



Suivi des métaux et métalloïdes dans les effluents de centres de stockage de déchets : Spéciation et devenir des composés de l'arsenic et de l'étain dans les lixiviats et les biogaz

Pauline Pinel-Raffaitin

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THESE

pour obtenir le grade de

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Pauline PINEL-RAFFAITIN

**Suivi des métaux et métalloïdes dans les effluents de centres de
stockage de déchets :
spéciation et devenir des composés de l'arsenic et de l'étain dans
les lixiviats et les biogaz**

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INTRODUCTION

Introduction

De nos jours, la gestion des déchets ménagers est au cœur des problématiques environnementales. La prise de conscience d'une meilleure évaluation des impacts environnementaux est d'autant plus importante que leur production a doublé dans les quarante dernières années. Ainsi la quantité de déchets ménagers produits par les Français dépasse aujourd'hui 1 kilogramme par personne et par jour. Malgré le développement du recyclage et des traitements biologiques, le stockage représente avec l'incinération encore plus de 80% du devenir de l'ensemble des déchets ménagers. Au niveau terminologique, le stockage a connu de nombreuses évolutions dans le temps. Anciennement appelé décharge puis centre d'enfouissement technique, le terme le plus usité actuellement est « installation de stockage de déchets non dangereux » ou « centre de stockage de déchets (CSD) ménagers et assimilés ». Dans cette nomenclature, il est important de préciser la nature des déchets stockés : les déchets ménagers et assimilés sont dans la catégorie de déchets non dangereux (classe II) et sont différenciés des déchets dangereux (classe I) et des déchets inertes (classe III).

Au cours de la dégradation des déchets stockés dans les CSD, deux effluents sont produits: les lixiviats et les biogaz. Le contact entre les effluents et l'écosystème environnant est en théorie évité grâce aux aménagements qui garantissent l'étanchéité des casiers contenant les déchets et grâce à la présence de drains qui permettent de collecter les effluents. Les risques de diffusion des biogaz à travers la couche de terre végétale et les risques de fuite de lixiviat au fond des casiers ne peuvent cependant pas être négligés. Le suivi de ces effluents est donc nécessaire afin de mieux maîtriser leur traitement et afin de prévenir les risques sanitaires et environnementaux.

Les métaux et métalloïdes représentent en poids humide 4% de la composition des déchets ménagers. Ils sont présents dans les emballages, les papiers, les matières plastiques, les produits manufacturés et les putrescibles. Ce stock d'éléments métalliques doit être pris en compte dans la gestion des CSD. En effet une fraction de ces métaux peut se retrouver dans les lixiviats et les biogaz. Les concentrations des métaux et métalloïdes dans ces effluents varient en fonction de la nature des déchets, du mode de gestion et des conditions climatiques. A ceci s'ajoute le fait que les éléments présentent une toxicité plus ou moins importante en fonction de la forme chimique sous laquelle l'élément est présent. Selon l'International Union of Pure and Applied Chemistry, la spéciation d'un élément est définie comme la distribution

de cet élément parmi différentes formes chimiques dans un système, sachant que les formes chimiques peuvent être différenciées selon la composition isotopique, l'état d'oxydation et leur présence sous forme de complexes ou de structure moléculaire. Parmi les métaux et métalloïdes présents dans les effluents de CSD, les études menées dans le cadre de ce travail ont été focalisées sur deux éléments : l'arsenic et l'étain. En effet, leur abondance dans les effluents, leur existence sous forme de nombreux composés, la toxicité avérée de certaines de leurs formes chimiques ainsi que les compétences spécifiques du laboratoire ont motivé l'étude approfondie de ces deux éléments.

Le projet, soutenu par l'Agence De l'Environnement et de la Maîtrise de l'Energie, s'appuie sur la collaboration avec deux CSD aquitains. De part leur différence de taille (30000 t/an et 150000 t/an), de déchets enfouis (déchets ultimes ou ordures ménagères brutes), de localisation géographique (Béarn et Gironde) et de gestion, ces deux CSD ont permis de prendre en compte la variabilité des effluents dans le suivi des métaux et métalloïdes. Du fait de sa proximité avec le laboratoire, le site béarnais a fait l'objet d'un suivi saisonnier. Complémentairement, du fait de sa taille et de sa gestion par casier, le site girondin a fait l'objet d'une étude plus globale sur l'impact de l'âge des déchets dans la composition des effluents. Aux échantillons de ces deux sites, s'est ajouté un lixiviat provenant d'un site d'Ile de France dont l'utilisation en tant que matériau de référence de laboratoire est le fruit de la collaboration avec l'Unité Hydrosystèmes et Bioprocédés du CEMAGREF (Institut de recherche pour l'ingénierie de l'agriculture et de l'environnement) d'Antony.

L'objectif de cette étude a été d'améliorer les connaissances au niveau des lixiviats et des biogaz en terme de composition en métaux et métalloïdes mais aussi d'appréhender les cycles des éléments en étudiant leurs devenir dans les différentes phases. En effet, les processus physico-chimiques qui interagissent au sein du système complexe constitué par les déchets, les lixiviats et les biogaz conditionnent la composition des effluents. De meilleures connaissances sur ces processus peuvent permettre de mieux adapter les traitements des effluents et de prédire le devenir du système à long terme.

Avant toute description des résultats, une synthèse bibliographique met en évidence les enjeux liés au suivi des métaux et des métalloïdes dans les effluents de CSD. Nous avons tout d'abord présenté le contexte lié à la gestion des effluents de centres de stockage des déchets

ménagers en France. Ensuite, un zoom sur l'arsenic et l'étain a été réalisé en prenant en compte leurs impacts possibles sur l'environnement liés à leur présence dans les CSD. Enfin, nous nous sommes focalisés sur les techniques analytiques de quantification des métaux et métalloïdes et plus particulièrement de l'arsenic et de l'étain aussi bien en analyse élémentaire qu'en analyse de spéciation dans les matrices complexes telles que les lixiviats et les biogaz.

Les résultats obtenus lors de cette thèse sont présentés dans ce mémoire sous forme de publications. L'étude s'articule en trois parties.

La première partie porte sur l'évaluation des stratégies analytiques dans le but d'accéder à la contamination des lixiviats. Pour cela, les étapes critiques du protocole de préparation et d'analyse des échantillons sont testées afin de mettre en évidence les précautions nécessaires pour une détermination significative des concentrations en métaux et métalloïdes dans les lixiviats.

La deuxième partie est consacrée à l'étude de l'arsenic et de ces composés dans le système déchets - lixiviats - biogaz. Les premiers efforts ont porté sur le développement d'une méthode d'analyse de spéciation de l'arsenic dans les lixiviats. Dans un second temps, c'est l'évolution et le devenir de ces composés ainsi que leurs homologues présents en phase gazeuse qui a retenu notre attention.

L'analyse des composés organostanniques constitue le troisième volet de ce mémoire avec tout d'abord une partie consacrée à la mise en place d'une méthode d'analyse de spéciation spécifiquement adaptée aux lixiviats. Enfin, la dernière partie s'intéresse de manière plus globale à la réactivité des composés organostanniques dans le système complexe que constituent les lixiviats et les biogaz.

PROBLEMATIQUES SCIENTIFIQUES

I. Problématiques scientifiques

I.1. Les centres de stockage de déchets ménagers et assimilés

I.1.1 Problématique liée aux centres de stockage de déchets ménagers et assimilés

I.1.1.1 Quelques chiffres clés

L'article premier de la loi du 15 juillet 1975 (n°75-633, J.O. du 16 juillet 1975) définit un déchet comme « tout résidu d'un processus de production, de transformation ou d'utilisation, toute substance, matériau, produit ou plus généralement bien meuble abandonné ou que son détenteur destine à l'abandon ».

La mise en centre de stockage constitue en France le mode de gestion dominant d'élimination des déchets ménagers et assimilés. Ainsi, en 2004, 47% de ces déchets ménagers et assimilés ont été stockés dans des centres de stockage (CSD) (Figure I.1.1). Ce mode de gestion apparaît comme l'option la plus économique tout en permettant à la plupart des ordures ménagères d'être décomposées en matériaux relativement inertes et stabilisés.

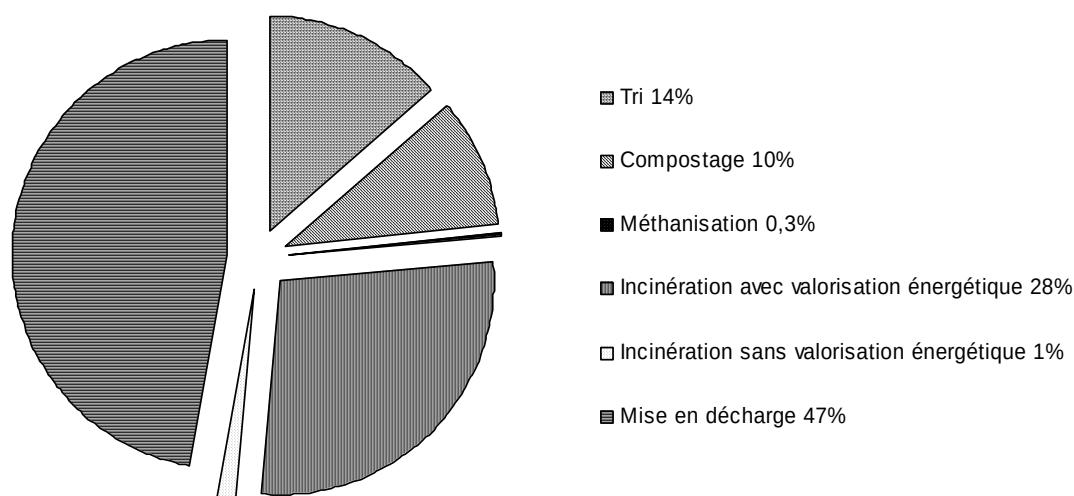


Figure I.1.1 Répartition par mode de traitement des tonnages traités en 2004 [1]

Les installations de stockage pour déchets ménagers et assimilés accueillent essentiellement les ordures ménagères (OM) et les déchets industriels banals (DIB). Les OM représentent 42% de la totalité des déchets pris en charge dans les CSD. Les autres flux qui alimentent les CSD sont les refus de tri et de compostage ainsi que les résidus de méthanisation et les mâchefers d'incinération, comme l'illustre la Figure I.1.2.

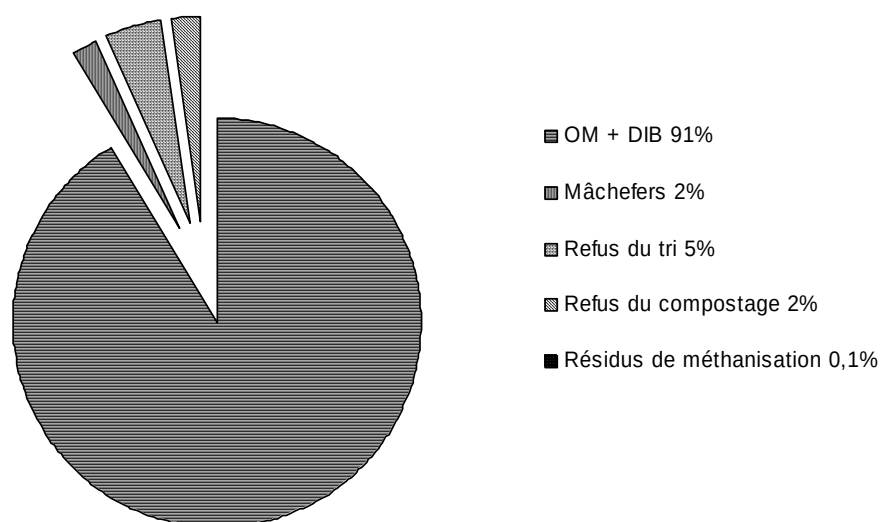


Figure I.1.2 Provenance des déchets entrants dans les CSD [1]

Malgré la mise en place du tri sélectif et du recyclage des déchets, encore près de 30% de déchets putrescibles et un tiers de poids des ordures ménagères proviennent des emballages. Le Tableau I.1.1 donne la répartition des déchets en fonction des différentes catégories issue d'une enquête de l'ADEME réalisée en 1993 [2].

Tableau I.1.1 Composition des OM en France [2]

Types de déchets	% du poids humide
Déchets putrescibles	29
Papiers / cartons	25
Verre	13
Plastiques	11
Métaux	4
Textiles	3
Autres*	15

*Textiles, combustibles et incombustibles divers, matériaux complexes, déchets dangereux des ménages

La production totale d'ordures ménagères en France en 2004 est de 21 millions de tonnes. Cela correspond à environ 1.2 kg / habitant / jour. En ce qui concerne les CSD d'une capacité supérieure à 3000t/an, les 361 sites français ont reçu, en 2004, 22 millions de tonnes de déchets sur les 47 millions de tonnes de déchets ménagers et assimilés entrant dans des unités de traitement. Sur le reste des déchets, 13 millions de tonnes ont été incinérées, 4.6 millions de tonnes traitées biologiquement et 6.3 millions de tonnes ont été recyclés.

I.1.1.2 Dégradation des déchets dans les CSD

I.1.1.2.1 Présentation d'un centre de stockage de déchets

Un centre de stockage de déchets constitue un réacteur complexe avec des flux de solides, de liquides et de gaz. Les déchets, les lixiviats et les biogaz constituent les trois compartiments du système. Ils sont indissociables et interagissent tout au long de la dégradation des déchets. La Figure I.1.3 représente schématiquement un centre de stockage de déchets.

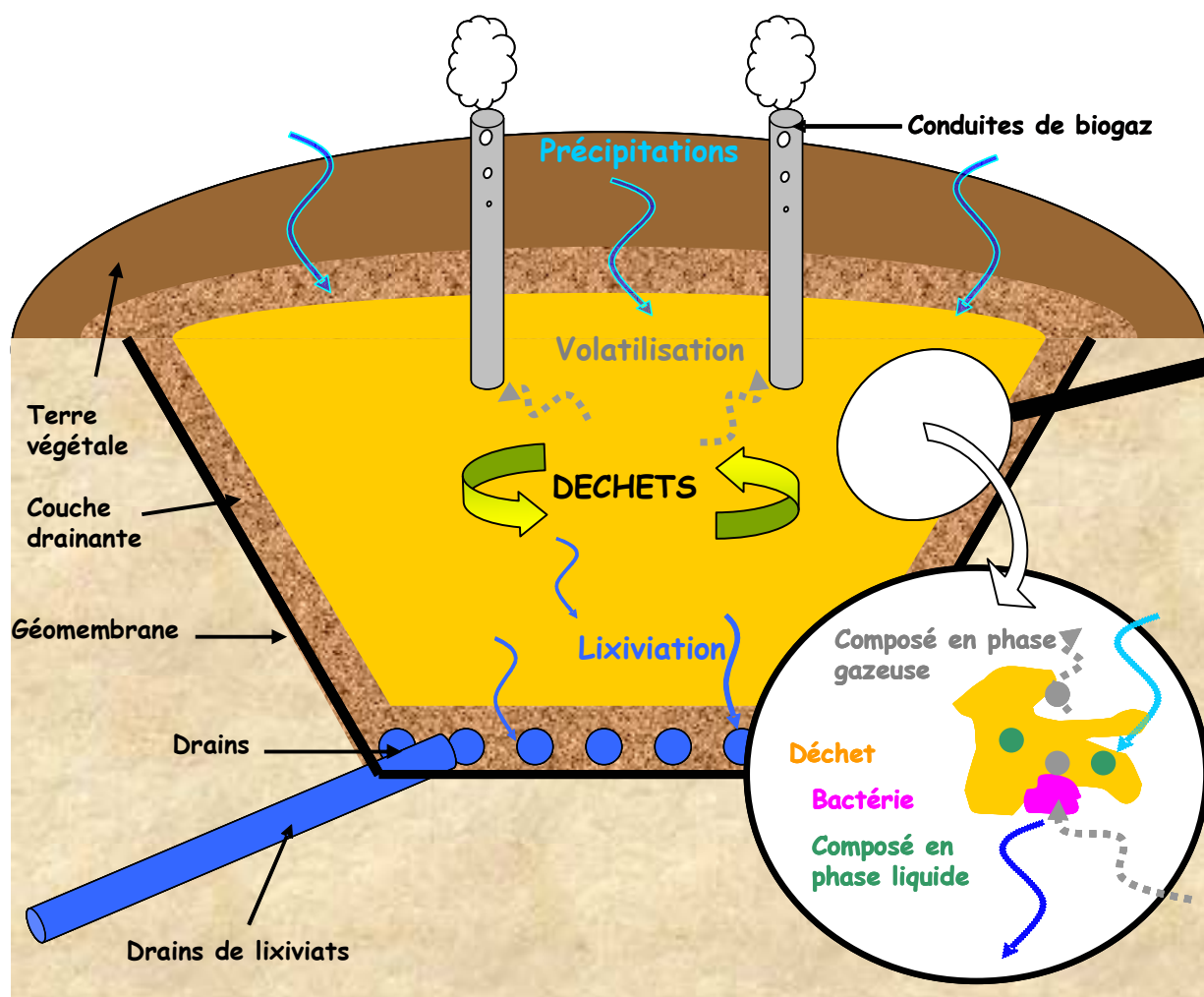


Figure I.1.3 Schéma de principe d'un centre de stockage de déchets

Ce schéma donne une représentation schématique d'un CSD comme un système régi par des phénomènes qui permettent de caractériser l'évolution globale d'une installation de stockage de déchets :

- les matières biodégradables subissent une évolution biologique sous l'action des bactéries aérobies et anaérobies ;

-l'eau qui s'écoule à travers la masse de déchets produit des lixiviats en se chargeant de substances chimiques ou biologiques ;

-la combinaison des contraintes physiques et chimiques conduit à la destruction partielle de la matière et à la solubilisation de certaines espèces ou à leur transformation en gaz ;

-l'hétérogénéité des déchets stockés et des sols environnants peut entraîner des tassements au niveau des alvéoles et des casiers qui modifient les caractéristiques mécaniques et géotechniques.

I.1.1.2.2 *Processus physico-chimiques*

La dégradation des déchets est dépendante de nombreux paramètres comme l'humidité, la température, le pH, le potentiel d'oxydo-réduction, la présence de différentes populations bactériennes, la présence d'inhibiteurs. Elle est caractérisée par trois grandes étapes qui sont représentées schématiquement dans la Figure I.1.4. Ces trois phases sont indissociables et forment un tout appelé fermentation méthanique.

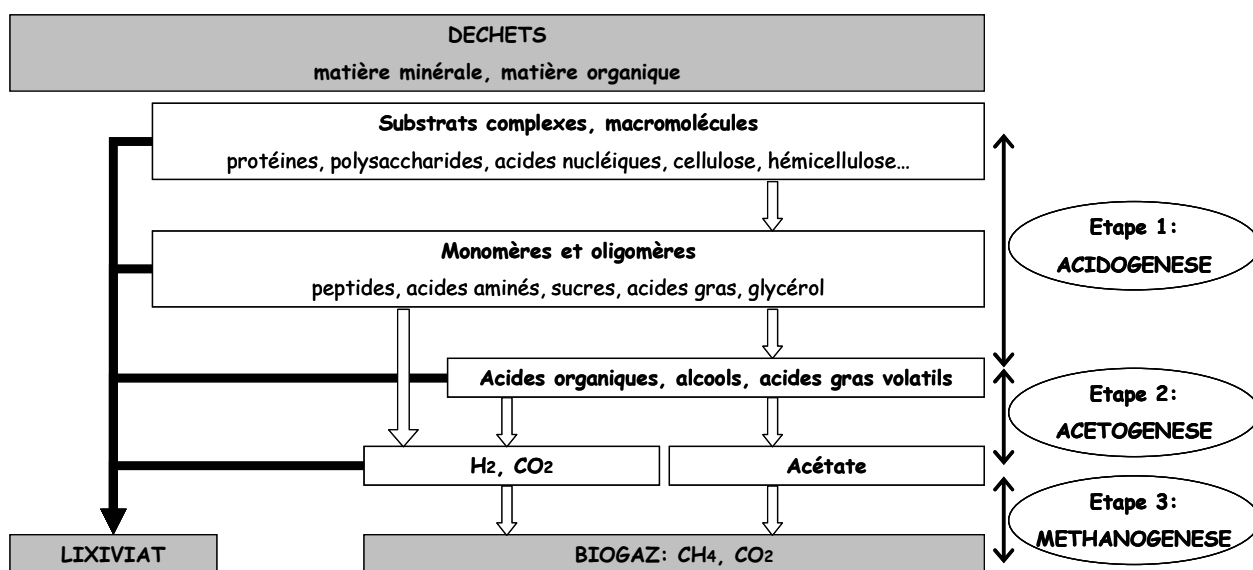


Figure I.1.4 Les étapes de la dégradation des déchets d'après Poulleau[3]

La première phase de la décomposition anaérobie des déchets est une fermentation acide. Lors de celle-ci, les matières organiques complexes sont hydrolysées en acides carboxyliques, acides aminés, alcools et acides gras. L'acidité du milieu favorise la solubilisation des métaux dans les lixiviats.

Lors de la deuxième étape ce sont des bactéries acétogènes qui se développent dans le milieu anaérobie, riche en dioxyde de carbone. Elles transforment les divers composés en précurseurs directs du méthane : dioxyde de carbone, dihydrogène et acétate.

La dernière phase du processus de décomposition est la méthanogénèse : les bactéries méthanogènes qui sont strictement anaérobies et qui se développent dans des milieux réducteurs digèrent les précurseurs pour former du méthane, du dioxyde de carbone et de l'eau.

La composition des effluents est très intimement liée avec ces processus et elle est donc spécifique à chaque système. Il apparaît intéressant d'évaluer si, malgré les différences apparentes certains mécanismes de dégradation se reproduisent dans différents sites et si les composés résultants se retrouvent d'un site à l'autre ou bien sont spécifiques à chaque CSD.

I.1.2 Réglementation

En 25 ans, la quantité de déchets ménagers a triplé. Cette augmentation a été accompagnée par une série d'arrêtés visant à développer une meilleure gestion des ordures ménagères.

Chaque centre de stockage des déchets est régi par un arrêté préfectoral. Celui-ci est spécifique au site et détermine notamment les déchets acceptés et les divers modes de fonctionnement.

I.1.2.1 Réglementation relative aux sites de stockage

I.1.2.1.1 Loi du 15 juillet 1975 (n°75-633, J.O. du 16 juillet 1975)

La loi du 15 juillet 1975 est relative à l'élimination des déchets et à la récupération des matériaux. Elle définit la notion de déchets et précise les responsabilités et les obligations des producteurs de déchets, ainsi que les sanctions qui peuvent leur être appliquées. Elle impose aux communes ou groupements de communes d'assurer la collecte et le traitement des déchets des ménages.

Par ailleurs, cette loi stipule la mise en place de plans départementaux (décret du 18 novembre 1996). Ces plans ont pour objet de coordonner les actions à mener tant par les pouvoirs publics que par les organismes privés afin d'assurer la gestion des déchets ménagers et assimilés. Ils fixent les orientations spécifiques au département en matière de tri, de recyclage, de collecte et de traitement. Les plans départementaux doivent, de plus, faire une énumération des installations et des quantités de déchets.

I.1.2.1.2 *Loi du 13 juillet 1992 (n°92-646, J.O. du 14 juillet 1992)*

Elle limite l'enfouissement aux seuls déchets ultimes à partir du 1er juillet 2002. Cette loi est précisée par une circulaire d'avril 1998. Selon le code de l'environnement, le déchet dit ultime est : « un déchet résultant ou non du traitement d'un déchet, qui n'est plus susceptible d'être traité dans les conditions techniques et économiques du moment, notamment par extraction de la part valorisable ou par réduction de son caractère polluant ou dangereux. »

I.1.2.1.3 *Arrêté du 9 septembre 1997 (J.O. du 2 octobre 1997)*

Il est relatif aux nouvelles installations de stockage de déchets ménagers et assimilés et à leur mise en conformité. Ce texte définit les prescriptions minimales à respecter : le confinement, l'isolement du site, la collecte et le traitement des effluents, la prévention des risques et les responsabilités, la surveillance des sites (pendant une période d'au moins trente ans). De plus, cet arrêté demande un effort d'intégration paysagère.

I.1.2.2 Réglementation relative aux lixiviats

Le Tableau I.1.2 présente les critères minimaux applicables aux rejets d'effluents liquides dans le milieu naturel (arrêté du 9 septembre 1997 modifié par l'arrêté du 31/12/01).

Tableau I.1.2 Valeurs limites appliquées aux rejets d'effluents liquides dans le milieu naturel

Critère	Valeur limite	
Matières en suspension totale	< 100 mg L ⁻¹	(si flux journalier max < 15kg)
	< 35 mg L ⁻¹	(si flux journalier max > 15kg)
Carbone organique total	< 70 mg L ⁻¹	
Demande chimique en oxygène	< 300 mg L ⁻¹	(si flux journalier max < 100kg)
	< 125 mg L ⁻¹	(si flux journalier max > 100kg)
Demande biologique en oxygène	< 100 mg L ⁻¹	(si flux journalier max < 30kg)
	< 30 mg L ⁻¹	(si flux journalier max > 30kg)
Azote total	< 30 mg L ⁻¹	(concentration moyenne mensuelle, si flux journalier max > 50kg)
Phosphore total	< 10 mg L ⁻¹	(concentration moyenne mensuelle, si flux journalier max > 15kg)
Phénols	< 0.1 mg L ⁻¹	(si le rejet journalier > 1g)
Métaux totaux (Pb, Cu, Cr, Ni, Zn, Mn, Sn, Cd, Hg, Fe, Al)	< 15 mg L ⁻¹	
Cr (VI)	< 0.1 mg L ⁻¹	(si le rejet journalier > 1g)

Cd	$< 0.2 \text{ mg L}^{-1}$	
Pb	$< 0.5 \text{ mg L}^{-1}$	(si le rejet journalier $> 5\text{g}$)
Hg	$< 0.05 \text{ mg L}^{-1}$	
As	$< 0.1 \text{ mg L}^{-1}$	
Fluor	$< 15 \text{ mg L}^{-1}$	(si le rejet journalier $> 150\text{g}$)
Cyanures libres	$< 0.1 \text{ mg L}^{-1}$	(si le rejet journalier $> 1\text{g}$)
Hydrocarbures totaux	$< 10 \text{ mg L}^{-1}$	(si le rejet journalier $> 100\text{g}$)
Composés organiques halogénés	$< 1 \text{ mg L}^{-1}$	(si le rejet journalier $> 30\text{g}$)

Les lixiviats ne peuvent être rejetés dans le milieu naturel que s'ils respectent les valeurs présentées dans le Tableau I.1.2. La dilution et l'épandage (sauf cas particulier) des lixiviats sont interdits.

I.1.2.3 Réglementation relative aux biogaz

D'après l'arrêté du 9 septembre 1997 modifié par l'arrêté du 31/12/01, l'exploitant doit analyser périodiquement le biogaz capté dans son installation ; il se doit de déterminer la teneur en CH_4 , CO_2 , O_2 , H_2S , H_2 , et H_2O .

En cas de destruction par combustion, les gaz doivent être portés à une température minimale de 900°C pendant une durée supérieure à 0.3 seconde. La température doit être mesurée en continu. Par ailleurs, les émissions de SO_2 , CO , HCl et HF issues des dispositifs de combustion doivent être analysées une fois par an par un organisme extérieur. La teneur limite en CO devra être inférieure à 150mg m^{-3} .

I.1.3 Caractérisation des lixiviats de CSD

I.1.3.1 Formation des lixiviats

Les précipitations, l'eau apportée par les déchets et les eaux de ruissellement favorisent la transformation bio-physico-chimique des déchets. C'est la décomposition des déchets conjuguée avec l'action de l'eau de pluie qui produit un lixiviat. Tout au long de la percolation, ce liquide se charge en substances organiques et minérales. Sa composition dépend de nombreux facteurs: la composition des déchets, le bilan hydrique, le mode d'exploitation de la décharge, les conditions climatiques, l'épaisseur de la couche de déchets, la nature de la couverture, l'âge de la décharge [4] [5]. Il en résulte qu'un lixiviat peut être variable d'une décharge à l'autre mais aussi au sein même d'une décharge.

La production de lixiviats est reconnue aujourd'hui comme un des problèmes environnementaux majeurs dans la mesure où ces liquides sont susceptibles de polluer les sols, les eaux de surface et les eaux souterraines. La collecte des lixiviats commence dès le début du stockage des déchets dans un casier. Le niveau de lixiviat dans les casiers ne doit pas excéder 50cm (arrêté du 09/09/1997, J.O. du 2 octobre 1997). Après la collecte, l'exploitant est tenu de traiter ces lixiviats sur site, selon les directives fixées par l'arrêté préfectoral qui définit l'activité de chaque CSD. Les installations de traitement sont généralement les mêmes que celles utilisées dans les stations d'épuration des eaux usées (traitement physico-chimique et traitement biologique).

I.1.3.2 Composition métallique et organométallique des lixiviats

Les lixiviats issus des centres de stockage de déchets constituent des matrices complexes composées de matière organique et de matière minérale, dissoute et/ou colloïdale. Les métaux et les métalloïdes font l'objet d'un suivi dans les centres de stockages de déchets du monde entier. Ils ne sont pas souvent au centre même des études réalisées sur les lixiviats mais sont régulièrement indiqués par les auteurs. Le Tableau I.1.3 donne un aperçu des larges gammes de concentrations en métaux mesurées dans les lixiviats.

