0	6.39	0.51	231	0.41	1.60	0.79	49.3	<L.D.	8.6	59	54.9	8	3	
PN21-5-H5	2.8	138	0.25	<L.D.	<L.D.	3.99	24.5	0.90	7.0	5.4	0.12	0.96	<L.D.	0.79	2.60	11.2	31	40.0	0.9	4.46	0.34	291	0.27	1.03	0.65	32.8	<L.D.	5.4	36	36.8	4	2	
PN21-5-H6	11.7	207	0.97	0.12	0.17	6.90	33.6	3.43	41.3	7.43	0.64	1.47	<L.D.	2.69	3.71	15.4	443	51.0	10.5	5.75	2.28	234	0.37	3.61	2.41	45.5	<L.D.	8.15	63.2	54.8	47	19	
PN21-6-H1	6.65	436	0.57	0.06	0.05	12.1	58.6	1.85	16.0	14.7	0.41	2.98	<L.D.	0.89	6.55	22.1	218	85.8	1.28	11.75	0.59	147	0.63	2.35	0.88	81.4	<L.D.	17.2	111	111	14	1	
PN21-6-H2	8.90	470	0.59	0.07	0.07	13.2	63.5	2.01	16.7	16.0	0.47	3.30	<L.D.	0.92	7.13	25.2	278	92.0	1.86	13.19	0.86	150	0.70	2.53	0.91	88.4	<L.D.	19.3	104	127	16	2	
PN21-6-H3	8.93	416	0.55	0.07	0.04	12.5	58.2	1.85	20.7	14.4	0.42	2.94	<L.D.	0.88	6.34	24.9	128	82.5	1.49	12.00	0.76	182	0.61	2.32	0.86	80.2	<L.D.	16.0	83.9	111	8	2	
PN21-6-H4	9.89	433	0.56	0.07	0.05	13.5	62.3	1.97	21.1	15.2	0.46	2.78	<L.D.	0.96	6.62	27.2	100.0	86.5	1.51	12.30	0.85	174	0.63	2.45	1.02	83.2	<L.D.	16.6	85.8	104	6	2	
PN21-6-H5	7.21	216	0.40	0.05	<L.D.	8.72	41.9	1.40	15.9	10.0	0.26	1.84	<L.D.	0.97	4.50	18.0	17.5	61.0	0.81	8.35	0.63	229	0.46	1.70	0.83	56.4	<L.D.	10.9	57.6	69.2	2	1	
PN21-6-H6	7.37	206	0.41	0.05	<L.D.	8.30	40.8	1.51	16.8	9.65	0.27	1.75	<L.D.	0.97	4.44	18.2	11.5	62.1	0.67	7.80	0.61	225	0.45	1.65	0.82	56.5	<L.D.	9.60	55.3	65.3	1	1	
PN17-R-07	31.1	1065	1.57	0.19	3.29	16.1	15.3	4.38	71.5	5.97	3.00	1.39	0.10	1.37	1.86	11.9	29846	73.9	128	1.50	9.21	16.5	0.26	3.55	0.98	11.6	1.21	7.11	125	45.8			
PN21-R-05	18.0	103	0.15	12.3	3.47	11.8	10.3	0.33	2018	0.59	1.82	0.16	0.34	1.37	0.22	46.0	71384	5.49	112	1.07	2.45	70.9	0.04	0.48	0.73	1.7	<L.D.	13.1	111	4.54			
PN21-R-05-1	3.9	89	<L.D.	20.9	4.23	9.4	7.1	0.08	1647	0.30	0.59	0.10	0.06	<L.D.	0.10	27.9	44077	2.58	54	0.62	0.44	25.8	0.02	0.07	0.15	<L.D.	<L.D.	6.4	58	5.58			
PN21-R-05-4	1004.1				8.33	31.5			2844						54.1	78872	3.26	561															
PN21-SCO-01	31.1	80285	1.13	0.19	0.21	83.7	144	3.31	239	9.14	1.61	5.57	0.92	14.0	5.05	21.1	108418	48.2															

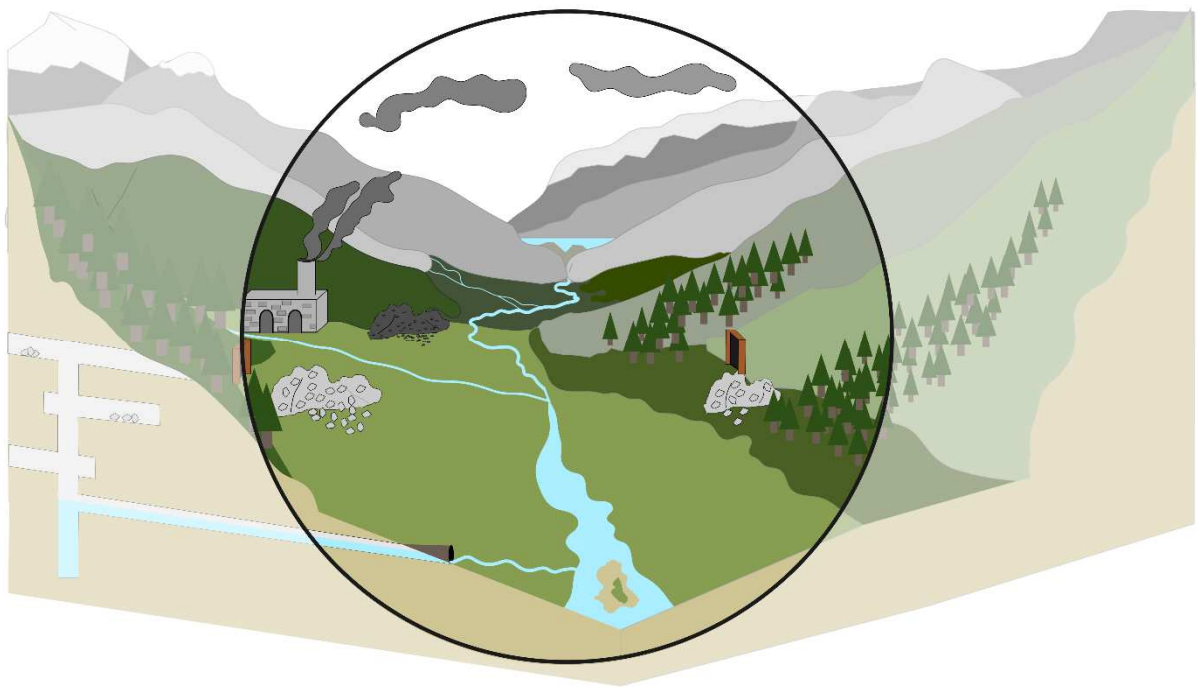
Table S3. Physico-chemical properties of soil horizons.

Profile/ Soil Type	Horizon	Depth cm	Particle size distribution			pH	CEC cmol.kg ⁻¹	CaCO _{3T} %	COT %	Ca _{ox} g.kg ⁻¹	Mg _{ox} g.kg ⁻¹	Mn _{ox} g.kg ⁻¹	K _{ox} g.kg ⁻¹	Na _{ox} g.kg ⁻¹
			Clays %	Silt %	Sand %									
P1/ Technosol	A	0-20	13.3	46.4	40.3	6.2	37.7	0.4	13.2	30.08	5.62	0.16	0.19	0.11
	Bu1	20-25	8.8	37.1	54.1	7.0	16.7	2.7	7.8	13.11	1.94	0.02	0.06	0.09
	Bu2	25-35	6.3	55.5	38.2	7.0	45.1	0.5	14.3	39.28	5.06	0.06	0.05	0.11
	Bw1	35-43	8	44.7	47.3	7.3	18.3	1.4	5.0	14.75	2.26	0.03	0.04	0.01
	Bw2	43-60	7.1	45.2	47.7	7.4	7.2	0.1	0.7	5.31	1.30	0.03	0.02	0.02
	C	60-75	5.8	44.6	49.6	7.6	7.5	0.9	0.9	6.00	1.39	0.02	0.03	0.02
P2/ Calcaric Cambisol	A	0-14	17	60.4	22.6	7.4	32.6	10.9	10.1	27.01	5.57	<0.005	0.17	0.05
	Bw1	14-20	9.5	66.9	23.6	7.7	25.9	9.8	7.0	21.32	4.03	<0.005	0.05	0.05
	Bw2	20-30	7.6	64.8	27.6	8.1	19.0	21.5	6.6	17.02	2.57	<0.005	0.03	0.03
	C	30-40	5	57.8	37.2	8.7	4.7	60.0	3.4	5.61	0.57	<0.005	<0.02	0.01
	C	40-55	5.1	69	25.9	8.5	7.9	44.4	4.7	8.16	0.95	<0.005	<0.02	0.01
P3/ Dystric Cambisol	A	0-5	16.4	47.5	36.1	6.6	16.5	0.1	4.6	13.29	2.94	0.05	0.45	0.09
	A/B	5-25	14.5	46.8	38.7	6.6	12.6	0.2	2.9	9.74	2.40	0.04	0.13	0.03
	Bw	25-45	11.8	47.4	40.8	6.7	8.5	<1	1.1	6.34	1.56	0.03	0.03	0.06
	C	45-60	7.2	43.4	49.4	6.9	7.2	<1	0.8	5.49	1.23	0.02	0.04	0.02
P4/ Dystric Cambisol	A	0-5	15.4	49.6	35	6.3	20.0	<1	6.2	16.43	2.67	0.07	0.16	0.12
	A/B	5-12	13.1	49.7	37.2	6.6	18.2	0.1	4.7	14.86	1.88	0.04	0.07	0.06
	Bw	12-25	7	51.4	41.6	7.1	14.1	0.1	2.1	12.28	1.01	0.03	0.03	0.03
	C	25-60	4.9	42.5	52.6	7.8	6.9	0.6	0.8	6.23	0.52	<0.005	<0.02	0.09
P5/ Calcaric Cambisol	A	0-7	15.7	63.1	21.2	7.7	25.0	13.3	9.0	21.18	4.01	<0.005	0.19	0.06
	Bw	7-17	14.2	65.3	20.5	7.8	22.3	12.2	8.2	19.01	3.47	<0.005	0.13	0.05
	C	17-27	6.7	61.7	31.6	8.3	11.9	34.4	5.8	11.14	1.44	<0.005	0.06	0.01
	2Bw	27-39	7.5	70.6	21.9	8.3	12.3	35.0	6.0	11.45	1.60	<0.005	0.03	0.02
	2C	39-53	4.7	42.1	53.2	8.6	3.8	65.0	2.4	4.65	0.45	<0.005	<0.02	0.01
	3Bw	53-57	4.9	57.3	37.8	8.3	10.6	60.0	2.5	10.69	1.21	<0.005	<0.02	0.02
	3C	57-70	3.5	48	48.5	8.7	2.1	66.6	2.0	3.33	0.29	<0.005	<0.02	0.01
P6/ Calcaric Cambisol	A	0-5	17.4	62.3	20.3	7.5	26.0	16.2	7.6	20.82	5.83	<0.005	0.13	0.11
	Bw	5-27	16.7	62.9	20.4	7.8	21.3	18.7	5.5	17.10	4.08	<0.005	0.05	0.09
	C	27-33	11.6	67.2	21.2	8.2	15.1	25.2	4.2	13.10	2.59	<0.005	0.03	0.06
	2Bw	33-42	8.8	72.6	18.6	8.1	14.7	25.3	4.0	12.35	2.59	<0.005	0.02	0.07
	2C	42-54	4.8	64.5	30.7	8.3	7.3	51.1	2.5	7.31	1.28	<0.005	0.04	0.04
	3Bw	54-80	6.5	74.2	19.3	8.5	6.0	48.9	3.0	6.23	0.93	<0.005	<0.02	0.04

Chapitre 6 |
Inventaire du Pb à l'échelle du
bassin versant

Chapitre 6 | Inventaires du plomb à l'échelle du bassin versant

Les chapitres précédents ont permis de discuter du degré de contamination des sols et de la part des différentes sources impliquées (déchets miniers et métallurgiques vs fumées). Ce chapitre vise à évaluer les inventaires (stocks) de Pb anthropique présents dans les sols du site minier d'une part, et dans les sols du bassin versant du Lac de La Plagne d'autre part, afin de les comparer à la quantité de Pb produit par la mine.



L'étude des sols de l'ancien site minier et métallurgique de Peisey-Nancroix, situés à proximité et en aval des haldes de roches stériles et de scories, a montré une contamination importante en Pb (Chapitre 3). Les concentrations mesurées en Pb sont de l'ordre de plusieurs % pour les sols développés à proximité immédiate des tas de scories, et une majeure partie des sols de surface présentent des teneurs entre 500 et 1500 mg.kg⁻¹ de Pb. Les mécanismes de transfert du Pb anthropique dans les sols de surface résultent d'une part de la dispersion de particules de déchets miniers et métallurgiques et d'autre part de la lixiviation de ces particules et des haldes de déchets. Les sols de surface (0-20 cm) du bassin versant du lac de La Plagne, situé 7 kilomètres en amont du site minier et métallurgiques, montrent quant à eux un enrichissement modéré à sévère en Pb par rapport au fond géochimique non-minéralisé. Sur ce bassin versant, l'apport anthropique de Pb correspond au Pb issu des fumées métallurgiques (Chapitre 4). Enfin, les sédiments de rivière et les eaux du Ponturin ne sont que peu impactés par la dispersion du Pb anthropique (Chapitre 5).

La comparaison des stocks actuels de Pb anthropique (Pb_{ANTH}) entre les sols du site minier et ceux du bassin versant du Lac de La Plagne permettra de comparer les quantités de Pb anthropique dispersées par voie aérienne (fumées métallurgiques) et les quantités de Pb anthropique remobilisées à partir des déchets miniers et métallurgiques. L'*inventaire* (encore appelé *stock métallique*) permet de comparer, à épaisseur égale, une quantité de Pb (en grammes voire tonnes) accumulée par unité de surface (mètres carrés voire hectare), en s'affranchissant de la variabilité de densité des sols. Semali et al. (2002) utilisent cette approche pour mesurer quantitativement les redistributions des éléments traces métalliques lors de la pédogénèse et estimer les parts exogènes d'un andosol développé sur des scories basaltiques. Les concentrations sont de bons indicateurs du degré de contamination mais ne permettent pas de saisir l'importance de celle-ci par rapport à la quantité de métaux produit par l'exploitation de la mine (21 500 tonnes de Pb et 52 t d'argent à la mine de Peisey-Nancroix). Dans ce chapitre, nous avons cherché à estimer l'inventaire en Pb anthropique des sols de surfaces du site minier et du bassin versant du Lac de La Plagne, soit ce qui revient à quantifier l'excès de Pb_{ANTH} accumulé à l'échelle du bassin versant à partir des fumées atmosphériques (contamination pendant et après la période d'exploitation) et de la remobilisation des déchets miniers (contamination post-mine). Afin d'estimer la proportion relative de Pb anthropique généré par les activités minières et métallurgiques par différents modes de transfert, il est nécessaire de distinguer les apports anthropiques des éléments issus du fond géochimique naturel. Dans le cas d'une zone minéralisée, il faut considérer le fond géochimique comme étant le fond géochimique minéralisé mesuré en dehors de toute perturbation anthropique (p. ex. dépôts

de déchets miniers ou métallurgique). L'inventaire de Pb pour la partie superficielle des sols est alors calculé à l'aide de la formule suivante :

$$\text{Inventaire} = \text{Teneur en Pb} * \text{Epaisseur du sol} * \text{masse volumique du sol} \quad (\text{équation 1})$$

avec l'*inventaire* (stock métallique) exprimé en mg.m^{-2} , la *teneur en Pb* exprimée en mg.kg^{-1} , l'*épaisseur du sol* exprimée en cm, et la *masse volumique du sol* (appelée aussi densité apparente) en g.cm^{-3} . Le but de la démarche consiste à établir des ordres de grandeur pour les deux zones ciblées et non de dresser un modèle précis.

6.1 Choix du fond géochimique pour chacun des sites

Le choix du fond géochimique est crucial pour déterminer la part de Pb anthropique présent dans les sols. Comme l'ont montré les isotopes du Pb (Chapitre 5), il existe deux fonds géochimiques à l'échelle du bassin versant, le fond géochimique dit global, non impacté par la présence de la minéralisation de Pb-Ag en son sous-sol, et le fond géochimique local minéralisé qui justifie la présence de la mine.

Table 6-1: Teneurs élémentaires en plomb et éléments lithogènes et leurs ratios élémentaires associés, pour différents échantillons pouvant servir de fond géochimique

Type d'échantillons	Teneurs (mg.kg^{-1})				Ratios élémentaire		
	Pb	Rb	Zr	Th	Pb/Rb	Pb/Zr	Pb/Th
Croûte continentale	17	82	193	11	0.2	0.09	1.5
<i>Zone minéralisée (site minier)</i>							
Sol de référence (REF-TOPSOIL, 0-20 cm)	83	70	237	6	1.2	0.4	14
Horizon sol profond Profil 3 (Dystric cambisol)	156	102	193	9	1.5	0.8	17
Horizon sol profond Profil 6 (Calcaric cambisol)	12	62	65	2	0.3	0.3	6
<i>Zone non minéralisée (site du Lac de La Plagne)</i>							
Horizon sol profond Profil A5 (cargneule)	36	132	164	13	0.3	0.2	3
Horizon sol profond Profil B6 (20-40 cm, till)	26	88	107	10	0.3	0.2	3
Horizon sol profond Profil B6 (40-60 cm, cargneule)	20	112	50	7	0.2	0.4	3
Sédiments de lac profond (n=14)	31±1.5	98±7	185 ±29	7±0.5	0.3	0.2	4.6
Sédiment de rivière en amont du site minier (SED-12)	12	74	202	8	0.2	0.06	1.5

Les sols du bassin versant du lac de La Plagne, ainsi que les sédiments de rivière prélevés en amont du site minier, et les sédiments lacustres profonds (anté-mine) montrent des ratio Pb/Rb proches de ceux de la moyenne des roches crustales. Ils représentent le fond géochimique non minéralisé. Les dystric cambisols développés sur le site minier ont quant à eux un ratio Pb/Rb environ 4 fois plus élevé que les calcaric cambisols (Table 6-1), probablement du fait de proximité de la minéralisation. On les considèrera comme représentant le fond géochimique minéralisé pour les dystric cambisols. Les sols profonds des calcaric cambisols sont considérés comme référence (peu minéralisée) pour ce type de sols.

6.2 Stock de plomb anthropique généré par les haldes (sols du site minier)

Les teneurs mesurées dans les sols de la zone prairiale située en contrebas des tas de déchets miniers et métallurgiques sont très supérieures à celles observées dans les horizons profonds et dans le sol de surface considéré comme référence, suggérant que la contamination par les remobilisation des déchets miniers et métallurgiques est très nettement supérieure au fond géochimique qu'il soit minéralisé ou non. L'étude de la distribution du Pb dans les sols de surface a permis de visualiser l'étendue de la contamination ainsi que les zones non ou peu impactées, c'est-à-dire qui tendent vers les valeurs du fond géochimiques minéralisés.