Tableau I.1.3 Composition des lixiviats de divers CSD

Paramètre	Concentrations en mg L ⁻¹ (sauf pour pH)	Référence
pH	5.7-8.5	[4, 7-14]
Fe	0.3-250	
Zn	0.080-5.6	
Mg	5-443	[4, 7-10, 12, 14]
Ca	5-3324	
Cu	0.002-6.0	[7-12, 14]
Ni	0.01-7.8	
Pb	0.002-2.1	
Cd	0.02-6.5	[8-12, 14]
Mn	0.02-38	
Cr	0.005-3.7	[8-14]
Al	0.1-4.5	[7, 8, 10]
Cl ⁻	260-16700	[4, 8-11, 14]

Afin d'illustrer la diversité de la matrice lixiviat elle-même, deux paramètres sont ajoutés aux métaux. Le pH est un paramètre très important car il est un indicateur de la phase de dégradation des déchets et il fixe ainsi les caractéristiques globales de la matrice. Les chlorures indiquent quant à eux la charge minérale du lixiviat et sont généralement considérés comme un paramètre conservatif dans les études hydrologiques [6].

Pour certains éléments tels que l'antimoine ou l'étain il n'y a pas de données dans la littérature. Dans les données compilées par Baun et Christensen, la gamme de concentrations donnée pour l'arsenic varie entre 0.5 et 130 $\mu\text{g L}^{-1}$ [15]. Le Tableau I.1.3 donne un aperçu de la grande variabilité des éléments selon les sites et leurs caractéristiques : les gammes de concentration varient de un ordre de grandeur (pour Al) à trois ordres de grandeur (pour Fe, Cu, Pb et Mn). Une attention toute particulière doit donc être portée aux protocoles analytiques qui permettent de quantifier les teneurs élémentaires en métaux et métalloïdes afin qu'ils soient efficaces en terme de simplification de la matrice et robustes pour s'adapter aux différences de concentration.

Par ailleurs, afin de mieux connaître les lixiviats et leurs impacts environnementaux, l'analyse de spéciation des espèces métalliques permet de compléter les données d'analyse élémentaire. En ce qui concerne les lixiviats, il n'existe à notre connaissance qu'une seule étude portant sur les organoétains. Mersiowsky *et al.* ont détectés des espèces méthylées, butylées et octylées d'étain dans des concentrations de l'ordre du $\mu\text{g L}^{-1}$ dans des lixiviats provenant de plusieurs CSD européens [16].

I.1.4 Caractérisation des biogaz de CSD

I.1.4.1 Formation des biogaz

Les gaz de décharge, appelés biogaz, sont issus de la fermentation anaérobie de la matière organique contenue dans les déchets. Les deux composés majoritaires du biogaz sont le méthane et le dioxyde de carbone, formés lors de la dernière étape de décomposition des déchets. Les composés minoritaires sont l'azote, l'eau, le monoxyde de carbone et l'hydrogène. Les composés à l'état de traces sont les composés organiques volatils, les composés halogénés, les composés soufrés ainsi que les composés métalliques et organométalliques (métaux et métalloïdes).

L'extraction du biogaz dans le CSD est généralement réalisée par le biais d'un réseau de canalisations raccordées à des drains qui permettent son acheminement soit vers des torchères, soit vers des unités de valorisation comme des chaudières ou des groupes électrogènes.

I.1.4.2 Composition métallique et organométallique des biogaz

L'analyse élémentaire des métaux et métalloïdes fait l'objet de très peu de travaux dans les biogaz issus de CSD. En ce qui concerne l'analyse de spéciation, un plus grand nombre de données sont disponibles du fait notamment du travail de l'équipe de recherche de l'université de Duisburg-Essen en Allemagne [17].

I.1.4.2.1 Analyse élémentaire

A titre de comparaison, le Tableau I.1.4 présente les teneurs pour différents éléments métalliques dans des gaz issus de CSD et les concentrations moyennes mondiales dans des zones polluées ou non. Les valeurs proposées par Reimann and Caritat permettent de définir un référentiel et de mesurer l'importance du traitement des biogaz par torchère afin de minimiser les émissions de composés métalliques. En effet, pour certains éléments comme As, Sn et Sb les concentrations mesurées dans les biogaz sont de 10 à 1000 fois supérieures à celles mesurées dans les zones polluées référencées [18].

Tableau I.1.4 Concentrations élémentaires des métaux et métalloïdes dans différentes atmosphères

Elément	Concentration (ng m ⁻³)				
	Zones non polluées	Zones polluées	Gaz de CSD		
	[18]	[18]	[19] [20] [21]	[3]	[22]
As	0.007-2.3	1.5-190	Pas de données	16200	16000-50000
Se	0.006-1.4	0.09-30	Pas de données	<3100	3-4
Sn	Pas de données	1.5-800	Pas de données	<600	8600-35000
Sb	0.0005-0.93	0.08-55	Pas de données	30500	24000-72000
Te	Pas de données	Pas de données	Pas de données	600	50-75
Hg	0.01-0.06	0.09-38	~ 1000	<1600	50-130
Pb	0.03-21	45-13000	Pas de données	4400	13-33
Bi	Pas de données	Pas de données	Pas de données	Pas de données	310-900
Cr	0.005-0.7	1-300	Pas de données	41300	Pas de données

I.1.4.2.2 Analyse de spéciation

En ce qui concerne les analyses de spéciation, plusieurs études permettent d'avoir une vision large des composés organométalliques volatils qui peuvent être présents dans les biogaz. Dans le Tableau I.1.5, les données sont exprimées en ordre de grandeur car seule une semi-quantification est possible compte tenu du manque d'étalons volatils commercialement disponibles.

Tableau I.1.5 Espèces identifiées et quantifiées dans des gaz de CSD

Elément	Espèce	Ordre de grandeur	Référence
Sn	SnH_4 , $\text{Sn}(\text{CH}_3)_4$, $\text{Sn}(\text{C}_4\text{H}_9)_3$, $\text{Sn}(\text{C}_4\text{H}_9)_2\text{H}_2$	$\mu\text{g m}^{-3}$	[17]
Pb	$\text{Pb}(\text{CH}_3)_4$, $\text{Pb}(\text{C}_2\text{H}_5)_4$	ng m^{-3}	
As	AsH_3 , $\text{As}(\text{CH}_3)_3$, $\text{As}(\text{C}_2\text{H}_5)_3$, $\text{As}(\text{CH}_3)_2\text{H}$, $\text{As}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$	$\mu\text{g m}^{-3}$	
Sb	$\text{Sb}(\text{CH}_3)_3$, SbH_3	$\mu\text{g m}^{-3}$	
Te	$\text{Te}(\text{CH}_3)_2$	ng m^{-3}	
Bi	$\text{Bi}(\text{CH}_3)_3$	$\mu\text{g m}^{-3}$	
Se		ng m^{-3}	
Hg	$\text{Hg}(\text{CH}_3)_2$	ng m^{-3}	[17, 20]
Mo	$\text{Mo}(\text{CO})_6$	mg m^{-3}	[23]
W	$\text{W}(\text{CO})_6$	$\mu\text{g m}^{-3}$	

Plus précisément l'étain a fait récemment l'objet d'une étude au cours de laquelle de nouvelles espèces ont été détectées, identifiées et quantifiées, parmi lesquelles les espèces propylées et éthylées (Tableau I.1.6).

Tableau I.1.6 Espèces d'étain identifiées et quantifiées dans biogaz par Mitra et al. [24]

Espèces	Concentrations ($\mu\text{g Sn m}^{-3}$)
$(\text{CH}_3)_4\text{Sn}$	12 – 1050
$(\text{C}_4\text{H}_9)\text{SnH}_3$	nd - 0.06
$(\text{C}_2\text{H}_5)\text{Sn}(\text{CH}_3)_3$	0.9 – 55
i- $(\text{C}_3\text{H}_7)\text{Sn}(\text{CH}_3)_3$	0.06 – 0.5
n- $(\text{C}_3\text{H}_7)\text{Sn}(\text{CH}_3)_3$	0.2 – 120
$(\text{C}_2\text{H}_5)_2(\text{CH}_3)_2\text{Sn}$	0.2 – 13
$(\text{C}_4\text{H}_9)\text{Sn}(\text{CH}_3)_3$	0.06 – 0.3
$(\text{C}_2\text{H}_5)_3\text{Sn}(\text{CH}_3)$	0.08 - 20

Pour conclure sur les biogaz, peu de travaux portent sur l'analyse des métaux et métalloïdes, que ce soit en analyse élémentaire ou en analyse de spéciation. D'un point de vue environnemental, il semble que de nombreux éléments sont susceptibles d'être présent dans les biogaz et notamment sous forme de composés méthylés qui peuvent être issus de processus liés à l'activité biologique (biométhylation).

I.2. Arsenic et étain : toxicité et impacts environnementaux engendrés par leur présence dans les effluents de CSD

L'arsenic et l'étain font l'objet de très nombreuses études dans les différents compartiments de la géosphère (atmosphère, eaux, sols, biosphère). Les sources et les mécanismes à l'origine de la présence de leurs espèces chimiques dans les différents milieux sont très documentés. Dans cette partie, nous nous proposons de rappeler brièvement les principales formes chimiques de ces deux éléments et leurs sources potentielles dans les déchets et les effluents de CSD. L'objectif est d'apporter des informations générales quant à leur toxicité et leurs possibles impacts environnementaux sur les milieux aquatiques et l'atmosphère.

I.2.1 Présence de l'arsenic

I.2.1.1 Milieux aquatiques terrestres

I.2.1.1.1 Formes chimiques

L'arsenic est un métalloïde présent majoritairement sous deux degrés d'oxydation : +III et +V. Les principales espèces sont exposées dans le Tableau I.2.1. Elles sont caractérisées par de très grandes différences de toxicité.

Tableau I.2.1 Espèces d'arsenic et leur toxicité

Espèce	Nature chimique	Notation	DL ₅₀ (souris) en mg(As) kg ⁻¹ [25, 26]
Acide arsénieux	AsOOH	AsIII	8
Acide arsénique	AsO(OH) ₃	AsV	22
Acide monométhylarsonique	AsO(OH) ₂ (CH ₃)	MMA	916
Acide diméthylarsinique	As ⁺ (OH) ₂ (CH ₃) ₂	DMA	648
Ion tétraméthylarsonium	As ⁺ (CH ₃) ₄	TMAAs ⁺	580
Oxyde de triméthylarsine	As ⁺ (CH ₃) ₃ OH	TMAO	5500
Arsénobétaine	As ⁺ (CH ₃) ₃ CH ₂ COOH	AsB	>4260
Arsénocholine	As ⁺ (CH ₃) ₃ CH ₂ CH ₂ OH	AsC	6540

En ce qui concerne les milieux aquatiques, les espèces majoritairement détectées sont les espèces inorganiques (AsIII et AsV) avec une répartition différente selon les conditions redox, le pH, la présence d'activité biologique. Les espèces mono- et diméthylées (MMA et DMA) sont plus rarement présentes dans les échantillons d'eaux de rivière et d'eaux souterraines

[30-32]. Les eaux usées, dont la matrice est plus proche de celle des lixiviats, ont fait l'objet de quelques études dans lesquelles seules les espèces inorganiques sont détectées [33, 34].

I.2.1.1.2 Sources

L'utilisation anthropique de l'arsenic est répandue dans le domaine agricole en tant que pesticide et agent de protection du bois, dans le domaine de la fabrication du verre, dans le domaine des semi-conducteurs, mais aussi dans le domaine médical [28, 29]. Ces applications peuvent générer directement des émissions d'arsenic dans les milieux aquatiques ou indirectement comme dans les CSD où l'arsenic peut être mobilisé durant la dégradation des produits manufacturés qui contiennent de l'arsenic (verres, emballages de produits agricoles, objets métalliques).

L'arsenic est naturellement présent dans les eaux. Cependant, les concentrations sont très variables du fait de la nature du milieu et de l'activité humaine. Dans les eaux souterraines, les concentrations en arsenic varient généralement entre 0.01 et 10 $\mu\text{g L}^{-1}$ [18, 27]. Dans les eaux douces de surface, les concentrations moyennes varient entre 1 et 10 $\mu\text{g L}^{-1}$ pour des zones non polluées et jusqu'à 100-5000 $\mu\text{g L}^{-1}$ dans des zones d'exploitation minière et/ou naturellement riches en arsenic [27, 28]. Le facteur d'émission global de l'arsenic lié aux lixiviats de CSD n'est pas référencé, par contre pour les eaux usées il est compris entre 0.02 et 0.1 ng (As) L^{-1} d'eaux usées [35].

I.2.1.2 Atmosphère

I.2.1.2.1 Formes chimiques

La présence de l'arsenic dans l'atmosphère revêt deux formes. Il est majoritairement adsorbé sur des particules sous forme inorganique (AsIII, AsV) [28] mais il peut être directement en phase gazeuse. Sous forme gazeuse, les espèces majoritaires sont l'arsine (AsH_3) et la triméthylarsine ($\text{As}(\text{CH}_3)_3$). Le suivi de ces espèces volatiles d'arsenic est justifié par leur toxicité variable : elle (DL_{50}) varie de 20000 mg L^{-1} pour la triméthylarsine à 5-45 mg L^{-1} pour l'arsine [36]. Du fait de leur toxicité, de nombreuses études se sont intéressées aux mécanismes de formation des espèces volatiles par voie microbienne [36, 38-41]. Les processus de production de ces composés sont attribués à la biométhylation qui se traduit par la substitution successive des groupements hydroxydes ou des hydrogènes par des groupements méthyls, comme le montre la Figure I.2.1

		Inorganic compounds	Methylated compounds		
			1 CH ₃	2 CH ₃	3 CH ₃
gaseous	hydrogen	As ₂ H ₄ (b.p. 100°C), AsH ₃ (b.p. -62.5°C)	CH ₃ AsH ₂ (b.p. -2°C)	(CH ₃) ₂ AsH (b.p. 36°C)	(CH ₃) ₃ As (b.p. 52°C)
aqueous	As(III)	H ₃ AsO ₃	CH ₃ As(OH) ₂	(CH ₃) ₂ AsOH	
	As(V)	H ₃ AsO ₄	CH ₃ AsO(OH) ₂	(CH ₃) ₂ AsOOH	(CH ₃) ₃ AsO

Figure I.2.1 Mécanismes de formation par biométhylation des espèces volatiles d'arsenic à partir de celles en phase aqueuse d'après Planer-Friedrich et al. [36]

I.2.1.2.2 Sources

Les sources naturelles d'arsenic atmosphérique ne sont pas très bien identifiées (activité volcanique, érosion, volatilisation...) et contribuent très minoritairement au bilan de l'arsenic atmosphérique en comparaison avec les sources anthropiques comme la métallurgie ou la transformation d'énergie [37].

Les concentrations moyennes en As dans l'air varient entre 0.007 ng m⁻³ et 2.3 ng m⁻³ dans les zones non polluées et de 1.5 ng m⁻³ à 190 ng m⁻³ dans les zones polluées (Tableau I.1.4) [18]. Il n'y a pas de données concernant les émissions atmosphériques d'arsenic liées à la gestion des déchets ménagers dans les CSD, par contre en ce qui concerne l'incinération des déchets, le facteur d'émission de l'arsenic (inorganique) est estimé à 1.1 g t⁻¹ de déchets incinérés [42].

I.2.2 Présence de l'étain

I.2.2.1 Milieux aquatiques terrestres

I.2.2.1.1 Formes chimiques

La forme oxydée de l'étain (+IV) est très largement majoritaire en phase aqueuse par rapport à la forme réduite (+II). Contrairement aux formes inorganiques, qui sont non toxiques, les composés organostanniques sont très toxiques ce qui justifie leur étude. Dans le Tableau I.2.2 sont présentées les espèces alkylées d'étain d'intérêt et leur toxicité. Celle-ci dépend à la fois de la nature des groupements alkyls et du degré de substitution de l'atome d'étain. Ainsi, plus le degré de substitution augmente, plus la toxicité est avérée.

Tableau I.2.2 Espèces d'étain et leur toxicité [43]

Espèce	Nature chimique (X=OH, Cl ...)	Notation	DL ₅₀ (rats) en mg (Sn) kg ⁻¹	
Etain inorganique	SnX ₄	ISn		
Monométhylétain	Sn(CH ₃)X ₃	MMT	1370	X=Cl
Diméthylétain	Sn(CH ₃) ₂ X ₂	DMT	74	X=Cl
Triméthylétain	Sn(CH ₃) ₃ X	TMT	13	X=Cl
			9	X=OAc
Monoéthylétain	Sn(C ₂ H ₅)X ₃	MET	Pas de données	
Diéthylétain	Sn(C ₂ H ₅) ₂ X ₂	DET	Pas de données	
Triéthylétain	Sn(C ₂ H ₅) ₃ X	TET	4	X=OAc
Monobutylétain	Sn(C ₄ H ₉)X ₃	MBT	2140	X=Cl
Dibutylétain	Sn(C ₄ H ₉) ₂ X ₂	DBT	100	X=Cl
Tributylétain	Sn(C ₄ H ₉) ₃ X	TBT	380	X=OAc

La plupart des travaux sur l'analyse de spéciation des organoétains traite des butylétains. Dans les eaux usées, l'occurrence des espèces butylées [52, 53] ainsi que celle des espèces méthylées [45] est avérée. A ce jour, la seule étude sur les lixiviats [16] a révélé la présence de composés méthylés, butylés et octylés.

I.2.2.1.2 Sources

Les composés alkylés de l'étain ont de très nombreuses applications anthropiques. Les composés mono- et di-alkylés (méthyl, butyl ou octyl) entrent dans la formulation de polymères plastiques (PVC, silicone, polyuréthane) en tant que stabilisants [43] [50, 51]. Les composés mono- et dibutylés sont utilisés dans les procédés de traitement du verre [44]. Par ailleurs, les propriétés biocides des organoétains sont à l'origine de leur utilisation en tant qu'antifongiques pour l'agriculture (tributylétain) et en tant qu'agents de protection du bois (tributylétain). Ces applications peuvent générer directement des émissions d'organoétains dans les milieux aquatiques ou indirectement comme dans les CSD où ils peuvent être mobilisés à partir des déchets ménagers.

Naturellement, l'étain existe dans les milieux aquatiques essentiellement sous forme inorganique. Dans certains milieux, des composés méthylés peuvent être produits à partir d'étain minéral par méthylation biotique [44] [45] [46] ou abiotique [47-49].

Dans les eaux souterraines et les eaux de surface, les concentrations moyennes d'étain total varient entre 0.01 et 5 $\mu\text{g L}^{-1}$ [18, 50]. Les teneurs en butylétains, dont la provenance est uniquement d'origine anthropique, varient entre 0.001 et 1 $\mu\text{g(Sn) L}^{-1}$ dans les eaux de surfaces. Dans les eaux usées et les lixiviats, les concentrations en butylétains sont généralement inférieures à 0.5 $\mu\text{g(Sn) L}^{-1}$ [16, 43, 71].

I.2.2.2 Atmosphère

I.2.2.2.1 Formes chimiques

De la même manière que pour l'arsenic, l'étain peut, soit être adsorbé sur des particules et être ainsi transporté dans les effluents gazeux, soit se retrouver directement en phase gazeuse. En effet, l'étain au degré d'oxydation +IV est en phase gazeuse tétra-substitué par des groupements hydrures, méthyls, éthyls, propyls ou butyls (Tableau I.1.6).

De nombreuses études se sont intéressées aux mécanismes de formation des espèces volatiles par voies biotiques et abiotiques. Les processus de méthylation et de volatilisation par hydruration des espèces ont été proposés pour expliquer la présence de certaines espèces organostanniques volatiles [45, 46, 49, 54, 55].

I.2.2.2.2 Sources

Les sources naturelles d'étain atmosphérique (érosion, agriculture) contribuent très minoritairement au bilan de l'étain atmosphérique en comparaison avec les sources anthropiques comme la métallurgie, le raffinage, la combustion d'énergie fossile ou encore l'incinération des déchets [50].

Les concentrations atmosphériques moyennes d'étain dans des zones polluées varient entre 1.5 ng m^{-3} et 800 ng m^{-3} (Tableau I.1.4) [18]. Il n'y a pas de données concernant les émissions atmosphériques d'étain liées à la gestion des déchets ménagers dans les CSD, par contre en ce qui concerne l'incinération des déchets, le facteur d'émission de l'étain (inorganique) est estimé à 1.0 g t^{-1} de déchets incinérés [42].

I.3. Méthodes analytiques pour l'étude des éléments traces dans les matrices complexes

I.3.1 Analyse élémentaire des métaux et métalloïdes dans les lixiviats

La caractérisation des éléments métalliques est délicate dans une telle matrice dans la mesure où de nombreuses précautions doivent être prises tout au long de la chaîne analytique afin d'avoir des résultats représentatifs de la matrice initiale. Du prélèvement sur le terrain à l'analyse au laboratoire, il faut veiller à minimiser les modifications subies par l'échantillon.

I.3.1.1 Du prélèvement à l'analyse

Les étapes de prélèvement et de stockage sont essentielles lorsque l'on veut connaître les concentrations en éléments métalliques dans des matrices complexes. Dans le cas précis des lixiviats de CSD, très peu d'auteurs donnent des précisions quant au matériel utilisé lors du prélèvement, aux conditions du prélèvement (aéré ou non, à l'abri de la lumière...), et aux traitements appliqués à l'échantillon dès le prélèvement (acidification, filtration...). En revanche, le type de conditionnement et les conditions de stockage sont souvent précisés (Tableau I.3.1).

Tableau I.3.1 Conditionnement des lixiviats

Nature du flacon de prélèvement	Volume (L)	Température de stockage (°C)	Référence
Polyéthylène	2	+4	[10]
	1		[9]
	Non précisé		[8]
	1	-18	[4]
Plastique (non précisé)	20	+4	[9]
Acier inoxydable	20	+15	[14]
Non précisé	Non précisé	+4	[12]
Non précisé	Non précisé	-20	[56]

S'agissant des lixiviats de CSD, les études se reportant à l'analyse des métaux et métalloïdes ne précisent pas de manière précise les étapes de prélèvement et de stockage des échantillons. Ce manque de protocole peut être la source d'erreurs lors de l'interprétation des résultats et lors de leur comparaison avec les données de la littérature.

I.3.1.2 Analyse

Malgré leur suivi régulier dans les lixiviats de CSD, peu d'études portent précisément sur l'analyse des métaux et métalloïdes dans ces matrices complexes. Les études portent généralement sur moins d'une dizaine d'éléments et de ce fait, ce sont les techniques monoélémentaires de type spectrométrie d'absorption atomique (AAS) à four graphite (GFAAS) ou flamme (FAAS) qui sont le plus souvent utilisées. Les techniques multi-élémentaires telles que la spectrométrie de masse à plasma induit et la spectrométrie d'émission atomique à plasma induit sont plus rarement citées. Le Tableau I.3.2 présente les éléments et les techniques d'analyse dans différents travaux portant sur les lixiviats.

Tableau I.3.2 Eléments détectés dans les lixiviats et techniques analytiques

Eléments analysés	Techniques	Référence
Al Ca Cu Fe Mg Pb Ni Zn	AAS (non précisé)	[7]
Ca Cd Cr Cu Fe Mg Mn Ni Pb Zn	AAS (non précisé)	[9]
Cd Cu Ni Pb Zn	FAAS	[56]
Cd Cr Cu Fe Mn Ni Pb Zn	FAAS	[11]
Cd Cr Cu Ni Pb Zn	GFAAS	[14]
Al Ca Cd Cr Cu Fe Mg Mn Ni Pb Zn	ICPAES	[8]
Al Cd Co Cr Cu Fe Mn Ni Pb Zn	ICP (MS ou AES)	[10]
Cd Cu Fe Zn	ICPMS	[4]

Afin de mener à bien l'analyse des métaux dans les lixiviats, il peut être nécessaire de réaliser au préalable une étape de digestion de l'échantillon afin de simplifier la matrice. Cecen *et al.* et Tatsi *et al.* préconisent une digestion à l'acide nitrique [9, 11]. En ce qui concerne les autres études qui portent sur l'analyse des métaux dans les lixiviats, aucun détail n'est donné à propos d'un éventuel traitement de l'échantillon avant analyse.

I.3.2 Analyse de spéciation dans les matrices liquides environnementales

L'analyse chimique de spéciation consiste à coupler une technique séparative à un détecteur spécifique des éléments d'intérêt. Selon la nature de l'élément et de ses espèces et la compatibilité des réactifs utilisés lors des étapes de préparation des échantillons avec les outils analytiques, plusieurs techniques sont susceptibles d'être utilisées.

Pour des échantillons liquides, les techniques de chromatographie en phase liquide haute performance (HPLC) ou en phase gazeuse (GC) après dérivation des composés sont les plus couramment utilisées pour les analyses de l'arsenic et de l'étain respectivement. La

spectrométrie de masse à plasma induit (ICPMS) permet la détection aussi bien des espèces d'arsenic que celles d'étain, tandis que la spectrométrie de fluorescence atomique (AFS) est spécifique à l'arsenic et la spectrométrie d'émission atomique à plasma induit par micro-ondes (MIPAE) et la spectrophotométrie à flamme pulsée (PFPD) sont spécifiquement utilisées pour l'étain.

I.3.2.1 Cas de l'arsenic

I.3.2.1.1 Du prélèvement à l'analyse

L'analyse de spéciation requiert une préservation de l'échantillon afin d'éviter les modifications de forme chimique des espèces (oxydation, réduction, transalkylation...). Dans le cas des matrices liquides aqueuses, aucune extraction préalable n'est généralement préconisée pour l'analyse de spéciation de l'arsenic. Pour préserver la spéciation, un intérêt tout particulier doit être porté aux conditions de stockage. Quelques auteurs se sont focalisés sur l'impact de la nature du contenant sur la stabilité des espèces de l'arsenic : les échantillons aqueux sont le plus couramment conservés dans des flacons en polypropylène [57-59] ou en polyéthylène [60, 61]. Il n'existe à notre connaissance aucun travail portant sur les lixiviats. Une acidification des échantillons avec de l'acide sulfurique, de l'acide chlorhydrique ou encore de l'acide nitrique a été appliquée sur des échantillons d'eaux pour stopper l'activité bactérienne ou éviter la co-précipitation de l'arsenic avec le fer [32]. Cependant ce procédé peut entraîner des interférences au niveau de l'analyse ou encore modifier les conditions redox de l'échantillon (oxydation de AsIII en AsV) [34]. Pour ces raisons, certains auteurs n'appliquent aucun traitement à l'échantillon mais le conservent à plus basse température [31, 62]. En effet, comme les micro-organismes sont susceptibles de métaboliser ou de transformer les espèces, une diminution de la température est nécessaire pour inhiber l'activité biologique. La température de -20°C permet d'assurer la stabilité de nombreuses espèces (AsV, MMA, DMA, AsB et AsC) dans diverses matrices comme l'eau désionisée et l'urine [61].

I.3.2.1.2 Analyse

L'arsenic peut être présent dans les matrices liquides sous forme organique et/ou inorganique, oxydé et/ou réduit. Les principaux modes de séparation utilisés pour la spéciation des espèces d'arsenic sont l'échange d'ions et l'appariement d'ions [58] [63].

De part leurs propriétés acido-basiques, la majorité des composés arséniés présentent des caractères ioniques différents en fonction du pH. Cette caractéristique fait de la chromatographie d'échange d'ions la technique séparative la plus fréquemment utilisée.

Echange d'anions

La chromatographie d'échange d'anions est la plus adaptée pour la séparation des espèces inorganiques et mono- et di-méthylées. La colonne Hamilton PRP-X100 (phase stationnaire en polystyrène divinylbenzène avec greffons triméthylammonium) est la colonne la plus utilisée. Le Tableau I.3.3 présente des exemples récents de méthodes développées pour l'analyse des espèces arsénisées par le mécanisme d'échange d'anions.

Tableau I.3.3 Exemples de conditions de chromatographie d'échange d'anions

Colonne	Phase mobile	Détection	Espèces séparées	Matrice	Référence
Hamilton PRP-X100	Nitrate d'ammonium (gradient, pH 8.7)	ICPMS	AsIII, DMA, MMA, AsV	Eaux de surface	[31]
Hamilton PRP-X100	Phosphate d'ammonium (isocratique, pH =5.6)	ICPMS	AsIII, DMA, MMA, AsV	Eaux de surface	[57]
Hamilton PRP-X100	Phosphate d'ammonium (gradient, pH =5.7)	HG-ICPMS	AsIII, DMA, MMA, AsV	Eaux de surface et souterraines	[30]
Dionex IonPak AS7	Acide nitrique (gradient : pH 3.4-1.8)	ICPMS	AsIII, MMA, DMA, AsV, Roxarsone		
Hamilton PRP-X100	Phosphate de potassium (isocratique, pH = 5.8)	HG-ICPMS	AsIII, DMA, MMA, AsV	Eaux (rivière, estuaire)	[64]
Hamilton PRP-X100	Phosphate de potassium (isocratique, pH = 6.25)	HG-AFS	AsIII, DMA, MMA, AsV	Eaux de mer	[65]
Hamilton PRP-X100	Phosphate d'ammonium (isocratique, pH =6.0)	HG-AFS	AsIII, DMA, MMA, AsV	Eaux usées	[34]
Hamilton PRP-X100	Phosphate de sodium (gradient, pH =6.0)	UV-HG-AFS	AsC~AsB, DMA, MMA, AsV	Eaux	[66]
Hamilton PRP-X100	Phosphate d'ammonium (gradient : pH : 4.8-8.0)	HG-AFS	AsIII, DMA, MMA, AsV	Eaux (rivière, consommation)	[32]
Dionex IonPak AS7	Acide nitrique (gradient : pH 3.4-1.8)	ICPMS	AsIII, MMA, DMA, AsV, AsB, AsC	Eaux (pluie, rivière)	[60]

Comme le montrent les exemples du Tableau I.3.3, la séparation avec la colonne PRP-X100 se limite généralement (pH autour de 6) à quatre espèces (AsIII, AsV, MMA et DMA) qui sont les espèces les plus couramment recherchées dans les matrices liquides environnementales. Cette colonne ne permet pas de séparer correctement les espèces organiques telles que AsB, AsC ou TMAO. Ces espèces sous forme de cations ou de zwitterions aux pH généralement utilisés ne sont que peu ou pas retenues par cette colonne.