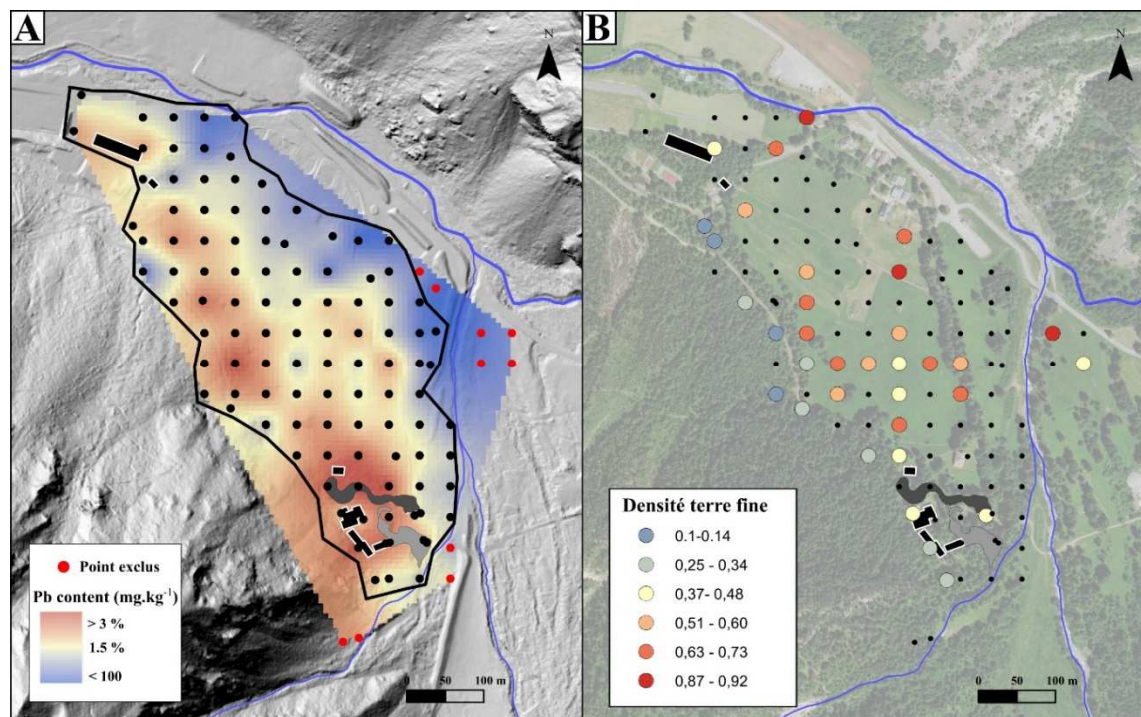


Figure 6.1: A) Distribution spatiale de la teneur en Pb totale et cadre restreint des points de sol de surface sélectionnés pour le calcul des inventaires. B) Distribution des points de mesure de masse volumique (densité apparente de terre fine), répartie entre la zone prairiale et la partie forestière.

D'après la visualisation spatiale des teneurs et l'étude des rapports Pb/Rb, les zones peu à pas contaminées, dont les valeurs de Pb dans les sols se rapprochent de celle du fond géochimique local, ont été exclues (Figure 6.1A). Les inventaires de Pb_{ANTH} et de Pb_{TOTAL} ont été calculés et interpolés.

6.2.1 Méthode de calcul et d'interpolation

D'après l'équation 1, l'inventaire de Pb total ou de Pb anthropique (g.m⁻²) est calculé pour chacun des sols de surface en utilisant l'équation :

$$Inventaire_{Pb_X} = Pb_X * \rho_{TERRE_FINE} * e \quad \text{équation 2}$$

avec Pb_X la concentration de Pb_{TOTAL} ou de Pb_{ANTH} de l'échantillon (mg.kg⁻¹), ρ_{TERRE_FINE} la masse volumique du sol (kg.m⁻³), qui est égale au ratio du poids de terre sèche de la fraction fine du sol (< 2mm; Semlali et al., 2002), et e la hauteur de sol prélevée à la tarière manuelle (0-20 cm). La concentration de Pb anthropique (Pb_{ANTH}) est calculée à partir de la méthode élémentaire qui se base sur un ratio élément contaminant/élément lithogène d'un échantillon de référence (méthode détaillée dans le Chapitre 4) :

$$Pb_{ANTH} = Pb_{TOTAL} - \left(Rb_{TOTAL} * \left(\frac{Pb_{BKG}}{Rb_{BKG}} \right) \right) \quad \text{équation 3}$$

avec Pb_{BKG} et Rb_{BKG} les teneurs en plomb et rubidium de l'échantillon de référence choisi (BKG, *background*). Le thorium, utilisé dans la méthode élémentaire pour les sédiments lacustres et les sols du bassin versant du lac de La Plagne (Chapitre 4), n'ayant pas été analysé par WDS-XRF dans les échantillons de sols de surface du site minier, le Rb est utilisé ici comme élément lithogène.

Deux types de sols ont été mis en évidence sur le site minier : des calcaric et des dystric cambisols, issus de deux matériaux parents différents (Chapitres 3). L'étude de la distribution du Pb des sols en profondeur a mis en évidence des ratios Pb/Rb différents pour les deux types de sols (Chapitre 5 ; Table 6-1). Ainsi pour le calcul du Pb_{ANTH}, des ratios différents ont été attribués aux sols de surface, selon la typologie du sol (Figure 3.2). Comme pour le Chapitre 4, nous utiliserons ici l'horizon profond du profil P6 comme échantillon de référence pour les calcaric cambisols et l'horizon profond du profil P3 comme échantillon de référence pour les dystric cambisols (Table 6-1). L'ensemble des points d'inventaire de Pb total et anthropique a été interpolé spatialement par krigeage ordinaire pour obtenir un ordre de grandeur des stocks de Pb en surface intégré à la surface

choisie (inventaire). La collection de fonction (*package*) *automap* du logiciel R a été utilisé pour réaliser un krigeage automatique (R Core Team, 2022).

6.2.2 Inventaires de Pb interpolés

Dans le calcul des inventaires, la plus grosse marge d'incertitude provient de la mesure de la masse volumique. L'étude de la variabilité de la masse volumique en fonction des différents types de sols a été étudiée ; la Figure 6.1B présente les points de sol échantillonnés pour les mesures densité apparente (masse volumique). Les sols localisés à proximité des rivières ont une densité apparente élevée, égale à 0.91 (n=2) alors que les échantillons prélevés sous le couvert forestier ont une densité apparente faible, égale à 0.23 (n=11, min =0.10 et max =0.37). Les sols de la zone prairiale représentent la majeure partie des sols du site, et leur densité apparente varie entre 0.41 et 0.87, avec une moyenne de 0.58 (n=21). A partir des valeurs minimums, maximums et moyennes des densité apparentes de terre fine, les inventaires de Pb_{ANTH} et de Pb_{TOTAL} ont pu être interpolés sur une surface totale de 15.9 ha (Figure 6.2). Les inventaires de Pb_{ANTH} et de Pb_{TOTAL} varient entre des valeurs proches de zéro jusqu'à plus de 3000 g.m⁻². La distribution de la teneur en Pb total des sols de surface (Figure 6.1A) est similaire à la distribution des inventaires en surface (Figure 6.2).

Table 6-2: Comparaison des inventaires de Pb_{TOTAL} et de Pb_{ANTH} intégrés sur la zone étudiée

	Inventaire de Pb _{ANTH}		Inventaire de Pb _{TOTAL}	
	g	t	g	t
Estimation maximum	2777512	2.8	2831610	2.8
Estimation minimum	1499490	1.5	1526970	1.5
Estimation moyenne	2021132	2.0	2064219	2.1

Les inventaires de Pb_{ANTH} et de Pb_{TOTAL} calculés et intégrés sur la surface contaminée (15.9 ha) sont identiques (Table 6-2). Ils varient entre 1.5 t et de 2.8 t de Pb considérant respectivement les densité apparentes minimales ou maximales, et de 2.1 t pour une densité apparente moyenne (Figure 6.2). Les sols de surface sont fortement contaminés ; la part naturelle a ainsi peu d'influence sur les inventaires de Pb total et de Pb anthropique de la zone, qui sont équivalents.

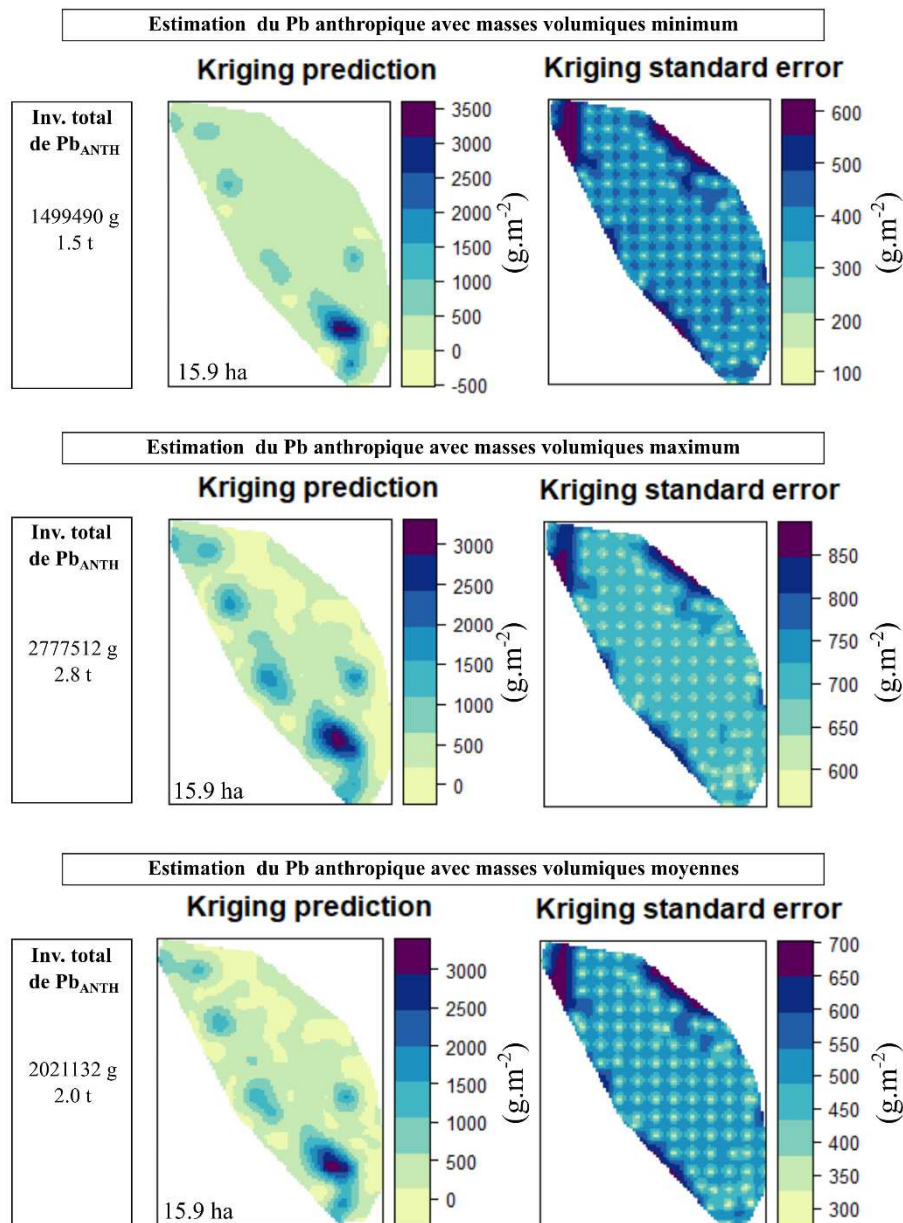


Figure 6.2: Cartes d'interpolation des inventaires (stocks) de Pb anthropique obtenus par krigeage standard (à gauche) et l'erreur standard associée en fonction de la densité apparente des sols considérée (à droite).

6.3 Inventaire de plomb anthropique généré par l'émission de fumées lors de la pyrométallurgie

Les sédiments lacustres du lac de la Plagne ont enregistré l'augmentation de la concentration en Pb atmosphérique causée par la fusion du minerai sur le site minier et métallurgique, situé 7 km en aval du lac de La Plagne (Figure 4.1). La datation des sédiments lacustres a permis de transformer la concentration en Pb total (mg de Pb par kg de sédiments) en taux d'accumulation de Pb

($\text{mg}\cdot\text{m}^{-2}\cdot\text{an}^{-1}$), puis en taux d'accumulation de Pb anthropique par des méthodes élémentaires (cf. Chapitre 4 ou équation 1 de ce chapitre), confirmé par la méthode isotopique (Chapitre 4).

Cette partie vise à estimer les inventaires de Pb anthropique déposés sur les sols du bassin versant du lac de La Plagne au cours de la période de fusion du minerai, et de les comparer aux stocks actuels des sols de surface. La comparaison avec l'inventaire de Pb anthropique du lac pour la période post-fusion, provenant de la remobilisation du Pb par l'érosion des sols, permettra de discuter ces résultats. Pour ce faire, les calculs présentés par la suite reposent sur plusieurs hypothèses fortes : (i) les taux d'accumulation de Pb anthropiques mesurés pendant la période de fusion du minerai correspondent aux flux atmosphériques déposés à la surface du lac et de son bassin versant, (ii) le flux atmosphérique de Pb anthropique, estimé à partir des sédiments lacustres, est considéré constant et homogène sur toute la surface du bassin; et (iii) l'inventaire du Pb anthropique mesuré dans la carotte PLG-03 est représentatif de l'inventaire du Pb anthropique à tout endroit du lac.

6.3.1 Reconstruction de l'inventaire de Pb anthropique déposé initialement sur les sols autour de Lac de la Plagne

A partir du taux d'accumulation de Pb anthropique mesuré au cours de la période de fusion du minerai (Figure 4.7), le flux atmosphérique moyen au cours des périodes de fusion du minerai a pu être estimé (Figure 6.3). Un flux de Pb_{anth} de $112 \text{ mg}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$ a été estimé pendant la période la plus productrice de 1745 à 1795, et un flux de Pb_{anth} de $74 \text{ mg}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$ a été estimé pour la seconde période de production (1804 et 1824 ; Figure 4.7). Le cumul des flux de Pb anthropique sur le nombre d'années de fusion du minerai conclut à une estimation moyenne d'un dépôt de $7 \text{ g}\cdot\text{m}^{-2}$ de Pb anthropique (entre 4 à $11 \text{ g}\cdot\text{m}^{-2}$) déposé au cours des 70 années d'activités métallurgiques (Table 6-3). Ces valeurs sont du même ordre de grandeur que les inventaires de Pb anthropiques calculés actuellement dans les sols du bassin versant, qui sont compris entre $1.6 \text{ g}\cdot\text{m}^{-2}$ et $9.0 \text{ g}\cdot\text{m}^{-2}$ (Table 4.4, $n=13$). Les sols du bassin versant du lac de la Plagne représentent une source secondaire de Pb anthropique. Les inventaires de Pb_{ANTH} estimés s'être déposés au cours des activités métallurgiques sont multipliés par la surface du bassin versant du lac de La Plagne (1742 ha). afin d'en évaluer la quantité (en tonnes) et de la comparer à la quantité de Pb anthropique toujours présente dans les sols (Table 6-4). A l'échelle du bassin versant du lac de La Plagne, cela représente entre 61 à 186 t (124 t en moyenne) de Pb anthropique qui se sont déposées pendant l'activité métallurgique. L'inventaire du Pb anthropique actuellement présent dans les sols du bassin versant

varie entre 28 et 157 tonnes, pour une valeur moyenne de 82 t. Ainsi, une partie du Pb anthropique déposé lors des activités métallurgiques a été remobilisée et évacuée du bassin versant (Table 6-4).

Table 6-3: Flux moyen de Pb anthropique estimé d'après le taux d'accumulation du Pb anthropique dans les sédiments lacustres. Estimations basées sur l'incertitude du modèle d'âge (estimation moyenne, basse et haute) et les inventaires de Pb anthropiques.

	Flux moyen de Pb anthropique		Inventaire de Pb anthropique	
	1745-1795 (50 ans)	1804-1824 (20 ans)	(70 ans)	
	mg.m ⁻² . y ⁻¹		mg.m ⁻²	g.m ⁻²
estimation moyenne	112	74	7104	7.1
estimation basse	56	35	3517	3.5
estimation haute	169	113	10690	10.7

Table 6-4 : Quantité initiale de Pb anthropique déposée sur les sols du bassin versant du lac de La Plagne (1742 ha) d'après l'estimation moyenne, minimale et maximale des inventaires de Pb anthropique réalisées à partir des sédiments lacustres, la quantité actuelle de Pb anthropique calculée à partir des inventaires de Pb anthropiques de sol moyen ($Pb_{anth} = 4.6 \text{ g.m}^{-2}$), minimum ($Pb_{anth} = 1.6 \text{ g.m}^{-2}$) et maximum ($Pb_{anth} = 9 \text{ g.m}^{-2}$, Table 4.4) et par différence, la quantité de Pb anthropique qui a été lessivée.

	Quantité initiale de Pb anthropique déposée (t) <i>mesuré d'après les sédiments lacustres</i>	Quantité actuelle de Pb anthropique estimée (t) <i>mesuré à partir des sols</i>	Quantité de Pb anthropique lessivé (t)	% Pb lessivé
estimation moyenne	124	82	42	34 %
estimation basse	61	28	33	54 %
estimation haute	186	157	29	16 %

6.3.2 Inventaire de Pb anthropique du lac de La Plagne issu de la remobilisation des sols par érosion

A partir de l'inventaire du Pb anthropique mesuré dans les sédiments lacustres, nous pouvons calculer l'inventaire de Pb anthropique stocké dans le lac lors de la période post-fusion, où en absence de dépôts atmosphériques la remobilisation du Pb_{ANTH} résulte uniquement de l'érosion des sols (Figure 6.3). L'inventaire de Pb_{ANTH} mesuré pendant la période post-fusion (1824-2019) est égal à 10.7 g.m^{-2} , que l'on rapporte à la surface totale du lac (hypothèse iii) : soit un total de 0.8 t de Pb_{ANTH} (Figure 6.3). Cette quantité de Pb_{ANTH} accumulée dans le lac par l'érosion des sols du bassin

versant est faible vis-à-vis de la quantité de Pb_{ANTH} initialement déposée (Table 6-4). En considérant la quantité estimée la plus haute et la plus basse, cela représente entre 0.4 à 1.3 % de la quantité de Pb_{ANTH} déposé sur les sols et susceptibles d'avoir été remobilisé pour sédimenter dans le lac, et 1.9 à 2.76% du Pb anthropique qui a été lessivé par érosion des sols depuis plus de 200 ans. Les données du chapitre 4 montrent que le Pb des sols du lac de La Plagne n'est pas transféré en profondeur. Aussi, nous avons fait l'hypothèse que le flux atmosphérique correspond au flux atmosphérique enregistré par les sédiments, or il est certain que la majeure partie du flux atmosphérique à la surface du lac et traversant la colonne d'eau reste en solution et est transférée vers l'exutoire. Ainsi, le Pb anthropique a été en grande partie emporté par les eaux et la quantité de Pb anthropique calculée ici et estimée s'être déposée sur les sols du bassin versant est sûrement minorée.