L'utilisation d'une colonne de type AS7 permet d'obtenir la séparation d'un plus grand nombre d'espèces. Cette colonne présente en fait un caractère mixte avec un caractère d'échange d'anions combiné à un caractère hydrophobe (phase stationnaire en copolymère styrène-divinylbenzène greffé d'ammoniums quaternaires alkylés). C'est la raison pour laquelle les espèces cationiques telles que AsB et AsC peuvent être retenues. Ce type de colonne a pour inconvénient d'être très onéreuse, ce qui peut empêcher son utilisation pour des analyses de routine de matrices complexes, telles que les lixiviats.

Echange de cations

Les méthodes de chromatographie d'échange de cations permettent de séparer principalement les espèces organoarséniées du fait de leur caractère cationique dans un domaine de pH. La majorité des méthodes développées sont dédiées à l'analyse de matrices « marines » de type algue, poisson, mollusque où ces espèces sont majoritaires. Sachant que les conditions chromatographiques sont susceptibles d'être appliquées à des matrices liquides environnementales, un aperçu de ces méthodes est proposé dans le Tableau I.3.4. Les méthodes de séparation les plus fréquentes sont basées sur l'utilisation de la colonne Hamilton PRP-X200 (phase stationnaire en polystyrène divinylbenzène avec greffons sulfonates) et de la colonne Supelcosil LC-SCX (phase stationnaire en silice greffée d'acide benzène sulfonique).

Tableau I.3.4 Exemples de conditions de chromatographie d'échange de cations

Colonne	Phase mobile	Détection	Espèces séparées	Matrice	Référence
Hamilton PRP-X200	Acide nitrique et nitrate d'ammonium (gradient ; pH = 2.5)	UV-HG- AFS	AsIII~MMA~AsV, DMA, AsB, AsC	Eaux	[66]
Hamilton PRP-X200	Pyridine (isocratique; pH = 2.8)	ICPMS	AsIII, AsB, DMA+MMA+AsV	Riz, poisson, sol, poulet	[67]
Varian IonoSpher-5C	Pyridine (gradient ; pH = 2.7)	ICPMS	DMA, AsB, TMAO, AsC, TMA ^{s+}	Echantillons marins	[68]
Supelcosil LC-SCX	Pyridine (gradient ; pH = 2.6)	ICPMS	AsB, AsC, TMAO, TMA ^{s+}	Sédiments et tissus biologiques	[69]

Le mécanisme d'échange de cations est appliqué le plus fréquemment à la séparation d'AsB, AsC et TMAO. Ce type de colonne ne permet généralement pas la séparation des espèces inorganiques et mono- ou di-méthylées. En général, les auteurs qui souhaitent réaliser une analyse complète des espèces organiques et inorganiques combinent une analyse sur chacune des deux colonnes à échange d'ions [66, 67, 69] ou utilisent une colonne mixte comme l'AS7 [60, 70].

I.3.2.2 Cas de l'étain

Le développement de méthodes d'analyse de spéciation de l'étain est consécutif à la prise de conscience des impacts environnementaux liés à la large utilisation du TBT en tant que biocide. La très grande majorité des méthodes mises en œuvre est donc spécifiquement adaptée à l'analyse des butylétains.

I.3.2.2.1 Du prélèvement à l'analyse

Les eaux douces ou de mer sont les matrices liquides les plus documentées [71-73] sur l'analyse de spéciation de l'étain. Ces échantillons souvent faiblement concentrés ne subissent généralement pas de traitement préalable afin d'extraire les espèces de la matrice. Dans le cas des lixiviats de CSD, une étape d'extraction des composés organostanniques peut s'avérer nécessaire. Une telle extraction peut être réalisée par un mélange méthanol/hydroxyde de potassium [16] ou comme pour les matrices solides (sols, sédiments, biota) par de l'acide acétique [71, 74] pouvant être assistée par l'action ou non d'un champ micro-ondes [75].

L'analyse des composés organostanniques par chromatographie en phase gazeuse (GC) nécessite une étape de dérivation afin de rendre les composés extractibles par une phase organique compatible avec l'analyse en GC. Cette étape consiste à substituer sur l'atome d'étain un ou plusieurs groupements non alkylés (chlorure, hydroxyde...) par un ou plusieurs groupements éthyls [16, 71, 72, 75] ou propyls [73, 74]. Les espèces sont ainsi pré-concentrées dans un petit volume de solvant organique et peuvent être injectées et séparées par chromatographie gazeuse.

I.3.2.2.2 *L'analyse*

Technique analytique

La séparation par chromatographie en phase gazeuse des composés organostanniques est la méthode la plus répandue car après dérivation les espèces tétraalkylées sont facilement séparées par leur point d'ébullition.

Le Tableau I.3.5 présente des exemples de conditions d'analyse des composés organostanniques par chromatographie en phase gazeuse. Les colonnes capillaires de 30m utilisées ont toutes une composition proche de type méthylphénylsiloxane. La plupart des programmes de température appliqués sont adaptés soit aux composés « lourds » de type butylétain, phénylétain ou octylétain, soit aux composés « légers » de type méthyl : pour la séparation de toute la gamme de composés le gradient en température est allongé (de 40°C à 250°C).

Tableau I.3.5 Exemples de conditions d'analyse des composés organostanniques

Colonne capillaire	Programme de température	Détection	Espèces séparées	Matrice	Référence
HP-5 30 x 0.32 x 0.25*	50°C (0.5min)-30°C/min- 250°C (2min)	ICPMS	MBT, DBT, TBT	Sédiments	[76]
HP-5 30 x 0.32 x 0.25*	60°C (0.5min)-30°C/min- 255°C (1min)	ICPMS	MBT, DBT, TBT	Eaux de mer	[74]
SPB1 30 x 0.32 x 0.25*	40°C (1min)-10°C/min- 150°C (2min)	PFPD	MMT, DMT, TMT	Sédiments	[77]
SPB1 30 x 0.32 x 0.25*	75°C (0.85min)-10°C/min- 250°C (5min)	PFPD	MBT, DBT, TBT, MPHT, DPhT, TPhT	Eaux de mer, sédiments, biota	[78]

MXT 30 x 0.53 x 1*	60°C (0min)-60°C/min- 250°C (2min)	ICPMS	MBT, DBT, TBT	Tissus d'huîtres, neige, eaux de mer	[75, 79]
DB5 30 x 0.32 x 0.25*	40°C (2min)-6°C/min- 220°C-12°C/min-300°C (5min)	PFPD	MMT, DMT, MBT, DBT, TBT, MOT, DOT	Lixiviats de décharge	[16]
HP-5 30 x 0.32 x 0.25*	50°C (3min)-30°C/min- 320°C	ICPMS	MMT, DMT, MBT, DBT, TBT, MOT, DOT	Eaux de pluie, sols	[74, 80]
Methylsilicone (Quadrex) 30 x 0.35 x 0.25*	80°C (0min) -30°C/min - 180°C 10°C/min -270°C	PFPD	MBT, DBT, TBT, MPHT, DPhT, TPhT, MOT, DOT, TOT	Sédiments, eaux de rivière, eaux usées, sable, huîtres	[71, 81]

*longueur (m) x diamètre interne (mm) x épaisseur (μm)

Du fait de sa bonne sensibilité, de sa spécificité et de sa possibilité d'analyse multi-isotopique, l'ICPMS est le détecteur de choix pour l'analyse de spéciation de l'étain. Un des grands problèmes des analyses de spéciation réside dans l'insuffisante assurance sur les résultats en terme de justesse et de traçabilité des protocoles analytiques. L'utilisation des matériaux de référence est généralement la méthode de choix pour la validation de la chaîne analytique. Du fait du manque de matériau de référence certifié pour des espèces d'étain dans des matrices environnementales représentatives, il est nécessaire d'inter-comparer les résultats obtenus par différents modes de quantification. De part sa détection multi-isotopique, l'ICPMS permet d'ajouter la dilution isotopique aux méthodes de quantification classiques que sont l'étalonnage externe, l'étalonnage interne et les ajouts dosés.

Quantification par dilution isotopique

La dilution isotopique s'apparente à l'étalonnage interne avec la spécificité d'être menée grâce à des espèces isotopiquement marquées. Elle permet de compenser les erreurs dues à des préparations d'échantillon non quantitatives ou à des pertes pendant le traitement de l'échantillon. La dilution isotopique est basée sur le dopage de l'échantillon par une quantité précise d'une forme isotopiquement marquée d'une espèce. Cette espèce utilisée comme traceur est enrichie de telle sorte que son empreinte isotopique soit différente de celle de

l'espèce naturellement présente. La quantification est basée sur le calcul des rapports isotopiques : à partir du rapport isotopique du traceur enrichi, de la quantité de ce traceur ajoutée à l'échantillon et du rapport isotopique de l'échantillon non dopé (rapport isotopique naturel), il est possible de déterminer la quantité de composé dans l'échantillon.

Etant donné que les espèces enrichies, qui sont de même nature que l'espèce d'intérêt, sont présentes dans l'échantillon initial, elles ont l'avantage de se comporter de la même manière que le composé initialement dans la matrice. Ce mode d'étalonnage a pour autre avantage de ne pas être affecté par les étapes de préparation (extraction, dérivation) car la quantification est réalisée de manière relative par rapport à l'étalon enrichi qui permet de doper l'échantillon [82]. Elle peut permettre aussi de détecter les réactions de dégradation ou de réarrangement des analytes. Dans les travaux qui portent sur la dilution isotopique de l'étain, les auteurs utilisent des espèces butylées enrichies en ^{117}Sn [75] [83] ou en ^{119}Sn [76] pour quantifier les composés butylés dans leurs échantillons en

I.3.3 Analyse de spéciation des espèces volatiles des métaux et métalloïdes dans des matrices gazeuses environnementales

I.3.3.1 Du prélèvement à l'analyse

Lorsque l'on souhaite échantillonner des gaz dans le but de réaliser une analyse de métaux et de métalloïdes, trois techniques peuvent être utilisées. Une première technique consiste à piéger les éléments métalliques dans un liquide (généralement un mélange acide/oxydant) au moyen d'un système de bullage. C'est la méthode de référence en ce qui concerne l'analyse des métaux totaux dans les gaz dans la législation française (norme française pour la mesure des métaux, NF X 43-05). La deuxième technique s'appuie sur les propriétés d'adsorption des métaux sur des adsorbants chimiques ; ce type d'échantillonnage est limité par le caractère plus ou moins sélectif des adsorbants. En ce qui concerne le mercure, cette technique est très utilisée car les pièges en or présentent une très forte sélectivité vis à vis du mercure (formation d'un amalgame). Enfin, la troisième et plus récente technique est le piégeage cryogénique qui a l'avantage de constituer un piège physique et donc universel des espèces organométalliques volatiles. Ces différentes techniques ont toutes été appliquées aux effluents gazeux issus des CSD (Tableau I.3.6).

Tableau I.3.6 Techniques de prélèvement des échantillons de biogaz

Biogaz	Prélèvement		Objectif d'analyse	Référence
Torchère de CSD	Module de	HNO ₃ + KCrO	Mercure	[3]
	barbotage	HNO ₃ + H ₂ O ₂	Métaux et métalloïdes	
Torchère de CSD	Pièges	Charbon actif iodé et or	Mercure total	[20]
	spécifiques	Carbotrap (Supelco)	Diméthylmercure	
Torchère de CSD	Sac Tedlar (4L)		Composés organométalliques	[84, 85]
Bullage dans zones marécages	Chambre à flux + Sac Tedlar			
Station d'épuration	Sac Tedlar (80L)			
				[23]

Les échantillons prélevés dans les sacs Tedlar sont transportés au laboratoire dans des sacs noirs afin d'éviter une dégradation par les rayonnements UV [23, 84, 85]. L'inconvénient de ce type d'échantillonnage avec les sacs en Tedlar est qu'il est nécessaire de réaliser l'analyse dans la journée suivant le prélèvement pour être sûr de conserver l'intégrité de l'échantillon [86]. Cette technique a pour avantage la simplicité d'utilisation et la variété de volume que l'on peut prélever (de 1 à 100L).

La technique de pré-concentration par piégeage cryogénique a l'avantage de constituer un piège physique et donc universel des espèces organométalliques volatiles. Les espèces sont piégées en fonction de leur température d'ébullition et non en fonction de leur affinité chimique par rapport à une phase stationnaire. La Figure I.3.1 présente un schéma de principe de du montage de pré-concentration des échantillons gazeux développé dans notre laboratoire. Le piégeage cryogénique des échantillons gazeux est réalisé à -80°C sur une colonne de laine de verre silanisée. Cette température est choisie afin de ne pas piéger le dioxyde de carbone qui est avec le méthane un des composés majoritaires de ce type de gaz. L'échantillon gazeux passe au préalable dans un piège à eau maintenu à -20°C par un mélange d'acétone et de glace afin d'éviter la formation d'un bouchon de glace à l'entrée de la colonne. Après pré-concentration, les colonnes sont conservées dans un cryoconservateur à -196°C .

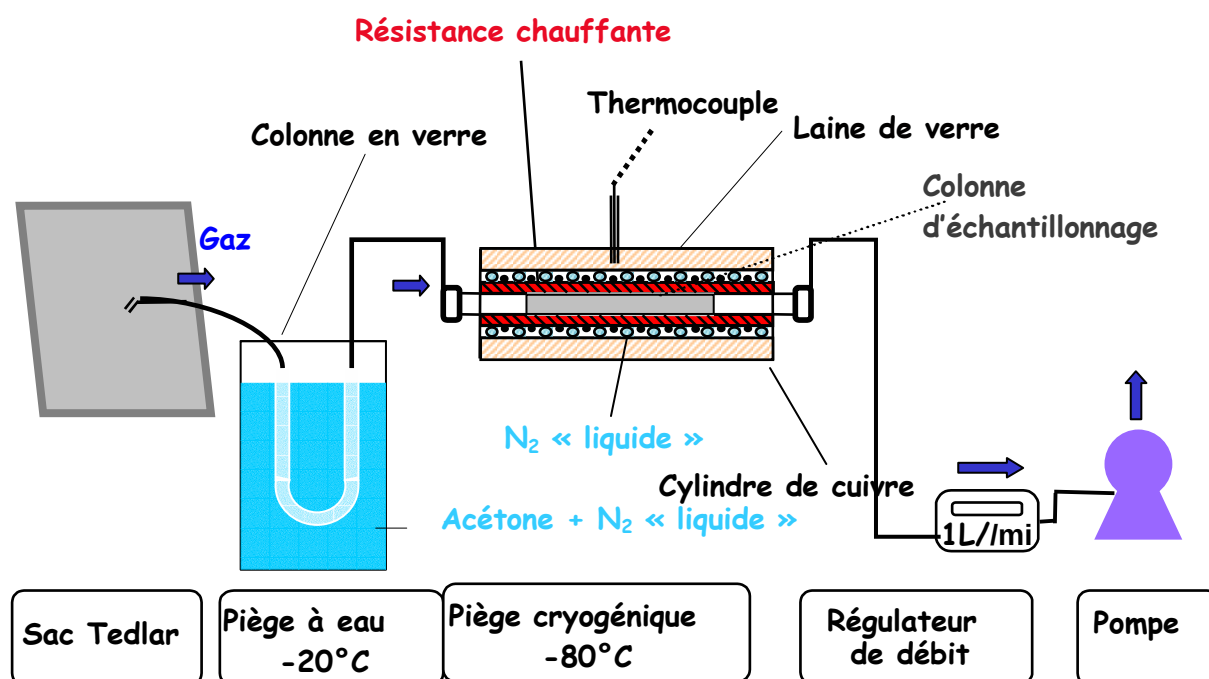


Figure I.3.1 Schéma de principe d'un système de pré-concentration des échantillons gazeux par piège cryogénique d'après Pécheyran *et al.* [87]

I.3.3.2 Analyse

I.3.3.2.1 Technique analytique

Il existe peu d'articles en ce qui concerne l'analyse de spéciation des composés métalliques volatils dans les gaz issus des décharges ou des stations d'épuration (même type de gaz). Cependant, les techniques analytiques sont similaires à celles utilisées pour les analyses d'air ou d'autres gaz. L'une des principales méthodes préconisées aujourd'hui et développée dans notre laboratoire est le piégeage cryogénique couplé à la chromatographie en phase gazeuse elle-même couplée à un spectromètre de masse à plasma induit (C-GC-ICPMS). Elle a déjà été appliquée pour l'analyse d'air ambiant [87-89] et l'analyse de gaz issus de CSD ou de station d'épuration [17, 22, 23, 84, 85].

Les gaz piégés sur les colonnes de laine de verre sont désorbés par augmentation de la température puis piégés une nouvelle fois sur une colonne chromatographique non polaire placée dans de l'azote liquide (-196°C) (Figure I.3.2). La séparation chromatographique est réalisée par chauffage de la colonne de -196°C à environ 150°C. Le gaz vecteur utilisé est l'hélium [23, 84, 85] ou l'argon [17, 90].

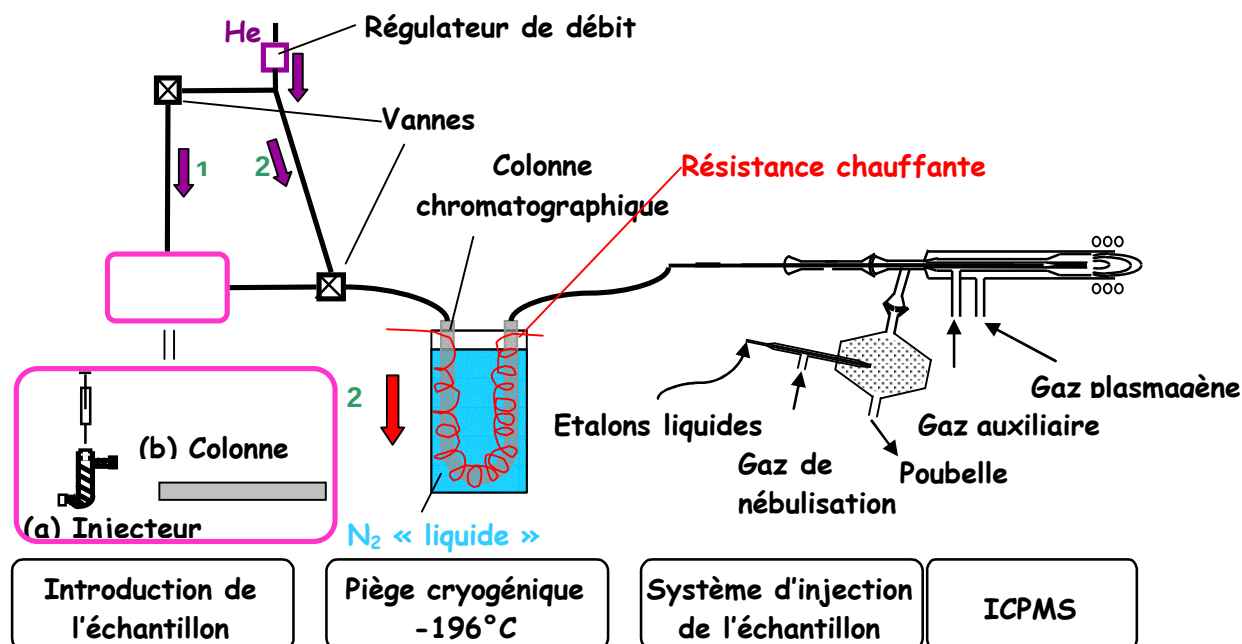


Figure I.3.2 Schéma de principe du système de chromatographie gazeuse avec piège cryogénique couplée à l'ICPMS [87]

I.3.3.2.2 Identification et quantification des composés organométalliques volatils

Le couplage à l'ICPMS permet l'analyse d'un grand nombre d'éléments. Il est donc possible de détecter une grande variété d'espèces organométalliques volatiles (Tableau I.1.5). Pour une minorité d'espèces, les étalons gazeux sont commercialement disponibles [89] : ainsi les espèces peuvent être correctement identifiées et quantifiées. Par contre, pour toutes les autres espèces ces deux étapes sont plus délicates.

L'identification est réalisée par le calcul de la température d'ébullition des composés inconnus à partir de la relation de linéarité entre le temps de rétention et la température d'ébullition pour une même famille de composés. En effet, en supposant que la séparation chromatographique est régie principalement par la température d'ébullition, les auteurs déterminent la relation de linéarité entre les deux grandeurs et l'extrapolent aux espèces inconnues [22, 39, 88]. Cette méthode d'identification permet d'avoir une idée plus précise des espèces susceptibles d'être présentes dans les échantillons.

L'utilisation d'une torche double entrée permet de nébuliser une solution simultanément à l'injection de matrices gazeuses (Figure I.3.2). Des étalons liquides peuvent ainsi être injectés pour réaliser une semi-quantification (30% d'erreur) des espèces volatiles [84]. Il s'agit alors de calculer le rendement de nébulisation qui indique la quantité réellement injectée par rapport à la quantité consommée et ce par unité de temps. Les concentrations en composé peuvent être évaluées en utilisant la relation linéaire entre l'aire du pic et la quantité injectée. Cette méthode nécessite que les conditions du plasma soient les mêmes pour l'injection des étalons en phase liquide et l'injection des échantillons en phase gazeuse : ainsi une solution aqueuse avec ou non un étalon interne est injectée tout au long de l'analyse des échantillons gazeux.

I.4. Démarche scientifique

Ainsi, malgré leur importance croissante dans les enjeux environnementaux les centres de stockages de déchets constituent encore de nos jours des «boîtes noires » dans lesquelles des phénomènes physiques, chimiques et biologiques interviennent simultanément. Parmi les composés présents dans les déchets, les métaux et métalloïdes, en particulier l'arsenic et l'étain, peuvent être à l'origine de risques sanitaires et environnementaux. Les connaissances concernent essentiellement les teneurs élémentaires dans les effluents produits par les CSD. Ces données sont insuffisantes lorsqu'il s'agit d'évaluer leurs impacts environnementaux car les comportements et les toxicités des métaux et métalloïdes sont très variables en fonction des formes chimiques sous lesquelles ils sont présents. En terme d'analyse de spéciation, les lixiviats souffrent d'un manque de protocoles spécifiquement adaptés. Par contre, les protocoles développés pour l'analyse de l'air ont déjà été adaptés à des matrices gazeuses aussi complexes que les biogaz.

Ce travail a donc eu pour objectif d'étudier le devenir des métaux et métalloïdes dans les effluents de CSD. Le schéma de la Figure I.4.1 synthétise la démarche qui a été mise en œuvre au cours de la thèse. Les étapes de préparation de l'échantillon et de l'analyse ont été testés à partir des nombreuses données bibliographiques sur les eaux et/ou les sédiments afin d'optimiser les conditions les plus adaptées aux lixiviats. Après validation, la méthodologie a été appliquée aux échantillons des deux sites. La deuxième partie du travail a consisté à suivre les éléments étudiés au sein des CSD en intégrant les caractéristiques des sites ainsi que des paramètres globaux tels que les données hydrologiques. La répartition des différentes espèces de l'étain et de l'arsenic a été examinée en tenant compte de leur occurrence initiale dans les déchets et de leur devenir dans le système complexe constitué par les lixiviats et les biogaz. Enfin, l'élargissement du cadre de l'étude a permis d'estimer et de caractériser les émissions potentielles de ces deux éléments dans les milieux aquatiques et atmosphériques.

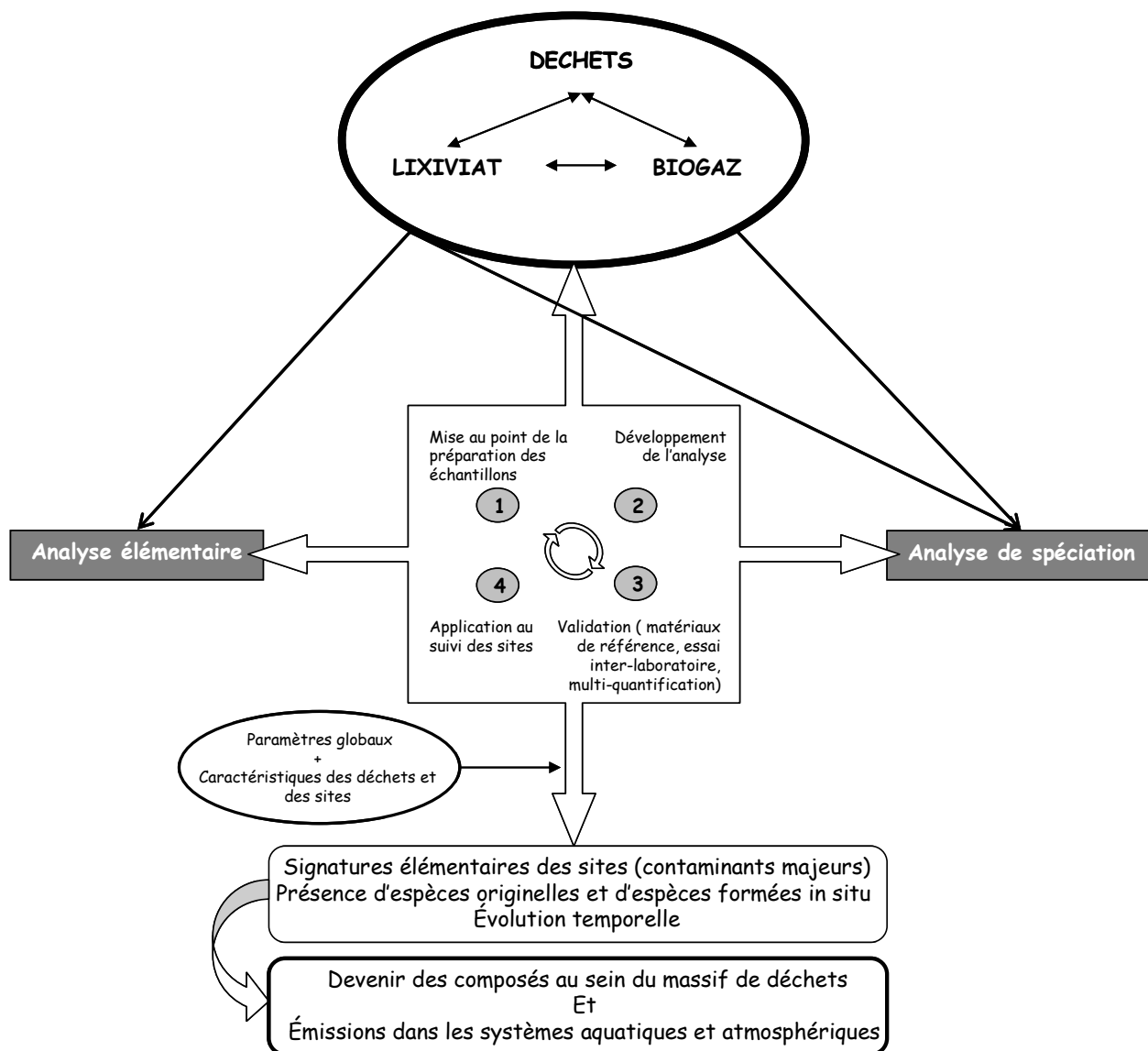


Figure I.4.1 : Représentation schématique de la démarche scientifique mise en œuvre

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SIGNATURES ELEMENTAIRES DES LIXIVIATS

II. Détermination des concentrations en métaux et métalloïdes dans les lixiviats de centres de stockage de déchets

Même si une grande partie des métaux reste piégée dans le massif de déchets, une fraction plus ou moins importante est mobilisée dans les lixiviats. Des phénomènes complexes qui combinent des processus physiques (lixiviation...), des processus chimiques (oxydo-réduction...) ainsi que des processus biologiques (biodégradation de la matière organique...) interviennent tout au long de la formation et de l'évolution des lixiviats. A ceci s'ajoutent les d'autres paramètres tels que la nature des déchets, le mode de gestion du site et les conditions climatiques qui contribuent aussi aux variations de composition de ces effluents complexes.

Ce chapitre présente les travaux de mise en place pour la détermination de la composition en métaux et métalloïdes des lixiviats. Nous nous sommes, tout d'abord, focalisés sur la préparation de l'échantillon. La synthèse bibliographique a mis en évidence une grande disparité dans les protocoles pour ce type de matrices. Les différentes étapes de la chaîne analytique (aération, filtration, stockage...) sont testées afin de définir les plus critiques en ce qui concerne l'analyse des métaux et métalloïdes. Le protocole analytique retenu est ensuite validé grâce à l'utilisation complémentaire de deux matériaux de référence certifiés et d'un échantillon de référence de laboratoire, qu'il s'est avéré nécessaire de développer à partir d'un lixiviat réel. Enfin, l'applicabilité de la méthodologie est évaluée sur le suivi saisonnier des lixiviats d'un CSD.

Evaluation of analytical strategies for the determination of metal concentrations to assess landfill leachate contamination

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Due to the complex nature of landfill leachates, metal and metalloid analyses prove to be tricky and suffer from a lack of standard protocols. A complete approach has been adopted to investigate the influence of the different steps during the sample processing of French landfill leachates. The validation of the entire protocol has been achieved using a laboratory reference material. This material, which is a real landfill leachate, is representative of real samples. Its evaluation has allowed a quality control for metal and metalloid analyses in landfill leachates. Precautions concerning storage temperature, aeration and filtration are proposed to perform accurate metal analyses in these complex matrices. The sample processing has been applied to the seasonal monitoring of a French landfill. The assessment of major leachate metallic contaminants such as As, Cr, Sb, Sn, has been performed by evaluating the relative enrichment of metals and metalloids in comparison with rain water and groundwater. In addition hydrological data are useful and complementary information to point out the main factors affecting metal concentrations and thus their potential remobilisation pathways.