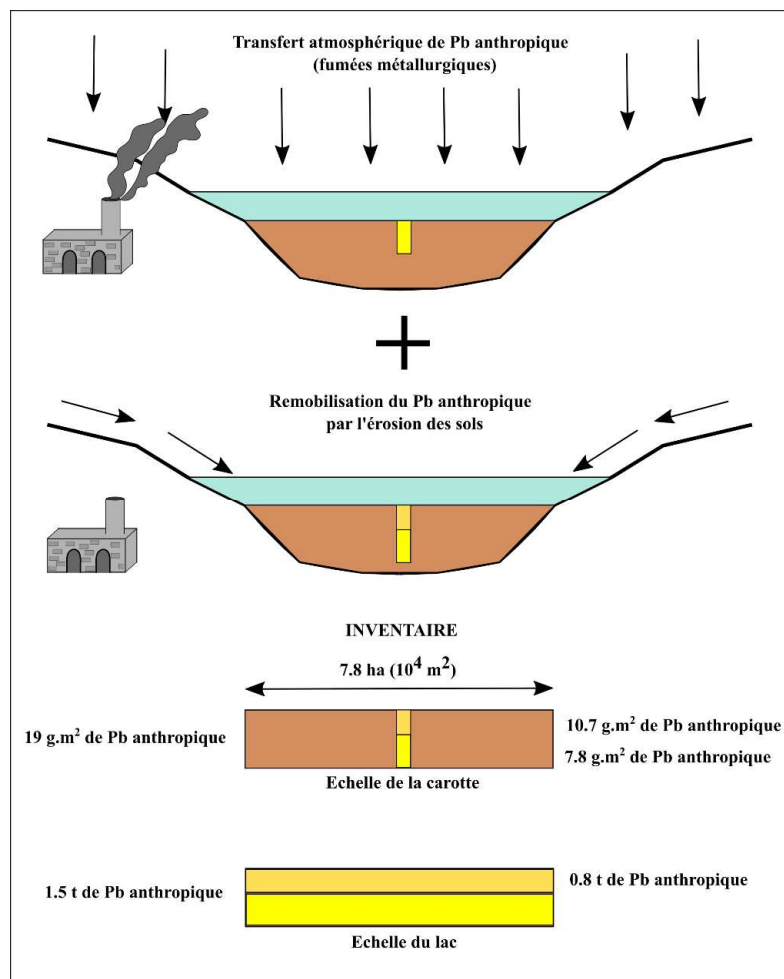


Figure 6.3: Schéma explicatif de la démarche de calcul de l'inventaire du Pb anthropique

6.4 Comparaison

Les calculs d'inventaire de Pb anthropique indiquent la présence de 2 t de Pb sur le site minier et métallurgique de Peisey-Nancroix, pour une surface de 15 ha, et du dépôt de 124 t dans les sols du bassin versant du lac de La Plagne, dont 66 % est encore persistant plus de 200 ans après l'arrêt des activités. Si la totalité de la surface du bassin versant avait été étudiée, les inventaires auraient au minimum doublé avec la surface prise en compte. Le flux atmosphérique étant sans doute bien supérieur à proximité de la mine et de la fonderie à celui estimé dans le bassin versant du lac de La Plagne (Cloquet et al., 2006a), la quantité de Pb anthropique dispersée dans l'environnement est probablement sous-estimée ici.

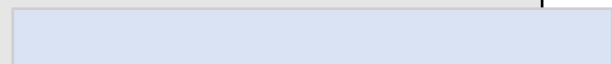
Ces calculs d'inventaire démontrent que l'étude des contaminations liées aux activités minières et métallurgiques doivent prendre en compte autant la contamination diffuse engendrée par les fumées issues du traitement pyrométallurgiques que la contamination ponctuelle générée par le stockage de déchets sur le long-terme. Dans le cas d'un site minier et métallurgique, les émissions de métaux par les fumées métallurgiques ne devraient pas être sous-estimées car ces métaux sont susceptibles d'être remobilisés et transportés plus loin ou bien accumulés sur le long terme dans des zones de replat ou encore des pièges comme les lacs.

A RETENIR

- Environ 2 t de Pb anthropique stockés dans les sols du site minier.
- Environ 124 t de Pb anthropique déposé dans le bassin versant du Lac de La Plagne.
- Lessivage d'environ 34% du Pb anthropique déposé par le lessivage des sols
- Seuls 1% du Pb anthropique lessivé est resté stocké dans le lac de La Plagne, le reste ayant été évacué dans le Ponturin par l'exutoire.

Chapitre 7 |

Conclusions & Perspectives



Chapitre 7 | Conclusion et Perspectives

Cette thèse avait pour but d'étudier **l'héritage minier à long-terme** (>200 ans) à partir de **l'étude de la dispersion à long-terme des ETM dans les différents compartiments de la zone critique**. Les principaux objectifs étaient de déterminer et de quantifier : (i) la part de la contamination naturelle versus la contamination anthropique, (ii) les éventuelles remobilisations d'ETM et (iii) la part de chaque source dans la contamination anthropique (déchets miniers minéralisés, scories et fumées métallurgiques), et (iv) les modes de dispersion des ETM dans l'environnement. Pour cela, une **approche source-puits, multi-compartiments** (source de contamination, sols, sédiments lacustres, sédiments de rivière et eaux) et **multi-échelles spatiales** (du site minier et métallurgique au bassin versant) a été mise en œuvre, combinant des observations et analyses minéralogiques, géochimiques et isotopiques. L'étude s'est focalisée sur l'ancien site minier et métallurgique de Pb-Ag de Peisey-Nancroix (Savoie, XVII^e-XIX^e siècle) abandonné il y a plus de 170 ans, où 21 500 t de Pb et 52 t d'Ag ont été produites. Le minerai a été traité sur place par pyrométallurgie pendant 70 ans. Aujourd'hui, on retrouve sur le site les vestiges des infrastructures ainsi que plusieurs tonnes de déchets miniers (roches minéralisées) et métallurgiques (scories) enrichis en ETM. Cette thèse s'est focalisée sur le Pb et Sb du fait de leur toxicité et de leur abondance dans la minéralisation du site étudié.

7.1 Les contaminations des différents compartiments autour du site minier

Au niveau du site minier et métallurgique, les sols correspondent au compartiment le plus contaminé en Pb et en Sb avec des teneurs en ETM élevées à très élevées (Chapitre 3) : elles atteignent jusqu'à 3 wt. % de Pb et 190 mg.kg⁻¹ de Sb au niveau des sols de surface développés sur ou situés à proximité immédiate des haldes de déchets miniers et métallurgiques. Dans la zone prairiale située à quelques dizaines de mètres de la zone de stockage des déchets, des teneurs en Pb comprises entre 500 et 5000 mg.kg⁻¹ et des teneurs en Sb comprises entre 1.5 et 147 mg.kg⁻¹ ont été mesurées. Cependant la contamination des sols diminue rapidement vers des valeurs proches du fond géochimique en contre-bas de la zone prairiale (Chapitre 3, Figure 3.4). Les profils de sols

réalisés dans les sols prairiaux montrent que les deux horizons les plus superficiels sont les plus contaminés, et que la contamination diminue très rapidement en profondeur pour atteindre également des valeurs proches de celles du fond géochimique (Chapitre 5, Figure 5.2). Ainsi, le transfert vertical des ETM reste limité à l'exception des technosols développés à proximité des haldes de déchets qui ont servi comme zone de grillage du minerai (présence importante de charbon). Le gradient horizontal de contamination depuis les zones de déchets vers l'aval, ainsi que le fort gradient vertical indiquent clairement une contamination superficielle d'origine anthropique dont la dispersion spatiale reste cependant très limitée.

Outre les sols, l'ensemble des compartiments étudiés (sédiments et eaux de rivières, sédiments lacustres) sont contaminés par le stockage à long-terme des déchets miniers et métallurgiques (> 170 ans), et/ou par l'émission à court-terme de fumées métallurgiques (1745-1824) et/ou par la remobilisation de minerai au niveau des exhaures. Les eaux et sédiments d'exhaure d'anciennes galeries d'exploration, situées sur les rives du Ponturin, sont enrichis en Pb et en Sb par rapport au signal amont du bassin versant (i.e.; référence non contaminée, Figure 5.1). Seule, la galerie d'exhaure provenant de la mine présente des teneurs particulièrement élevées en Pb et en Sb dans les eaux et les sédiments. Les eaux de ces galeries rejoignent la rivière principale, le Ponturin, dont les sédiments prélevés quelques centaines de mètres après le site minier montrent des valeurs qui se rapprochent du fond géochimique, montrant la dilution rapide de la contamination.

Enfin, les sédiments lacustres du Lac de La Plagne (7 km en amont du site minier et métallurgique, sous le vent) ont enregistré la contamination en Pb lors de la période de traitement du minerai par pyrométallurgie. Ainsi, pendant la période d'exploitation, les sédiments lacustres présentent des teneurs en Pb 5 fois plus élevées que le fond géochimique non contaminé (Chapitre 4). Les sédiments du bassin versant du Lac de La Plagne ont également enregistré les retombées atmosphériques et sont encore contaminés en Pb anthropique d'origine pyrométallurgique.

7.2 Le problème de la caractérisation du fond géochimique local

La définition d'un fond géochimique est un préalable à l'étude d'une contamination en ETM dans l'environnement ; sa valeur fait office de référence pour évaluer le degré d'une contamination d'origine anthropique, comme les activités minières et métallurgiques, pour calculer des facteurs d'enrichissement (EF) ou de facteurs de concentration (CF) pour les différents compartiments de l'environnement. Présents à l'état de traces dans les roches de la croûte continentale, la présence

d'une minéralisation peut augmenter la concentration en ETM des compartiments de l'environnement à proximité de celle-ci (Galuszka et al., 2015; Galán et al., 2008).

L'estimation du fond géochimique est particulièrement complexe et peut être soumise à débats, notamment d'ordre méthodologique. Cette estimation est particulièrement complexe dans les zones de montagne en raison de la présence de lithologies de natures très variées. Dans le cas du bassin versant du site minier de Peisey-Nancroix, le socle Varisque composé de diverses roches cristallines (schistes, roches mafiques et ultramafiques, gneiss silicatés), est juxtaposé à des roches siliceuses du permo-Trias et à des roches carbonatées (cargneules ; Figure 3.1). La présence de dépôts quaternaires (tills + cônes de déjection + éboulis + alluvions) contribue à redistribuer ces lithologies ; les différents dépôts pouvant également se superposer et s'intercaler (ex. profils P5 et P6 où superposition de dépôts de cône alluvial silicaté et d'éboulis carbonaté).

La présence d'une mine sur un territoire est synonyme de sous-sol minéralisé, dont l'altération géochimique est potentiellement une source de contamination naturelle des sols, et en particulier des horizons profonds. Puisqu'il serait vain de déterminer une contamination en-deçà de sa contamination naturelle, la détermination du fond géochimique local représente un prérequis indispensable avant toute quantification d'une contamination en ETM liée à des activités minières et métallurgiques. L'étude de la dispersion verticale des ETM au sein d'un profil de sols (Chapitre 5) s'est avérée utile à l'identification d'une contamination provenant de la surface. En effet, dans le cas des sites anciens comme le site de Peisey-Nancroix, il est commun de trouver des déchets miniers (roches plus ou moins minéralisées) et de déchets métallurgiques (scories et fumées pyrométallurgiques) en surface. Ils sont néanmoins similaires par le cortège métallique qu'ils portent, ce qui ne favorise pas leur distinction dans l'environnement par des méthodes géochimiques ou isotopiques classiques.

7.3 La caractérisation des sources de contamination anthropique & des modes de dispersion

7.3.1 L'apport du couplage isotopie Pb-Sb pour caractériser les sources de contaminants

Les isotopes de l'antimoine ont été utilisés pour la première fois dans un contexte métallurgique dans ces travaux de thèse. Le fractionnement des isotopes de Sb lors de processus pyrométallurgique a ainsi été mis en évidence : les déchets métallurgiques sont enrichis en isotopes lourds ($\delta^{123}\text{Sb}_{\text{SCORIE}} = 0.75 \pm 0.07 \text{ ‰}$) par rapport au minerai qui en est appauvri ($\delta^{123}\text{Sb}_{\text{MINERAI}} = -$

0.11 ± 0.17 ‰). Leur utilisation a permis de distinguer les sources métallurgiques (scories ; contamination anthropique) des sources porteuses de minerai (contamination naturelle et/ou anthropique).

L'ensemble des profils de sols analysés présente une part de contamination par les scories qui est d'autant plus importante à mesure que le profil se rapproche du tas de déchets, avec une contribution comprise entre 56 et 89 % pour les sols les plus proches des déchets métallurgiques, et une contribution de 12 à 63 % pour le profil le plus éloigné. Toutefois, les variations de $\delta^{123}\text{Sb}$ au sein d'un même profil suggèrent également des processus biogéochimiques responsables du fractionnement des isotopes au-delà du simple mélange de source de contamination, mais qui n'ont pas fait l'objet d'une étude détaillée dans cette thèse. En effet, les horizons profonds du profil 1 (P1) montrent des signatures isotopiques plus proches de la valeur des scories que les horizons superficiels alors que la concentration en Sb diminue en profondeur. La tendance inverse est observée pour P3 suggérant potentiellement un mélange entre la signature isotopique des scories et le fond géochimique. Le profil développé à partir d'un matériel parental constitué de roches carbonatées, montre une signature isotopique constante des horizons. Ainsi, les processus (bio)-géochimiques de l'antimoine dans les sols devraient être mieux documentés.

Le couplage des systèmes isotopique du Pb et du Sb est un outil prometteur pour évaluer la part des déchets et fumées métallurgiques dans la contamination anthropique (Figure 7.1). Sur le site minier et métallurgique, il est possible de quantifier la part des déchets métallurgiques (scories) stockés à long terme en surface des sols. L'étude d'un bassin versant situé en amont du site minier permet d'évaluer uniquement la part des fumées métallurgiques émises à court terme dans l'environnement. Malheureusement, l'identification de la signature isotopique en Sb des fumées pyrométallurgiques n'a pas été mise en évidence dans les sédiments lacustres du lac de la Plagne.

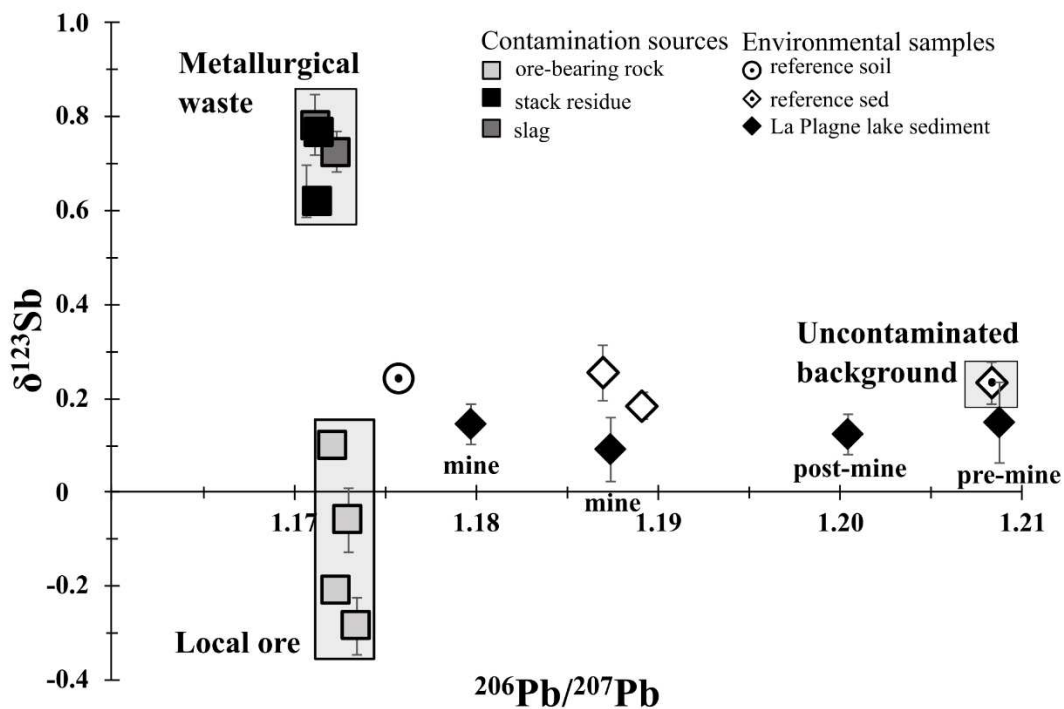


Figure 7.1 : Couplage des isotopes du Pb et de Sb montrant la signature des sédiments lacustres du lac de La Plagne

7.3.2 Dispersion des déchets miniers et métallurgiques sur le site

L'étude des profils verticaux de sols du site minier et métallurgique de Peisey-Nancroix montre que la contamination anthropique domine par rapport à la contamination naturelle (Chapitre 5). Considérant la contamination naturelle comme négligeable, deux sources de contamination anthropique ont été identifiées : les scories et les déchets miniers minéralisés (les fumées métallurgiques n'ont pas pu être distinguées ici, bien que très probablement présentes). Les résultats montrent que jusqu'à 89 % de la contamination des sols du site de Peisey-Nancroix provient des scories.

L'étude minéralogique des sols montre une remobilisation aussi bien des scories que du minerai en aval des haldes (Chapitre 3). La présence de particules primaires issues des haldes de déchets (galène et scories) met en évidence la présence de transport particulaire. La présence de phases secondaires (principalement en cérusite et Pb associé aux oxydes Mn) témoigne de l'altération par lixiviation des déchets, de leur transfert en solution et de processus de précipitation dans les sols.

7.3.3 Dispersion des fumées pyrométallurgiques

Les sédiments lacustres du lac de La Plagne ont enregistré le Pb anthropique issu des fumées métallurgiques, portant la signature du minerai local de Pb-Ag. Une contribution à hauteur de 84 % du Pb total met évidence une contamination atmosphérique, vieille de 200 ans et dispersé sur au moins 7 à 10 km du site minier. Les fumées métallurgiques se seraient aussi déposées sur les sols du site minier, mais la contamination engendrée par les déchets miniers et métallurgiques ne permet pas d'appréhender leur existence. Plus de 200 ans après l'arrêt des activités métallurgiques, les sols du bassin versant du lac sont toujours marqués par la signature du minerai de Peisey-Nancroix ($^{206}\text{Pb}/^{207}\text{Pb} = 1.172 \pm 0.002$). Néanmoins, cette contamination persistante représente de faibles teneurs entre 30 et 130 mg.kg⁻¹ de Pb. L'étude de la contamination des différents compartiments a montré que les activités minières et métallurgiques de Peisey-Nancroix au cours du XVIII^e et XIX^e siècles sont toujours prégnants dans l'environnement.

Au niveau du site, il est souvent difficile de différencier les contaminations liées à la présence de minéralisation en sous-sol, du stockage en surface des déchets métallurgiques et miniers. Bien que les données géochimiques et minéralogique mettent en évidence une contamination anthropique liée au stockage des déchets porteurs de phases en Pb et Sb, il est impossible de quantifier la part des sources de contaminations métallurgiques (scories) des contaminations minières (roches stériles porteuses de minéralisation). Ce constat d'autant plus vérifié pour les horizons profonds de sols, où les concentrations diminuent et la distinction avec le fond géochimique minéralisé peut être fine. Néanmoins, les données isotopiques montrent que ces sols sont contaminés.

7.4 Relations entre mobilité, biodisponibilité et minéralogie des ETM

Les phases porteuses de la minéralisation sont des témoins des processus de dispersion et de remobilisation des ETM dans l'environnement. Des particules grossières de scories ou des déchets miniers sont observées dans les sols du site minier et témoignent de la dispersion et de la remobilisation des déchets depuis les zones de stockage. La présence de phases secondaires pseudomorphosés met en évidence des processus de lixiviation à l'origine de la redistribution du Pb dans les sols sur le long terme. Parallèlement, la distribution des phases porteuses de Pb le long du gradient de contamination des sols s'accompagne par une diminution de la part remobilisable du Pb (Chapitre 3). Les phases primaires s'altèrent en phases secondaires plus stables comme les (hydr-) oxydes de Mn-Pb, qui sont les plus représentés dans les sols distants de la zone de stockage. Cette diminution de la mobilité du Pb des sols est favorisée par la nature alcaline des sols. Des tests

de lixiviation ont montré que plus la teneur en Pb du sol est importante plus la part mobile du Pb est importante. Ces résultats suggèrent que la teneur en Pb des phases riches Pb présentes dans les sols est mobilisable à long terme. Ainsi les sols contaminés représentent une potentielle source secondaire de Pb anthropique.