II.1. Introduction

Municipal solid waste management is to date one of the most critical concerns of our society as the production of domestic wastes is continuously increasing. Even if new technologies, such as sorting, composting or recycling, are promoted, at present the most common approaches for waste management are still incineration and landfilling. Waste disposal is more particularly the predominant alternative in most countries¹. This is partly due to the low cost and the simplicity of this technology, coupled to a relatively good degradation and stabilisation of the majority of municipal solid wastes.

Landfilling is a source of three major types of nuisance to the environment, namely gases (odorous, inflammable, toxic and greenhouse gases), liquid effluents (nutrient rich and toxic leachates) and landscape alterations. In developed countries, leachates are now regulated in terms of collection and treatment. Leachates have to be collected during the entire cell filling. After collection, they have to be treated in the same way as waste waters, before being discharged in the natural environment.

Landfill leachate composition monitoring is important as their environmental impacts last from beginning of cell filling, to many years after^{2,3}. Physical, chemical and microbiological processes in the waste mass are the cause of exchanges between the solid, the liquid and the gaseous phases. During their formation by water (water contained in wastes and rain water) percolation, leachates become more complex with a high organic and inorganic content^{4,5,6}. Leachate composition can be highly variable depending on landfill location⁷, waste composition⁸, and management⁸. The observed variations can also be due to the lack of standard protocols for sampling, storage and treatment of leachate samples. As an example, the concentrations of metals measured in a sample with colloids will change depending on the sampling technique used^{4,5} due to the high affinity of heavy metals for colloids⁹ and due to the sensitivity of colloids to sampling conditions. Among the various parameters which should be taken into account, metals and metalloids are still recognized as priority pollutants. In opposition to most of organic pollutants, metals and metalloids cannot be degraded in the waste deposit. They are thus maintained in the waste disposal and further mobilized in liquid or gaseous phases. The ranges of concentrations in leachates reported in the literature are considerable such as for Cd 0.2-20µg/L, Cr 5-600µg/L, Mn 0.01-70mg/L, Fe 0.3-220mg/L¹⁰⁻

¹³.

Landfill leachates are complex matrix halfway between water and sludge. Known methods for sample treatment and sample analysis should be thus adapted for such a miscellaneous matrix. Nevertheless, few studies ^{4, 6, 11, 13} are directly focused on metal analyses in landfill leachates. Metal composition is often only a part of the analyses performed and no detail is given concerning the sampling protocol, the sample treatment or the sample analysis. Only one research team ¹³ has published and focused its attention on sampling protocols. In this intensive study, leachates were carefully sampled monitoring continuously the turbidity, pH, specific conductivity and temperature. The conditions applied to preserve the *in situ* chemistry have allowed evaluation of the metal fractionation between colloid and dissolved phases.

The use of certified reference materials (CRMs) is required to ensure the measurement accuracy ¹⁴. Only two certified reference landfill leachates are available (LGC 6175 and LGC 6177 (Promochem)). The concentrations are certified for B, Ca, Fe, K, Mg, Mn, Na, Ni P and Zn. These CRMs are unfortunately not certified for the most environmentally problematic metals and metalloids such as Hg, Pb, Cd, Sn, As and Cr (European Pollutant Emission Register, 2000/479/EC). Moreover, the pre-treatment applied to ensure the stability of these two CRMs (acidification and filtration) leads to a modification of the matrix. Precipitation of organic matter (humic acids) due to acidification ¹⁵ can form aggregates, in which particulate metals can be trapped. This treatment can lead to a loss of metals during filtration. The development of a representative laboratory reference material appears to be necessary to complete the quality control of the entire analytical procedure for metal analysis in landfill leachates.

The purpose of this paper is to assess the complete processing of metals and metalloids analyses in landfill leachates. The first part of this work is focused on the evaluation of critical steps during sampling and sample processing. Based on initial results on the influence of sample processing on metal analyses in landfill leachates ¹⁶, the objective is to highlight the precautions required for metal analyses in such complex samples. The second part presents the conception of a laboratory reference material (LRM) using a bulk landfill leachate. Although the feasibility of such LRM has been checked by an inter-laboratory comparison ¹⁷, its relevance is evaluated here for quality control in routine analyses of metal in leachates. Finally, the methodology is applied for the seasonal monitoring of metal and metalloids in landfill leachates. In this last part the assessment of metal contamination for such landfill is discussed through the evolution of leachate composition together with background concentration and hydrological conditions.

II.2. Experimental

II.2.1 Sampling

II.2.1.1 Sampling sites and sample collection

I.2.1.1.1 Landfill sites description

Leachates are sampled in a French landfill which receives only municipal wastes. This landfill, named hereafter as L.F.1, is small: 10000 tons of wastes per year are disposed. This site is composed of three cells: the first one has been filled from 1989 to 1999, the second one from 1999 to 2003 and the exploitation of the third one started in 2004 (during the year 2003-2004 the site has been modernized). The total precipitations and the mean atmospheric temperature of the 30 days period preceding each sampling campaigns are noted (Météo France).

For the creation of the laboratory reference material, the leachate originates from a French landfill, named hereafter as L.F.2, where 200000 tons per year of municipal solid wastes are disposed.

I.2.1.1.2 Sample collection

Leachates of the second cell of L.F.1 have been sampled. Concerning the sampling technique, no pumping is applied and no perturbation of the outflow is induced: leachates are simply collected at the extremity of the leachate pipe. Leachate from L.F.2 is collected in the leachate well with a pump.

Leachates from L.F.1 and L.F.2 are collected in polyethylene containers (1L for L.F.1 and 20L for L.F.2).

Sampling bottles and plastic ware throughout this work were all, before use, rinsed with a detergent and warm water, then decontaminated with diluted (10%) nitric acid (Baker Analysed, 65%) and finally rinsed three times with ultrapure water (Millipore 18M Ω). All bottles are filled with ultrapure water and transported to the landfill. One of the bottles is left with pure water to constitute a “landfill blank” following all the critical steps.

II.2.1.2 Sampling evaluation strategy

A complete sampling strategy is performed on one landfill leachate sample from L.F.1. To evaluate the impacts of sample processing steps on metal and metalloid determination, a

reference protocol for this type of complex matrix is established. Figure I.1.1 presents a general scheme of the sample process pathways including the experimental approach performed in this study. The first step aims to evaluate the impacts of sample conditioning, i.e. with or without aeration. The aeration is carried out by bubbling oxygen in the leachate. Each aliquot is then filtered or not with 0.2 μ m filters (vinyl polyfluoride, Durapore). The filtration is performed on-line (polysulfone device) and under pressure (nitrogen, 99.9990%). Finally, long-term storage temperatures are evaluated. For each protocol, 15 aliquots of 5mL or 10mL (polypropylene vials) are sub-sampled. Each protocol is tested in triplicate to obtain a specific standard deviation.

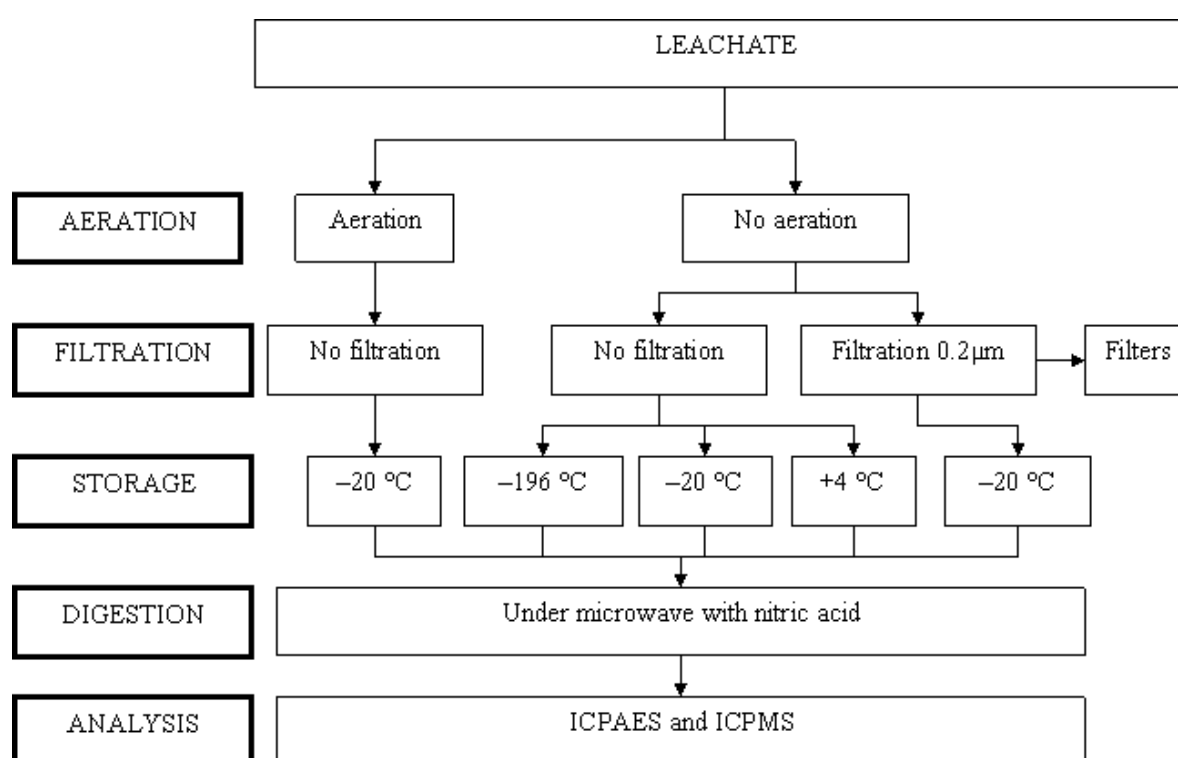


Figure II.2.1 General scheme of sample processing strategy

II.2.2 Reagents and certified reference materials

All reagents used are analytical grade and ultrapure water is obtained from a MilliQ system (18M Ω , Millipore). For microwave digestion, nitric acid (Baker Instra-Analysed, 70%) is used. To cover all the range of elements, three multi-elemental solutions are obtained from Analab (CCS-4, CCS-5 and CCS-6).

For quality control, a landfill leachate LGC 6177 (LGC Promochem) with eleven certified elements (B, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, P, Zn) and a waste water SPSWW1 (LGC Promochem) with eleven certified elements (As, Zn, Ni, Al, Pb, Mn, Cd, Co, Cr, Cu, Fe) are

used in this work. The certified landfill leachate LGC 6177 is preferred to the LGC 6175 because it presents more certified elements. The certified waste water allows analysis of six additional elements.

II.2.3 Physical and chemical parameters

Complementary characterization of the leachate samples is obtained through the determination of the following parameters: pH (pH-meter Metrohm 691), Total Organic Carbon and Inorganic Carbon by a TOC analyser (TOC-VCSn Shimadzu), anions (Cl^- , F^- , Br^- , NO_3^- , SO_4^{2-} , ΣPO_4) by ionic liquid chromatography (Dionex DX120 Ion Chromatograph), sodium and potassium (Na^+ , K^+) by flame photometry (Corning 410). The determination of all these parameters has been performed using standard methodology¹⁸.

During the evaluation of the sampling and the sample treatment strategies, the filters used for the filtration of the leachate samples have been analysed by an Environmental Scanning Electron Microscope.

II.2.4 Sample digestion

Leachates are digested using microwave systems. Open (Microdigest 3.6, Prolabo) and closed (Ethos, Milestone and MDS-2000, CEM) systems have been tested during validation of the protocol and give similar results¹⁷. 5mL of the leachate are placed in the vessel with 5mL of HNO_3 (Baker Instra-Analysed, 70%). The digestion is complete within 15 minutes at an irradiation power of 62W (opened system) or with a temperature of 110°C (closed system). After cooling at room temperature, the sample is transferred in a polyethylene flask (35mL) and diluted five times with ultrapure water. Before analyses by Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES) and Inductively Coupled Plasma Mass Spectrometry (ICPMS), samples are diluted two times and twenty times, respectively, and filtered (0.45 μm , cellulose acetate filters) to remove remaining suspended particles.

Digestion blanks are made by replacing leachate by ultrapure water. The same digestion protocol, dilution and filtration are applied to check potential contamination from all these steps.

II.2.5 Analytical procedure

II.2.5.1 Instrumentation

For total metal concentrations, two complementary techniques are used: Inductively Coupled Plasma Mass Spectrometry (ICPMS) (Agilent, 7500ce) and Inductively Coupled Plasma

Atomic Emission Spectrometry (ICPAES) (Panorama, Jobin-Yvon). The analytical sample introduction system is composed of a Micromist nebuliser and a Scott chamber for ICPMS, and composed of a cyclonic chamber and a Meinhard nebuliser for ICPAES. During protocol validation, additional techniques such as Graphite Furnace Atomic Absorption Spectrometry noted GFAAS (SpectrAA220Z, Varian), and Flame Atomic Absorption Spectrometry noted FAAS (SpectrAA220FS, Varian), have also been used following standard procedure ¹⁸. Fe and Zn are analysed using FAAS, whereas Cd, Cr, Cu, Ni, Mn and Pb are analysed by GFAAS.

Table II.2.1 Analysis parameters

Element	ICPAES			ICPMS		
	Wavelength	Detection	Isotopes	Collision cell		Detection
	(nm)	limit (µg/L)		mode		limit (µg/L)
				OFF	ON	
As	189.0	5.5	⁷⁵ As		H ₂	0.06
Sn	189.9	5.4	¹¹⁷ Sn, ¹¹⁸ Sn, ¹²⁰ Sn		He	0.03
Se	196.0	20.5	⁷⁸ Se, ⁸⁰ Se, ⁸² Se		H ₂	0.20
Zn	213.9	1.6	⁶⁶ Zn, ⁶⁷ Zn		He	0.08
Pb	220.5	11.4	²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb	X		0.09
Cd	226.5	1.1	¹¹¹ Cd, ¹¹³ Cd		H ₂	0.01
Mn	257.6	0.4	⁵⁵ Mn	X		0.02
Fe	259.9	1.7	⁵⁶ Fe, ⁵⁷ Fe		H ₂	0.80
Cr	267.7	3.2	⁵² Cr, ⁵³ Cr		H ₂	0.045
Cu	324.8	2.7	⁶³ Cu, ⁶⁵ Cu		H ₂	0.09
Al	396.2	11.1	²⁷ Al	X		0.98
Sr	407.8	0.1	⁸⁸ Sr		H ₂	0.07
Sb	206.8	11.1	¹²¹ Sb	X		0.09
Co	228.6	2.2				
Ni	231.6	5.2				
Ca	317.9	8.5				
Mg	279.6	0.4				

For ICPAES analysis, 15 elements are monitored whereas for ICPMS only 13 elements are monitored (Table II.2.1). The operating conditions are typical for the two analytical apparatus (cooling argon: 15L/min, nebulization argon: 0.7-1.2L/min, RF Power: 1000W (ICPAES) and 1500W (ICPMS)). For ICPMS, a collision cell is used to avoid polyatomic interferences (multi-tune mode). Analysis of each element can be performed with or without collision cell

(using hydrogen or helium; gas flow: 3.5-5mL/min). Table 1 outlines the appropriate wavelengths for ICPAES, the ICPMS isotopes and the collision cell modes. Tuning of the ICPAES is made with a 5 mg/L solution of Pb whereas tuning of ICPMS is made with a 1µg/L solution of Li, Y and Tl. Blanks of the whole sample processing are determined to check for any contamination. Storage blanks are also performed to avoid any bias due to metal release by storage vials.

II.2.5.2 Quantification

The difficulty of elemental analysis of metals and metalloids in landfill leachate is mainly related to the large concentration range. For example, Cd amount is below 1µg/L whereas Fe concentration can reach up to 4500µg/L. For this reason, in order to give accurate results, analyses of leachates and CRMs have been performed and quantified by external calibration with matrix reconstitution but also by standard addition to check any matrix effect.

II.2.5.3 Analytical performances

Detection limits (LD) are calculated from three times the standard deviation of matrix reconstitution blanks. ICPMS is much more sensitive than ICPAES, as shown in Table II.2.1 with the comparison of LD. Detection limits vary from 0.01µg/L for Cd by ICPMS to 20µg/L for Se by ICPAES. This underlines the complementarity of these two techniques for samples with a wide range of concentrations.

Considering the ranges of concentrations, respectively for ICPMS from 0.1µg/L to 20µg/L and for ICPAES from 100µg/L to 5000µg/L, the linear regression factors exceed 0.99. For ICPAES, the relative standard deviation for a multi elemental standard at 250µg/L varies from 9% for Cr to 24% for Se. For ICPMS, the relative standard deviation for a multi elemental standard at 1µg/L varies from 4% for Cd, Cr, Mn, Sb, Se, Sn, and Sr to 25% for Al and Fe.

II.3. Results and discussion

II.3.1 Validation of analytical techniques with available CRM

Two certified reference materials have been used for the validation of the analytical techniques (Table II.3.1). A relative standard deviation of 10% for the certified concentrations can be accepted, to evaluate metal contaminations in such complex matrices.

II.3.1.1 Certified reference landfill leachate

The concentrations of Cr, Mn and Ni measured by the three analytical methods (GFAAS, ICPMS and ICPAES) are within the certified confidence interval. The three techniques give similar results for Zn (mean value= $225 \pm 15 \mu\text{g/L}$) but the range of concentration is slightly lower than the certified confidence interval ($260 \pm 20 \mu\text{g/L}$). Only ICPMS gives a concentration of Fe outside the certified confidence interval. The same dilution for all the elements was made to evaluate analytical protocols for routine analysis in such complex matrices. The lack of accuracy observed is due to this dilution, which is not sufficient for Fe to fall within the range of the standard calibration.

II.3.1.2 Certified reference waste water

The determinations of Cd, Co, As, Cr and Al are performed with a deviation of 10% for the three analytical techniques. The concentrations of Pb, Mn, Cu and Ni measured by ICPAES do not overlap the 10% confidence interval. Only ICPMS concentration for Fe and ICPAES concentration for Zn are within the confidence interval.

Table II.3.1 Validation with certified reference materials (concentration in $\mu\text{g/L}$)

Element	LGC 6177				SPS WW1			
	Certified value	^a GFAAS or ^b FAAS	ICPAES	ICPMS	Certified value	^a GFAAS or ^b FAAS	ICPAES	ICPMS
Cd					20.0 ± 0.1	^a 20 ± 1	20 ± 1	25 ± 2
Co					60.0 ± 0.3		65 ± 2	
Pb					100.0 ± 0.5	^a 113 ± 4	74 ± 4	115 ± 3
As					100.0 ± 0.5		74 ± 20	123 ± 14
Cr	180 ± 20	^a 202 ± 2	188 ± 10	190 ± 13	200 ± 1	^a 215 ± 2	220 ± 1	213 ± 3
Mn	140 ± 20	^a 155 ± 3	156 ± 7	153 ± 7	400 ± 2	^a 434 ± 3	477 ± 1	427 ± 6
Cu					400 ± 2	^a 411 ± 21	472 ± 4	468 ± 23
Zn	260 ± 20	^b 226 ± 14	230 ± 2	219 ± 11	600 ± 6	^b 491 ± 1	621 ± 6	527 ± 8
Ni	210 ± 20	^a 207 ± 9	213 ± 12		1000 ± 5	^a 1052 ± 8	1157 ± 9	
Fe	3800 ± 200	^b 4048 ± 175	4153 ± 200	4392 ± 180	1000 ± 5	^b 660 ± 62	1837 ± 65	1180 ± 77
Al					2000 ± 10		2016 ± 93	2352 ± 141

These two CRMs reflect the difficulty of measuring a large number of metals and metalloids with a wide range of concentrations using simple methods. Systematic errors are indeed inherent in multi-elemental analytical techniques. This evaluation shows the importance of confronting the different analytical systems to provide accurate results.

II.3.2 Multi-elemental analytical verification using a Laboratory Reference Material (LRM)

As the matrices of the two available CRMs are not representative of a real landfill leachate, a landfill leachate characterized by two independent laboratories with different analytical techniques has been developed in order to be used as a laboratory reference material (LRM). Different sample preparations are tested to control homogeneity and stability of this material¹⁷. To obtain a reference material with a matrix as close as possible from the leachates one, the “bulk” sample is chosen as the laboratory reference material to control each leachate analysis and to validate result accuracy. This leachate sample is stored in 5mL propylene flasks at -20°C without any treatment.

Table II.3.2 Validation of the LRM (bulk sample) with mean value ($\mu\text{g/L}$) determined during intercomparison work (ICPMS, GFAAS or FAAS and ICPAES) and three standard deviations obtained during intercomparison work, during homogeneity tests ($n=10$, ICPMS) and during one year stability test ($n=6$, ICPMS)

	Mean value ($\mu\text{g/L}$)	Standard deviation in $\mu\text{g/L}$ (relative standard deviation in %)			
		Intercomparability	Homogeneity	Stability	
Fe	3363	285 (8%)	98 (3%)	357	(11%)
Cr	907	118 (13%)	17 (2%)	192	(21%)
As	578 ^a	12 ^a (2%)	6 (1%)	69	(12%)
Zn	192	18 (9%)	6 (3%)	57	(30%)
Sn	142 ^a	35 ^a (25%)	7 (5%)	22	(15%)
Mn	134	17 (13%)	8 (6%)	15	(11%)
Cu	111	16 (14%)	4 (4%)	22	(20%)
Pb	16 ^b	3 ^b (19%)	0.6 (4%)	4	(25%)
Cd	0.7 ^b	0.3 ^b (43%)	0.1 (14%)	0.1	(14%)

^a Inter-comparison between ICPAES and ICPMS

^b Inter-comparison between GFAAS and ICPMS

II.3.2.1 Evaluation of analytical procedure

The development of the laboratory reference material allows to evaluate not only analytical techniques but also sample processing. In fact, the two laboratories have used different approaches for analytical protocols (e.g. open and closed microwave systems, different quality of nitric acid). Mean values obtained for the bulk sample with the three analytical techniques (ICPMS, ICPAES and GFAAS) are presented in Table II.3.2 along with the

standard deviation. For Pb and Cd, the indicated mean value corresponds only to ICPMS and GFAAS because their concentrations are lower than the detection limit of ICPAES. For As and Sn, the indicated mean value correspond only to ICPAES and ICPMS. Analytical performances of the three analytical techniques (ICPAES, ICPMS and GFAAS) depend on the ranges of concentration, in addition to the specific sensitivity of each analytical system. For the four most concentrated elements (Fe, Cr, As, Zn), the standard deviation is around 10%, whereas for Cd the precision is worse and the relative standard deviation reaches 43%.

II.3.2.2 Homogeneity of LRM

The homogeneity test allows the evaluation of the repeatability of the analytical protocol using the LRM. The external homogeneity of the LRM is tested among the different vials stored at -20°C. This external homogeneity is measured by ICPMS by reproducing the analysis on 10 independent samples. Standard deviations are presented in Table II.3.2. Results obtained exhibit a standard deviation lower than 5% except for Mn (6%) and Cd (14%). These standard deviations are lower than those obtained during the intercomparison work. The Laboratory Reference Material is assumed to be sufficiently homogeneous.

II.3.2.3 Stability of LRM

The LRM is not chemically modified, conversely to certified reference materials which are often acidified. For this reason, the stability versus time of the bulk sample stored at -20°C must be tested. The evolution of concentrations measured using ICPMS in this sample is monitored during one year (6 analyses). A new LRM vial is defrosted, digested and analysed (Table II.3.2) for each analysis date. This stability test corresponds to a reproducibility test of the global protocol. For all the elements the standard deviation over one year is comprised between 11% (Fe and Mn) and 30% (Zn), and therefore always larger than the homogeneity standard deviation. The variability measured over one year for Mn, Sn and Cd is lower than the standard deviation measured during the intercomparison work. For these elements no significant instability can be outlined. The case of Cd is particular, because the concentration in the sample is closer to the detection limit. The high standard deviation prevents an assessment of its stability. For Fe, As, Cr, Zn, Cu and Pb, the variability measured on six analyses over one year is larger than the standard deviation measured during the intercomparison work. This result suggests that metal species in LRM are not totally stabilised during storage. Plotting the concentrations measured versus time does not show however any specific trends. There is neither increase nor decrease of the concentrations

measured. It can be concluded that the metal concentrations may exhibit larger uncertainties than expected but the LRM does not present a significant instability with time.

II.3.3 Evaluation of sampling and sample treatment strategies

To control the entire protocol for metal analyses in leachates, the different steps presented in Figure II.2.1 are evaluated.

II.3.3.1 Sampling and storage

The aeration does not affect the determination of metal concentrations (Table II.3.3). No significant differences can be observed for all the 13 element concentrations measured by ICPMS. This observation is probably linked to the landfill equipment itself. Indeed, the leachates are not preserved from aeration during their collection in the leachate pipe. The impact of aeration is not significant. Leachate matrices can be different from one landfill to another and some elements such as iron and manganese are dependent on redox conditions. Maintaining no head-space above the liquid phase is suggested to avoid air contact in the storage vial.

Table II.3.3 Results for the different ways of leachate sample processing (concentrations in $\mu\text{g/L}$, measured by ICPMS)

Elements	Concentrations in $\mu\text{g/L}$				
	Aeration No Filtration	No Aeration No Filtration	No Aeration No Filtration	No Aeration No Filtration	No Aeration Filtration
	-20°C	+4°C	-20°C	-196°C	-20°C
Cd	0.21 ± 0.02	0.27 ± 0.04	0.25 ± 0.07	0.24 ± 0.04	$0.12 \pm .001$
Se	0.33 ± 0.06	0.34 ± 0.01	0.36 ± 0.04	0.33 ± 0.06	0.23 ± 0.04
Pb	5.0 ± 0.6	2.5 ± 0.2	5.6 ± 0.3	5.3 ± 0.6	4.1 ± 0.01
Sb	13 ± 1	14 ± 1	14 ± 2	14 ± 1	13 ± 1
Cu	12 ± 1	13 ± 1	14 ± 1	14 ± 1	11 ± 1
As	62 ± 1	58 ± 1	61 ± 1	62 ± 6	60 ± 1
Zn	96 ± 3	85 ± 2	93 ± 1	101 ± 13	80 ± 1
Mn	539 ± 1	477 ± 19	544 ± 1	551 ± 65	511 ± 1
Sn	300 ± 4	291 ± 1	316 ± 2	308 ± 22	280 ± 2
Cr	691 ± 20	727 ± 28	709 ± 2	713 ± 58	659 ± 2
Al	1144 ± 46	1113 ± 39	1208 ± 12	1417 ± 49	958 ± 6
Sr	2537 ± 142	1716 ± 210	2557 ± 12	2578 ± 27	2486 ± 9
Fe	3415 ± 50	3378 ± 157	3465 ± 8	3488 ± 286	3190 ± 33

There are no significant differences between the three tested storage temperatures (-196°C, -20°C and +4°C) after six months of storage, except for Mn, Al and Sr where the concentrations are slightly lower for the +4°C-stored sample (Table II.3.3). Leachates samples are generally stored at +4°C as water samples and are analysed soon after sampling^{6, 10, 11}. The question of long-term storage has thus not been investigated. Storage at -20°C is generally rejected because of the changes that can occur during one or more freezings and defrosts. It is possible to avoid such problem by transferring the leachates in 5mL aliquots just after sampling and storing them at -20°C for single analysis of each vial.

II.3.3.2 Sample treatment

Leachates are commonly treated as other aqueous samples between sampling and analysis. Filtration just after sampling is therefore tested. The influence of 0.22µm filtration is linked to the characteristics of the matrix, more particularly the presence of colloids and suspended solids. For example, the size of iron hydroxide colloid varies from nanometers to microns¹⁹. Depending on the distribution of the colloids and the cut-off limit chosen for the filter, the amount trapped on the filter varies. The leachate L.F.1 is filtrated just after sampling. The filtrated sample is analysed in terms of metal composition and can be compared to the bulk content (Table II.3.3). Four groups of elements can be differentiated. The ratio between filtered and bulk contents is higher than 95% for As and Sr. Then, for five elements (Sb, Cr, Mn, Fe, and Sn), difference between filtered and bulk samples ranges between 85% and 95%. The third group composed of Cu, Pb, Al and Zn is more affected by filtration with a ratio between 75% and 85%. Finally, the analytical error made on the determination of Cd and Se concentrations (around 1µg/L), do not allowed an accurate measurement of the ratio between filtered and bulk samples. Thus the major part of the elements is dissolved or bound to the colloidal fraction smaller than 0.22µm. These results are similar to the results obtained for Mn, Cu, Cr and Zn in four Danish landfills¹³, even if the cut-off limit is not the same as here (0.40µm).

The fraction trapped on the filter is very thin. Filters have been analysed by Environmental Scanning Electron Spectroscopy, in order to have qualitative information of material trapped on the filter. Only crystalline structure can be observed and the elemental analysis allows identifying chloride salts as the major particulate component. Such analyses were performed by Jensen *et al.*¹³ and they assumed that the main part of colloidal material above 0.40µm was different and characterised by clay minerals with a high content of Si.

This evaluation shows that the impact of filtration on landfill leachates is element dependent. No treatment is thus required when the aim is the determination of metal concentrations in landfill leachates.

II.3.4 Applicability of the methodology to assess metal contamination in a landfill leachate

In order to apply the developed methodological approach, L.F.1 has been monitored seasonally during 14 months (2004-2005). Five sampling campaigns were performed on 12/10/2004, 25/04/2005, 11/07/2005, 22/09/2005 and 06/12/2005. Leachates samples were analysed for metals and metalloids using the previously validated protocol and following the described guidelines Metal and metalloid (Se, Cd, Pb, Cu, Sb, As, Zn, Sn, Mn, Cr, Fe, Sr, Al) concentrations are given in Figure II.3.1 in $\mu\text{g/L}$.

Complementary determinations of hydrological parameters were performed on leachates from L.F.1 such as pH, Total Organic Carbon (TOC), Inorganic Carbon (IC), major cations and anions (Table II.3.4).

Table II.3.4 General composition of leachates from L.F.1

	pH	Rain (mm)	Temperature (°C)	TOC (mgC/L)	IC (mgC/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	Br ⁻ (mg/L)	ΣPO ₄ (mg/L)	F ⁻ (mg/L)
12-oct-04	8.5	70	18.4	812	1090	1482	745	1300	441	n.d.	4.6	7.6	1.4
25-avr-05	7.5	197	10.3	694	301	290	282	224	192	128	0.8	4.2	0.4
11-juil-05	8.4	76	20.0	1865	1023	859	862	927	179	5.6	3.0	20.6	0.4
22-sept-05	8.1	158	17.5	1757	981	831	738	954	286	1.8	2.9	22.4	0.5
06-déc-05	7.1	227	6.6	632	220	208	138	144	338	n.d.	n.d.	n.d.	n.d.

II.3.4.1 Identification of metal contaminants

In terms of legislation, landfill leachates are concerned by the European directive (1999/31/CE) and by the French decree (09/09/1997) on waste landfilling. The total amount of Pb, Cu, Cr, Ni, Zn, Mn, Sn, Cd, Hg, Fe and Al must not reach the limit fixed at 15mg/L, which is the case for the all five sampling periods. Indeed, the total concentration of these elements varies between 2.60mg/L (22/09/2005) and 6.20mg/L (12/10/2004)). Nevertheless, this limit does not reflect any potential risk because it only gives an indication of the global metal load. For Cd, Pb, and As which are mentioned in the regulation, the concentrations

measured are lower than the regulated threshold (Cd: 0.2 mg/L, Pb: 0.5 mg/L, As: 0.1 mg/L) for the five campaigns. The important variations observed over one year suggest that an integrated monitoring must be performed combining monthly sampling and intensive daily study to better reflect the real impact of total metal content in this type of complex effluent.

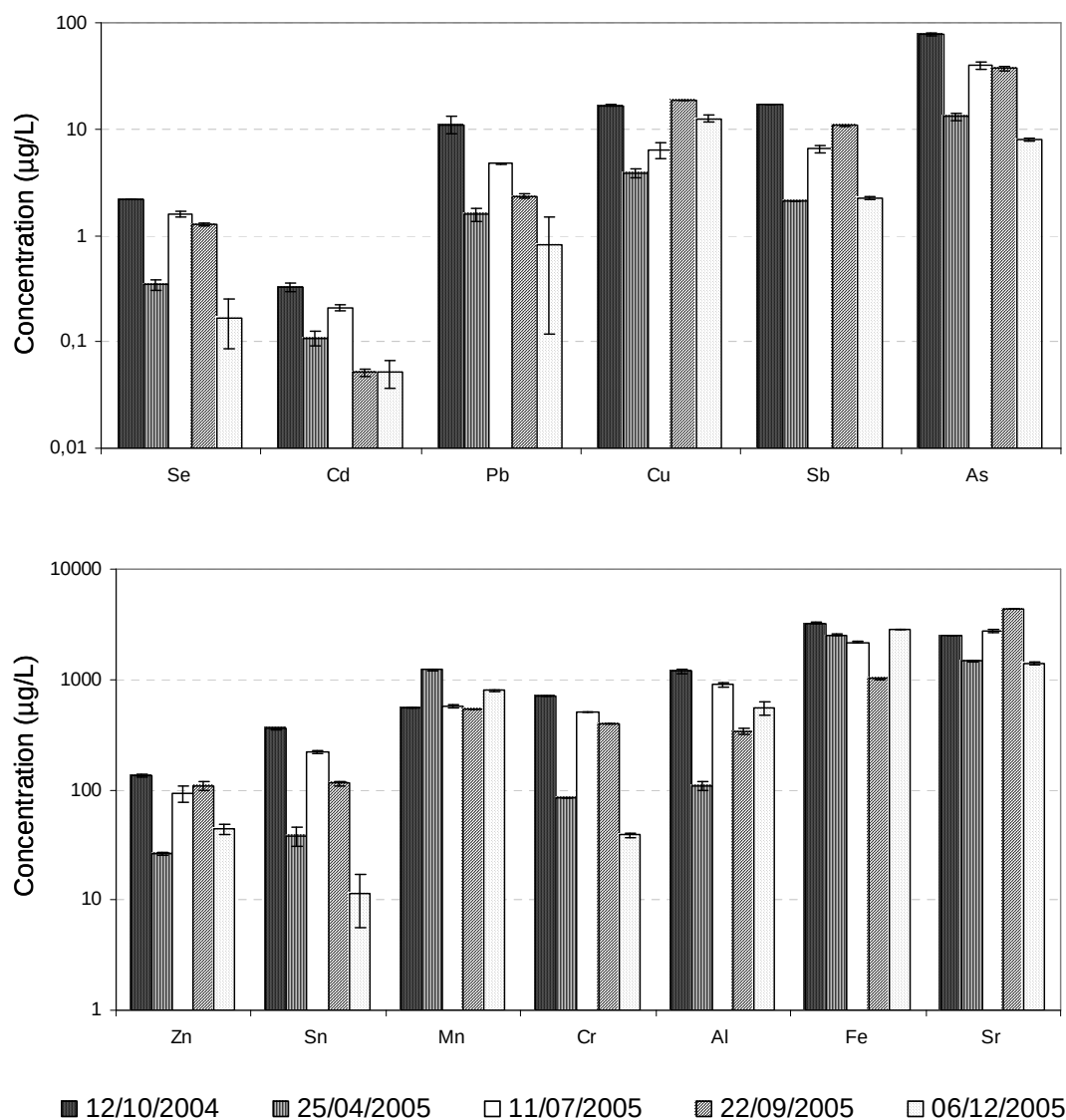


Figure II.3.1 Metal and metalloid composition (µg/L) of leachate from L.F.1 for the five sampling campaigns

In order to consider the environmental impacts bound to leachates, it is important to evaluate concentration factors in relation to rain water and to ground water. Indeed, rain water highly contributes to water balance whereas ground water can be polluted by landfill leachates. Ranges of concentrations (µg/L) of our leachate samples are compared (Table II.3.5) to rain water and ground water ranges or mean concentrations²⁰ and to leachates concentrations²¹.

For all the elements that have been previously measured, the concentrations in leachates from L.F.1 are within the range of values reviewed by Baun *et al.*²¹ (Table II.3.5). Different groups of elements appear by comparing metals and metalloids concentrations with rain water amounts and ground water amounts. First, Cd is the only element for which the concentration in leachate is within the range of rain water. A second group composed of Se, Pb, Cu, Zn, Mn, and Al is characterised by concentrations with same orders of magnitude as those found in ground water. For these elements, the contamination in leachate can be stated as not significantly important. A last group is composed of six elements: Sb, As, Sn, Cr, Fe and Sr. The concentration factors of these elements related to ground water vary from 2 for Sr, to more than 100 for Sn and Cr. The contamination from such metals in this leachate can thus be relatively significant. Some chemical forms of As, Sn, Cr, Sb are also especially recognised as toxic substances (arsenite, tributyltin²²...). The chemical efficiency of leachate treatment has to be carefully checked for such metals and associated compounds to avoid any pollution of the environment.

Table II.3.5 Orders of magnitude of metal and metalloids in µg/L in leachates from L.F.1 compared to literature data for rain water, ground water and leachate

Element	Concentrations range (µg/L)			
	Leachate	Rain water	Ground-water	Leachate
	This study (5 campaigns)	Reimann <i>et al.</i> ²⁰		Baun <i>et al.</i> ²¹
Se	0.2 - 2.2	0.5	0.01 - 4.8	no data
Cd	0.1 - 0.3	0.02 - 0.3	0.002 - 5.5	0.02 - 130
Pb	0.8 - 11.0	0.1 - 1.4	0.03 - 44	0.5 - 1500
Cu	3.9 - 19	0.2 - 1.8	0.4 - 1332	0.5 - 1300
Sb	2.1 - 17	0.03 - 0.4	0.2 - 0.8	no data
As	8.0 - 77	0.05 - 0.2	0.03 - 11	0.5 - 130
Zn	26 - 135	2.5 - 14	0.5 - 1324	0.05 - 7200
Sn	11.3 - 355	no data	0.01 - 2.3	no data
Mn	540 - 1213	0.5 - 6	0.1 - 2975	10 - 23200
Cr	39 - 703	0.2 - 0.2	0.1 - 5.9	0.5 - 1300
Fe	1011 - 3225	10	5 - 323	80 - 2100000
Sr	1397 - 4316	0.10 - 0.4	0.9 - 1871	no data
Al	108 - 1184	0.9 - 9	2 - 2537	no data

II.3.4.2 Interpretation with hydrological data

Some general trends stand out from metal concentration monitoring during one year. Different groups of elements can be identified by taking into account similar evolutions of metal concentrations.

The major group is composed of Se, Sb, As, Zn, Sn and Cr. The evolution of these elements is characterised by two low concentrations in April 2005 and December 2005, just after the two rainiest periods. This general trend is the same for inorganic carbon, sodium, potassium, chloride, bromide and pH. Chloride is usually employed as a conservative compound in hydrological studies such as in landfill leachate plumes²³. The linear dependence ($R^2=0.81$, $p<0.01$, STATBOX Bravais Pearson test) of chloride concentration with wet deposition can be thus simply explained by leachate dilution by rainwater. The linear relationship between pH and precipitations ($R^2=0.92$, $p<0.01$) can be explained similarly by the pH-difference between rain water (5.5) and leachate (8.5). Linear regression coefficients (R^2) range from 0.54 ($p=0.059$) for Sb to 0.90 ($p<0.01$) for Se, Sn and Cr with wet deposition. This statistical data is an indication of co-variation of these metals and metalloids which is mainly due to the physical dilution of leachates by rainwater (minus evapotranspiration). The strong influence of wet deposition on leachate general composition (physico-chemical parameters) was already studied^{24, 25, 26}. The only work which focuses on metal composition describes a similar influence on metal composition²⁶.

Sr, Al, Cd and Pb do not present exactly the same evolution as the first group. The three first campaigns follow the same evolution with a decrease followed by an increase but the two last campaigns present different evolutions. These elements are thus not only controlled by the dilution with rainwater.

The three last elements are Cu, Fe and Mn. For Cu, the best linear regression is obtained with sulphate ($R^2=0.95$, $p<0.01$, without the data from 22/09/2005). Only nitrate is found to be correlated to Mn with a regression coefficient of 0.86 ($p<0.01$). As for Mn, Fe presents a singular profile and is not particularly correlated to any elements or parameters. These elements are thus not only physically controlled but also in interaction with the waste system. Chemical or microbiological processes can be considered. Indeed bacteria respiration uses first oxygen but when the system becomes anaerobic, other electron acceptors such as NO_3^- , Mn, Fe and SO_4^{2-} are used. Christensen *et al.*²³ had also highlighted the simultaneous occurrence of different redox zones in landfill sites with the predominant role of these four electron acceptors for microbial communities (methanogens, SO_4^{2-} -reducers, Fe-reducers, Mn-reducers and denitrifiers).

II.4. Conclusion

This study has led to the determination of some recommendations for leachate processing adapted to total metal analyses. Leachates have to be preserved from aeration by avoiding any head-space above the liquid in sampling bottles, especially if redox sensitive species are of interest. Just after sampling, leachates can be transferred in low volume vials for subsequent single analysis (one analysis = one vial). Leachates can be stored at +4°C and -20°C, especially if analysis can not be performed rapidly. Landfill leachate sampling strategy has been validated through the development of the laboratory reference material (LRM). The relevance of this landfill leachate reference material is complementary to the use of certified reference materials to perform a comprehensive quality control of metal and metalloid analyses in these complex matrices.

The applicability of this complete methodology has been achieved by the evaluation of metal contamination in a landfill site. The comparison of metallic composition between landfill leachates and biogeochemical background is proposed as a way to underline the possible contaminants and to avoid misinterpretation associated with different levels of concentration. In the studied landfill, the more significantly concentrated elements are As, Sn, Sb and Cr. These elements are also characterised by chemical species with large differences of toxicity and bio-availability. The analyses of these elements in terms of chemical speciation appear now to be a necessity to have a more precise evaluation of environmental impacts related to these effluents.

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Ce chapitre a fait apparaître l'importance de la définition de protocoles analytiques spécifiquement adaptés aux lixiviats de CSD afin d'assurer la représentativité des résultats d'analyse des métaux et métalloïdes. De plus, cette première étape a permis de mettre en évidence la présence de deux éléments, en concentrations relativement importantes, qui sont susceptibles de poser problème en raison de leur caractère toxique : l'arsenic et l'étain. Pour ces éléments, qui font l'objet d'une étude approfondie dans la suite de ces travaux, la démarche mise en œuvre est identique. Tout d'abord, les efforts sont concentrés sur la mise en place de protocoles analytiques spécifiquement adaptés à leur spéciation dans les lixiviats. Dans un second temps, le travail consiste à examiner le devenir de leurs composés à l'intérieur et à l'extérieur du système constitué par les déchets, les lixiviats et les biogaz.

**SPECIATION ET DEVENIR DE L'ARSENIC
DANS LES LIXIVIATS ET LES BIOGAZ**

III. Spéciation et devenir de l'arsenic dans les lixiviats et les biogaz de CSD

Dans les déchets ménagers, les sources de l'arsenic sont majoritairement les verres et les formulations métalliques. Au cours de leur dégradation, l'arsenic peut être mobilisé dans les lixiviats et les biogaz. Le but de ce chapitre est d'approfondir les connaissances des formes chimiques sous lesquelles l'arsenic est présent dans ces effluents, et des processus associés.

Avant de s'intéresser au devenir de l'arsenic dans les deux compartiments, il a été nécessaire de mettre en place une méthode d'analyse de spéciation de l'arsenic dans les lixiviats. Le choix s'est porté sur une séparation par chromatographie en phase liquide par échange de cations (colonne Hamilton PRP-X200) suivie d'une analyse par spectrométrie de masse à plasma induit (ICPMS). Les conditions chromatographiques sont optimisées afin de réaliser simultanément la séparation d'un maximum d'espèces d'arsenic. Finalement, aux six espèces quantifiées (AsIII, AsV, MMA, DMA, TMA^s⁺ et AsB), s'ajoutent deux autres espèces dont les pics se superposent en partie (TMAO et AsC). Le critère important pour l'évaluation du protocole de préparation des échantillons est la préservation des espèces couplée à la minimisation des effets de matrice. La validation de l'étape d'analyse de spéciation est réalisée par l'utilisation d'un matériau de référence certifié et par la confrontation de deux méthodes de quantification (étalonnage externe et ajouts dosés). La simplicité de mise en œuvre et la robustesse de ce protocole permettent son application au suivi des espèces de l'arsenic dans les lixiviats des deux sites d'étude. En complément, les espèces volatiles d'arsenic ont été analysées dans les biogaz au moyen de la technique de chromatographie en phase gazeuse avec piège cryogénique couplée à l'ICPMS. A partir du bilan sur les espèces susceptibles d'être présentes dans les déchets, les voies possibles de formation et de mobilisation des espèces de l'arsenic dans les effluents sont évaluées.

III.1. Analyse de spéciation de l'arsenic dans les lixiviats de centres de stockage de déchets

Article soumis à Water Research

Speciation analysis of arsenic in landfill leachate

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As environmental impacts of landfill last from beginning of cell filling to many years after, there is an increasing interest in monitoring landfill leachate composition especially with regards to metals and metalloids. High-Performance Liquid Chromatography (HPLC) coupled with Inductively Coupled Plasma Mass Spectrometry (ICPMS) has been applied to the speciation of arsenic in landfill leachates. The difficulty is related to the complexity and heterogeneity of leachate matrices. A soft sample preparation protocol with water-dilution and filtration of leachates has proved to be sufficient for the achievement of identification and quantification of arsenic species without matrix effect. The cationic-exchange separation method developed has enabled the detection of six arsenic species (AsIII, MMA, AsV, DMA, AsB, TMAO) in different landfill leachates. The wide range of concentrations of arsenic species (from 0.2 $\mu\text{g As L}^{-1}$ to 250 $\mu\text{g As L}^{-1}$) and their repartition illustrate the high variability of these effluents depending on the nature of the wastes, the landfill management, the climatic conditions, the degradation phase... These results provide new information about the chemical composition of these effluents which is useful to better adapt their treatment and to achieve the risk assessment of landfill management.

III.1.1 Introduction

Landfill leachates are mainly generated by excess rainwater percolating through the waste layers. In the waste, combined physical, chemical and microbial processes transfer pollutants from the waste material to the percolating water (Christensen et al., 2001). Among metals and metalloids present in wastes, arsenic concentration reaches 5 mg kg^{-1} of dry waste, according to the French Agency for the Environment and Energy Management (ADEME). The main origin of arsenic is glasses (79% of As present in the waste) and metallic components (12% of As). In leachates the arsenic concentrations vary significantly from one landfill to another, as the global composition of landfill leachates is dependent on many factors such as the origin and the age of wastes, the climatic conditions or the landfill management (Mahler et al., 2005; Clement, 1995). Baun and Christensen (2003) report concentrations of arsenic between 0.0005 to 1.6 mg L^{-1} in landfill leachates from different countries.

Although arsenic is pointed out by the European Pollutant Emission Register (2000/479/EC) as one of the potential inorganic contaminant in the landfill leachate, no study has investigated the arsenic speciation in such matrix. Speciation of arsenic in environmental samples is however very important as the physical and chemical properties, the toxicity and the bioavailability are related to the chemical forms. The inorganic species, arsenite (AsIII) and arsenate (AsV), are considered carcinogenic, whereas the toxicity of the organic species is variable. TMA^+ (tetramethylarsonium ion), MMA (monomethylarsonic acid), DMA (dimethylarsinic acid) and TMAO (trimethylarsine oxide) are less acutely toxic than inorganic arsenic, whereas AsB (arsenobetaine) and AsC (arsenocholine) are considered to be non-toxic. For example, the lethal dose which causes the death of 50% of a population of tested mice (LD50) is 8 mg kg^{-1} , 22 mg kg^{-1} , 916 mg kg^{-1} , 5500 mg kg^{-1} for AsIII, AsV, MMA and TMAO respectively (Craig, 1986; Hughes, 2002).

Speciation analysis of arsenic requires proper sampling and storage (Segura et al., 2002) and the coupling of two techniques, a technique to separate the different arsenic species and a sensitive and specific mean of detection. The separation of the chemical forms of arsenic is usually based on High-Performance Liquid Chromatography (HPLC). The ion-exchange chromatography is the most extensively used technique, following by ion-pair in reverse mode chromatography. As detection mean, inductively coupled plasma mass spectrometry (ICPMS) (B'Hymer and Caruso, 2004) and the hydride generation atomic fluorescence spectrometry (HG-AFS) are the most frequently used technique.

The challenge in arsenic speciation analysis lies on the chemical nature of the arsenic compounds with different charges, pKa values, molecular sizes and functional groups. The

study of organic and inorganic species is usually performed by combining two chromatographic mechanisms. Vilano et al. (2000) propose the use in parallel of anionic and cationic exchange column to separate six arsenic species (AsIII, AsV, MMA, DMA, AsB and AsC). In their separation on the cationic column, the resolution of AsIII, MMA and AsV peaks is not achieved. Other studies combine anion and cation exchange chromatography in series or in column switching system (Teräsahde et al., 1996; Suner et al., 2001). Simon et al. (2004) use a column combining strong anion exchange and hydrophobic characteristics associated to HG-AFS detection, allowing the separation of twelve arsenic species with a single column.

A large variety of samples has been studied: water (groundwater, fresh water and sea water), sediment, fish, chicken, plant, body fluids (B'Hymer and Caruso, 2004; Guérin et al., 1999; Gong et al., 2002). Nevertheless no study on arsenic speciation in landfill leachate has been performed despite the occurrence of arsenic in the waste. Landfill leachates are complex matrix due to their high concentrations of salts and organic matter so that an adaptation of existing protocols is necessary.

The aim of the present study is to perform a screening investigation regarding the occurrence of arsenic compounds in the leachate of various French landfill sites. The first and fundamental stage of this work is the analytical adaptation of the protocol to the complex matrices that are the leachates. The speciation analysis of arsenic implies a soft sample preparation to preserve arsenic species integrity. The separation protocol using HPLC coupled with ICPMS, allowing both the separation of six arsenic species and the identification of two other less resolved species with a single cationic column, has been first optimized on standard solution and then applied to various landfill leachates.

III.1.2 Experimental

III.1.2.1 Standard substances and chemicals

All reagents used are of analytical grade. 1000 mg L⁻¹ arsenic stock solutions are prepared by dissolving NaAsO₂ (Aldrich, 98%) for AsIII, Na₂HAsO₄·7H₂O (Prolabo, >98%) for AsV, CH₃AsO(ONa)₂·6H₂O (Carlo Erba, >98%) for MMA and (CH₃)₂AsO(ONa)·3H₂O (Fluka, >98%) for DMA in high quality ultrapure water from a MilliQ system (18MΩ, Millipore).

Arsenobetaine (AsB), arsenocholine (AsC), trimethylarsine oxide (TMAO), tetramethylarsonium ion (TMAs⁺) were kindly donated by Professeur K.A. Francesconi, Karl-Franzens University, Graz, Austria. All the arsenic solutions are stored in the dark at 4°C.

The HPLC eluent is prepared by dissolving appropriate amounts of ammonium nitrate (Sigma Aldrich, 99.5%) and ultrapure nitric acid (Baker, 70%) in ultrapure water from a MilliQ system.

III.1.2.2 Instrumentation

Total arsenic concentrations are measured with an ICPMS (Agilent, 7500ce) after microwave digestion (Ethos, Milestone) of the sample (nitric acid digestion) (Pinel-Raffaitin et al., 2006 II p53).

The HPLC system consists of an Agilent 1100 gradient solvent delivery pump and a Hamilton PRP-X200 cationic-exchange column protected by a Hamilton guard column, at room temperature. The optimized elution program is presented in Table III.1.1. The column is conditioned with the mobile phase A for at least 4 hours before analysis. The outlet of the column is connected to an ICPMS (Agilent, 7500ce). The ICPMS settings are detailed in Table III.1.1.

Table III.1.1 Instrumental settings and HPLC conditions

HPLC (Agilent 1100)	
Cationic exchange column	Hamilton PRP-X200 (25cm x 4,1 mm)
Mobile phase	- solution A : HNO ₃ 4mmol L ⁻¹ - solution B : HNO ₃ 4mmol L ⁻¹ + NH ₄ NO ₃ 20mmolL ⁻¹
Injected volume	100µL
Flow rate	1 mL min ⁻¹
pH solution A and B	2.5
Gradient elution	- 0 to 2 min: 100% sol. A - 2.1 to 6.1 min: 20% sol. A and 80% sol. B - 6.2 to 17. 2 min : 100% sol. B - 17.3 to 25 min : 100% sol. A
ICPMS (Agilent 7500ce)	
Sampler/skimmer cones	Ni
Power	1500 W
Nebulizer	Micromist
Spray chamber	Scott ; Temperature : 2°C
Nebulizer flow	Ar : 0.8-1.2 L min ⁻¹

III.1.2.3 Landfill leachate samples

III.1.2.3.1 Landfill sites description

Leachates were sampled in three French landfills which receive only municipal wastes. In the first landfill, named hereafter as L.A, 200000 tons of wastes per year are disposed. The second one, named hereafter L.B is small: 10000 tons of wastes per year are disposed. This site is composed of three cells: the studied one has been filled from 1999 to 2003. The third landfill, named hereafter L.C, receives 150000 tons of wastes per year and is composed of seven cells. The 1st cell has been filled from 1995 to 2000 (L.C1) and each of the six following cells has been filled during one year (L.C2 to L.C6).

Additionally, leachates from an experimental landfill (L.D) testing different kind of waste management have been sampled. The wastes used have been homogenized before the filling of the different experimental cells. Three cells were investigated: a reference one without any treatment, a biological pre-treatment cell with a first step of waste degradation by composting and a bioreactor cell with leachate recirculation.

III.1.2.3.2 Sample collection

Concerning the sampling technique, no pumping is applied and no perturbation of the outflow is induced: leachates are simply collected at the extremity of the leachate pipe and immediately transported in 1L polyethylene bottle in ice-box. Then, leachates are transferred in 5mL polypropylene vials and frozen at -20°C.

Sampling bottles and plastic ware throughout this work were all, before use, rinsed with a detergent and warm water, then decontaminated with diluted (10%) nitric acid (Baker Analyzed, 65%) and finally rinsed three times with ultrapure water (Millipore 18MΩ). All bottles are filled with ultrapure water and transported to the landfill. One of the bottles is left with pure water to constitute a “landfill blank” following all the critical steps.

III.1.2.3.3 Sample preparation

For total arsenic determination, leachates are digested using a closed microwave system. The investigated protocol was presented elsewhere (Pinel-Raffaitin et al., 2006).

For speciation analysis, the leachate samples are diluted with ultrapure water. The dilution depends on total As concentration and on the ICPMS working range which is comprised between 0.25 and 20 µg As L⁻¹ (the dilution factor varies between 5 and 40). Leachate

samples are then filtered through a 0.45µm cellulose acetate filter just before injection in the HPLC system. 100µL aliquots of sample solution are injected in the chromatographic system.

III.1.3.1.4 *Quantification*

In order to give accurate results, quantitative analyses are performed by external calibration but also by standard addition to check any matrix effect. Standard solution of TMAO is partly degraded in DMA, its quantification is indicative. The total arsenic concentration of each digested sample is also quantified by these two calibration methods. The tuna fish tissue certified reference material BCR-627 is used for the validation of the quantification of the two species DMA and AsB for which it is certified.

III.1.3 **Results and discussion**

III.1.3.1 Optimization of the analytical method

III.1.3.1.1 *Separation of arsenic compounds*

Analytical parameters of mobile phase were optimized to obtain the best resolution between all peaks with the shorter analysis duration (Table III.1.1). The final elution gradient allows the complete separation of six species in 25 minutes with a light peak overlap between AsIII and MMA. Two others species (AsC and TMAO) have been separated from the six others but their resolution is not achieved. A typical chromatogram of a standard solution with AsIII, MMA, AsV, DMA, AsB, TMA⁺, AsC and TMAO is presented Figure III.1.1.

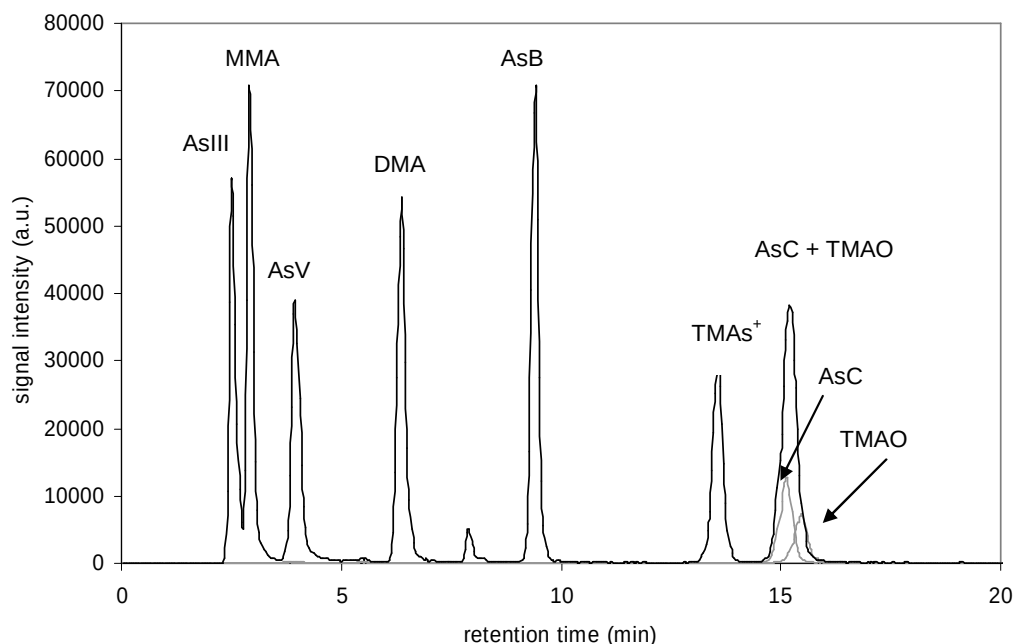


Figure III.1.1 In black, chromatogram of a standard solution at $10 \mu\text{g As L}^{-1}$ of AsIII, MMA, AsV, DMA, AsB, AsC and TMAO and at $5 \mu\text{g As L}^{-1}$ of TMAAs⁺; in gray, chromatograms of AsC and TMAO injected separately at $5 \mu\text{g As L}^{-1}$

On this chromatogram, AsC and TMAO are eluted together in a broad peak. When they are injected separately at lower concentration, (chromatograms in gray), there is a lag between their elutions. Retention times are 2.5, 2.9, 4.1, 6.5, 9.5, 13.7, 15.2 and 15.7 minutes for AsIII, MMA, AsV, DMA, AsB, TMAAs⁺, AsC and TMAO respectively. This analysis is original because of the simultaneous separation of six species and two others less resolved species on a cationic-exchange column. AsC and TMAAs⁺ are positively charged, independently of pH, which means that their cationic-exchange separation is function of their ionic radius. For the others species, the charge is pH-dependent: they can be neutral, anionic, cationic or zwitterionic. At pH 2.5, TMAO is positively charged and AsB is a zwitterion. Therefore, the retention time of AsB is shorter than the one of the three cationic species. At this pH, AsIII, DMA and MMA are neutral; thus the hydrophobic interaction with the column material allows the separation. The case of AsV is more difficult to understand because this pH is closer to the pKa value, so that the species is in equilibrium between a neutral and an anionic species. The retention time expected should be similar to the one of AsIII. The longer retention time of AsV could be attributed to interactions between this compound and the polymer of the column.