Dans les sédiments lacustres déposés récemment, environ 20 % du Pb total est d'origine anthropique (Chapitre 4). Malgré des teneurs en Pb total des sols du bassin versant qui restent dans des gammes de valeurs « naturelles », la part de Pb anthropique est importante et remobilisable sur le long terme, comme l'indiquent les données isotopiques. Plus de 200 ans après l'arrêt de la pyrométallurgie dans le bassin versant du Ponturin et 150 ans après la fermeture définitive de la mine, des stocks de Pb anthropique d'une centaine de tonnes perdurent dans les sols du bassin versant du lac de La Plagne (Chapitre 6). Toutefois, environ un tiers du Pb anthropique déposé a été lixivié, dont une faible part (de l'ordre du pourcent) a été piégé dans le lac. Ainsi les fumées métallurgiques représentent aussi un héritage à long terme des activités minières et métallurgiques, invisible, contrairement aux déchets abandonnés en surface.

Différents modes de transfert des ETM d'origine anthropique ont causé leur dispersion dans l'environnement et contribuent à la contamination de la zone critique à l'échelle de tout le bassin versant. L'altération chimique et l'érosion des haldes de déchets représente une estimation d'environ 2 t de Pb sur une surface de 15 ha alors que les fumées métallurgiques transportées dans l'atmosphère sur plusieurs kilomètres ont engendré une contamination d'un ordre de grandeur ~100 t sur 1700 ha. Bien que les concentrations ne soient pas comparables, il s'avère important d'évaluer les inventaires de Pb anthropique dans l'environnement et de les mettre en regard de la production industrielle de Pb (ici 21 500 t de Pb). Ainsi, les stocks de Pb anthropique dans l'environnement représentent quelques pourcents du Pb produit (chiffres sous-estimés, car tout le Pb produit n'a pas été traité sur site). La part de la contamination diffuse, non matérialisée par la présence de déchets, représente donc une part importante de la contamination globale engendrée par les activités minières et métallurgiques. Cette étude montre le rôle d'accumulateur des sols dans des environnements extrêmement contaminés. Pour avoir une vision globale des flux entrants et sortants, il faudrait également évaluer les stocks de Pb contenus dans les déchets miniers et métallurgiques.

7.5 Messages à retenir

Les principaux résultats à retenir à l'issue des travaux de recherche doctorale sur le site minier de Peisey-Nancroix (Savoie) sont les suivants :

- L'ensemble des compartiments de la zone critique montrent une contamination anthropique rémanente, mais d'intensité et d'extension spatiale variable.
- D'important stocks de Pb anthropique sont présents sur l'ensemble du bassin versant.
- Le couplage isotopique Pb-Sb permet de distinguer les sources de contamination anthropiques
- Les déchets métallurgiques (scories) sont la principale source de contamination anthropique des sols de surface, bien que le Pb des déchets miniers soit également remobilisé.
- Le Pb anthropique issu des fumées métallurgiques est remobilisé par l'érosion des sols depuis 200 ans.
- Les fumées métallurgiques sont une importante source de contamination diffuse sur le long terme (> 200 ans).
- La mobilité du Pb diminue avec le degré de contamination.

L'héritage minier des sites anciens représente donc une source en ETM remobilisable sur le long-terme par des processus de lixiviation ou détritique. Plus de 150-170 ans après l'arrêt de la métallurgie et la fermeture de la mine de Peisey-Nancroix, l'héritage environnemental demeure important, avec de potentiels effets sur les écosystèmes (ANNEXE C).

7.6 Perspectives

7.6.1 Perspectives à l'échelle du site de Peisey-Nancroix

Plusieurs perspectives pour l'étude du site minier et métallurgique de Peisey-Nancroix émergent à l'issue de ce travail de thèse :

- Le développement d'une approche multi-élémentaire (Pb, Sb, Cu, Zn) de la contamination des sols pour appréhender les différences de trajectoires spatiales et temporelles des ETM depuis leur source.

- La nécessité d'estimer des stocks de Pb et Sb dans les déchets miniers et métallurgiques afin d'améliorer le raisonnement en flux et en inventaires amorcé par ce travail de thèse.
- L'impossibilité de déterminer à partir des sédiments lacustres la signature isotopique de l'antimoine des fumées, qui invite à la recherche de nouveaux proxys sur le site qui auraient préservé cette signature.
- L'évaluation spatiale de la contamination liée aux fumées pyrométallurgiques et la quantification de leur remobilisation par l'érosion des sols. Il pourrait être envisager d'établir différents transects partant de l'ancienne fonderie pour améliorer les calculs d'inventaire de Pb anthropique rémanent à l'échelle d'un bassin versant, et avoir une meilleure spatialisation de la contamination. A cela, pourrait se combiner l'utilisation de traceurs d'érosion des sols, comme le $^{210}\text{Pb}_{\text{ex}}$ (Matisoff, 2014) afin d'identifier des potentiels puits intermédiaires de contamination dans les sols (Figure 7.2).

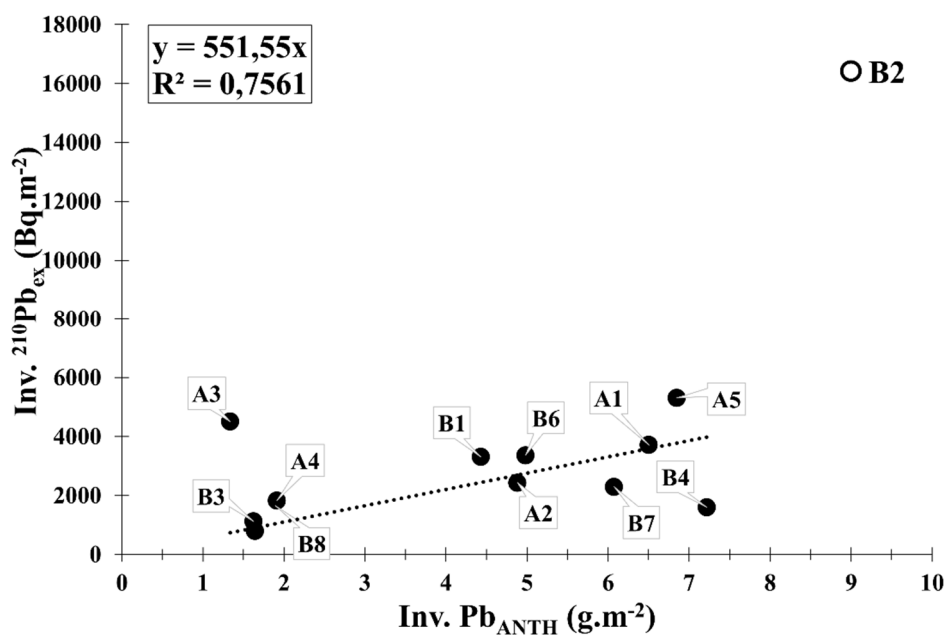


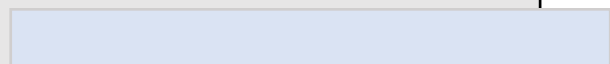
Figure 7.2 : Inventaire du Pb anthropique (g.m^{-2}) en fonction de l'inventaire du $^{210}\text{Pb}_{\text{ex}}$ (Bq.m^{-2}) dans les sols de surface autour du lac de La Plagne.

7.6.2 Perspectives globales

Plusieurs perspectives plus générales émergent de ce travail de thèse :

- Avoir confirmation du fractionnement isotopique de Sb lors de la pyrométallurgie à partir d'autres études et essayer d'appliquer le couplage Pb-Sb ailleurs
- Révéler l'importance de l'héritage laissé par la multitude de mines abandonnées de tailles modeste à l'échelle régionale (arc alpin) par rapport aux déchets miniers restés en surface.
- Outre les activités minières, différentes industries utilisent les substances métalliques qui sont potentiellement dispersées dans l'environnement. Les activités minières et métallurgiques sont parmi les plus anciennes activités humaines, pourrait-on utiliser la méthode mise en place au cours de cette thèse à d'autres industries qui s'installent durablement et contribuent également à la dispersion des ETM dans l'environnement (p. ex. les pesticides, les usines de recyclages des métaux, etc.) ?

REFERENCES |



REFERENCES

- Académie Des Science, 1998. Contamination des sols par les éléments en traces: Les risques et leur gestion, Tec et Doc (Eds.).
- Adriano, D.C., 2001. Trace Elements in Terrestrial Environments. Springer New York, New York, NY. <https://doi.org/10.1007/978-0-387-21510-5>
- Agricola, G., 1556. De Re Metallica.
- Akcil, A., Koldas, S., 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. Journal of Cleaner Production, Improving Environmental, Economic and Ethical Performance in the Mining Industry. Part 2. Life cycle and process analysis and technical issues 14, 1139–1145. <https://doi.org/10.1016/j.jclepro.2004.09.006>
- Allan, R., 1997. Introduction: Mining and metals in the environment. Journal of Geochemical Exploration 58, 95–100. [https://doi.org/10.1016/S0375-6742\(97\)00004-6](https://doi.org/10.1016/S0375-6742(97)00004-6)
- Alloway, B.J. (Ed.), 2013. Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability, Environmental Pollution. Springer Netherlands, Dordrecht. <https://doi.org/10.1007/978-94-007-4470-7>
- Ancel, B., Py, V., 2008. L'abattage par le feu: une technique minière ancestrale. Archéopages : archéologie & société.
- Anderson, S.P., von Blanckenburg, F., White, A.F., 2007. Physical and Chemical Controls on the Critical Zone. Elements 3, 315–319. <https://doi.org/10.2113/gselements.3.5.315>
- Antoniadis, V., Thalassinos, G., Levizou, E., Wang, J., Wang, S.-L., Shaheen, S.M., Rinklebe, J., 2022. Hazardous enrichment of toxic elements in soils and olives in the urban zone of Lavrio, Greece, a legacy, millennia-old silver/lead mining area and related health risk assessment. Journal of Hazardous Materials 434, 128906. <https://doi.org/10.1016/j.jhazmat.2022.128906>
- Aplin, A.C., Matenaar, I.F., McCarty, D.K., van der Pluijm, B.A., 2006. Influence of mechanical compaction and clay mineral diagenesis on the microfabric and pore-scale properties of deep-water Gulf of Mexico mudstones. Clays and Clay Minerals 54, 500–514. <https://doi.org/10.1346/CCMN.2006.0540411>
- Appleby, P.G., Richardson, N., Nolan, P.J., 1991. ²⁴¹Am dating of lake sediments. Hydrobiologia 214, 35–42. <https://doi.org/10.1007/BF00050929>
- Arnaud, F., Lignier, V., Revel, M., Desmet, M., Beck, C., Pourchet, M., Charlet, F., Trentesaux, A., Tribovillard, N., 2002. Flood and earthquake disturbance of ²¹⁰Pb geochronology (Lake Anterne, NW Alps). Terra Nova 14, 225–232. <https://doi.org/10.1046/j.1365-3121.2002.00413.x>
- Arnaud, F., Revel-Rolland, M., Bosch, D., Winiarski, T., Desmet, M., Tribovillard, N., Givelet, N., 2004. A 300 year history of lead contamination in northern French Alps reconstructed from distant lake sediment records. J. Environ. Monit. 6, 448–456. <https://doi.org/10.1039/B314947A>
- Arnaud, F., Serralongue, J., Winiarski, T., Desmet, M., Paterne, M., 2006. Pollution au plomb dans la Savoie antique (II–IIIe s. apr. J.-C.) en relation avec une installation métallurgique de la cité de Vienne. Comptes Rendus Geoscience 338, 244–252. <https://doi.org/10.1016/j.crte.2005.11.008>
- Asare, M.O., Afriyie, J.O., 2021. Ancient Mining and Metallurgy as the Origin of Cu, Ag, Pb, Hg, and Zn Contamination in Soils: A Review. Water Air Soil Pollut 232, 240. <https://doi.org/10.1007/s11270-021-05166-4>
- Bacardit, M., Camarero, L., 2010. Modelling Pb, Zn and As transfer from terrestrial to aquatic ecosystems during the ice-free season in three Pyrenean catchments. Science of The Total Environment, Special Section: Integrating Water and Agricultural Management Under Climate Change 408, 5854–5861. <https://doi.org/10.1016/j.scitotenv.2010.07.088>
- Bacardit, M., Krachler, M., Camarero, L., 2012. Whole-catchment inventories of trace metals in soils and sediments in mountain lake catchments in the Central Pyrenees: Apportioning the anthropogenic and natural contributions. Geochimica et Cosmochimica Acta, Environmental Records of Anthropogenic Impacts 82, 52–67. <https://doi.org/10.1016/j.gca.2010.10.030>
- Baieta, R., Mihaljević, M., Ettler, V., Vaněk, A., Penížek, V., Trubač, J., Kříbek, B., Ježek, J., Svoboda, M., Sracek, O., Nyambe, I., 2021. Depicting the historical pollution in a Pb–Zn mining/smelting site in Kabwe (Zambia) using tree rings. Journal of African Earth Sciences 181, 104246. <https://doi.org/10.1016/j.jafrearsci.2021.104246>

REFERENCES

- Baize, D., 2000. Teneurs totales en “ métaux lourds ” dans les sols français : résultats généraux du programme ASPITET. *Le Courrier de l’environnement de l’INRA* 39–54.
- Baize, D., 1997. Teneurs totales en éléments traces métalliques dans les sols (France) - Références et stratégies d’interprétation. Programme ASPITET, INRA. ed, Un point sur... Quae.
- Bajard, M., Etienne, D., Quinsac, S., Dambrine, E., Sabatier, P., Frossard, V., Gaillard, J., Develle, A.-L., Poulenard, J., Arnaud, F., Dorioz, J.-M., 2018. Legacy of early anthropogenic effects on recent lake eutrophication (Lake Bénit, northern French Alps). *Anthropocene* 24, 72–87. <https://doi.org/10.1016/j.ancene.2018.11.005>
- Bao, Z., Al, T., Couillard, M., Poirier, G., Bain, J., Shrimpton, H.K., Finck, Y.Z., Lanzirrotti, A., Paktunc, D., Saurette, E., Hu, Y., Ptacek, C.J., Blowes, D.W., 2021. A cross scale investigation of galena oxidation and controls on mobilization of lead in mine waste rock. *Journal of Hazardous Materials* 412, 125130. <https://doi.org/10.1016/j.jhazmat.2021.125130>
- Barbier, V. (1828-1898) A. du texte, 1875. La Savoie industrielle. Mines et métaux. Chaux, ciments, plâtres, poteries et tuileries. Horlogerie. Industries diverses
- Baron, S., Carignan, J., Laurent, S., Ploquin, A., 2006. Medieval lead making on Mont-Lozère Massif (Cévennes-France): Tracing ore sources using Pb isotopes. *Applied Geochemistry* 21, 241–252. <https://doi.org/10.1016/j.apgeochem.2005.09.005>
- Bertauts, M., Janots, E., Rossi, M., Duhamel-Achin, I., Boiron, M.-C., Airaghi, L., Lanari, P., Lach, P., Peiffert, C., Magnin, V., 2022. A New Alpine Metallogenic Model for the Pb-Ag Orogenic Deposits of Macôt-la Plagne and Peisey-Nancroix (Western Alps, France). *Geosciences* 12, 331. <https://doi.org/10.3390/geosciences12090331>
- Bigalke, M., Weyer, S., Kobza, J., Wilcke, W., 2010. Stable Cu and Zn isotope ratios as tracers of sources and transport of Cu and Zn in contaminated soil. *Geochimica et Cosmochimica Acta* 74, 6801–6813. <https://doi.org/10.1016/j.gca.2010.08.044>
- Blaauw, M., 2010. Methods and code for ‘classical’ age-modelling of radiocarbon sequences. *Quaternary Geochronology* 5, 512–518. <https://doi.org/10.1016/j.quageo.2010.01.002>
- Boyle, J., Chiverrell, R., Schillereff, D., 2015. Lacustrine Archives of Metals from Mining and Other Industrial Activities—A Geochemical Approach, in: Blais, J.M., Rosen, M.R., Smol, J.P. (Eds.), *Environmental Contaminants: Using Natural Archives to Track Sources and Long-Term Trends of Pollution, Developments in Paleoenvironmental Research*. Springer Netherlands, Dordrecht, pp. 121–159. https://doi.org/10.1007/978-94-017-9541-8_7
- Brännvall, M.-L., Bindler, R., Emteryd, O., Nilsson, M., Renberg, I., 1997. Stable Isotope and Concentration Records of Atmospheric Lead Pollution in Peat and Lake Sediments in Sweden. *Water, Air, & Soil Pollution* 100, 243–252. <https://doi.org/10.1023/A:1018360106350>
- Brännvall, M.-L., Bindler, R., Emteryd, O., Renberg, I., 2001. Four thousand years of atmospheric lead pollution in northern Europe: a summary from Swedish lake sediments. *Journal of Paleolimnology* 25, 421–435. <https://doi.org/10.1023/A:1011186100081>
- Brännvall, M.-L., Bindler, R., Renberg, I., Emteryd, O., Bartnicki, J., Billström, K., 1999. The Medieval Metal Industry Was the Cradle of Modern Large-Scale Atmospheric Lead Pollution in Northern Europe. *Environ. Sci. Technol.* 33, 4391–4395. <https://doi.org/10.1021/es990279n>
- Brantley, S.L., Goldhaber, M.B., Ragnarsdottir, K.V., Anderson, S.P., White, A.F., Chorover, J., Kretzschmar, R., Garcia-Pichel, F., Sparks, D.L., Amundson, R., Richter, D.D., Humphreys, G.S., Jobbágy, E.G., Gaillardet, J., Derry, L.A., Chadwick, O.A., 2007. Crossing Disciplines and Scales to Understand the Critical Zone.
- Brown, G.E., Foster, A.L., Ostergren, J.D., 1999. Mineral surfaces and bioavailability of heavy metals: A molecular-scale perspective. *PNAS* 96, 3388–3395. <https://doi.org/10.1073/pnas.96.7.3388>
- Bruel, R., Sabatier, P., 2020. serac: an R package for Shortlived RADionuclide chronology of recent sediment cores. *Journal of Environmental Radioactivity* 225, 106449. <https://doi.org/10.1016/j.jenvrad.2020.106449>
- Brugam, R.B., Ketterer, M., Maines, L., Lin, Z.Q., Retzlaff, W.A., 2012. Application of a simple binary mixing model to the reconstruction of lead pollution sources in two Mississippi River floodplain lakes. *J Paleolimnol* 47, 101–112. <https://doi.org/10.1007/s10933-011-9562-5>
- Buatier, M.D., Sobanska, S., Elsass, F., 2001. TEM-EDX investigation on Zn- and Pb-contaminated soils. *Applied Geochemistry* 16, 1165–1177. [https://doi.org/10.1016/S0883-2927\(01\)00015-4](https://doi.org/10.1016/S0883-2927(01)00015-4)