III.1.3.1.2 *Void volume determination*

The void volume has been estimated by the comparison of AsIII and DMA retentions when changing the concentration of the mobile phase. With the injection of 100% of phase B (HNO_3 4mmol L^{-1} + NH_4NO_3 20mmol L^{-1}), the retention time of the first specie (AsIII) does not change whereas the retention time of the DMA decreases. The inorganic species is thus eluted in the void volume corresponding to a retention time of 2.5min. The identification of this species could then be controversial. Nevertheless on the chromatograms presented in this work, the peak with a retention time of 2.5 min will be attributed to AsIII. In fact, it will be assumed that all the other arsenic species should present a different charge and a different molecular mass inducing stronger interactions with the stationary phase of the column.

III.1.3.1.3 *Arsenic interferences*

During HPLC–ICPMS runs, a number of isotopic masses have been monitored to evaluate possible interferences at the ^{75}As mass. The main interference at m/z 75 is from the formation of the polyatomic ion $^{40}\text{Ar}^{35}\text{Cl}^+$ resulting from the combination in the plasma of argon (from plasma) and chloride (from samples). This occurs when high chloride matrix is present in the samples, which is the case for landfill leachates. The monitoring of ^{77}Se and ^{82}Se is a way to determine whether possible $^{40}\text{Ar}^{37}\text{Cl}^+$ formation occurs and whether changes in the m/z 75 signal are due to chloride interferences.

To investigate the time retention of chloride, a sodium chloride solution has been injected. The elution of the chloride ion is monitored as $^{35}\text{Cl}^{16}\text{O}^+$ at m/z 51. The retention time of chloride is measured at 5.5 minutes, so the chloride peak is completely separated from those of the arsenic species.

III.1.3.1.4 *Analytical validation and performances*

Only three reference materials certified for arsenic species exist: there are all fish tissues. The analytical separation and quantification have been validated using BCR-627 (certified for AsB and DMA concentrations). Species are extracted from the sample with a mixture of ultrapure water and methanol. After ultrasonication and centrifugation, samples are stored at 4°C until analysis. The certified species are well quantified (standard addition): $2.3 \pm 0.2 \mu\text{mol kg}^{-1}$ for DMA (certified value: $2.0 \pm 0.3 \mu\text{mol kg}^{-1}$) and $50 \pm 4 \mu\text{mol kg}^{-1}$ for AsB (certified value: $52 \pm 3 \mu\text{mol kg}^{-1}$). Because of the lack of liquid certified reference material, this validation only concerns the analytical procedure and not the whole protocol, as our samples are prepared differently.

Detection limits are calculated using the I.U.P.A.C. (International Union of Pure and Applied Chemistry) definition as three times the standard deviation of noise level. Relative detection limits vary between 11 ng As L⁻¹ for DMA to 27 ng As L⁻¹ for AsV. In terms of quantification limits, it corresponds to a range between 36 ng As L⁻¹ and 90 ng As L⁻¹.

III.1.3.2 Application to real landfill leachate matrix

III.1.3.2.1 Achievement of arsenic speciation in leachate sample

Due to their high organic matter content and their high salt concentration, the applicability to landfill leachate of the optimized separation is not obvious and therefore it has to be checked. The method application to a landfill leachate from L.A is illustrated by the chromatogram Figure III.1.2. Three defined peaks with similar retention time to MMA (2.9 min), AsV (4.1 min) and DMA (6.9 min) have been identified. Five other little peaks appear on the chromatogram, the first one corresponding to AsIII retention time (2.5 min) and the last one to TMAO (15.7 min) retention time. The identification of this last compound has been achieved by retention time comparison and checked by addition of both AsC and TMAO separately. There are also three species with a retention time not matching with any of the standards. The first one at 5.5 minutes corresponds to chloride interference. The two other species (X₁ eluted at 8.5 min and X₂ at 10.9 min) seem to be minor species but their identification is not already achieved.

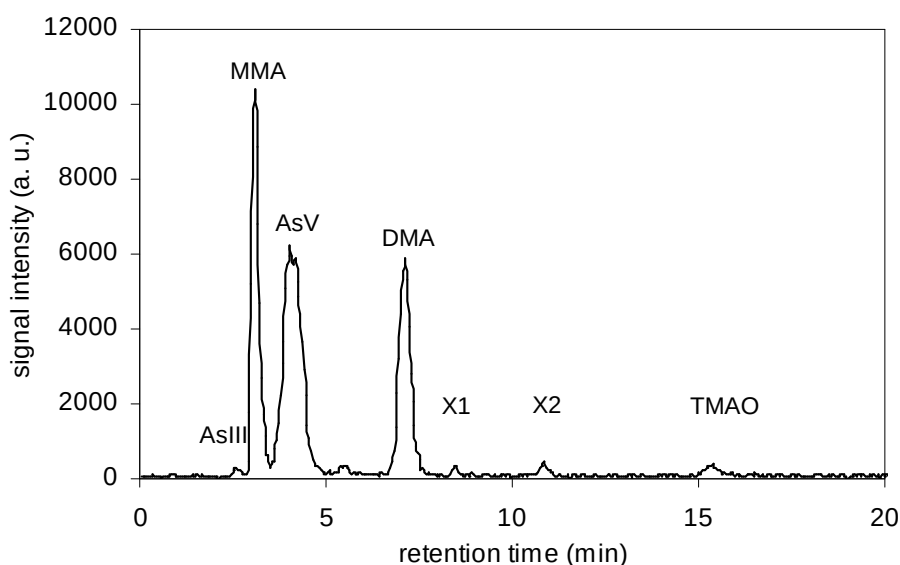


Figure III.1.2 Arsenic species separation in leachate from L.A using the optimized conditions

III.1.3.2.2 *Comparison of calibration methods: any matrix effect?*

To evaluate the possible matrix effects, the quantification of arsenic compounds is performed by standard additions. The concentrations measured by external calibration and standard addition are presented in Table III.1.2. The results match very well. The slopes of the two calibration methods are similar with less than 6% of relative difference. For this sample, no significant matrix effect interferes on the arsenical species separation and quantification. External calibration is then suitable for the quantification of arsenic species, even if a checking with standard addition is performed for each new sample.

Total arsenic concentration indicated in Table III.1.2 has been previously determined by an intercomparison work (Pinel-Raffaitin et al., 2006, II p53). Because two unidentified species are not quantified and some species are probably not eluted with these chromatographic conditions, there is a 10% difference between the sum of arsenical species and total arsenic measured after digestion. The chromatographic conditions permit thus to give a nearly complete view of the arsenic composition.

Table III.1.2 Arsenic species concentrations and calibration slopes measured by external calibration (Ext. Cal.) and standard addition (Std. Add.) in leachate from L.A diluted in ultrapure water. Total As concentration previously determined (Pinel-Raffaitin et al., 2006, II p53).

Species	Concentration ($\mu\text{g As L}^{-1}$)		Calibration slope	
	Ext. Cal.	Std. Add.	Ext. Cal.	Std. Add.
As III	4.0 ± 0.2	4.0 ± 0.1	2.7E+04	2.5E+04
MMA	154 ± 4	158 ± 2	2.7E+04	2.6E+04
As V	237 ± 2	233 ± 3	2.7E+04	2.5E+04
DMA	136 ± 5	134 ± 2	2.7E+04	2.8E+04
Sum of As species	530 ± 10	529 ± 6		
Ratio versus total As	92%	92%		
Total As	578 ± 69			

III.1.3.2.3 *Influence of sample pH on chromatographic separation*

The pH of the different leachate samples is around 6 – 8 while the pH of the mobile phase is 2.5. The impact of the elution solution pH has to be checked on arsenic speciation. Same samples have been diluted with ultrapure water and with the elution solution. Arsenic speciation and quantification by external calibration have been compared in the two cases. The relative deviation between the concentrations measured in the samples varies from 3% for

DMA to 9% for AsIII which is the less concentrated species. Considering the relative standard deviation of external calibration (between 1% and 6%, Table III.1.2), the difference between the results obtained in the sample diluted with water and in the same sample diluted with mobile phase (HNO_3 4mmol L^{-1}) is not significant. Consequently, landfill leachate dilution can be performed with ultrapure water.

III.1.3.3 Investigation of arsenic speciation in French landfill leachates

The particularity of the arsenic speciation method developed specifically for landfill leachate sample is its faculty to be carried out easily: leachate is diluted with water and filtered before the achievement of its speciation analysis with a single injection on HPLC-ICPMS. The objective is to assess if this method is suitable for the routine analyses of landfill leachates originating from different sites.

III.1.3.3.1 Assessment of arsenic species repartition in landfill leachates

The three chromatograms shown in Figure III.1.3 are obtained from leachates from two landfills L.B and L.C. The proposed protocol is fully relevant to describe the difference from one sample to another in species repartition and quantification. Table III.1.3 presents the arsenic distributions in a leachate from L.B sampled in October 2004 and in leachates from the six L.C landfill cells (LC1 to LC6) sampled in July 2005. These samples illustrate the diversity of arsenic species distribution: for L.A (Table III.1.2), L.B, L.C2 and L.C5, the predominant species are AsV and MMA, for L.C3 and L.C4, they are the two inorganic species and for L.C1 and L.C6, the predominant species is TMAO. Considering simultaneously the two most toxic species which are AsIII and AsV, their amount vary between 20% to 98% of the sum of the arsenic species.

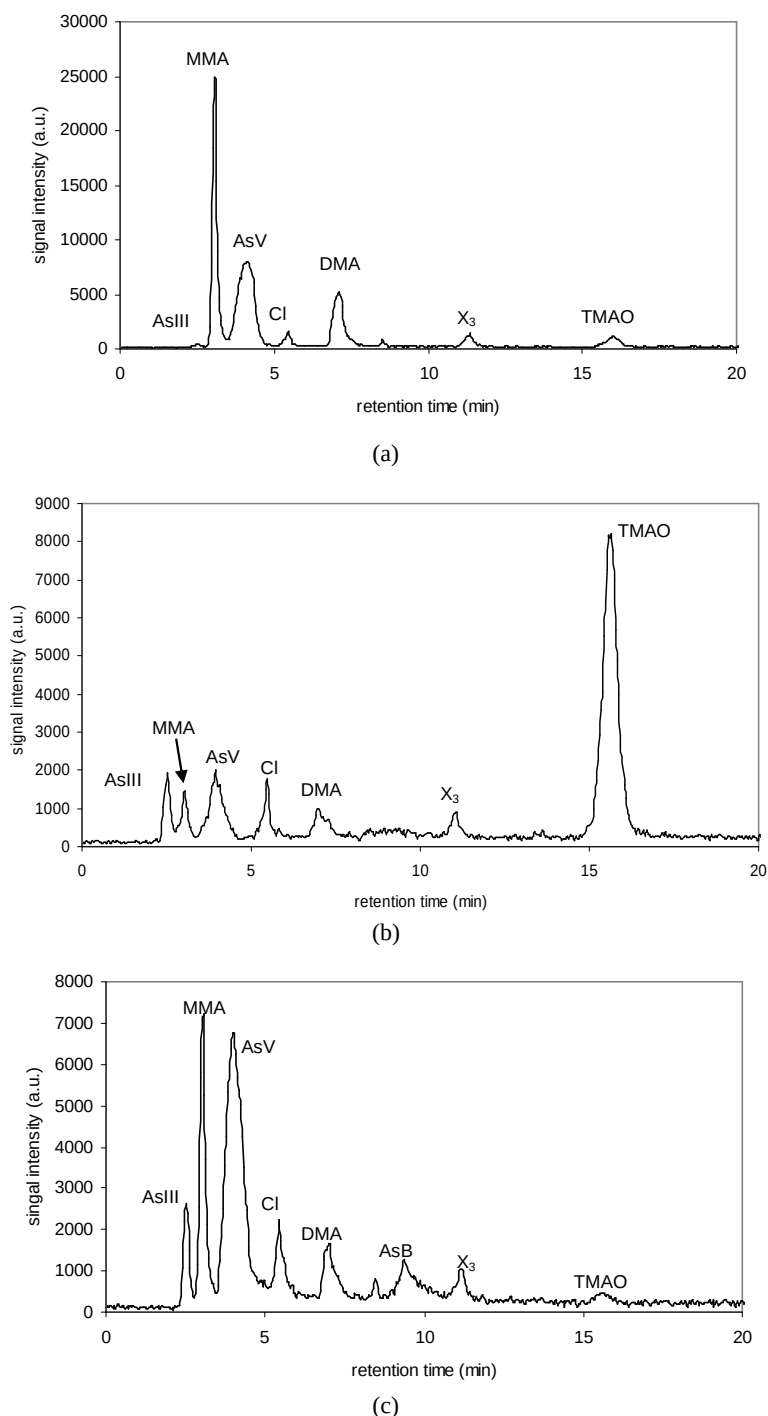


Figure III.1.3 Chromatograms of landfill leachates: (a) leachate from landfill L.B sampled in October 2004, named hereafter L.B.; (b) leachate from landfill L.C sampled in July 2005 in the 1st cell (filled from 1995 to 2000), L.C1; (c) leachate from landfill L.C sampled in July 2005 in the 5th cell (filled from 2003 to 2004), L.C.5

Landfill leachates are concerned by the European directive (1999/31/CE) and by the French decree (09/09/1997) on waste landfilling which fixes the total arsenic concentration limit at $100\mu\text{g L}^{-1}$ for the effluent after treatment. All the studied samples except L.A present concentrations below this limit value. However, the observed differences between the species

repartition highlight the necessity of speciation analysis for the risk assessment of these leachates. More than that, the speciation analysis can be a tool for a better adaptation of landfill leachate treatment.

Table III.1.3 Examples of arsenic species distribution (concentration in $\mu\text{g As L}^{-1}$) in different landfill leachates
(Nd: not detected)

Species	Concentration in $\mu\text{g As L}^{-1}$ in leachate samples						
	L.B	L.C.1	L.C.2	L.C.3	L.C.4	L.C.5	L.C.6
As III	0.3±0.1	0.8±0.1	1.4±0.1	1.9±0.1	4.4±0.4	3.4±1.5	0.2±0.1
MMA	23.2±0.7	0.5±0.1	4.1±0.3	0.5±0.1	0.2±0.1	6.1±1.3	0.2±0.1
As V	20.9±0.1	1.9±0.2	5.1±0.5	2.7±0.1	5.6±1.1	16.7±0.1	0.9±0.7
DMA	8.6±0.5	0.6±0.1	3.3±0.4	0.3±0.1	Nd	2.0±0.6	0.6±0.1
AsB	Nd	Nd	Nd	Nd	Nd	2.3±0.9	Nd
TMAO	2.2±0.1	10.5±0.7	0.9±0.1	Nd	Nd	0.8±0.1	2.9±0.5
Σ As species	55.1±0.1	14.3±0.5	14.8±0.2	5.6±0.2	10.2±0.7	30.9±1.8	4.9±0.5
Ratio vs total As	71%	46%	42%	30%	60%	46%	94%
Total As	77.4±0.5	31.4±0.4	35.3±0.1	18.9±0.7	16.9±0.6	67.6±1.7	5.2±0.5

III.1.3.3.2 Assessment of arsenic species repartition in landfill leachates

Landfill cells are complex anaerobic systems in which conditions of reduction reactions and methylation are gathered. Nevertheless, before sampling the leachates are aerated in the leachate drains so that the species could be oxidized. The samples show a high diversity of species: reduced, methylated and oxidized species. The occurrence of the most reduced species (AsIII) can indicate that the leachate is stable enough and the speciation is not completely modified during the leachate draining and sampling. The presence of methylated species could indicate that all the conditions for biomethylation are gathered in landfill systems. Some works on landfill biogases have already observed methylated compounds in the gaseous phase, indicating the possibility of such phenomenon in these complex reactors that are landfills (Feldmann and Hirner, 1995; Hirner, 2003; Pinel et al., 2005).

III.1.3.3.3 Assessment of arsenic species repartition in landfill leachates

The study of the experimental landfill (L.D) allows the evaluation of the impact of waste management on arsenic speciation in the landfill leachate. Arsenic speciation chromatograms

of leachates originating from the experimental landfill (L.D) are presented Figure III.1.4((a) reference cell, (b) biological pre-treatment cell, (c) bioreactor cell).

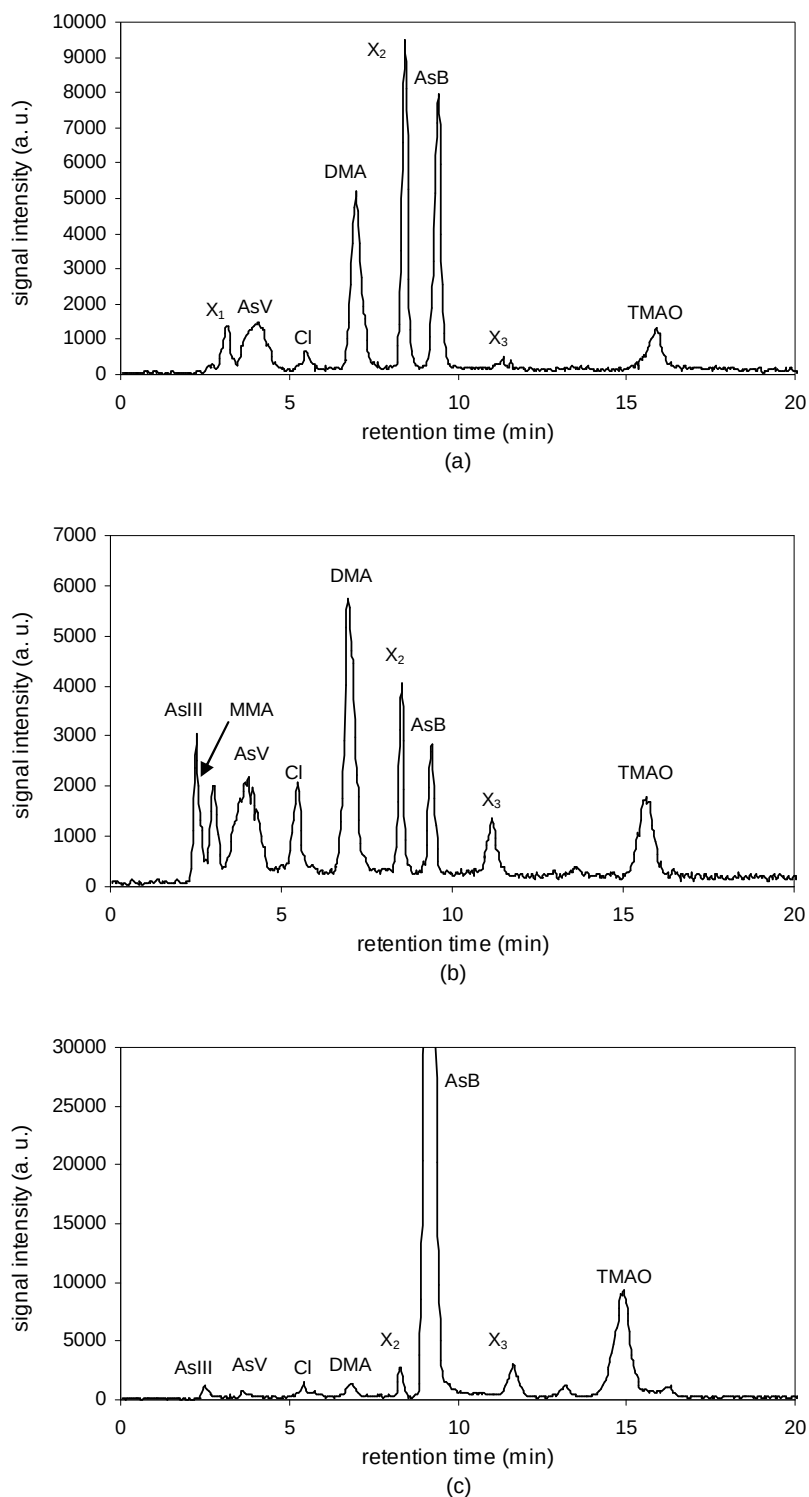


Figure III.1.4 Chromatograms of leachates from the experimental landfill: (a) reference cell, (b) pre-treatment cell, (c) bioreactor cell

Inorganic (AsIII and AsV) as well as organic species (MMA, DMA, AsB and TMAO) are present in the three leachates but in different proportions. The presence of arsenobetaine

(AsB), generally predominant species in marine organisms, in the leachates can be due to the disposal of marine biological wastes (algae, fish) in the cells, as the investigated site is in a coastal area. This species is known to be non toxic. The arsenic species distributions in the reference and in the biological pre-treatment cells are relatively closed. The main difference is observed in the leachate from the bioreactor cell with the presence of arsenobetaine as the dominant species. With this first observation an impact of the waste management on arsenic speciation can be envisaged. As a preliminary explanation, the leachate recirculation can enhance biological activity and then can favor the degradation of complex organic arsenic species (perhaps arsenosugars or arsenoproteins) or the biotransformation of inorganic species, until AsB formation. AsB is rather stable and is supposed to be the end-product of a series of degradations as it has already been suggested in marine environment (Francesconi et al., 1994). Nevertheless, with the available experimental data, and the coastal properties of the wastes, a simple leaching of the AsB induced by the leachates recirculation can not be excluded.

III.1.4 Conclusions

This study has lead to the development of an arsenic speciation method adapted to landfill leachates. The chromatographic conditions provide the separation of six arsenic species within 25 minutes and the identification of two others which are not completely resolved. Despite the high complexity of leachate matrix, no matrix effect has been pointed out. The applicability of the analytical protocol has been achieved by the evaluation of arsenic species distributions in several landfill leachates. The developed method has the advantages to require a soft and rapid sample preparation and to enable within a single analysis the repartition determination of the most environmentally significant arsenic species. The recovery of most of the total arsenic content is obtained for some leachates. The results show the wide diversity of arsenic speciation depending on the nature of waste, and landfill management. This first screening of arsenic speciation in leachates highlights the presence of both inorganic and organic species in different proportions. These observations induce differences of environmental and sanitary impacts related to these effluents and are relevant for the choice of leachate treatment protocol.

III.1.5 Acknowledgements

The authors are grateful to F. Seby and UT2A for the reference material. P. Pinel-Raffaitin acknowledges the French Environmental agency (ADEME) for her financial support.

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III.2. Devenir des espèces inorganiques et organiques de l'arsenic dans les lixiviats et les biogaz de centres de stockage de déchets

Article en cours de soumission

Distribution and fate of inorganic and organic arsenic species in landfill leachates and biogases

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The potential landfill release of arsenic, which is one of the most environmentally problematic elements, requires a special attention with increasing global municipal solid waste production. The determination of arsenic species in both leachates and biogases has been performed in this work to achieve the fate of arsenic in landfill. Both inorganic and methylated arsenic species occur in leachates with concentrations varying from $0.1\mu\text{g(As)}\text{L}^{-1}$ to $80\mu\text{g(As)}\text{L}^{-1}$. These species are representative of the leachate arsenic composition as the mean recovery obtained for the speciation analyses is 67% of the total arsenic determined in elementary analyses. In biogases, both methylated and ethylated volatile arsenic species have been identified and semi-quantified ($0\text{-}15\mu\text{g(As)}\text{m}^{-3}$). The landfill monitoring has emphasized close relationships between the concentrations of mono-, di- and tri-methylated arsenic compounds in leachates. Biomethylation pathway has thus been proposed as a source of these methylated compounds in the leachates from the waste arsenic, which is supposed to be in major part under inorganic forms. In addition, peralkylation mechanisms of both biomethylation and bioethylation have been suggested to explain the occurrence of the identified volatile species. This combined speciation approach provides a qualitative and quantitative characterization of the potential emissions of arsenic from domestic waste disposal in landfill.

III.2.1 Introduction

Even though municipal solid waste (MSW) disposal in landfill is one of the most common waste management pathway throughout the world, its potential release of major contaminants such as arsenic in both atmosphere and aquatic ecosystems is not documented. As a comparison, the incineration arsenic global emission in the atmosphere was 87 tons per year in the mid 1990's and the corresponding emission factor was ranging between 1.1 and 2.8 g of arsenic per tons of incinerated MSW (Pacyna and Pacyna, 2001) (Nriagu and Pacyna, 1988). With the increasing global waste production and the well-known toxicity of arsenic, this potential diffuse source of arsenic in the environment is gaining importance. Our recent work has pointed out arsenic as a main leachate contaminant among metals and metalloids (Pinel-Raffaitin et al. 2006, II p53). Furthermore, simulated arsenic leaching studies (Ghosh et al., 2006) have to be completed with speciation analyses of real samples to improve the understanding of arsenic fate in landfill.

Taking into account the main anthropogenic uses of arsenic, its sources in municipal solid waste are supposed to be glasses, metallic components and agricultural products (Mandal and Suzuki, 2002; Bissen and Frimmel, 2003). According to the French Agency for the Environment and Energy Management, the total arsenic concentration in municipal solid wastes reaches 5 mg kg⁻¹ of dry waste (ADEME, 1993). The information concerning the characterization of arsenic forms in MSW is scarce. In glasses, arsenic acid (acid form of arsenate, AsV) is nowadays preferred to arsenic trioxide (As₂O₃) (Loebenstein, 1994). In metallic components (alloy, semi-conductors), arsenic is supposed to be under inorganic forms such as GaAs (Carter et al., 2003). Arsenic agricultural applications include wood preservatives, herbicides and insecticides, in which arsenic can be under different forms such as inorganic arsenic or mono- and di-methylated species (Loebenstein, 1994; Mandal and Suzuki, 2002).

Complex physical, chemical and biological processes interact in landfill during waste degradation. As well as other metals and metalloids, arsenic can potentially be transferred from the waste to leachates and biogases. In the waste mass, the presence of microorganisms combined to reducing conditions enhances the potential transformation of arsenic by bioalkylation or hydride generation pathways (Michalke et al., 2000; Hirner, 2003). More particularly, the Challenger's biomethylation mechanism still remains topical nowadays in order to explain the formation of methylated compounds from inorganic arsenic by combining reactions of reduction and methylation (Craig, 1986). The potential pathways of these

microbial processes have been widely studied (Cullen and Reimer, 1989; Bentley and Chasteen, 2002). The difference of toxicity between the methylated forms in comparison with the inorganic forms in both liquid and gaseous phase remains significant. The lethal dose which causes the death of 50% of a population of tested mice (LD_{50}) is as low as 8 mg kg^{-1} for arsenite (AsIII) and rises up to 5500 mg kg^{-1} for trimethylarsine oxide (TMAO) (Hughes, 2002). Similarly, LD_{50} tremendously decreases from 20000 mg L^{-1} for trimethylarsine down to $5\text{-}45 \text{ mg L}^{-1}$ for arsine (AsH_3) (Planer-Friedrich et al., 2006). Such observations have suggested that biomethylation of arsenic can be thus considered as a detoxification mechanism (Bentley and Chasteen, 2002).

Both liquid and gaseous arsenic species determinations appear to be necessary for the assessment of environmental and sanitary impacts of landfill. Even if arsenic speciation analysis in liquid samples has been widely studied for example in waters (Bohari et al., 2001; Bednar et al., 2004) and in wastewaters (Segura et al., 2002; Yu et al., 2003), it is noteworthy that no data upon arsenic species occurrence in landfill leachates is available, to the best of our knowledge. In opposition, some works have already reported the occurrence of some volatile arsenic species in landfill biogases (Feldmann and Hirner, 1995; Hirner, 2003) such as hydride, methylated and ethylated forms.

This work is based on the specific developments of arsenic speciation analyses in both landfill leachates (Ponthieu et al. submitted, III.1 p76) and biogases (Feldmann et al. 1994). A reliable analytical protocol for the determination of up to eight arsenic species has been developed and is applied for the leachate monitoring collected in two MSW landfills. In addition, the corresponding biogases are examined in terms of volatile arsenic species composition. The main objective of the present work is to propose possible sources and pathways to explain the occurrence of the identified species in landfill effluents. In this way, the results of arsenic speciation analyses in both gaseous and liquid phases have been combined to outline the main factors that influence the formation and the evolution of the arsenic species. Finally, the global emissions of arsenic related to waste disposal in landfill have been evaluated in a risk assessment point of view.

III.2.2 Material and methods

III.2.2.1 Reagents

Ultrapure water was obtained from a MilliQ system (18M Ω , Millipore). All reagents used are of analytical grade. Nitric acid (70% Baker Instra-Analysed) was used for the microwave assisted extraction. Arsenite (AsIII), arsenate (AsV), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) were obtained respectively from Aldrich (NaAsO₂, 98%), Prolabo (Na₂HAsO₄·7H₂O, >98%), Carlo Erba (CH₃AsO(ONa)₂·6H₂O, >98%) and Fluka ((CH₃)₂AsO(ONa)·3H₂O, >98%). Arsenobetaine (AsB), arsenocholine (AsC), trimethylarsine oxide (TMAO), tetramethylarsonium ion (TMA⁺) were kindly donated by Professeur K.A. Francesconi (Karl-Franzens University, Graz, Austria). Elemental arsenic standard was obtained from Analab (CCS-4). All the arsenic solutions are stored in the dark at 4°C. The High-Performance Liquid Chromatography eluent is prepared by dissolving appropriate amounts of ammonium nitrate (Sigma Aldrich, 99.5%) and ultrapure nitric acid (Baker, 70%) in ultrapure water from a MilliQ system.

III.2.2.2 Sampling sites and procedures

III.2.2.2.1 Landfill sites description

Leachates and biogases were sampled in two different French landfills which receive only municipal solid wastes (Table III.2.1).

The first landfill, named hereafter as L.A, receives 150000 tons of wastes per year and is composed of seven cells. The 1st cell has been filled from 1995 to 2000 (named hereafter LA¹) and each of the three following cells has been filled during one year until 2003 (named hereafter LA², LA³ and LA⁴). The second landfill, named hereafter as L.B, has been filled with 10000 tons of wastes per year from 1999 to 2002.

III.2.2.2.2 Leachate sampling

In order to avoid the perturbation of the outflow no pumping was applied during sampling. In this way, the leachates were simply collected at the extremity of the leachate pipe and immediately transported in 1L polyethylene bottle using ice-boxes. Then, the leachates were transferred into 5mL polypropylene vials and frozen at -20°C until analysis. In all cases, the sampling bottles and the plastic ware used throughout this work were rinsed with detergent and warm water, decontaminated with diluted (10%) nitric acid and finally rinsed three times with ultrapure water before use. All bottles were filled with ultrapure water and transported to

the landfill keeping one of the bottles filled with ultrapure water during the whole sampling and transportation in order to constitute the “landfill blank” (following all the subsequent sample preparation steps).

Leachates samples were collected four times in landfill L.A (10/01/2005; 04/07/2005; 08/12/2005; 29/05/2006) and five times in landfill L.B (12/10/2004; 25/04/2005; 11/07/2005; 22/09/2005; 06/12/2005). The corresponding leachate samples are LA^1_A to LA^4_A for 10/01/2005, LA^1_B to LA^4_B for 04/07/2005, LA^1_C to LA^4_C for 08/12/2006, LA^1_D to LA^4_D for 29/05/2006 and LB_A , LB_B , LB_C , LB_D , LB_E for the five campaigns in L.B (Table III.2.1). For all the analysed samples, the entire sample protocol was done in duplicate.

Table III.2.1 Presentation of the sampling campaigns on the two landfills and the corresponding wet deposition.

Landfill	Waste cells (filling period)	Leachate and biogas sampling campaigns					
		10/01/2005	04/07/2005	08/12/2005	29/05/2006		
L.A.	LA^1 (1995-2000)	LA^1_A	LA^1_B	LA^1_C	BgA^1_D	LA^1_D	
	LA^2 (2000-2001)	LA^2_A	LA^2_B	LA^2_C	BgA^2_D	LA^2_D	
	LA^3 (2001-2002)	LA^3_A	LA^3_B	LA^3_C	BgA^3_D	LA^3_D	
	LA^4 (2002-2003)	LA^4_A	LA^4_B	LA^4_C	BgA^4_D	LA^4_D	
Wet deposition (mm)		63	40	159		51	
		12/10/2004	25/04/2005	11/07/2005	22/09/2005	06/12/2005	
L.B.	LB (1999-2002)	LB_A	LB_B	BgB_C	LB_C	LB_D	LB_E
Wet deposition (mm)		70	197	76	158	227	

III.2.2.2.3 Biogas sampling

The two sites are equipped with drain to collect and then flare the biogases. Biogases were sampled at the drain's bleed. Ten-litres Tedlar bags were filled using a laboratory-made box which provides a clean sampling as it is depressurised indirectly with a vacuum pump. After collection, bags were placed immediately in the dark to avoid photochemical degradations and kept at room temperature until pre-concentration step. For each sampling campaign, the first and the last samples were ambient air samples to check the landfill background.

One sampling campaign has been done on each site (Table III.2.1). For L.A, two Tedlar bags were used for each of the four cells sampled (29/05/2006): BgA^1_D , BgA^2_D , BgA^3_D and BgA^4_D . For L.B, five Tedlar bags were filled on 11/07/2005 (BgB_C).

III.2.2.2.4 *Cryogenic pre-concentration of volatile species*

Cryogenic pre-concentration was performed within 2 hours after the on-site collection. Each Tedlar bag was directly connected to a cryogenic pre-concentration system via its valve (Péchevran et al., 1998). The aspiration flow rate for the gas pumping was fixed at 800 mL min⁻¹. Gas samples were dried by passing through an empty U-shaped glass tube maintained at -20°C (mixture of ice and acetone) before being cryofocused at -80°C in glass wool columns (i.d. 5mm, 17.5cm of length). This temperature was chosen to avoid the condensation of both carbon dioxide (Boiling point = -80°C) and methane (Boiling point = -164°C), which represent 50-80% of the total biogas content. For each Tedlar bag, three columns were used to pre-concentrate different volumes of biogas (four and two litres). For ambient air, the gas volume pre-concentrated was 8L. After cryofocusing, the cryotrap was closed with Teflon caps and immediately transferred to a dry atmosphere cryogenic container. Volatile arsenic species were extracted from leachate samples from L.A (29/05/2006) using a purge system connected to the previously cited cryogenic pre-concentration system. The principle of the purge is described elsewhere (Amouroux et al., 1998), although the apparatus has been slightly modified (Pinel-Raffaitin et al. submitted, IV.2 p134).

III.2.2.3 *Arsenic speciation analyses*

III.2.2.3.1 *Dissolved arsenic species determination by HPLC-ICPMS analysis*

The analytical method for the speciation analysis of arsenic consists in the coupling of High-Performance Liquid Chromatography (HPLC) to Inductively Coupled Plasma Mass Spectrometry (ICPMS) (Agilent Technologies) (Ponthieu et al., submitted, III.1 p76). The chromatographic conditions on a cationic exchange column (PRP-X200) provide the separation of six arsenic species (AsIII, MMA, AsV, DMA, AsB, TMAs⁺) within 25 minutes and the identification of two others which are not completely resolved (AsC and TMAO). Despite the high complexity of leachate matrix, no matrix effect has been pointed out. The developed method has the advantages to require a soft and rapid sample preparation and to enable within a single analysis the repartition determination of the most environmentally significant arsenic species.

III.2.2.3.2 *Dissolved total arsenic determination by ICPMS analysis*

To check the efficiency of arsenic speciation analysis in landfill leachates, total arsenic concentrations are measured with an ICPMS (Agilent Technologies) after nitric acid

microwave digestion (Ethos, Milestone) of the sample. The investigated protocol was presented elsewhere (Pinel-Raffaitin et al., 2006, II p53).

III.2.2.3.3 *Volatile arsenic species determination by CT-GC-ICPMS analysis*

The cryogenic trapping-gas chromatography (CT-GC) system is detailed elsewhere (Péchevran et al., 1998). The volatile species are thermally flash desorbed from the cryotrap into the chromatographic column (Chromosorb WHP, 60-80 mesh, 10% SP2100 Supelco) maintained at -196°C with nitrogen, are subsequently eluted and separated in the column heated up to 250°C. This cryogenic trapping system is hyphenated to an X series ICPMS (Thermo Electron Corp).

The identification of arsenic volatile species ($\text{As}(\text{CH}_3)_3$, $\text{As}(\text{CH}_3)(\text{C}_2\text{H}_5)_2$, $\text{As}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$, $\text{As}(\text{C}_2\text{H}_5)_3$, $\text{As}(\text{CH}_3)_2\text{H}$) is performed following the methodology based on the relationship between the boiling point and the retention time (Feldmann and Hirner, 1995). The raise of one alkyl group from one species to another, leads to a correlation (logarithmic) between retention time and boiling point. The boiling points calculated here for the identification of these species are consistent with those cited by Feldmann and Hirner as reference boiling points: 50-51°C for $\text{As}(\text{CH}_3)_3$, 87°C for $\text{As}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$, 140°C for $\text{As}(\text{C}_2\text{H}_5)_3$, and 35-37°C for $\text{As}(\text{CH}_3)_2\text{H}$ (Table III.2.4).

The calibration method is based on the use of a double-entrance plasma torch which provides the simultaneous injection of liquid solutions and gases. In this way, liquid internal standard is injected continuously during the analyses of the gas samples to check the sensitivity and the stability of the ICPMS. For the quantification, aqueous arsenic solutions are injected at different concentrations with the same plasma conditions. The detailed method has proved to be efficient for a semi-quantification of the species with less than 30% of error (Feldmann and Cullen, 1997).

III.2.3 Results and discussion

III.2.3.1 *Distribution and fate of arsenic species in landfill leachates*

III.2.3.1.1 *Occurrence of both inorganic and organic arsenic species*

The results of the four campaigns in landfill L.A and the five campaigns in landfill L.B are summarised in the Table III.2.2 with the indication of the minimal and maximal concentrations of each arsenic species detected in the samples. The investigation of more than forty samples has highlighted the presence of up to six arsenic species. In addition to arsenite

(AsIII) and arsenate (AsV), methylated arsenic species with the three substitution degrees have been found in the leachates samples: monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and trimethylarsine oxide (TMAO). In some samples from L.A, arsenobetaine (AsB) has also been detected. To our knowledge, all these results of arsenic species occurrence in landfill leachates can not be compared to any other study due to the lack of available data. Our results can nevertheless be compared to wastewater measurements. According to the literature data upon wastewater, only inorganic species (AsV and AsIII) have been detected (Segura et al., 2002) (Yu et al., 2003), without any report on the presence of organoarsenic compounds.

Table III.2.2 Arsenic species concentrations ($\mu\text{g (As) L}^{-1}$) in landfill leachates from L.A and L.B

Concentrations ($\mu\text{g (As) L}^{-1}$) for four campaigns (LA ^x) and five campaigns (LB)							
Species (abbreviation)		Mean	LA ¹ _{A-D}	LA ² _{A-D}	LA ³ _{A-D}	LA ⁴ _{A-D}	LB _{A-E}
			min-max	min-max	min-max	min-max	min-max
		n [*] = 42	n [*] = 8	n [*] = 8	n [*] = 8	n [*] = 8	n [*] = 10
As(OH) ₃	(AsIII)	1.4	0.4-0.9	0.3-1.9	0.3-1.9	3.6-4.2	0.1-2.6
AsO(OH) ₂ CH ₃	(MMA)	6.5	0.4-10.5	0.1-4.3	0.5-3.2	0.2-28	2.9-23
AsO(OH) ₃	(AsV)	7.2	0.3-8.1	1.7-5.6	0.5-21	6.4-13	2.2-21
AsO(OH)(CH ₃) ₂	(DMA)	4.6	0.6-13.9	n.d ^{**} -3.6	n.d ^{**} -2.5	n.d ^{**} -22	0.8-8.6
As ⁺ (CH ₃) ₃ CH ₂ COOH	(AsB)	0.2	n.d ^{**} -0.7	n.d ^{**} -0.4	n.d ^{**} -0.5	n.d ^{**} -0.6	n.d ^{**}
As ⁺ (OH)(CH ₃) ₃	(TMAO)	5.7	0.3-82	n.d ^{**} -1.0	n.d ^{**} -0.3	n.d ^{**} -2.0	0.5-2.4
Σ species (X)	(mean)		41	8	14	42	24
total As (Y)	(mean)		42	18	24	51	35
X/Y (%)	(mean)		74	45	52	81	69

n^{*} number of samples; ** n.d: not detected.

III.2.3.1.2 Arsenic species concentrations

Landfill leachates from the two studied sites present a qualitatively as well as quantitatively diversified composition. As shown in Table III.2.2, the screening of the samples exhibits AsV as the major species with a mean contribution of 23% of the total arsenic. The second predominant species is MMA with a mean contribution to 15% of the total arsenic. AsIII and AsB are always minor components (less than 5% of the total arsenic). In the same way, the contribution of TMAO to total arsenic is less than 5%, except for LA¹ for which it is the predominant species with more than 40% of the total arsenic. The concentrations of the two most toxic species which are AsIII and AsV vary from 0.1 $\mu\text{g (As) L}^{-1}$ to 4.2 $\mu\text{g (As) L}^{-1}$ and

from $0.3 \mu\text{g (As) L}^{-1}$ to $21 \mu\text{g (As) L}^{-1}$ respectively. These concentrations are higher than those measured in wastewater, which are around $0.5 \mu\text{g (As) L}^{-1}$ for AsIII and $5 \mu\text{g (As) L}^{-1}$ for AsV (Segura et al., 2002) (Yu et al., 2003). The proportion of the inorganic species relatively to the sum of the arsenic species is highly variable (5% to 98%). The high variability of this proportion and its related potential toxicity highlights the necessity of arsenic composition assessment in landfill leachates.

The mean recoveries of the speciation analysis in comparison with the total arsenic are ranging between 45% and 80% depending on the landfill cell samples. Two main reasons can be suggested. Firstly, during the speciation analysis, some minor species are detected but still remain unidentified. Secondly, some heavier species are probably not eluted from the chromatographic column. The recovery average of 67% for all the samples gives however satisfaction, as most of the samples have been significantly examined for the most environmentally problematic arsenic species.

III.2.3.1.3 Seasonal evolution

The five sampling campaigns performed on landfill L.B constitute a seasonal monitoring of the arsenic compounds in leachates.

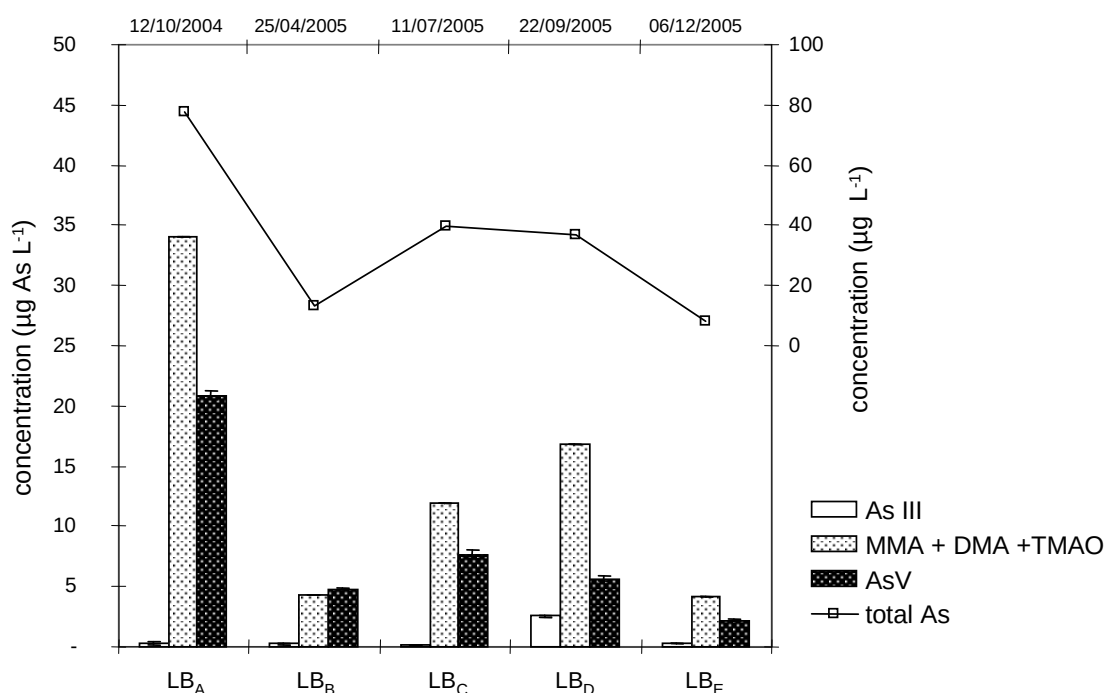


Figure III.2.1 Concentrations of arsenic species (AsIII, AsV and methylated species) and total arsenic in the five seasonal campaigns on landfill L.B

As shown Figure III.2.1 with the representation of both total arsenic and arsenic species concentrations for the five campaigns, the seasonal variations of the species follow the total arsenic seasonal variation, except AsIII. The total arsenic content variations are largely leaded by the hydrological conditions especially wet deposition (Pinel-Raffaitin et al., 2006, II p53) as shown Table III.2.3 with the Bravais-Pearson correlation matrix.

Table III.2.3 Bravais-Pearson correlation matrix for the five sampling campaigns on landfill L.B (significant correlation factors indicated in bold)

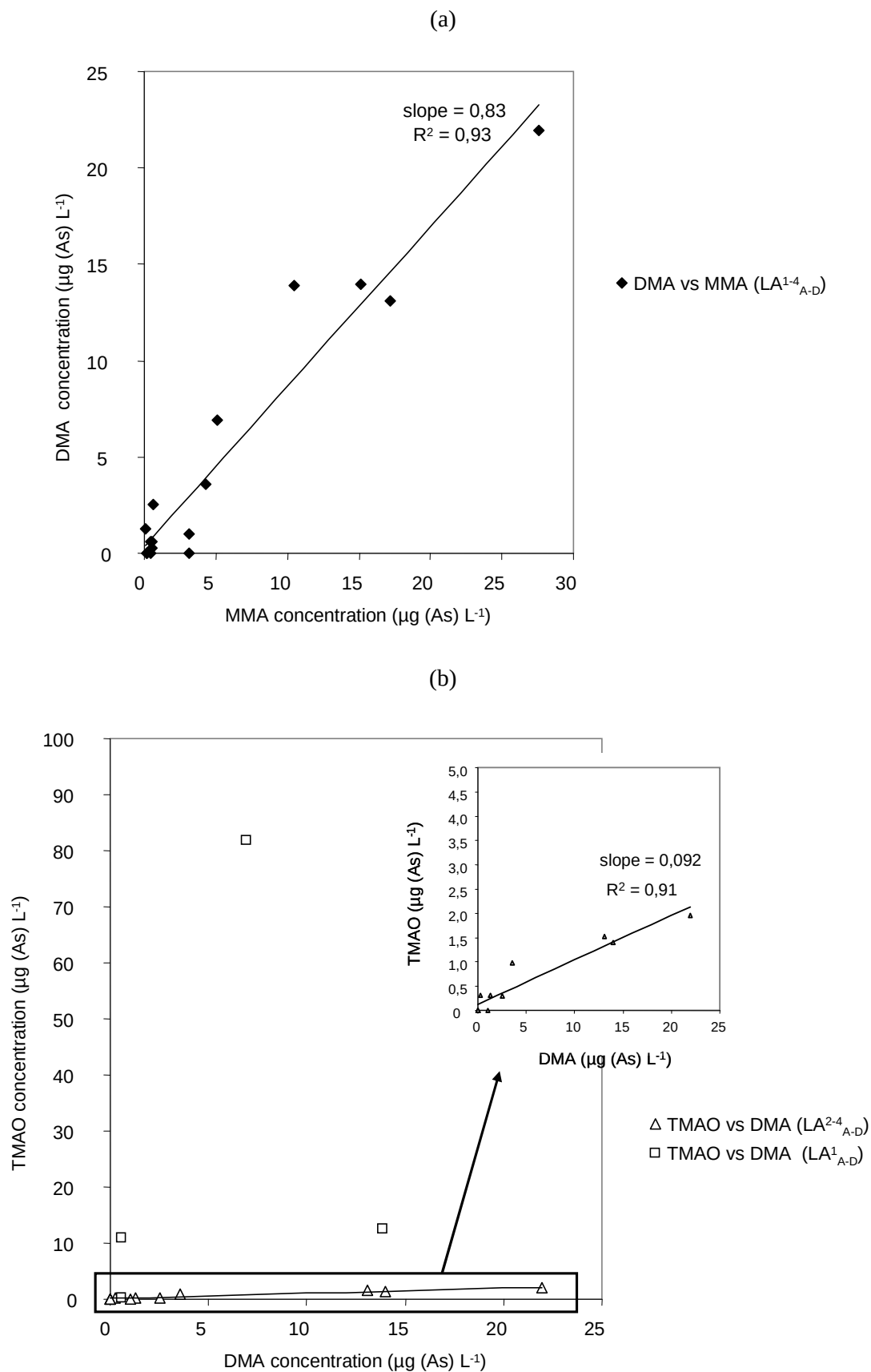
(n = 5)	AsIII	MMA	AsV	DMA	TMAO	Total As	Wet deposition
AsIII	1.00	-0.005	-0.20	0.27	0.66	0.03	0.10
MMA		1.00	0.97	0.96	0.75	0.99	-0.79
AsV			1.00	0.88	0.60	0.95	-0.78
DMA				1.00	0.90	0.94	-0.67
TMAO					1.00	0.76	-0.50
Total As						1.00	-0.88
Wet deposition							1.00

The correlation factors which are indicated in bold illustrate close relationships between the arsenic species. MMA, AsV and DMA concentrations are correlated to the total arsenic concentration. These three species are also correlated together especially AsV with MMA and MMA with DMA. For TMAO, the best correlation factor (0.90, $p < 0.05$) is obtained with DMA. AsIII is not correlated to any arsenic species. For this species the maximum of concentration occurs in the late summer period (Figure III.2.1) which corresponds to the highest reductive conditions within the landfill. This seasonal monitoring shows the influence of the hydrological conditions in particular wet deposition on the content of total arsenic. In addition, a close relationship between the methylated species concentrations has been highlighted.

III.2.3.1.4 Influence of waste degradation state

Taking into account the previous results, the study of the four cells of the landfill L.A has been focalised on the relationships between the concentrations of the three methylated species. The Figure III.2.2 shows the correlations curves between MMA, DMA and TMAO concentrations.

Figure III.2.2 Correlation curves between methylated species concentrations in the leachates from landfill L.A:
MMA versus DMA (a) and TMAO versus DMA (b).



For all the samples originating from the four cells, MMA and DMA seem to co-vary. The Bravais-Pearson correlation factor is 0.96 ($p < 0.05$) and the linear regression factor (R^2) is 0.93. In addition, a significant Bravais-Pearson correlation factor is obtained between the concentrations of DMA and TMAO (0.95, $p < 0.05$) by excluding the data from the first cell (LA¹) which presents a profile different from the three other cells. This cell corresponds to the oldest cell filling period from 1995 to 2000 (Table III.2.1) and is characterized by an advanced state of degradation with namely poor leachate production. The low leachate volume can thus lead to an enrichment of the species depending on their originating sources and processes. For the three more recent cells, the high interdependence of the methylated arsenic species contents illustrate that in the first stages of waste degradation the same factors influence the arsenic composition.

III.2.3.2 Distribution and fate of volatile arsenic species in landfill biogases

III.2.3.2.1 Gaseous and dissolved volatile species

Five volatile arsenic species have been semi-quantified in the biogas samples originating from the two sites (Table III.2.4). The most predominant species is trimethylarsine ($\text{As}(\text{CH}_3)_3$). The concentration of $\text{As}(\text{CH}_3)_3$ is from 100 to 1000 times higher than the other species, which are $\text{As}(\text{CH}_3)_2\text{H}$, $\text{As}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$, $\text{As}(\text{CH}_3)(\text{C}_2\text{H}_5)_2$ and $\text{As}(\text{C}_2\text{H}_5)_3$. Taking into account the occurrence of $\text{As}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$, and $\text{As}(\text{C}_2\text{H}_5)_3$, the presence of $\text{As}(\text{CH}_3)(\text{C}_2\text{H}_5)_2$ is expected even if it has never been reported in environmental samples, to our knowledge. The occurrence of $\text{As}(\text{CH}_3)_3$, $\text{As}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$, $\text{As}(\text{C}_2\text{H}_5)_3$ and $\text{As}(\text{CH}_3)_2\text{H}$ has already been reported by Feldmann and Hirner (Feldmann and Hirner, 1995).

Table III.2.4 Arsenic volatile species in landfill biogases from L.A and L.B and in landfill leachates from L.A

Volatile species (proposed)	$\text{As}(\text{CH}_3)_3$	$\text{As}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$	$\text{As}(\text{CH}_3)(\text{C}_2\text{H}_5)_2$	$\text{As}(\text{C}_2\text{H}_5)_3$	$\text{As}(\text{CH}_3)_2\text{H}$
Calculated boiling point (°C)	58	86	114	134	36
Gaseous samples		Ranges of concentration in $\mu\text{g}(\text{As})\text{m}^{-3}$			
BgA ¹ _D	n.d.	n.d.	n.d.	n.d.	n.d.
BgA ² _D	11.0-17.7	$3.8 \cdot 10^{-2}$ - $5.2 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$ - $8.9 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$0.5 \cdot 10^{-2}$ - $0.9 \cdot 10^{-2}$
BgA ³ _D	2.2-12.9	$0.2 \cdot 10^{-2}$ - $1.9 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$ - $1.8 \cdot 10^{-2}$	$0.5 \cdot 10^{-2}$	$0.1 \cdot 10^{-2}$ - $2.6 \cdot 10^{-2}$
BgA ⁴ _D	13.7	$5.5 \cdot 10^{-2}$	$14.9 \cdot 10^{-2}$	n.d.	$1.1 \cdot 10^{-2}$
BgB _C	$1.6 \cdot 10^{-3}$ - $3.0 \cdot 10^{-3}$	n.d.	n.d.	n.d.	n.d.
Ambient air (above landfill)	n.d.	n.d.	n.d.	n.d.	n.d.

The mean total volatile arsenic concentrations comprised between $2 \mu\text{g(As)}\text{m}^{-3}$ and $14.5 \mu\text{g(As)}\text{m}^{-3}$ correspond to a lower concentration range than the one reported for sewage and landfill biogases varying between $16 \mu\text{g (As) m}^{-3}$ and $48 \mu\text{g (As) m}^{-3}$ (Feldmann and Hirner, 1995). No volatile arsenic has been detected in the ambient air samples above the two landfills. It is noteworthy that no biogas treatment by flaring could induce in the surrounding atmosphere significant diffuse emission of volatile arsenic.

The analysis of the purges of landfill leachates has revealed the absence of volatile arsenic compounds dissolved in the aqueous phase, except $\text{As}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$ which was found in LA^1_{D} ($0.70 \pm 0.03 \text{ pg (As) L}^{-1}$ of leachate). The absence of arsenic volatile species dissolved in the landfill leachates illustrates the potential over-saturation of the gaseous phase in comparison with the liquid phase.

III.2.3.2.2 Influence of waste degradation state

The campaign on the landfill L.A allows the observation of the composition at a specified moment by fixing some parameters such as waste management, climatic conditions and waste general composition. For the biogas corresponding to the most degraded waste, no volatile arsenic species is detected (Table III.2.4). In contrast, in the three most recent cells (LA^2 , LA^3 , LA^4), the biogas is enriched in arsenic volatile species with concentrations reaching $15 \mu\text{g(As)}\text{m}^{-3}$. This is consistent with the fact that the maximum fermentation gas production is reached during the beginning of the exploitation of the landfill (Kjeldsen et al., 2002). It seems that the first cell LA^1 as well as the one of L.B is in a most advanced state of degradation, which is expressed by a poor volatilisation of arsenic species.

III.2.3.3 Sources and pathways of arsenic species in landfill effluents

The Table III.2.5 is a schematic representation of the three landfill compartments (waste, leachate biogas) and their occurring arsenic species. It summarizes the possible sources and processes that can be proposed for the understanding of effluent composition.

III.2.3.3.1 Anthropogenic sources from waste leaching

Arsenic known pools in wastes are glasses, metallic components and agricultural products in which arsenic is mainly under inorganic forms and a minor part under mono- or di-methylated

forms. In addition some punctual sources of arsenic could be proposed. As an example, in coastal area, as for landfill L.A, marine wastes could supply arsenic, as the occurrence of AsB especially in sea products such as algae, molluscs and fish is well-attested (Francesconi and Edmonds, 1994; Simon et al. 2004). The percolating water can thus provide the transfer of mainly AsV and perhaps AsIII and some organoarsenic compounds from the solid waste material into the leachates.

III.2.3.3.2 *Methylation and ethylation as sources of newly formed species*

The anthropogenic sources of arsenic are not sufficient for the explanation of all occurring arsenic species. During the degradation, the waste mass is under anaerobic conditions (Kjeldsen et al., 2002, Hirner, 2003). Under these reducing conditions, AsV can easily be transformed into AsIII. Besides its important anaerobic activity, landfill gathers all the conditions for the biomethylation of arsenic (Michalke et al., 2000, Hirner, 2003). The correlations between the methylated species observed in the two landfills (Table III.2.3 and Figure III.2.2) are consistent with successive biomethylation steps. As indicated Table 5, the proposed mechanism implies subsequent reduction steps after each methylation reactions. Reduced intermediates such as MMA^{III} or DMA^{III} are highly unstable and can not be detected with our analytical protocol. They are thus probably readily converted to their oxidised form before analysis (Gong et al., 2001). The successive reactions in liquid phase constitute a “detoxification” chain from inorganic arsenic to TMAO (Bentley and Chasteen, 2002) as the toxicity of organoarsenicals decreases with the increasing substitution (Hughes 2002). In leachates, peralkylation pathway seems to be not of concern as the tetramethylarsonium ion has not been detected in our samples (Table III.2.2). In opposition, the predominance of trimethylarsine (As(CH₃)₃) in comparison to dimethylarsine (As(CH₃)₂H) in landfill biogases (Table III.2.4) could mean that peralkylation is a major phenomenon in gaseous phase (Hirner, 2003). The observation of arsine and monomethylarsine by decreasing the pre-concentration temperature would probably confirm that As(CH₃)₃ is the most stable end-product of the biomethylation pathway (Planer-Friedrich et al., 2006).