REFERENCES

- Byrne, P., Wood, P.J., Reid, I., 2012. The Impairment of River Systems by Metal Mine Contamination: A Review Including Remediation Options. *Critical Reviews in Environmental Science and Technology* 42, 2017–2077. <https://doi.org/10.1080/10643389.2011.574103>
- Camizuli, E., Monna, F., Scheifler, R., Amiotte-Suchet, P., Losno, R., Beis, P., Bohard, B., Chateau, C., Alibert, P., 2014. Impact of trace metals from past mining on the aquatic ecosystem: A multi-proxy approach in the Morvan (France). *Environmental Research, Linking Exposure and Health in Environmental Public Health Tracking* 134, 410–419. <https://doi.org/10.1016/j.envres.2014.07.008>
- Camizuli, E., Rossi, M., Gasquet, D., 2021. Trace metals dispersion from 1000 years of mining activity in the northern French Alps. *The Extractive Industries and Society* 8, 135–146. <https://doi.org/10.1016/j.exis.2020.08.017>
- Camizuli, E., Scheifler, R., Garnier, S., Monna, F., Losno, R., Gourault, C., Hamm, G., Lachiche, C., Delivet, G., Chateau, C., Alibert, P., 2018. Trace metals from historical mining sites and past metallurgical activity remain bioavailable to wildlife today. *Scientific Reports* 8, 3436. <https://doi.org/10.1038/s41598-018-20983-0>
- Cappuyns, V., 2012. A Critical Evaluation of Single Extractions from the SMT Program to Determine Trace Element Mobility in Sediments. *Applied and Environmental Soil Science* 2012, e672914. <https://doi.org/10.1155/2012/672914>
- Carignan, J., Hild, P., Mevelle, G., Morel, J., Yeghicheyan, D., 2001. Routine Analyses of Trace Elements in Geological Samples using Flow Injection and Low Pressure On-Line Liquid Chromatography Coupled to ICP-MS: A Study of Geochemical Reference Materials BR, DR-N, UB-N, AN-G and GH. *Geostandards and Geoanalytical Research* 25, 187–198. <https://doi.org/10.1111/j.1751-908X.2001.tb00595.x>
- Causse, B., Spadini, L., Martins, J.M.F., Lenoir, T., Heyraud, A., Delolme, C., 2013. Xanthan exopolysaccharide: Acid–base reactivity related to structure and conformation. A model for understanding the reactivity of degraded and colloidal soil organic matter. *Chemical Geology* 359, 150–158. <https://doi.org/10.1016/j.chemgeo.2013.09.010>
- Chester, R., Stoner, J.H., 1973. Pb in Particulates from the Lower Atmosphere of the Eastern Atlantic. *Nature* 245, 27–28. <https://doi.org/10.1038/245027b0>
- Chopin, E.I.B., Alloway, B.J., 2007. Trace element partitioning and soil particle characterisation around mining and smelting areas at Tharsis, Riotinto and Huelva, SW Spain. *Science of The Total Environment* 373, 488–500. <https://doi.org/10.1016/j.scitotenv.2006.11.037>
- Chrastný, V., Čadková, E., Vaněk, A., Teper, L., Cabala, J., Komárek, M., 2015. Cadmium isotope fractionation within the soil profile complicates source identification in relation to Pb–Zn mining and smelting processes. *Chemical Geology* 405, 1–9. <https://doi.org/10.1016/j.chemgeo.2015.04.002>
- Christmann, P., 2018. Towards a More Equitable Use of Mineral Resources. *Nat Resour Res* 27, 159–177. <https://doi.org/10.1007/s11053-017-9343-6>
- Clary, E., Givélet, P., Palluel-Guillard, A., 1995. Les mines de Pesey et de Macôt, SOCIÉTÉ SAVOISIENNE D'HISTOIRE ET D'ARCHÉOLOGIE. ed, L'Histoire en Savoie.
- Cloquet, C., Carignan, J., Libourel, G., 2006a. Atmospheric pollutant dispersion around an urban area using trace metal concentrations and Pb isotopic compositions in epiphytic lichens. *Atmospheric Environment* 40, 574–587. <https://doi.org/10.1016/j.atmosenv.2005.09.073>
- Cloquet, C., Carignan, J., Libourel, G., Sterckeman, T., Perdrix, E., 2006b. Tracing Source Pollution in Soils Using Cadmium and Lead Isotopes. *Environ. Sci. Technol.* 40, 2525–2530. <https://doi.org/10.1021/es052232+>
- Cloquet, C., Estrade, N., Carignan, J., 2015. Ten years of elemental atmospheric metal fallout and Pb isotopic composition monitoring using lichens in northeastern France. *Comptes Rendus Geoscience, Geochemical and isotopic record of anthropogenic activities (Part 1)* 347, 257–266. <https://doi.org/10.1016/j.crte.2015.04.003>
- Corella, J.P., Sierra, M.J., Garralón, A., Millán, R., Rodríguez-Alonso, J., Mata, M.P., de Vera, A.V., Moreno, A., González-Sampérez, P., Duval, B., Amouroux, D., Vivez, P., Cuevas, C.A., Adame, J.A., Wilhelm, B., Saiz-Lopez, A., Valero-Garcés, B.L., 2021. Recent and historical pollution legacy in high altitude Lake Marboré (Central Pyrenees): A record of mining and smelting since pre-Roman times in the Iberian Peninsula. *Science of The Total Environment* 751, 141557. <https://doi.org/10.1016/j.scitotenv.2020.141557>
- Cortada, U., Hidalgo, M.C., Martínez, J., Rey, J., 2018. Impact in soils caused by metal(loid)s in lead metallurgy. The case of La Cruz Smelter (Southern Spain). *Journal of Geochemical Exploration* 190, 302–313. <https://doi.org/10.1016/j.gexplo.2018.04.001>

REFERENCES

- Cotter-Howells, J. d., Champness, P. e., Charnocky, J. m., Pattrick, R. a. d., 1994. Identification of pyromorphite in mine-waste contaminated soils by ATEM and EXAFS. *European Journal of Soil Science* 45, 393–402. <https://doi.org/10.1111/j.1365-2389.1994.tb00524.x>
- Cotter-Howells, J., Thornton, I., 1991. Sources and pathways of environmental lead to children in a Derbyshire mining village. *Environ Geochem Health* 13, 127–135. <https://doi.org/10.1007/BF01734304>
- Craddock, P.T., 2009. *Mining and Metallurgy*. Oxford University Press. <https://doi.org/10.1093/oxfordhb/9780199734856.013.0005>
- Csavina, J., Field, J., Taylor, M.P., Gao, S., Landázuri, A., Betterton, E.A., Sáez, A.E., 2012. A review on the importance of metals and metalloids in atmospheric dust and aerosol from mining operations. *Science of The Total Environment* 433, 58–73. <https://doi.org/10.1016/j.scitotenv.2012.06.013>
- Cui, J., Wu, X., 2011. AN EXPERIMENTAL INVESTIGATION ON LEAD ISOTOPIC FRACTIONATION DURING METALLURGICAL PROCESSES: Lead isotopic fractionation during metallurgical processes. *Archaeometry* 53, 205–214. <https://doi.org/10.1111/j.1475-4754.2010.00548.x>
- Davis, A., Drexler, J.W., Ruby, M.V., Nicholson, A., 1993. Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. *Environ. Sci. Technol.* 27, 1415–1425. <https://doi.org/10.1021/es00044a018>
- De Vleeschouwer, F., Gérard, L., Goormaghtigh, C., Mattielli, N., Le Roux, G., Fagel, N., 2007. Atmospheric lead and heavy metal pollution records from a Belgian peat bog spanning the last two millenia: Human impact on a regional to global scale. *Science of The Total Environment* 377, 282–295. <https://doi.org/10.1016/j.scitotenv.2007.02.017>
- Degryse, P., Shortland, A.J., Dillis, S., van Ham-Meert, A., Vanhaecke, F., Leeming, P., 2020. Isotopic evidence for the use of Caucasian antimony in Late Bronze Age glass making. *Journal of Archaeological Science* 120, 105195. <https://doi.org/10.1016/j.jas.2020.105195>
- Deloule, E., Allegre, C.J., Doe, B.R., 1986. Lead and sulfur isotope microstratigraphy in galena crystals from mississippi valley-type deposits. *Economic Geology* 81, 1307–1321. <https://doi.org/10.2113/gsecongeo.81.6.1307>
- Delplace, G., Viers, J., Schreck, E., Oliva, P., Behra, P., 2022. Pedo-geochemical background and sediment contamination of metal(loid)s in the old mining-district of Salsigne (Orbiel valley, France). *Chemosphere* 287, 132111. <https://doi.org/10.1016/j.chemosphere.2021.132111>
- Desaulty, A.-M., Petelet-Giraud, E., 2020. Zinc isotope composition as a tool for tracing sources and fate of metal contaminants in rivers. *Science of The Total Environment* 728, 138599. <https://doi.org/10.1016/j.scitotenv.2020.138599>
- Doebelin, N., Kleeberg, R., 2015. Profex: a graphical user interface for the Rietveld refinement program BGMN. *J Appl Cryst* 48, 1573–1580. <https://doi.org/10.1107/S1600576715014685>
- Doucet, F.J., Carignan, J., 2001. Atmospheric Pb isotopic composition and trace metal concentration as revealed by epiphytic lichens: an investigation related to two altitudinal sections in Eastern France. *Atmospheric Environment* 35, 3681–3690. [https://doi.org/10.1016/S1352-2310\(00\)00510-0](https://doi.org/10.1016/S1352-2310(00)00510-0)
- Dudka, S., Adriano, D.C., 1997. Environmental Impacts of Metal Ore Mining and Processing: A Review. *Journal of Environmental Quality* 26, 590–602. <https://doi.org/10.2134/jeq1997.00472425002600030003x>
- Elbaz-Poulichet, F., Guédron, S., Anne-Lise, D., Freydier, R., Perrot, V., Rossi, M., Piot, C., Delpoux, S., Sabatier, P., 2020. A 10,000-year record of trace metal and metalloid (Cu, Hg, Sb, Pb) deposition in a western Alpine lake (Lake Robert, France): Deciphering local and regional mining contamination. *Quaternary Science Reviews* 228, 106076. <https://doi.org/10.1016/j.quascirev.2019.106076>
- Elbaz-Poulichet, F., Resongles, E., Bancon-Montigny, C., Delpoux, S., Freydier, R., Casiot, C., 2017. The environmental legacy of historic Pb-Zn-Ag-Au mining in river basins of the southern edge of the Massif Central (France). *Environ Sci Pollut Res* 24, 20725–20735. <https://doi.org/10.1007/s11356-017-9669-y>
- Ettler, V., 2016. Soil contamination near non-ferrous metal smelters: A review. *Applied Geochemistry, Special issue of Applied Geochemistry on Environmental Impacts of Mining and Smelting* 64, 56–74. <https://doi.org/10.1016/j.apgeochem.2015.09.020>
- Ettler, V., Cihlová, M., Jarošíková, A., Mihaljevič, M., Drahot, P., Kříbek, B., Vaněk, A., Penížek, V., Sracek, O., Klementová, M., Engel, Z., Kamona, F., Mapani, B., 2019. Oral bioaccessibility of metal(loid)s in dust materials from mining areas of northern Namibia. *Environment International* 124, 205–215. <https://doi.org/10.1016/j.envint.2018.12.027>

REFERENCES

- Ettler, V., Johan, Z., 2014. 12 years of leaching of contaminants from Pb smelter slags: Geochemical/mineralogical controls and slag recycling potential. *Applied Geochemistry* 40, 97–103. <https://doi.org/10.1016/j.apgeochem.2013.11.001>
- Ettler, V., Tejnecký, V., Mihaljevič, M., Šebek, O., Zuna, M., Vaněk, A., 2010. Antimony mobility in lead smelter-polluted soils. *Geoderma* 155, 409–418. <https://doi.org/10.1016/j.geoderma.2009.12.027>
- Evangelou, V.P. (Bill), Zhang, Y.L., 1995. A review: Pyrite oxidation mechanisms and acid mine drainage prevention. *Critical Reviews in Environmental Science and Technology* 25, 141–199. <https://doi.org/10.1080/10643389509388477>
- Ferrari, C., Méheut, M., Resongles, E., Freydier, R., Casiot, C., 2022. Equilibrium mass-dependent isotope fractionation of antimony between stibnite and Sb secondary minerals: A first-principles study. *Chemical Geology* 611, 121115. <https://doi.org/10.1016/j.chemgeo.2022.121115>
- Ferrari, C., Resongles, E., Freydier, R., Casiot, C., 2021. Correction: A single-step purification method for the precise determination of the antimony isotopic composition of environmental, geological and biological samples by HG-MC-ICP-MS. *Journal of Analytical Atomic Spectrometry* 36, 2560–2560. <https://doi.org/10.1039/D1JA90048J>
- Flexer, V., Baspineiro, C.F., Galli, C.L., 2018. Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing. *Science of The Total Environment* 639, 1188–1204. <https://doi.org/10.1016/j.scitotenv.2018.05.223>
- Forget, M., 2015. Trajectoires territoriales d'un nouveau centre extractif mondialisé. L'exemple des Andes argentines septentrionales. *Journal of Alpine Research | Revue de géographie alpine*. <https://doi.org/10.4000/rga.2973>
- Froger, C., Ayrault, S., Evrard, O., Monvoisin, G., Bordier, L., Lefèvre, I., Quantin, C., 2018. Tracing the sources of suspended sediment and particle-bound trace metal elements in an urban catchment coupling elemental and isotopic geochemistry, and fallout radionuclides. *Environ Sci Pollut Res* 25, 28667–28681. <https://doi.org/10.1007/s11356-018-2892-3>
- Gabrieli, J., Barbante, C., 2014. The Alps in the age of the Anthropocene: the impact of human activities on the cryosphere recorded in the Colle Gnifetti glacier. *Rend. Fis. Acc. Lincei* 25, 71–83. <https://doi.org/10.1007/s12210-014-0292-2>
- Galán, E., Fernández-Caliani, J.C., González, I., Aparicio, P., Romero, A., 2008. Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South–West Spain. *Journal of Geochemical Exploration* 98, 89–106. <https://doi.org/10.1016/j.gexplo.2008.01.001>
- Galán, E., Gómez-Ariza, J.L., González, I., Fernández-Caliani, J.C., Morales, E., Giráldez, I., 2003. Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt. *Applied Geochemistry* 18, 409–421. [https://doi.org/10.1016/S0883-2927\(02\)00092-6](https://doi.org/10.1016/S0883-2927(02)00092-6)
- Galuszka, A., Migaszewski, Z.M., Dołęgowska, S., Michalik, A., Duczmal-Czernikiewicz, A., 2015. Geochemical background of potentially toxic trace elements in soils of the historic copper mining area: a case study from Miedzianka Mt., Holy Cross Mountains, south-central Poland. *Environ Earth Sci* 74, 4589–4605. <https://doi.org/10.1007/s12665-015-4395-6>
- Garçon, A.-F., 1995. Les métaux non ferreux en France aux XVIIIe et XIXe siècles : Ruptures, blocages, évolution au sein des systèmes techniques (These de doctorat). Paris, EHESS.
- Giguët-Covex, C., Arnaud, F., Poulenard, J., Disnar, J.-R., Delhon, C., Francus, P., David, F., Enters, D., Rey, P.-J., Delannoy, J.-J., 2011. Changes in erosion patterns during the Holocene in a currently treeless subalpine catchment inferred from lake sediment geochemistry (Lake Anterne, 2063 m a.s.l., NW French Alps): The role of climate and human activities. *The Holocene* 21, 651–665. <https://doi.org/10.1177/0959683610391320>
- Grimaldi, M., Guédron, S., Grimaldi, C., 2015. Impact of gold mining on mercury contamination and soil degradation in Amazonian ecosystems of French Guiana. Land-use change impacts on soil processes: tropical and savannah ecosystems, CABI Books 95–107. <https://doi.org/10.1079/9781780642109.0095>
- Guédron, S., Amouroux, D., Sabatier, P., Desplanque, C., Develle, A.-L., Barre, J., Feng, C., Guiter, F., Arnaud, F., Reys, J.L., Charlet, L., 2016. A hundred year record of industrial and urban development in French Alps combining Hg accumulation rates and isotope composition in sediment archives from Lake Luitel. *Chemical Geology* 431, 10–19. <https://doi.org/10.1016/j.chemgeo.2016.03.016>

REFERENCES

- Guillevic, F., Rossi, M., Develle, A.-L., Spadini, L., Martins, J.M.F., Arnaud, F., Poulencard, J., 2023. Pb dispersion pathways in mountain soils contaminated by ancient mining and smelting activities. *Applied Geochemistry* 105556. <https://doi.org/10.1016/j.apgeochem.2022.105556>
- Gupta, S.K., Vollmer, M.K., Krebs, R., 1996. The importance of mobile, mobilisable and pseudo total heavy metal fractions in soil for three-level risk assessment and risk management. *Science of The Total Environment, Harmonization of Leaching/Extraction Tests for Environmental Risk Assessment* 178, 11–20. [https://doi.org/10.1016/0048-9697\(95\)04792-1](https://doi.org/10.1016/0048-9697(95)04792-1)
- Guyard, H., Chapron, E., St-Onge, G., Anselmetti, F.S., Arnaud, F., Magand, O., Francus, P., Mélières, M.-A., 2007. High-altitude varve records of abrupt environmental changes and mining activity over the last 4000 years in the Western French Alps (Lake Bramant, Grandes Rousses Massif). *Quaternary Science Reviews* 26, 2644–2660. <https://doi.org/10.1016/j.quascirev.2007.07.007>
- Habashi, F., 2005. A short history of hydrometallurgy. *Hydrometallurgy, Teaching and Learning Hydrometallurgical Science and Engineering-Part I* 79, 15–22. <https://doi.org/10.1016/j.hydromet.2004.01.008>
- Hansson, S.V., Claustres, A., Probst, A., De Vleschouwer, F., Baron, S., Galop, D., Mazier, F., Le Roux, G., 2017. Atmospheric and terrigenous metal accumulation over 3000 years in a French mountain catchment: Local vs distal influences. *Anthropocene* 19, 45–54. <https://doi.org/10.1016/j.ancene.2017.09.002>
- Hansson, S.V., Grusson, Y., Chimienti, M., Claustres, A., Jean, S., Le Roux, G., 2019. Legacy Pb pollution in the contemporary environment and its potential bioavailability in three mountain catchments. *Science of The Total Environment* 671, 1227–1236. <https://doi.org/10.1016/j.scitotenv.2019.03.403>
- Heinrichs, H., Schulz-Dobrick, B., Wedepohl, K.H., 1980. Terrestrial geochemistry of Cd, Bi, Tl, Pb, Zn and Rb. *Geochimica et Cosmochimica Acta* 44, 1519–1533. [https://doi.org/10.1016/0016-7037\(80\)90116-7](https://doi.org/10.1016/0016-7037(80)90116-7)
- Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology* 25, 101–110. <https://doi.org/10.1023/A:1008119611481>
- Herath, I., Vithanage, M., Bundschuh, J., 2017. Antimony as a global dilemma: Geochemistry, mobility, fate and transport. *Environmental Pollution* 223, 545–559. <https://doi.org/10.1016/j.envpol.2017.01.057>
- Hernandez, L., Probst, A., Probst, J.L., Ulrich, E., 2003. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Science of The Total Environment* 312, 195–219. [https://doi.org/10.1016/S0048-9697\(03\)00223-7](https://doi.org/10.1016/S0048-9697(03)00223-7)
- Hettiarachchi, G.M., Pierzynski, G.M., Ransom, M.D., 2000. In Situ Stabilization of Soil Lead Using Phosphorus and Manganese Oxide. *Environ. Sci. Technol.* 34, 4614–4619. <https://doi.org/10.1021/es001228p>
- Hong, S., Candelone, J.-P., Patterson, C.C., Boutron, C.F., 1994. Greenland Ice Evidence of Hemispheric Lead Pollution Two Millennia Ago by Greek and Roman Civilizations. *Science* 265, 1841–1843. <https://doi.org/10.1126/science.265.5180.1841>
- Hudson-Edwards, K., 2016. Tackling mine wastes. *Science* 352, 288–290. <https://doi.org/10.1126/science.aaf3354>
- Hudson-Edwards, K.A., 2003. Sources, mineralogy, chemistry and fate of heavy metal-bearing particles in mining-affected river systems. *Mineralogical Magazine* 67, 205–217. <https://doi.org/10.1180/0026461036720095>
- Hudson-Edwards, K.A., Jamieson, H.E., Lottermoser, B.G., 2011. Mine Wastes: Past, Present, Future. *Elements* 7, 375–380. <https://doi.org/10.2113/gselements.7.6.375>
- INAP, 2009. *Global Acid Rock Drainage Guide (GARD Guide)*.
- Ineris, 2020. Synthèse des valeurs réglementaires pour les substances chimiques, en vigueur dans l'eau, les denrées alimentaires et dans l'air en France.
- Jébrak, M., Marcoux, É., 2008. *Géologie des ressources minérales*. Ministère des ressources naturelles et de la faune, Québec, Canada.
- JORF, 2006. Arrêté du 9 août 2006 relatif aux niveaux à prendre en compte lors d'une analyse de rejets dans les eaux de surface ou de sédiments marins, estuariens ou extraits de cours d'eau ou canaux relevant respectivement des rubriques 2.2.3.0, 4.1.3.0 et 3.2.1.0 de la nomenclature annexée au décret n° 93–743 du 29 mars 1993., *Journal Officiel de la République Française* 222.

REFERENCES

- Judet, P., 2014. Exploitation, abandon et patrimonialisation des mines savoyardes de 1750 à nos jours. Une introduction à une histoire longue et contrastée. Collection EDYTEM. Cahiers de géographie 17, 53–60. <https://doi.org/10.3406/edyte.2014.1273>
- Keim, M.F., Markl, G., 2015. Weathering of galena: Mineralogical processes, hydrogeochemical fluid path modeling, and estimation of the growth rate of pyromorphite. *American Mineralogist* 100, 1584–1594. <https://doi.org/10.2138/am-2015-5183>
- Khaska, M., Le Gal La Salle, C., Sassine, L., Cary, L., Bruguier, O., Verdoux, P., 2018. Arsenic and metallic trace elements cycling in the surface water-groundwater-soil continuum down-gradient from a reclaimed mine area: Isotopic imprints. *Journal of Hydrology* 558, 341–355. <https://doi.org/10.1016/j.jhydrol.2018.01.031>
- Killick, D., Fenn, T., 2012. Archaeometallurgy: The Study of Preindustrial Mining and Metallurgy. *Annual Review of Anthropology* 41, 559–575. <https://doi.org/10.1146/annurev-anthro-092611-145719>
- Kobayashi, H., Garnier, J., Mulholland, D.S., Quantin, C., Haurine, F., Tonha, M., Joko, C., Olivetti, D., Freydier, R., Seyler, P., Martinez, J.-M., Roig, H.L., 2023. Exploring a new approach for assessing the fate and behavior of the tailings released by the Brumadinho dam collapse (Minas Gerais, Brazil). *Journal of Hazardous Materials* 448, 130828. <https://doi.org/10.1016/j.jhazmat.2023.130828>
- Komárek, M., Ettler, V., Chrástný, V., Mihaljevič, M., 2008. Lead isotopes in environmental sciences: A review. *Environment International* 34, 562–577. <https://doi.org/10.1016/j.envint.2007.10.005>
- Komárek, M., Ratič, G., Vaňková, Z., Šípková, A., Chrástný, V., 2021. Metal isotope complexation with environmentally relevant surfaces: Opening the isotope fractionation black box. *Critical Reviews in Environmental Science and Technology* 0, 1–31. <https://doi.org/10.1080/10643389.2021.1955601>
- Kříbek, B., Majer, V., Knésl, I., Keder, J., Mapani, B., Kamona, F., Mihaljevič, M., Ettler, V., Penížek, V., Vaněk, A., Sracek, O., 2016. Contamination of soil and grass in the Tsumeb smelter area, Namibia: Modeling of contaminants dispersion and ground geochemical verification. *Applied Geochemistry, Special issue of Applied Geochemistry on Environmental Impacts of Mining and Smelting* 64, 75–91. <https://doi.org/10.1016/j.apgeochem.2015.07.006>
- Kříbek, B., Nyambe, I., Majer, V., Knésl, I., Mihaljevič, M., Ettler, V., Vaněk, A., Penížek, V., Sracek, O., 2019. Soil contamination near the Kabwe Pb-Zn smelter in Zambia: Environmental impacts and remediation measures proposal. *Journal of Geochemical Exploration* 197, 159–173. <https://doi.org/10.1016/j.gexplo.2018.11.018>
- Lahd Geagea, M., Stille, P., Gauthier-Lafaye, F., Perrone, Th., Aubert, D., 2008. Baseline determination of the atmospheric Pb, Sr and Nd isotopic compositions in the Rhine valley, Vosges mountains (France) and the Central Swiss Alps. *Applied Geochemistry* 23, 1703–1714. <https://doi.org/10.1016/j.apgeochem.2008.02.004>
- Lara, R.H., Briones, R., Monroy, M.G., Mullet, M., Humbert, B., Dossot, M., Naja, G.M., Cruz, R., 2011. Galena weathering under simulated calcareous soil conditions. *Science of The Total Environment* 409, 3971–3979. <https://doi.org/10.1016/j.scitotenv.2011.06.055>
- Le Berre, S., Bretesché, S., 2020. De la désindustrialisation au scandale de la France contaminée : médiatisation et controverses sur l'après-mine de l'uranium à Bessines (1991-2019). *vertigo* 20. <https://doi.org/10.4000/vertigo.28830>
- Le Roux, G., Hansson, S.V., Claustres, A., Binet, S., Vleeschouwer, F.D., Gandois, L., Mazier, F., Simonneau, A., Teisserenc, R., Allen, D., Rosset, T., Haver, M., Ros, L.D., Galop, D., Durantez, P., Probst, A., Sánchez-Pérez, J.M., Sauvage, S., Laffaille, P., Jean, S., Schmeller, D.S., Camarero, L., Marquer, L., Lofts, S., 2020. Trace Metal Legacy in Mountain Environments, in: *Biogeochemical Cycles*. American Geophysical Union (AGU), pp. 191–206. <https://doi.org/10.1002/9781119413332.ch9>
- Lê, S., Josse, J., Husson, F., 2008. FactoMineR: An R Package for Multivariate Analysis. *Journal of Statistical Software* 25, 1–18. <https://doi.org/10.18637/jss.v025.i01>
- Leblanc, M., Morales, J.A., Borrego, J., Elbaz-Poulichet, F., 2000. 4,500-YEAR-OLD MINING POLLUTION IN SOUTHWESTERN SPAIN: LONG-TERM IMPLICATIONS FOR MODERN MINING POLLUTION. *Economic Geology* 95, 655–662. <https://doi.org/10.2113/gsecongeo.95.3.655>
- Lejon, D.P.H., Martins, J.M.F., Lévêque, J., Spadini, L., Pascual, N., Landry, D., Milloux, M.-J., Nowak, V., Chaussod, R., Ranjard, L., 2008. Copper Dynamics and Impact on Microbial Communities in Soils of Variable Organic Status. *Environ. Sci. Technol.* 42, 2819–2825. <https://doi.org/10.1021/es071652r>

REFERENCES

- Leverington, D.W., Schindler, M., 2018. Delineating Areas of Past Environmental Degradation near Smelters using Rock Coatings: A Case Study at Rouyn-Noranda, Quebec. *Sci Rep* 8, 17364. <https://doi.org/10.1038/s41598-018-35742-4>
- Li, P., Cai, M., 2021. Challenges and new insights for exploitation of deep underground metal mineral resources. *Transactions of Nonferrous Metals Society of China* 31, 3478–3505. [https://doi.org/10.1016/S1003-6326\(21\)65744-8](https://doi.org/10.1016/S1003-6326(21)65744-8)
- Lobo, L., Degryse, P., Shortland, A., Eremin, K., Vanhaecke, F., 2014. Copper and antimony isotopic analysis via multi-collector ICP-mass spectrometry for provenancing ancient glass. *Journal of Analytical Atomic Spectrometry* 29, 58–64. <https://doi.org/10.1039/C3JA50303H>
- Lobo, L., Degryse, P., Shortland, A., Vanhaecke, F., 2013. Isotopic analysis of antimony using multi-collector ICP-mass spectrometry for provenance determination of Roman glass. *J. Anal. At. Spectrom.* 28, 1213–1219. <https://doi.org/10.1039/C3JA50018G>
- Lottermoser, B., 2010. *Mine Wastes*. Springer Berlin Heidelberg, Berlin, Heidelberg. <https://doi.org/10.1007/978-3-642-12419-8>
- Lynch, A.J., Rowland, C.A., 2005. *The history of grinding*. Society for Mining, Metallurgy, and Exploration, Littleton, Colo.
- MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. *Arch. Environ. Contam. Toxicol.* 39, 20–31. <https://doi.org/10.1007/s002440010075>
- Mackay, A.K., Taylor, M.P., Munksgaard, N.C., Hudson-Edwards, K.A., Burn-Nunes, L., 2013. Identification of environmental lead sources and pathways in a mining and smelting town: Mount Isa, Australia. *Environmental Pollution* 180, 304–311. <https://doi.org/10.1016/j.envpol.2013.05.007>
- MacKenzie, A.B., Pulford, I.D., 2002. Investigation of contaminant metal dispersal from a disused mine site at Tyndrum, Scotland, using concentration gradients and stable Pb isotope ratios. *Applied Geochemistry* 17, 1093–1103. [https://doi.org/10.1016/S0883-2927\(02\)00007-0](https://doi.org/10.1016/S0883-2927(02)00007-0)
- Macklin, M.G., Brewer, P.A., Hudson-Edwards, K.A., Bird, G., Coulthard, T.J., Dennis, I.A., Lechler, P.J., Miller, J.R., Turner, J.N., 2006. A geomorphological approach to the management of rivers contaminated by metal mining. *Geomorphology*, 37th Binghamton Geomorphology Symposium 79, 423–447. <https://doi.org/10.1016/j.geomorph.2006.06.024>
- Manhes, G., Allègre, C.J., Dupré, B., Hamelin, B., 1980. Lead isotope study of basic-ultrabasic layered complexes: Speculations about the age of the earth and primitive mantle characteristics. *Earth and Planetary Science Letters* 47, 370–382. [https://doi.org/10.1016/0012-821X\(80\)90024-2](https://doi.org/10.1016/0012-821X(80)90024-2)
- Mariet, A.-L., Gauthier-Manuel, H., Lagiewski, T., Bégeot, C., Walter-Simonnet, A.-V., Gimbert, F., 2020. Impact assessment of legacy wastes from ancient mining activities on current earthworm community. *Journal of Hazardous Materials* 393, 122369. <https://doi.org/10.1016/j.jhazmat.2020.122369>
- Mariet, A.-L., Monna, F., Gimbert, F., Bégeot, C., Cloquet, C., Belle, S., Millet, L., Rius, D., Walter-Simonnet, A.-V., 2018. Tracking past mining activity using trace metals, lead isotopes and compositional data analysis of a sediment core from Longemer Lake, Vosges Mountains, France. *J Paleolimnol* 60, 399–412. <https://doi.org/10.1007/s10933-018-0029-9>
- Mariet, A.-L., Sarret, G., Bégeot, C., Walter-Simonnet, A.-V., Gimbert, F., 2017. Lead Highly Available in Soils Centuries after Metallurgical Activities. *Journal of Environmental Quality* 46, 1236–1242. <https://doi.org/10.2134/jeq2016.12.0469>
- Marrugo-Negrete, J., Pinedo-Hernández, J., Díez, S., 2017. Assessment of heavy metal pollution, spatial distribution and origin in agricultural soils along the Sinú River Basin, Colombia. *Environmental Research* 154, 380–388. <https://doi.org/10.1016/j.envres.2017.01.021>
- Martínez Cortizas, A., López-Merino, L., Bindler, R., Mighall, T., Kylander, M.E., 2016. Early atmospheric metal pollution provides evidence for Chalcolithic/Bronze Age mining and metallurgy in Southwestern Europe. *Science of The Total Environment* 545–546, 398–406. <https://doi.org/10.1016/j.scitotenv.2015.12.078>
- Martínez-Cortizas, A., Pontevedra-Pombal, X., García-Rodeja, E., Nóvoa-Muñoz, J.C., Shotyk, W., 1999. Mercury in a Spanish Peat Bog: Archive of Climate Change and Atmospheric Metal Deposition. *Science* 284, 939–942. <https://doi.org/10.1126/science.284.5416.939>

REFERENCES

- Matisoff, G., 2014. 210Pb as a tracer of soil erosion, sediment source area identification and particle transport in the terrestrial environment. *Journal of Environmental Radioactivity* 138, 343–354. <https://doi.org/10.1016/j.jenvrad.2014.03.008>
- Maury-Brachet, R., Gentes, S., Dassié, E.P., Feurtet-Mazel, A., Vigouroux, R., Laperche, V., Gonzalez, P., Hanquiez, V., Mesmer-Dudons, N., Durrieu, G., Legeay, A., 2020. Mercury contamination levels in the bioindicator piscivorous fish *Hoplias aimara* in French Guiana rivers: mapping for risk assessment. *Environ Sci Pollut Res* 27, 3624–3636. <https://doi.org/10.1007/s11356-018-3983-x>
- Meloux, J., 1975. Alpes-Nord. Bilan Synthétique de Dix Années de Prospection. (No. n°75-RME-023-FE). BRGM, Orléans.
- Mihaljevič, M., Baieta, R., Ettlér, V., Vaněk, A., Kříbek, B., Penížek, V., Drahota, P., Trubač, J., Sracek, O., Chrástný, V., Mapani, B.S., 2019. Tracing the metal dynamics in semi-arid soils near mine tailings using stable Cu and Pb isotopes. *Chemical Geology* 515, 61–76. <https://doi.org/10.1016/j.chemgeo.2019.03.026>
- Mihaljevič, M., Zuna, M., Ettlér, V., Šebek, O., Strnad, L., Goliáš, V., 2006. Lead fluxes, isotopic and concentration profiles in a peat deposit near a lead smelter (Příbram, Czech Republic). *Science of The Total Environment* 372, 334–344. <https://doi.org/10.1016/j.scitotenv.2006.09.019>
- Monna, F., Camizuli, E., Revelli, P., Biville, C., Thomas, C., Losno, R., Scheifler, R., Bruguier, O., Baron, S., Chateau, C., Ploquin, A., Alibert, P., 2011. Wild Brown Trout Affected by Historical Mining in the Cévennes National Park, France. *Environ. Sci. Technol.* 45, 6823–6830. <https://doi.org/10.1021/es200755n>
- Monna, F., Hamer, K., Lévêque, J., Sauer, M., 2000. Pb isotopes as a reliable marker of early mining and smelting in the Northern Harz province (Lower Saxony, Germany). *Journal of Geochemical Exploration* 68, 201–210. [https://doi.org/10.1016/S0375-6742\(00\)00005-4](https://doi.org/10.1016/S0375-6742(00)00005-4)
- Morin, G., Juillot, F., Ildefonse, P., Calas, G., Samama, J.-C., Chevallier, P., Brown, G.E., 2001. Mineralogy of lead in a soil developed on a Pb-mineralized sandstone (Largentière, France). *American Mineralogist* 86, 92–104. <https://doi.org/10.2138/am-2001-0110>
- Mottes, C., Sabatier, P., Evrard, O., Cottin, N., Arnaud, F., Comte, I., Piot, C., Lesueur-Jannoyer, M., Lichtfouse, E., Poulénard, J., 2022. Pesticide resurrection. *Environ Chem Lett* 20, 3357–3362. <https://doi.org/10.1007/s10311-021-01347-z>
- Müller, G., 1979. Schwermetalle in den sediments des Rheins-Veränderungen seit 1971. *Umschau in Wissenschaft und Technik* 79.
- Navel, A., Uzu, G., Spadini, L., Sobanska, S., Martins, J.M.F., 2015. Combining microscopy with spectroscopic and chemical methods for tracing the origin of atmospheric fallouts from mining sites. *Journal of Hazardous Materials* 300, 538–545. <https://doi.org/10.1016/j.jhazmat.2015.07.035>
- Nriagu, J.O., 1974. Lead orthophosphates—IV Formation and stability in the environment. *Geochimica et Cosmochimica Acta* 38, 887–898. [https://doi.org/10.1016/0016-7037\(74\)90062-3](https://doi.org/10.1016/0016-7037(74)90062-3)
- Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333, 134–139. <https://doi.org/10.1038/333134a0>
- Ostergren, J.D., Brown, Gordon E., Parks, G.A., Tingle, T.N., 1999. Quantitative Speciation of Lead in Selected Mine Tailings from Leadville, CO. *Environ. Sci. Technol.* 33, 1627–1636. <https://doi.org/10.1021/es980660s>
- Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.* 9, 269–298. <https://doi.org/10.1139/a01-012>
- Paktunc, A.D., 1999. Mineralogical constraints on the determination of neutralization potential and prediction of acid mine drainage. *Environmental Geology* 39, 103–112. <https://doi.org/10.1007/s002540050440>
- Peloux, F., Bailly-Maître, M., Viallet, H., 2015. L'histoire si curieuse des mines de Brandes, PUG. ed, La pierre et l'écrit. Grenoble.
- Petruk, W., 2000. Applied mineralogy in the mining industry, 1st ed. ed. Elsevier Science BV, Amsterdam ; New York.
- Philippe, M., Le Pape, P., Resongles, E., Landrot, G., Freydier, R., Bordier, L., Baptiste, B., Delbes, L., Baya, C., Casiot, C., Ayrault, S., 2022. Fate of antimony contamination generated by road traffic – A focus on Sb geochemistry and speciation in stormwater ponds. *Chemosphere* 137368. <https://doi.org/10.1016/j.chemosphere.2022.137368>

REFERENCES

- Poulard, F., Daupley, X., Didier, C., Pokryska, Z., D'Hugues, P., Charles, N., Dupuy, J.-J., Save, M., 2017. Exploitation minière et traitement des minerais (No. Tome 6), Collection "La mine en France."
- Pulford, I.D., MacKenzie, A.B., Donatello, S., Hastings, L., 2009. Source term characterisation using concentration trends and geochemical associations of Pb and Zn in river sediments in the vicinity of a disused mine site: Implications for contaminant metal dispersion processes. *Environmental Pollution, Special Issue Section: Ozone and Mediterranean Ecology: Plants, People, Problems* 157, 1649–1656. <https://doi.org/10.1016/j.envpol.2008.12.018>
- Quevauviller, P., 1998. Operationally defined extraction procedures for soil and sediment analysis I. Standardization. *TrAC Trends in Analytical Chemistry* 17, 289–298. [https://doi.org/10.1016/S0165-9936\(97\)00119-2](https://doi.org/10.1016/S0165-9936(97)00119-2)
- R Core Team, 2022. R: A language and environment for statistical computing.
- Rao, C.R.M., Sahuquillo, A., Lopez Sanchez, J.F., 2008. A Review of the Different Methods Applied in Environmental Geochemistry For Single and Sequential Extraction of Trace Elements in Soils and Related Materials. *Water Air Soil Pollut* 189, 291–333. <https://doi.org/10.1007/s11270-007-9564-0>
- Ratié, G., Quantin, C., Jouvin, D., Calmels, D., Ettler, V., Sivry, Y., Vieira, L.C., Ponzevera, E., Garnier, J., 2016. Nickel isotope fractionation during laterite Ni ore smelting and refining: Implications for tracing the sources of Ni in smelter-affected soils. *Applied Geochemistry, Special issue of Applied Geochemistry on Environmental Impacts of Mining and Smelting* 64, 136–145. <https://doi.org/10.1016/j.apgeochem.2015.09.005>
- Reguera-Galan, A., Barreiro-Grille, T., Moldovan, M., Lobo, L., de Blas Cortina, M.Á., García Alonso, J.I., 2019. A Provenance Study of Early Bronze Age Artefacts Found in Asturias (Spain) by Means of Metal Impurities and Lead, Copper and Antimony Isotopic Compositions. *Archaeometry* 61, 683–700. <https://doi.org/10.1111/arcm.12445>
- Reimann, C., de Caritat, P., 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. *Science of The Total Environment* 337, 91–107. <https://doi.org/10.1016/j.scitotenv.2004.06.011>
- Reimer, P.J., 2020. Composition and consequences of the IntCal20 radiocarbon calibration curve. *Quaternary Research* 96, 22–27. <https://doi.org/10.1017/qua.2020.42>
- Renberg, I., Bindler, R., Brännvall, M.-L., 2001. Using the historical atmospheric lead-deposition record as a chronological marker in sediment deposits in Europe. *The Holocene* 11, 511–516. <https://doi.org/10.1191/095968301680223468>
- Renberg, I., Persson, M.W., Emteryd, O., 1994. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. *Nature* 368, 323–326. <https://doi.org/10.1038/368323a0>
- Resongles, E., Dietze, V., Green, D.C., Harrison, R.M., Ochoa-Gonzalez, R., Tremper, A.H., Weiss, D.J., 2021. Strong evidence for the continued contribution of lead deposited during the 20th century to the atmospheric environment in London of today. *Proceedings of the National Academy of Sciences* 118, e2102791118. <https://doi.org/10.1073/pnas.2102791118>
- Resongles, E., Freydier, R., Casiot, C., Viers, J., Chmeleff, J., Elbaz-Poulichet, F., 2015. Antimony isotopic composition in river waters affected by ancient mining activity. *Talanta* 144, 851–861. <https://doi.org/10.1016/j.talanta.2015.07.013>
- Reyss, J.-L., Schmidt, S., Legeleux, F., Bonté, P., 1995. Large, low background well-type detectors for measurements of environmental radioactivity. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 357, 391–397. [https://doi.org/10.1016/0168-9002\(95\)00021-6](https://doi.org/10.1016/0168-9002(95)00021-6)
- Rose, N.L., Yang, H., Turner, S.D., Simpson, G.L., 2012. An assessment of the mechanisms for the transfer of lead and mercury from atmospherically contaminated organic soils to lake sediments with particular reference to Scotland, UK. *Geochimica et Cosmochimica Acta, Environmental Records of Anthropogenic Impacts* 82, 113–135. <https://doi.org/10.1016/j.gca.2010.12.026>
- Rosman, K.J.R., Ly, C., Van de Velde, K., Boutron, C.F., 2000. A two century record of lead isotopes in high altitude Alpine snow and ice. *Earth and Planetary Science Letters* 176, 413–424. [https://doi.org/10.1016/S0012-821X\(00\)00013-3](https://doi.org/10.1016/S0012-821X(00)00013-3)
- Rossi, M., Camizuli, E., Gasquet, D., 2017. Le passé minier, la gestion de l'après-mine : exemple des Alpes du Nord françaises. *Mines & carrières, Revue de la société de l'industrie minière*.

REFERENCES

- Rouxel, O., Ludden, J., Fouquet, Y., 2003. Antimony isotope variations in natural systems and implications for their use as geochemical tracers. *Chemical Geology* 200, 25–40. [https://doi.org/10.1016/S0009-2541\(03\)00121-9](https://doi.org/10.1016/S0009-2541(03)00121-9)
- Rudnick, R., Gao, S., 2003. Composition of the Continental Crust. *Treatise on Geochemistry* 3, 1–64. <https://doi.org/10.1016/B0-08-043751-6/03016-4>
- Sabatier, P., Moernaut, J., Bertrand, S., Van Daele, M., Kremer, K., Chaumillon, E., Arnaud, F., 2022. A Review of Event Deposits in Lake Sediments. *Quaternary* 5, 34. <https://doi.org/10.3390/quat5030034>
- Sabatier, P., Poulenard, J., Fanget, B., Reyss, J.-L., Develle, A.-L., Wilhelm, B., Ployon, E., Pignol, C., Naffrechoux, E., Dorioz, J.-M., Montuelle, B., Arnaud, F., 2014. Long-term relationships among pesticide applications, mobility, and soil erosion in a vineyard watershed. *PNAS* 111, 15647–15652. <https://doi.org/10.1073/pnas.1411512111>
- Sahuquillo, A., Rigol, A., Rauret, G., 2003. Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. *TrAC Trends in Analytical Chemistry* 22, 152–159. [https://doi.org/10.1016/S0165-9936\(03\)00303-0](https://doi.org/10.1016/S0165-9936(03)00303-0)
- Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., Vivo, B.D., Vos, W.D., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T., 2005. *Geochemical Atlas of Europe. Part 1: Background Information, Methodology and maps.* Geological Survey of Finland.
- Semlali, R.M., Denaix, L., Oort, F., 2002. Estimation des stocks et des flux dans un Andosol jeune.
- Semple, Kirk.T., Doick, K.J., Jones, K.C., Burauel, P., Craven, A., Harms, H., 2004. Defining Bioavailability and Bioaccessibility of Contaminated Soil and Sediment is Complicated. *Environ. Sci. Technol.* 38, 228A-231A. <https://doi.org/10.1021/es040548w>
- Shiel, A.E., Weis, D., Orians, K.J., 2010. Evaluation of zinc, cadmium and lead isotope fractionation during smelting and refining. *Science of The Total Environment* 408, 2357–2368. <https://doi.org/10.1016/j.scitotenv.2010.02.016>
- Shotyk, W., Krachler, M., Chen, B., 2005. Anthropogenic impacts on the biogeochemistry and cycling of antimony. *Metal ions in biological systems* 44, 171–203.
- Shotyk, W., Rausch, N., Outridge, P.M., Krachler, M., 2016. Isotopic evolution of atmospheric Pb from metallurgical processing in Flin Flon, Manitoba: Retrospective analysis using peat cores from bogs. *Environmental Pollution* 218, 338–348. <https://doi.org/10.1016/j.envpol.2016.07.009>
- Shotyk, W., Weiss, D., Appleby, P.G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., Knaap, W.O.V.D., 1998. History of Atmospheric Lead Deposition Since 12,370 14C yr BP from a Peat Bog, Jura Mountains, Switzerland. *Science* 281, 1635–1640. <https://doi.org/10.1126/science.281.5383.1635>
- Simonneau, A., Chapron, E., Garçon, M., Winiarski, T., Graz, Y., Chauvel, C., Debret, M., Motelica-Heino, M., Desmet, M., Di Giovanni, C., 2014. Tracking Holocene glacial and high-altitude alpine environments fluctuations from minerogenic and organic markers in proglacial lake sediments (Lake Blanc Huez, Western French Alps). *Quaternary Science Reviews* 89, 27–43. <https://doi.org/10.1016/j.quascirev.2014.02.008>
- Sivry, Y., Riotte, J., Sonke, J.E., Audry, S., Schäfer, J., Viers, J., Blanc, G., Freydier, R., Dupré, B., 2008. Zn isotopes as tracers of anthropogenic pollution from Zn-ore smelters The Riou Mort–Lot River system. *Chemical Geology* 255, 295–304. <https://doi.org/10.1016/j.chemgeo.2008.06.038>
- Smith, J.N., 2001. Why should we believe 210Pb sediment geochronologies? *Journal of Environmental Radioactivity* 55, 121–123. [https://doi.org/10.1016/S0265-931X\(00\)00152-1](https://doi.org/10.1016/S0265-931X(00)00152-1)
- Sobanska, S., Ricq, N., Laboudigue, A., Guillermo, R., Brémard, C., Laureyns, J., Merlin, J.C., Wignacourt, J.P., 1999. Microchemical Investigations of Dust Emitted by a Lead Smelter. *Environ. Sci. Technol.* 33, 1334–1339. <https://doi.org/10.1021/es9805270>
- Spadini, L., Navel, A., Martins, J.M.F., Vince, E., Lamy, I., 2018. Soil aggregates: a scale to investigate the densities of metal and proton reactive sites of organic matter and clay phases in soil. *European Journal of Soil Science* 69, 953–961. <https://doi.org/10.1111/ejss.12695>
- Sterckeman, T., Gomez, A., Ciesielski, H., 1996. Soil and waste analysis for environmental risk assessment in France. *Science of The Total Environment, Harmonization of Leaching/Extraction Tests for Environmental Risk Assessment* 178, 63–69. [https://doi.org/10.1016/0048-9697\(95\)04798-0](https://doi.org/10.1016/0048-9697(95)04798-0)

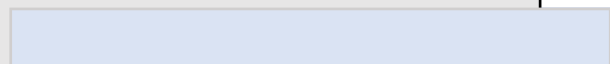
REFERENCES

- Stoffers, P., Glasby, G.P., Wilson, C.J., Davis, K.R., Walter, P., 1986. Heavy metal pollution in Wellington Harbour. *New Zealand Journal of Marine and Freshwater Research* 20, 495–512. <https://doi.org/10.1080/00288330.1986.9516169>
- Swęd, M., Uzarowicz, L., Duczmal-Czernikiewicz, A., Kwasowski, W., Pędziwiatr, A., Siepak, M., Niedzielski, P., 2022. Forms of metal(loid)s in soils derived from historical calamine mining waste and tailings of the Olkusz Zn–Pb ore district, southern Poland: A combined pedological, geochemical and mineralogical approach. *Applied Geochemistry* 139, 105218. <https://doi.org/10.1016/j.apgeochem.2022.105218>
- Thevenon, F., Graham, N.D., Chiaradia, M., Arpagaus, P., Wildi, W., Poté, J., 2011a. Local to regional scale industrial heavy metal pollution recorded in sediments of large freshwater lakes in central Europe (lakes Geneva and Lucerne) over the last centuries. *Science of The Total Environment* 412–413, 239–247. <https://doi.org/10.1016/j.scitotenv.2011.09.025>
- Thevenon, F., Guédron, S., Chiaradia, M., Loizeau, J.-L., Poté, J., 2011b. (Pre-) historic changes in natural and anthropogenic heavy metals deposition inferred from two contrasting Swiss Alpine lakes. *Quaternary Science Reviews* 30, 224–233. <https://doi.org/10.1016/j.quascirev.2010.10.013>
- Thienpont, J.R., Korosi, J.B., Hargan, K.E., Williams, T., Eickmeyer, D.C., Kimpe, L.E., Palmer, M.J., Smol, J.P., Blais, J.M., 2016. Multi-trophic level response to extreme metal contamination from gold mining in a subarctic lake. *Proceedings of the Royal Society B: Biological Sciences* 283, 20161125. <https://doi.org/10.1098/rspb.2016.1125>
- Thiombane, M., Di Bonito, M., Albanese, S., Zuzolo, D., Lima, A., De Vivo, B., 2019. Geogenic versus anthropogenic behaviour and geochemical footprint of Al, Na, K and P in the Campania region (Southern Italy) soils through compositional data analysis and enrichment factor. *Geoderma* 335, 12–26. <https://doi.org/10.1016/j.geoderma.2018.08.008>
- Thornton, I., 1996. Impacts of mining on the environment; some local, regional and global issues. *Applied Geochemistry, Environmental Geochemistry* 11, 355–361. [https://doi.org/10.1016/0883-2927\(95\)00064-X](https://doi.org/10.1016/0883-2927(95)00064-X)
- Tylecote, R.F., 2002. *History of Metallurgy*, 2nd edition. ed. Maney for the Institute Material, UK.
- van der Voet, E., Salminen, R., Eckelman, M., Norgate, T., Mudd, G., Hisschier, R., Spijker, J., Vijver, M., Selinus, O., Posthuma, L., de Zwart, D., van de Meent, D., Reuter, M., Tikana, L., Valdivia, S., Wäger, P., Hauschild, M.Z., de Koning, A., 2013. Environmental challenges of anthropogenic metals flows and cycles (Report No. 978-92-807-3266-5), Environmental challenges of anthropogenic metals flows and cycles. United Nations Environment Programme.
- Vaněk, A., Chrastný, V., Teper, L., Cabala, J., Penížek, V., Komárek, M., 2011. Distribution of thallium and accompanying metals in tree rings of Scots pine (*Pinus sylvestris* L.) from a smelter-affected area. *Journal of Geochemical Exploration* 108, 73–80. <https://doi.org/10.1016/j.jgexplo.2010.10.006>
- Vaněk, A., Grösslová, Z., Mihaljevič, M., Ettler, V., Trubač, J., Chrastný, V., Penížek, V., Teper, L., Cabala, J., Voegelin, A., Zádorová, T., Oborná, V., Drábek, O., Holubík, O., Houška, J., Pavlů, L., Ash, C., 2018. Thallium isotopes in metallurgical wastes/contaminated soils: A novel tool to trace metal source and behavior. *Journal of Hazardous Materials* 343, 78–85. <https://doi.org/10.1016/j.jhazmat.2017.09.020>
- Vaněk, A., Vejvodová, K., Mihaljevič, M., Ettler, V., Trubač, J., Vaňková, M., Goliáš, V., Teper, L., Sutkowska, K., Vokurková, P., Penížek, V., Zádorová, T., Drábek, O., 2021. Thallium and lead variations in a contaminated peatland: A combined isotopic study from a mining/smeltering area. *Environmental Pollution* 290, 117973. <https://doi.org/10.1016/j.envpol.2021.117973>
- Vuong, X.T., Prietzel, J., Heitkamp, F., 2016. Measurement of organic and inorganic carbon in dolomite-containing samples. *Soil Use and Management* 32, 53–59. <https://doi.org/10.1111/sum.12233>
- Wang, D., Mathur, R., Zheng, Y., Qiu, K., Wu, H., 2021. Redox-controlled antimony isotope fractionation in the epithermal system: New insights from a multiple metal stable isotopic combination study of the Zhaxikang Sb–Pb–Zn–Ag deposit in Southern Tibet. *Chemical Geology* 584, 120541. <https://doi.org/10.1016/j.chemgeo.2021.120541>
- Wang, L., Jin, Y., Weiss, D.J., Schleicher, N.J., Wilcke, W., Wu, L., Guo, Q., Chen, J., O'Connor, D., Hou, D., 2021. Possible application of stable isotope compositions for the identification of metal sources in soil. *Journal of Hazardous Materials* 407, 124812. <https://doi.org/10.1016/j.jhazmat.2020.124812>

REFERENCES

- Wen, B., Zhou, J., Tang, P., Jia, X., Zhou, W., Huang, J., 2022. Antimony (Sb) isotopic signature in water systems from the world's largest Sb mine, Central China: Novel insights to trace Sb source and mobilization. *Journal of Hazardous Materials* 130622. <https://doi.org/10.1016/j.jhazmat.2022.130622>
- Wen, B., Zhou, J., Zhou, A., Liu, C., Li, L., 2018. A review of antimony (Sb) isotopes analytical methods and application in environmental systems. *International Biodeterioration & Biodegradation, Remediation and Restoration of Polluted Mining Areas* 128, 109–116. <https://doi.org/10.1016/j.ibiod.2017.01.008>
- Wen, H., Zhang, Y., Cloquet, C., Zhu, C., Fan, H., Luo, C., 2015. Tracing sources of pollution in soils from the Jinding Pb–Zn mining district in China using cadmium and lead isotopes. *Applied Geochemistry* 52, 147–154. <https://doi.org/10.1016/j.apgeochem.2014.11.025>
- Wiederhold, J.G., 2015. Metal Stable Isotope Signatures as Tracers in Environmental Geochemistry. *Environ. Sci. Technol.* 49, 2606–2624. <https://doi.org/10.1021/es504683e>
- Wiklund, J.A., Kirk, J.L., Muir, D.C.G., Gleason, A., Carrier, J., Yang, F., 2020. Atmospheric trace metal deposition to remote Northwest Ontario, Canada: Anthropogenic fluxes and inventories from 1860 to 2010. *Science of The Total Environment* 749, 142276. <https://doi.org/10.1016/j.scitotenv.2020.142276>
- Wills, B.A., Finch, J.E., 2016. *Wills' mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery*, Eighth edition. ed. Elsevier, Amsterdam Boston, Mass Heidelberg.
- World Health Organization, 2022. *Guidelines for drinking-water quality : fourth edition incorporating the first and second addenda*. Geneva.
- Yang, H., Rose, N., 2005. Trace element pollution records in some UK lake sediments, their history, influence factors and regional differences. *Environment International* 31, 63–75. <https://doi.org/10.1016/j.envint.2004.06.010>
- Yang, H., Rose, N.L., Battarbee, R.W., 2002a. Distribution of some trace metals in Lochnagar, a Scottish mountain lake ecosystem and its catchment. *Science of The Total Environment* 285, 197–208. [https://doi.org/10.1016/S0048-9697\(01\)00931-7](https://doi.org/10.1016/S0048-9697(01)00931-7)
- Yang, H., Rose, N.L., Battarbee, R.W., Boyle, J.F., 2002b. Mercury and Lead Budgets for Lochnagar, a Scottish Mountain Lake and Its Catchment. *Environ. Sci. Technol.* 36, 1383–1388. <https://doi.org/10.1021/es010120m>
- Yin, N.-H., Lens, P.N.L., Sivry, Y., van Hullebusch, E.D., 2017. Lead and Zinc Metallurgical Slags Mineralogy and Weathering, in: Rene, E.R., Sahinkaya, E., Lewis, A., Lens, P.N.L. (Eds.), *Sustainable Heavy Metal Remediation: Volume 2: Case Studies, Environmental Chemistry for a Sustainable World*. Springer International Publishing, Cham, pp. 133–160. https://doi.org/10.1007/978-3-319-61146-4_5
- Zdanowicz, C.M., Banic, C.M., Paktunc, D.A., Kliza-Petelle, D.A., 2006. Metal emissions from a Cu smelter, Rouyn-Noranda, Québec: characterization of particles sampled in air and snow. *Geochemistry: Exploration, Environment, Analysis* 6, 147–162. <https://doi.org/10.1144/1467-7873/05-089>
- Zhai, D., Mathur, R., Liu, S.-A., Liu, J., Godfrey, L., Wang, K., Xu, J., Vervoort, J., 2021. Antimony isotope fractionation in hydrothermal systems. *Geochimica et Cosmochimica Acta* 306, 84–97. <https://doi.org/10.1016/j.gca.2021.05.031>
- Zhou, W., Zhou, A., Wen, B., Liu, P., Zhu, Z., Finckel, Z., Zhou, J., 2022. Antimony isotope fractionation during adsorption on aluminum oxides. *Journal of Hazardous Materials* 429, 128317. <https://doi.org/10.1016/j.jhazmat.2022.128317>

ANNEXES |



ANNEXES

ANNEXE A – Liste des laboratoires partenaires et collaborateur pour la réalisation des analyses.

ANNEXE B – Valorisation scientifique durant la thèse.

ANNEXE C – Proceeding of the 16th SGA Biennial Meeting

ANNEXE A - Liste des laboratoires partenaires et collaborateur pour la réalisation des analyses

Analyses	Date	Collaboration (Laboratoire)
<u>Échantillonnage :</u> - Source de contamination - Sols de surface (site minier, et autour du lac) - Profils de sol (site minier) - Sols de surface (autour du lac) - Sed. lacustres - Sed. Rivières et eaux	Juillet 2020, Mai 2021 Juillet 2020 Mai 2021 Octobre 2021 Juillet 2019 Mai 2021	Floriane Guillevic (FG), Magali Rossi (MR), Jérôme Poulenard (JP), Lise Marchal (MR) Avec la participation de Gél Monvoisin (GEOPS) et Eléonore Resongles (HSM)
<u>Préparation des échantillons :</u> - Tamisage - Broyage - Pastilles - Caractérisation physico-chimique -Pertes au Feu - Granulométrie - Datation	2020,2021,2022	FG,MR FG,MR FG Laboratoire externe INRAE FG FG Laboratoire externe POZNAN (Pologne)
<u>Quantification élémentaire :</u> - WDS-XRF	2020,2021,2022	FG, Anne-Lise Develle (ALD)
- ICP-MS	2020, 2021, 2022	Laboratoire externe SARM
<u>Minéralogie</u> - Microscopie optique - MEB - DRX	2020, 2021, 2022	FG FG Laboratoire externe ISTERRE
<u>Essais de lixiviation :</u> Préparation Réalisation Analyse lixiviat	2021	Collaboration avec IGE Jean M.F. Martins, Lorenzo Spadni 
<u>Isotopie du Sb</u> Minéralisation Séparation Analyses	Juin-Juillet 2021	Collaboration avec HSM Eléonore Resongles 
<u>Isotopie du Pb</u> Préparation Analyses	Octobre 2021	Collaboration avec GEOPS Cécile Quantin, Gaël Monvoisin 

ANNEXE B - Valorisation scientifique durant la thèse

Publication dans une revue à comité de lecture :

Guillevic, F., Rossi, M., Develle, A.-L., Spadini, L., Martins, J.M.F., Arnaud, F., Poulénard, J., 2023. Pb dispersion pathways in mountain soils contaminated by ancient mining and smelting activities. *Applied Geochemistry* 105556. <https://doi.org/10.1016/j.apgeochem.2022.105556>

Publication soumise à une revue à comité de lecture :

Guillevic, F., Rossi, M., Poulénard, J., Sabatier, P., Develle, A.-L., Quantin, C., Monvoisin, G., Arnaud, F., The Legacy of Metallurgical Atmospheric Contamination in a Mountainous Catchment: A Delayed Response of Pb Contamination. Soumis à *Science of the Total Environment*.

Publication en préparation :

Guillevic, F., Rossi, M., Resongles, E., Freyrier, R., Ferrari, C., Poulénard, J., Quantin, C., Monvoisin, G., Arnaud, F. Multi-isotope (Pb, Sb) approach to trace metallic contaminant sources at a historical mining and metallurgical site. En préparation pour soumission à *Chemical geology*.

Participations à des colloques internationaux :

Guillevic F., Rossi M., Arnaud F., Poulénard J. Trace metals dispersal from mine wastes to the critical zone: the example of the Pb-Ag mine of Peisey-Nancroix. Congrès EUROSOL, Geneva, Switzerland. 2021 (**Poster virtuel**).

Guillevic F., Rossi M., Poulénard J., Arnaud F., Gateuille D., Naffrechoux E., Martins J.M, Spadini L., Foulquier A, Lyautey E., Etienne D., Pesce S. The environmental trajectory of a former mining territory evidenced from an integrated and multidisciplinary approach: the case of Peisey-Nancroix Pb-Ag mine. Congrès Society for Geology Applied to Mineral Deposit (SGA), Rotorua, New Zealand. 2022 (**Communication orale virtuelle**)

Guillevic F., Rossi M., Poulénard J., Arnaud F., Quantin C., Monvoisin G. Persistent imprint of historical metallurgy in an alpine watershed evidenced from lake sediments Pb isotopes. Congrès European Geosciences Union (EGU), Vienna, Austria. 2022 (**Communication orale**)

Guillevic F., Rossi M., Poulenard J., Arnaud F., Resongles, E., Freydier R., Quantin C., Monvoisin G. Pb and Sb transfer processes and persistence in soils contaminated by ancient mining activities. Congrès World Science Congress of Soil Science (WCSS), Glasgow, UK. 2022 (**Communication orale**).

Participations à des colloques nationaux :

Guillevic F., Rossi M., Poulenard J., Arnaud F. La dispersion des ETMs dans la zone critique depuis les déchets miniers : Exemple de la mine de Pb-Ag de Peisey-Nancroix. Congrès Réunion des Sciences de la Terre (RST), Lyon, France. 2021 (**Communication orale**).

ANNEXE C - Proceeding of the 16th SGA Biennial Meeting

The environmental trajectory of a former mining territory evidenced from an integrated and multidisciplinary approach: the case of Peisey-Nancroix Pb-Ag mine

Floriane Guillevic, Magali Rossi, Jérôme Poulenard, Fabien Arnaud, David Gateuille, Emmanuel Naffrechoux
Univ. Savoie Mont-Blanc, CNRS, EDYTEM, Chambéry, France

Jean Martins, Lorenzo Spadini
Univ. Grenoble Alpes, CNRS, G-INP, IRD, IGE, Grenoble, France

Arnaud Foulquier
Univ. Grenoble Alpes, CNRS, Univ. Savoie Mont-Blanc, Grenoble, France

Emilie Lyautey, David Etienne
Univ. Savoie Mont-Blanc, INRAE, CARRTEL, Chambéry France

Stéphane Pesce
INRAE, UR RiverLy, Villeurbanne, France

Abstract. Mining produces mine wastes (waste dumps, tailings) and metallurgical wastes (slags and fumes) enriched in trace metals (TMs, e.g. Pb, Cu, As, Zn, Cd and Sb) that are mobilized by leaching and particle translocation in the critical zone long after mine closure. A multi-compartments study, integrating ore, slags, soils, stream sediments, lake sediments, and vegetation, has been developed to better understand the transfer mechanisms and remobilization processes of TMs over time (>50 years) in the critical zone. An interdisciplinary approach was used, coupling geochemical analyses with mineralogical observations and ecotoxicology (i) to discuss the processes involved in TMs persistence and remobilization in each environmental compartment contaminated by mining activity, and (ii) to assess the effects of TMs contamination on biota and on the ecosystem functioning.

1 Introduction

The exploitation of mineral resources is one of the most disturbing forms of anthropogenic activity (Dudka and Adriano 1997) that leads to trace metals (TMs, e.g. Pb, Sb, As, Cd and Cu) dispersal in the critical zone (Fig. 1). Brantley et al (2007) describes the critical zone as a "system of coupled chemical, biological, physical, and geological processes operation together to support life at the Earth's surface". Mine wastes (waste dumps, tailings, slags) stored above ground are usually enriched in TMs, especially in ancient mining sites. Weathering of mine wastes induces TMs leaching and particle translocation, thus contributing to TMs dispersal in the critical zone during mining activity, but also long after mine closure (several hundred years; Galuszka et al. 2015; Camizuli et al. 2021). Atmospheric fallout

of TMs-rich fumes emitted during smelting contributes to TMs dispersal at a more regional scale (Arnaud et al. 2005; Guyard et al. 2007; Ettler 2016; Carvalho and Schulte 2020).

Mine wastes can be considered as a potential toxic heritage for future generations. To better constrain the environmental impacts of future mining activity, it appears necessary to understand the long-term TMs behaviour (dispersal and persistence) in the critical zone by developing studies on mining sites abandoned for several hundred years. A multi-compartments study, integrating ore, slags, soils, stream sediments, lake sediments, and vegetation, is necessary to characterize the environmental heritage of mining activity. Such an integrated approach is necessary to better understand the transfer mechanisms and remobilization processes of TMs over time in mining territories.

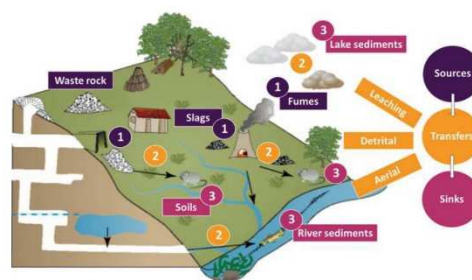


Figure 1. Sources and fates of trace metals in the environment of a mining system.

The aim of our project is to determine the spatial

and temporal trajectories of TMs in the critical zone using a source-sink approach (source = ore + slags; sinks = soils + stream sediments + lake sediments + vegetation cover; Fig. 2). For each compartment of the critical zone, the combination of geochemical data with mineralogical observations (especially the Pb-bearing phases) and microbial activity characterization contribute to determine the TMs mobility and circulation pathways, their bioavailability, and their biogeochemical cycle.

2 The Peisey-Nancroix Pb-Ag mine

Hundreds of abandoned metallic mines have been reported in the northern French Alps. They have been operated since Antiquity, but mining activity reached its maximum during the Middle-Ages and the 18th-19th centuries. Since mine closure, the mines have been abandoned and mine and metallurgical wastes have been left onsite.

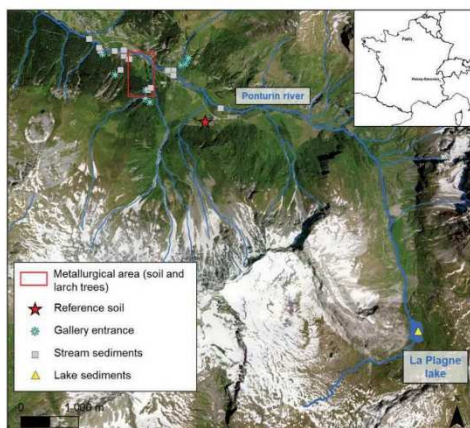


Figure 2. Overview of the Peisey-Nancroix watershed showing the location of the various samples collected (soils and larch trees in the metallurgical area, stream sediments, lake sediments).

The Peisey-Nancroix Pb-Ag mine is located at 1500 m a.s.l. along the Ponturin River, in the northern French Alps (Fig. 2). Artisanal mining of the Pb-Ag ore was already reported in 1644. From 1734 to 1865, industrial operation occurred: 22 000 t of Pb and 53 t of Ag were extracted during that period. Until 1824, smelting occurred onsite. Several tons of waste rocks and slags have been left abandoned onsite at mine closure (Fig. 3). Since mine closure, grassland production for livestock feeding as well as leisure activities (treetop adventure courses, hiking, cross-country skiing) have become the main economic activities in the vicinity of the former mining site.

The Pb-Ag ore is hosted in Triassic sandstones. It is composed of galena, associated with pyrite, μ -scale As-rich tetrahedrite and bournonite, sphalerite

and rare chalcocopyrite. Quartz is the main gangue mineral. Slags are significantly enriched in trace metals (Table 1).

Table 1. Metal contents of the Peisey-Nancroix ore and slags (ppm or % if indicated).

	Pb	Zn	As	Cu	Sb
Ore	1.9%	114	37	87	137
Slags	2.26%	5276	22	143	452
Soil ref.	87	126	14	15	2
River sediment ref.	8	61	10	14	1.5
Lake sediment ref.	34	130	140	27	2

3 Soils from the mining site

120 topsoils samples (0-20 cm) were collected downhill the mining site (main entrance, ore processing and metallurgical installations) to provide evidence of the TMs spatial distribution (Fig. 3). Ca- and Si-rich cambisols have been identified on site. Technosols developed on abandoned slags. 5 soil profiles were sampled along the contamination gradient in order to better understand the vertical distribution of TMs. Geochemical analyses were performed on all samples. Soil properties (e.g. pH, CEC, carbon content) and mineralogical observations were performed on selected samples depending on their Pb content, and the types of soils.

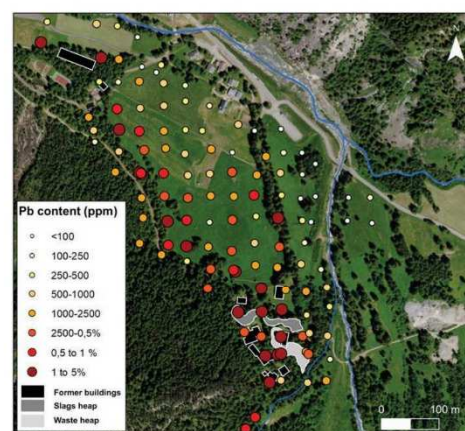


Figure 3. Pb content of topsoils from the Peisey-Nancroix mining site.

The spatial distribution of TMs content in topsoils indicates a clear anthropogenic contamination gradient from the mining site downwards (Fig. 3): Pb varies from 120 mg/kg to 3.4%, Sb from 1.5 to 630 mg/kg, As from 24 to 2269 mg/kg and Zn from 27 to 1578 mg/kg. Comparison of the soils TMs content with a reference sample allows enrichment factor and

Igeo index calculation and provide evidence of severe contamination in Pb between the smelting zone (south east) and the ore washing tank (northwest) only (Fig. 3).

Batch leaching tests were performed on selected samples along the contamination gradient. Pb appears to still be extractable and transferred more than 150 years after mine closure.

Mineralogical observations allowed identification of the Pb-bearing phases, which in turn allows discussing Pb mobility in soils. Detrital galena and slag fragments are only observed in the vicinity of the waste heaps. Further downward, Pb is essentially associated with Mn-Fe (hydr)-oxides suggesting leaching of the waste deposits, solute transportation and finally adsorption. Cerussite occurs as oxidation of galena and probably as secondary precipitation phase. Other Pb-bearing phases, such as pyromorphite, and Pb-associated with clays and organic matter have also been identified.

4 Lake sediments

The Peisey-Nancroix smelters emitted Pb-rich fumes, which were transported along prevailing wind currents. The sediments of La Plagne lake recorded the deposition of these atmospheric fluxes (Fig. 2 and 4). La Plagne Lake is located at 2,100 m a.s.l., 7 km uphill the Peisey-Nancroix mine, along the Ponturin valley.

Despite a globally low Pb content of lake sediments (Table 1), a clear Pb enrichment is observed during operation and smelting at the Peisey-Nancroix mining site (Fig.4). Isotopic data provide evidence of the metallurgical origin of this Pb and suggest its remobilization in recent times from the watershed due to soil erosion. Mineralogical observations suggest that Pb is essentially associated with infra μm -scale Mn-Fe (hydr)-oxides.

5 River sediments and water

17 stream sediments and 8 water samples were collected along the stream and drainage water system. In stream sediments, Pb varies from 12 to 2387 mg/kg, Sb varies from 2 to 8 mg/kg, As varies from 11 to 32 mg/kg and Zn varies from 82 to 216 mg/kg. In water, Pb varies from 0.06 to 7.27 $\mu\text{g/L}$, Sb varies from < L.D. to 1.59 $\mu\text{g/L}$, As varies from 0.19 to 3.53 $\mu\text{g/L}$ and Zn varies from 0.28 to 18.20 $\mu\text{g/L}$.

The highest metal contents are observed in dewatering waters and sediments. The Pb-content is rapidly diluted in stream waters due to the torrential stream dynamics.

6 Ecotoxicology

Microbial communities play an essential role in biogeochemical cycles and are sensitive to the health of the ecosystems. Microbial activities from soil

samples, stream sediments and lake sediments have been investigated to highlight the effects of trace metals contaminations on the communities functioning (enzymatic activities related to carbon, nitrogen and phosphate assimilation). High TMs content appear to have limited effects on most enzymatic activities for microbial communities hosted in soils and stream sediments.

The innovative Pollution-Induced Community Tolerance (PICT) experiments were performed to characterize the ecological state and the functional integrity of the compartment investigated by testing the communities' resistance and adaptation to TMs high level exposure. Results indicate that microbial communities of the most contaminated soils have developed the greatest tolerance to Pb.

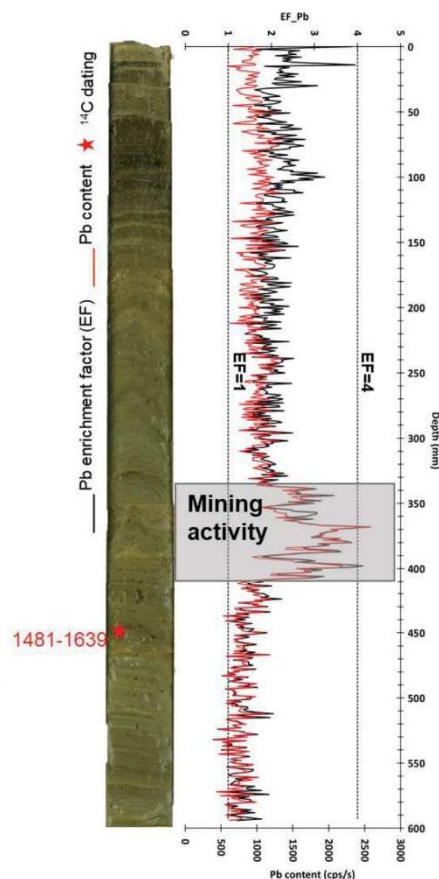


Figure 4. Reconstructed lake sediment core (the flood deposits have been removed) from the La Plagne Lake. The XRF Pb content is reported in red, and the calculated enrichment factor in black ($EF = (\text{Pb/Rb})_{\text{sample}} / (\text{Pb/Rb})_{\text{reference}}$).

7 Vegetation

An alley of larch trees was planted in the early 1800s along the main entrance of the mining site (Fig. 3). Tree cores were collected from recently cut tree stumps in order to investigate their recording of mining activity. Preliminary geochemical studies show variations in the Pb content in tree rings over time that can be correlated with the smelting and mining activities. Detailed investigations are being performed.

8 Conclusion

Our work demonstrates the persistence and remobilization of Pb in topsoils, stream and lake sediments more than 150 years after mine closure and its present-day impacts on soils microbial activity. A cross-disciplinary and integrated approach coupling biotic and abiotic proxies from various compartments of the critical zone was developed in order to better understand the long-term heritage of mining in the critical zone. Such knowledge is necessary to better anticipate the future environmental impacts of mining.

Acknowledgements

This work is supported by the French National Program EC2CO (Ecosphère Continentale et Côtière).

References

- Amaud F, Serralongue J, Winiarski T, Desmrt M, Paterne M (2006) Pollution au plomb dans la Savoie antique (II–IIIe s. apr. J.-C.) en relation avec une installation métallurgique de la cité de Vienne. *CR Geosci.* doi: 10.1016/j.crte.2005.11.008
- Brantley SL, Goldhaber MB, Ragnarsdottir KV (2007) Crossing Disciplines and Scales to Understand the Critical Zone. *Elements* 3:307–314
<https://doi.org/10.2113/gselements.3.5.307>
- Camizuli E, Rossi M, Gasquet D (2021) Trace metals dispersion from 1000 years of mining activity in the northern French Alps. *Extr. Ind. Soc.* doi: 10.1016/j.exis.2020.08.017
- Carvalho F, Schulte L (2020) Reconstruction of mining activities in the Western Alps during the past 2500 years from natural archives. *Sci Total Environ*
doi: 10.1016/j.scitotenv.2020.141208
- Dudka S, Adriano DC (1997) Environmental Impacts of Metal Ore Mining and Processing: a Review. *J Environ Qual*
doi: 10.2134/jeq1997.00472425002600030003x
- Ettler V (2016) Soil contamination near non-ferrous metal smelters: a review. *App Geochem*
doi: 10.1016/j.apgeochem.2015.09.020
- Gałaszka A, Mięgaszewski ZM, Dołęgowska S, Michalik A, Duczmal-Czernikiewicz A (2015) Geochemical background of potentially toxic trace elements in soils of the historic copper mining area: a case study from Miedzianka Mt., Holy Cross Mountains, south-central Poland. *Environ Earth Sci*
doi: 10.1007/s12665-015-4395-6
- Guyard H, Chapron E, St-Onge G, Anselmetti FS, Arnaud F, Magand O, Francus P, AntoinetteMélières M-A (2007) High-altitude varve records of abrupt environmental changes and mining activity over the last 4000 years in the Western

French Alps (Lake Bramant, Grandes Rousses Massif).
Quat Sci Rev doi: 10.1016/j.quascirev.2007.07.007

Financements

Cette thèse a été financée par une bourse doctorale du ministère de l'Enseignement supérieur et de la Recherche (allocation doctorale MESR). Les analyses ont pu être réalisées par l'obtention de financement des projets EC2CO (HERMIN) et MITI (HERMIN).