Table III.2.5 Propositions of sources and processes for the arsenic occurrence in waste, leachate and biogas

WASTE		LEACHATE			BIOGAS		
Species	Sources	Species	Sources	Processes	Species	Sources	Processes
$\text{AsO}(\text{OH})_3$	Glasses, metallic components; agricultural products	$\text{AsO}(\text{OH})_3$	Waste	Leaching			
		$\text{As}(\text{OH})_3$	Leachate	Oxidation			
$\text{As}(\text{OH})_3$		$\text{As}(\text{OH})_3$	Waste	Leaching			
			Leachate	Reduction			
$\text{AsO}(\text{OH})_2\text{CH}_3$	Agricultural products	$\text{AsO}(\text{OH})_2\text{CH}_3$	Waste	Leaching	$\text{As}(\text{CH}_3)_x(\text{C}_2\text{H}_5)_{3-x}$	Leachate	Ethylation
			Leachate	Methylation		Biogas	
		$\text{As}(\text{OH})_2\text{CH}_3$		Reduction			
$\text{AsO}(\text{OH})(\text{CH}_3)_2$	Agricultural products	$\text{AsO}(\text{OH})(\text{CH}_3)_2$	Waste	Leaching	$\text{As}(\text{CH}_3)_2\text{H}$	Leachate	Hydridation
			Leachate	Methylation			
		$\text{As}(\text{OH})(\text{CH}_3)_2$		Reduction			
		$\text{As}^+(\text{OH})(\text{CH}_3)_3$	Leachate	Methylation	$\text{As}(\text{CH}_3)_3$	Leachate	Volatilization
$\text{As}^+(\text{CH}_3)_3\text{CH}_2\text{COOH}$	Marine waste	$\text{As}^+(\text{CH}_3)_3\text{CH}_2\text{COOH}$	Waste	Leaching			
			Leachate	Alkylation cycle			

In addition, as it was already reported by Feldmann and Hirner (Feldmann and Hirner, 1995), bioethylation is also assumed to take place in landfill to explain the occurrence of volatile ethyl- or methylethyl-arsenic compounds in our biogas samples (Table III.2.4). As indicated in Table III.2.5, the hypothesis is that these per-alkylated species are formed from liquid or gaseous methylated species by reaction with an ethyl-donor. In fact methyl-donor such as halogenated compounds (Chen et al., 2006), fulvic and humic acids or different organometallic compounds could likewise be ethyl-donors under particular conditions. At the laboratory scale, the formation of the mixed alkylated volatile species has been observed in incubations of micro-organisms grown on ethylarsenic substrates (Bentley and Chasteen, 2002). Another study has demonstrated that some bacteria which can make methanogenesis have shown their capability of producing ethane (Belay and Daniels, 1988). Similarly, some bacteria which can methylate could be able to ethylate the arsenic species. But up to now, this hypothesis has not been confirmed by any identification of microorganisms in charge of bioethylation under simulated landfill conditions.

Biomethylation and bioethylation mechanisms in addition to waste leaching allow the explanation of the occurrence of all identified species. In addition, it is worth stressing that more complex bioalkylation cycle could occur in the waste mass generating other organoarsenic compounds.

III.2.3.4 Evaluation of potential emissions of arsenic compounds from landfill leachates and biogases

With a long-term approach, landfill constitutes the return to natural environment of anthropogenic wastes. In the case of arsenic, the waste degradation seems to induce the release of more environmentally friendly compounds. However, a special attention is required to evaluate the potential emissions of arsenic produced by this way of waste management which is used all around the world.

Leachate and biogas average annual concentrations of the two landfills are used to evaluate the potential emissions due to waste disposal by taking into account the annual volume of leachates and biogases. The potential atmospheric emissions extrapolated to the total municipal solid waste disposals in French landfills give a quantity of 6 kg (As) year⁻¹. It corresponds to 0.05% of the total atmospheric emissions of arsenic in France in 2004 (CITEPA, 2006). In the aquatic systems, the potential emissions of arsenic related to french municipal solid waste disposals, estimated in this work, are around 10 kg (As) year⁻¹ for inorganic arsenic and 20 kg (As) year⁻¹ for methylated arsenic. As a comparison, the

estimation of the global domestic waste water arsenic emissions is comprised between 2.10^6 and 8.10^6 kg (As) year⁻¹ (Nriagu and Pacyna, 1989). According to our study, the input of arsenic from waste disposals could be negligible in the total mass balance of arsenic emissions. However, MSW landfill can constitute a diffuse source of arsenic in the environment and the removal efficiency of arsenic from leachates and biogases during the treatment require a special attention.

III.2.4 Acknowledgements

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La mise en œuvre des protocoles d'analyse de spéciation de l'arsenic dans les lixiviats et les biogaz a permis d'étudier le devenir des espèces arsénées dans le système complexe constitué par les déchets, les lixiviats et les biogaz. Sur la Figure III.2.3 sont indiquées les espèces majeures de l'arsenic retrouvées dans les lixiviats (AsIII , AsV , MMA, DMA et TMAO) et dans les biogaz (TMA). Par ailleurs, cette figure illustre les phénomènes qui ont été proposés pour expliquer la présence dans les deux effluents : d'une part la mobilisation à partir des déchets (espèces inorganiques) et d'autre part la méthylation et la per-méthylation par voie biologique (espèces méthylées).

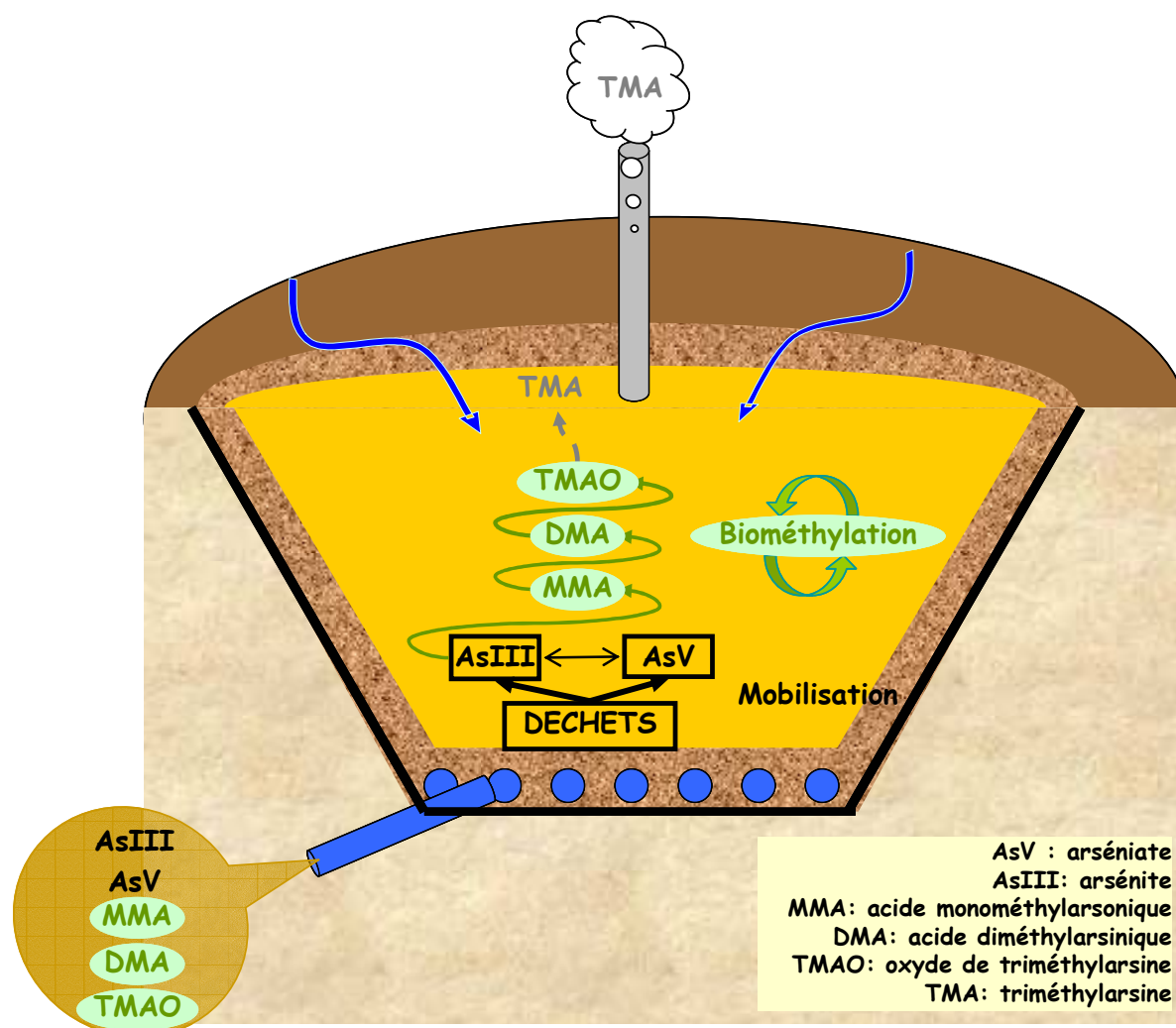


Figure III.2.3 : Représentation schématique d'un CSD et des processus à l'origine de la présence des espèces de l'arsenic dans les lixiviats et les biogaz

**SPECIATION ET DEVENIR DE L'ETAIN
DANS LES LIXIVIATS ET LES BIOGAZ**

IV. Spéciation et devenir de l'étain dans les lixiviats et les biogaz de CSD

De nombreuses catégories de déchets ménagers peuvent être à l'origine de la présence d'étain et en particulier de ses composés organiques dans les CSD. Les deux sources majeures peuvent être : les objets métalliques (cannettes, conserves...) à l'origine de l'étain minéral, et les formulations plastiques telles que le PVC, le silicone ou le polyuréthane (emballages, textiles...) qui contiennent des organoétains. Au cours de la dégradation des déchets, les composés de l'étain sont donc susceptibles d'être mobilisés dans les lixiviats et les biogaz. Le but de ce chapitre est d'approfondir les connaissances sur les formes sous lesquelles l'étain est présent dans les effluents, et les processus à l'origine de cette présence.

La mise en place d'une méthode d'analyse de spéciation des organoétains spécifiquement adaptée aux lixiviats fait l'objet de la première partie de ce chapitre. Le développement de la méthode au moyen du couplage de la chromatographie en phase gazeuse avec la spectrométrie de masse à plasma induit est focalisé, à l'issue d'essais préliminaires, sur les composés méthylés, éthylés et butylés. Les deux étapes critiques du protocole de préparation des échantillons (l'extraction et la dérivation) sont évaluées qualitativement et quantitativement en tenant compte de la complexité de la matrice des lixiviats. L'analyse est validée par une approche multi-quantitative qui combine les méthodes de calibration par étalonnage interne et externe et la méthode de dilution isotopique au moyen d'espèces butylées enrichies isotopiquement. L'application de cette méthodologie au suivi des espèces organostanniques dans les lixiviats est combinée à la caractérisation des espèces volatiles dans les biogaz au moyen de la technique de chromatographie en phase gazeuse avec piège cryogénique couplée à l'ICPMS. La discussion porte sur l'évolution et sur les mécanismes de mobilisation et de formation des espèces dans le massif des déchets.

IV.1. Détermination par GC-ICPMS des composés organostanniques dans les lixiviats de centres de stockage de déchets à l'aide d'espèces d'étain isotopiquement enrichies

Article accepté dans Journal of Analytical Atomic Spectrometry

Determination of alkylated tin compounds in landfill leachates using isotopically enriched tin species with GC-ICPMS detection

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A method for the simultaneous determination of methylated, ethylated and butylated tin compounds in landfill leachates has been developed in this work. The assessment of the organotin compound composition has been achieved by the development of a specific GC-ICPMS protocol adapted to these complex matrices. The analytical procedure consists in three major steps which have been carefully optimized taking into account the variety of alkyltin compounds and the high organic content of the leachate matrix: nitric acid extraction under microwave, derivatization using sodium tetrapropylborate and chromatographic separation. Different quantification approaches are proposed for the determination of the alkyltin species in the leachates. In this way, isotope dilution analyses in the species-specific and species-unspecific spiking modes have been found to provide results in agreement with external and internal calibration approaches. A single analysis with an addition of three isotopically enriched butyltin species is found to be suitable for the routine quantitative and semi-quantitative determination of all occurring alkyltin species in landfill leachates. The different qualitative and quantitative GC-ICPMS complementary approaches developed in this work allow the full organotin composition assessment of landfill leachates.

IV.1.1 Introduction

Municipal solid wastes contain a great diversity of chemical substances that can be released during their management. Landfilling is the predominant disposal pathway in Europe producing two effluents (leachates and biogases) that must be regularly monitored to evaluate their environmental, sanitary and toxicological impacts. During their percolation through the waste layers, landfill leachates are enriched in organic and inorganic compounds by combined physical, chemical and microbial processes. The chemical characterization of landfill leachates has been mainly focused on the occurrence and determination of metals and metalloids [1,2,3,4] whereas their chemical speciation analysis has been scarcely investigated [5]. Total metal analysis is not able to provide information about accumulation and toxicity of a given element, therefore speciation analysis is unquestionably required to provide a specific, reliable and complete understanding of the environmental impact of this kind of effluents.

The occurrence of organometallic compounds in landfill leachates is due to the fact that many wastes are composed of manufactured products in which organometallic species are present [6]. In particular, organotin compounds are used in a broad range of applications such as fungicides, pesticides, wood preservatives, PVC stabilisers or antifouling paints [7]. Moreover, their severe toxicity and their bioaccumulation potential have led to the control of their levels in different environmental compartments and have been regarded as priority pollutants by the European Union both in the Pollutant Emission Register (2000/479/EC) and in the Water Framework Directive (2000/60/EC).

Both the environmental and the analytical research in the field of organotin compounds are mainly restricted to butyltin compounds (particularly tributyltin, TBT) due to their widespread anthropogenic use and their persistence in the environment [8,9,10,11]. However, the microbiological degradation of wastes is a way of producing other organotin species by methanogenic and fermentative processes. Methyltin compounds are the only organotin species that can be naturally formed and have been identified in environmental samples such as sediment, soils or rain water [12,13]. Moreover, methylation processes have already been reported in waste water treatment plants [8,14] and assumed in landfill due to the presence of methylated species in gaseous [15,16] and liquid phases [5]. In their study on European landfill leachates, Mersiowsky *et al.* have detected mono- and dimethyltin in addition to butylated and octylated tin species [5]. The second study which has described the presence of organotin compounds in landfill leachates, is also focused on methyltin, butyltin and octyltin compounds in simulated landfills [17].

The speciation analysis of organotin compounds by Gas Chromatography (GC) coupled to Inductively Coupled Plasma Mass Spectrometer (ICPMS) [9,18] provides the possibility of applying species-specific isotope dilution analysis (SSIDA) for quantification. This calibration technique is not affected by the typical errors involved in the speciation analysis and has already been widely applied for the determination of butyltin compounds in different environmental matrices [7,9,10,11,18]. However, its main limitation relies on the required availability of all the species to be analysed in an isotopically labelled form.

In general, the analysis of landfill leachate is problematic due to the complexity of its matrix characterised by a high organic matter content and a high ionic strength level. However, in the particular case of organotin compounds speciation, those problems become even more serious due to the numerous species that may simultaneously occur in a single leachate. The major difficulty related to the screening of known and unknown species in complex matrices is the accurate quantification of the species. In fact, the adequate natural abundance standards are sometimes missing to perform conventional external and internal calibrations. As an example, tripropyltin cannot be used as internal standard when propylation is applied for derivatisation. In addition, SSIDA can not be performed for all the species due to the unavailability of the required isotopically enriched species. The two studies which have described the presence of organotin compounds in landfill leachates are both providing quantification of organotin compounds by internal calibration with tripropyltin (using ethylation for the derivatisation) [5] or triethyltin (using propylation for the derivatisation) [17].

In this work, the identification and quantification of nine different alkylated tin compounds in real landfill leachates by GC-ICPMS has been accomplished for the first time. Different and complementary quantification methodologies are proposed to overcome the limited availability of natural abundance or isotopically enriched organotin standards. For this purpose, a mixture of mono-di- and tributyltin enriched in the isotope 119 was employed not only for the quantification of these three species by applying SSIDA in the landfill leachates but also as a suitable internal standard both for the performance of internal calibration (IC) and a species-unspecific isotope dilution calibration (SUIDC). The objective of this work is the assessment of reliable and complementary analytical protocols adapted to these complex matrices. In this way, quantification using external calibration (EC) has been tested by comparison with SSIDA for butyltin compounds and IC using the ^{119}Sn -enriched MBT as a suitable internal standard. In addition, the efficiency of a species-unspecific isotope dilution calibration (SUIDC) using ^{119}Sn -enriched MBT and ^{119}Sn -enriched DBT has been evaluated

to quantify methyltin and ethyltin species. Finally, the applicability of the developed method has been illustrated with the determination of tin species repartition in different landfill leachates.

IV.1.2 Experimental

IV.1.2.1 Reagents and materials

Ultrapure water was obtained from a MilliQ system (18M Ω , Millipore USA). Analytical reagent-grade isooctane, sodium hydroxide, glacial acetic acid and sodium acetate were purchased from Sigma-Aldrich (Seelze, Germany). Nitric acid (J.T.Baker, Instra-Analyzed 70%, Atlantic Labo, France) was used for the microwave assisted extraction. Hydrochloric acid (J.T.Baker, Ultrex II Ultrapure reagent 33-36%) was used in order to adjust the pH and to break the emulsion after the liquid-liquid extraction. Buffer solution of pH 5 was prepared by dissolving sodium acetate (Sigma-Aldrich) in ultrapure water and adjusting to pH 5 with glacial acetic acid (Sigma-Aldrich). Sodium tetraethylborate (NaBEt₄) (purity 98%) and sodium tetrapropylborate (NaBPr₄) (purity 98%) were purchased from Galab (Geesthacht, Germany). NaBEt₄ and NaBPr₄ solutions (0.5% w/v) in MilliQ water were prepared every 6 hours and stored in the dark at +4°C.

Monomethyltin chloride (MMTCl), dimethyltin chloride (DMTCl), trimethyltin chloride (TMTCl) and triethyltin chloride (TETCl) were obtained from Strem Chemicals (Newburyport, USA) and diethyltin chloride (DETCl) from Ventron (Karlsruhe, Germany). Natural tributyltin chloride 96% (TBTCl), dibutyltin chloride 97% (DBTCl) and monobutyltin chloride 95% (MBTCl) were obtained from Sigma-Aldrich. Stock solutions of each species were prepared by dissolving the different powders in diluted hydrochloric acid or in glacial acetic acid with concentrations ranging from 100 mg Sn L⁻¹ to 1000 mg Sn L⁻¹ and stored at -20°C in the dark. A mixture solution of all species at 20 μ g L⁻¹ in 1% hydrochloric acid was daily prepared to perform external calibration whereas for SSIDA, IC and SUIDC, a ¹¹⁹Sn-enriched mixture of the three butyltin compounds described previously [18] was obtained from ISC-Science (Gijon, Spain).

IV.1.2.2 Instrumentation

An open focused vessel microwave oven Prolabo A301 (France) was used to carry out the extraction of the samples. The analysis of the samples was performed by using a gas

chromatograph Focus (Thermo Finnigan, Milan, Italy) equipped with an automatic injector and a capillary column Tr-5 from Thermo Finnigan (San Jose, CAL, USA) (cross-linked 5 % diphenyl, 95% dimethyl siloxane, 30 m x 0.25 mm i.d. x 0.25 µm coating) coupled to an X series inductively coupled plasma mass spectrometer (Thermo Electron Corp., Windsford, UK) via the commercial available interface provided by the company. The silcosteel capillary transfer line is inserted directly in a specifically defined torch. This instrumental configuration enables the dual introduction of gaseous samples and liquid standard solutions. The liquid nebulisation allows the optimization of the instrument performance and the measurement of $^{121}\text{Sb}/^{123}\text{Sb}$ for the correction of the mass-bias as well as the instrumental signal drift during the chromatographic runs. The temperature program consisted in a linear gradient between 40 and 270 °C at 30 °C/min with 1 minute as initial and final time and 1.5 mL/min as He carrier gas flow. Depending on the concentration of the samples, volumes of 1 or 2 µL were injected using in all cases a split/splitless injector with 1 min splitless time at 250°C. The isotopes measured for Sn were the 118, 119 and 120 using an integration time of 30 ms whereas 10 ms of integration time was employed for the Sb isotopes 121 and 123.

IV.1.2.3 Sampling

IV.1.2.3.1 Landfill sites description

Leachates were sampled in three different French landfills which receive only municipal wastes. A single leachate was sampled in the first landfill, named hereafter as L.A, in which 200000 tons of wastes per year are disposed. The second landfill, named hereafter as L.B, has been filled with 10000 tons of wastes per year from 1999 to 2002. Three campaigns have been realised in this site with the corresponding collected leachates: LB1 (sampled in October 2004), LB2 (sampled in April 2005) and LB3 (sampled in September 2005). The third landfill, named hereafter as L.C, has received 150000 tons of wastes per year and is composed of seven cells. The 1st cell has been filled from 1995 to 2000 and each of the six following cells has been filled during one year until 2006. LC1 and LC2 correspond to the leachates sampled in cell 3 in January 2005 and to the leachates sampled in cell 4 in May 2006, respectively.

IV.1.2.3.2 Sample collection

In order to avoid the perturbation of the outflow no pumping was applied during sampling. In this way, the leachates were simply collected at the extremity of the leachate pipe and immediately transported in 1L polyethylene bottle using ice-boxes. Then, the leachates were

transferred into 5mL polypropylene vials and frozen at -20°C until analysis. In all cases, the sampling bottles and the plastic ware were rinsed with detergent and warm water, decontaminated with concentrated nitric acid solution (J.T.Baker, Analyzed, 70%) and finally rinsed three times with ultrapure water (Millipore 18M Ω) before use. All bottles were filled with ultrapure water and transported to the landfill keeping one of the bottles filled with ultrapure water during the whole sampling and transportation in order to constitute the “landfill blank” (following all the subsequent sample preparation steps).

IV.1.2.4 Procedures

In order to decrease the matrix effects of the leachates all samples were microwave assisted extracted using nitric acid. For this purpose, the required volume of acid was directly added to the 5 mL volume of leachate previously stored at -20°C to obtain a 20% concentration of HNO₃ before carrying out the extraction. Then, the digested samples were adjusted to pH 5 [10] and the derivatisation was carried out after the addition of NaBPr₄ and isooctane by a manual shaking of the vials. However, due to the presence of organic matter in the leachates, the addition of hydrochloric acid and the centrifugation of the samples were necessary to break the resulting emulsion before collecting the organic phase. Finally, a volume between 100 μ L and 300 μ L of isooctane was collected and stored in the dark at -20°C until the GC-ICPMS determination. For SSIDA, IC and SUIDC, the mixture of ¹¹⁹MBT, ¹¹⁹DBT, ¹¹⁹TBT was added to the sample at the beginning of the sample preparation and the amount of enriched spike was carefully optimised according to the random error propagation theory [19].

IV.1.3 Results and discussion

IV.1.3.1 Determination of alkylated tin compounds in landfill leachates

IV.1.3.1.1 Chromatographic separation of methyltin, ethyltin and butyltin compounds

Using the chromatographic parameters described above the separation of eight organotin compounds within 8 minutes could be achieved. Figure IV.1.1 shows a typical GC-ICPMS chromatogram of 10 μ g (Sn) L⁻¹ standard solutions for the isotope 118 using ethylation (Figure IV.1.1a) and propylation (Figure IV.1.1b) as derivatisation approaches. As can be observed, ethylation does not lead to any gain in sensitivity in comparison with propylation but it provides a better chromatographic resolution. However, propylation of the leachates

was finally selected because NaBEt_4 does not provide a chromatographic resolution of endogenous ethyltin species and their discrimination from inorganic Sn (as all of them are finally converted to tetraethyltin).

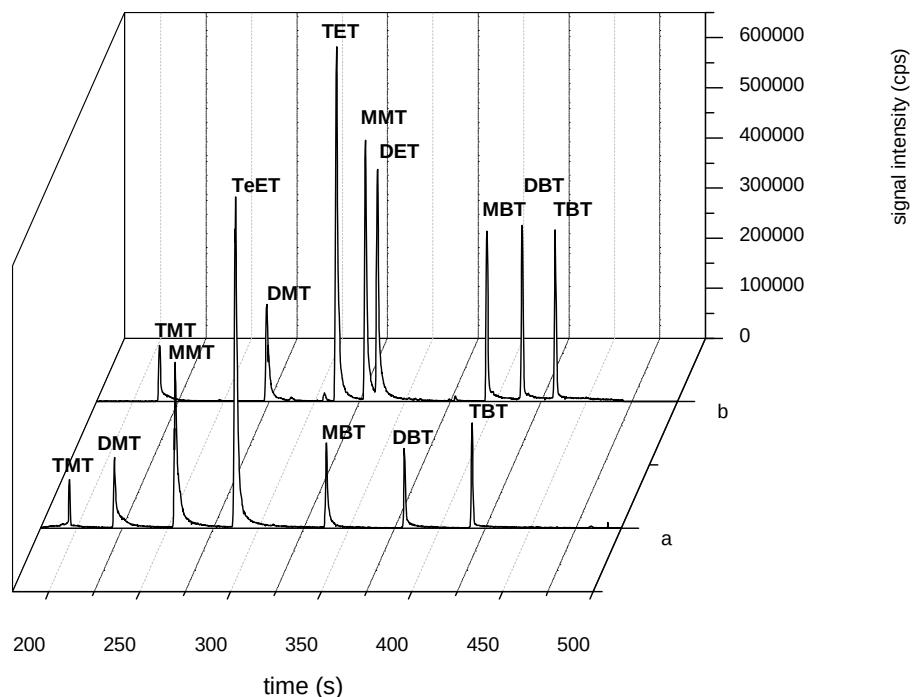


Figure IV.1.1 Chromatograms of standard mixture at $10 \mu\text{g (Sn) L}^{-1}$ after ethylation (a) and propylation (b)

This is also demonstrated in Figure IV.1.2, which shows the GC-ICPMS chromatograms for the isotope ^{118}Sn in a representative leachate sample from L.B and derivatised with NaBEt_4 (Figure 2a) and NaBPr_4 (Figure 2b). As can be observed, six species were detected for the propylated sample (MMT, DMT, TMT, MBT and two unidentified species names Sn3 and Sn4) whereas only five were observed when using ethylation as derivatisation procedure. According to this, it is well demonstrated that propylation is required to obtain the maximum information concerning the organotin distribution in the leachates.

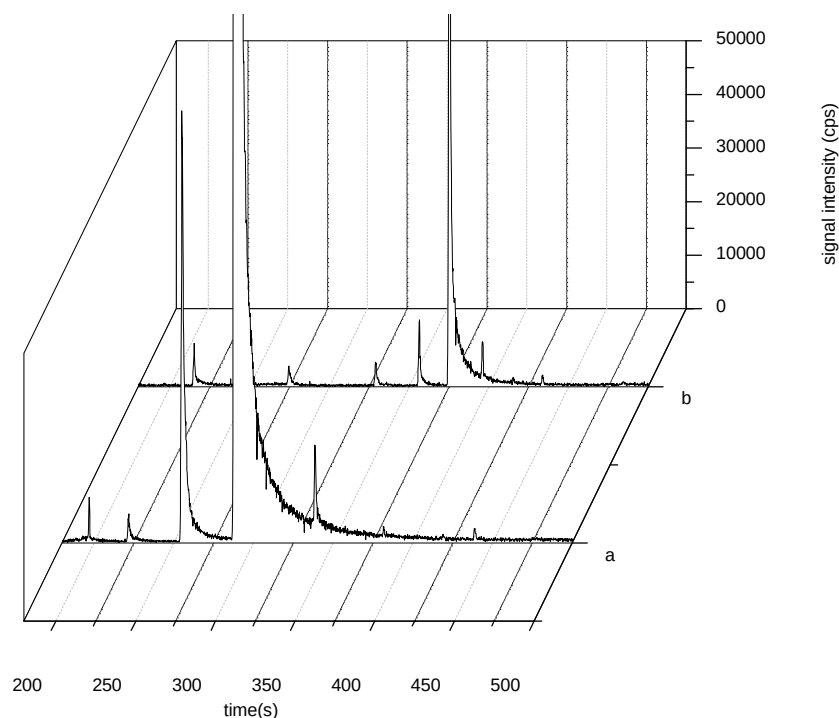


Figure IV.1.2 Chromatograms of directly-derivatised leachate LB1 from landfill L.B with NaBEt_4 (a) and NaBPr_4 (b)

IV.1.3.1.2 Identification of the alkylated tin compounds in landfill leachates

The identification of the organotin species in the samples was subsequently performed by the comparison of the retention times of the alkyltin species occurring in the leachates with those obtained in fortified samples. For this purpose the leachates were fortified with a $1 \mu\text{g (Sn) L}^{-1}$ standard containing TMT, DMT, TET, MMT, DET, MBT, DBT and TBT. The GC-ICPMS chromatograms of the fortified and the unfortified samples (Figure IV.1.3a and Figure IV.1.3b) were compared in terms of the species' retention times. Using the chromatographic conditions explained above, the retention times of the propylated species were found to be: 212 ± 0.3 s for TMT, 270 ± 0.1 s for DMT, 308 ± 0.2 s for TET, 324 ± 0.2 s for MMT, 331 ± 0.2 s for DET, 393 ± 0.3 s for MBT, 413 ± 0.3 s for DBT and 432 ± 0.4 s for TBT. As an example, Figure IV.1.3 shows a GC-ICPMS chromatogram for the isotope ^{118}Sn which illustrates the matching of the retention times of the occurring species in representative leachate. Figure IV.1.3a corresponds to the extracted LB1 and Figure IV.1.3b corresponds to the same extracted sample with the addition of the standard solution. As can be observed in Figure 3b there are two peaks (Sn3 and Sn4) that, according to the retention times, do not correspond to any standard. In the case of Sn4, its identification as inorganic tin is easily performed by injecting inorganic tin standard solution. In addition Figure IV.1.3c shows a GC-ICPMS chromatogram

of the microwave extracted leachate L.A in which the presence of two unknown tin species (Sn1 and Sn2) was also detected.

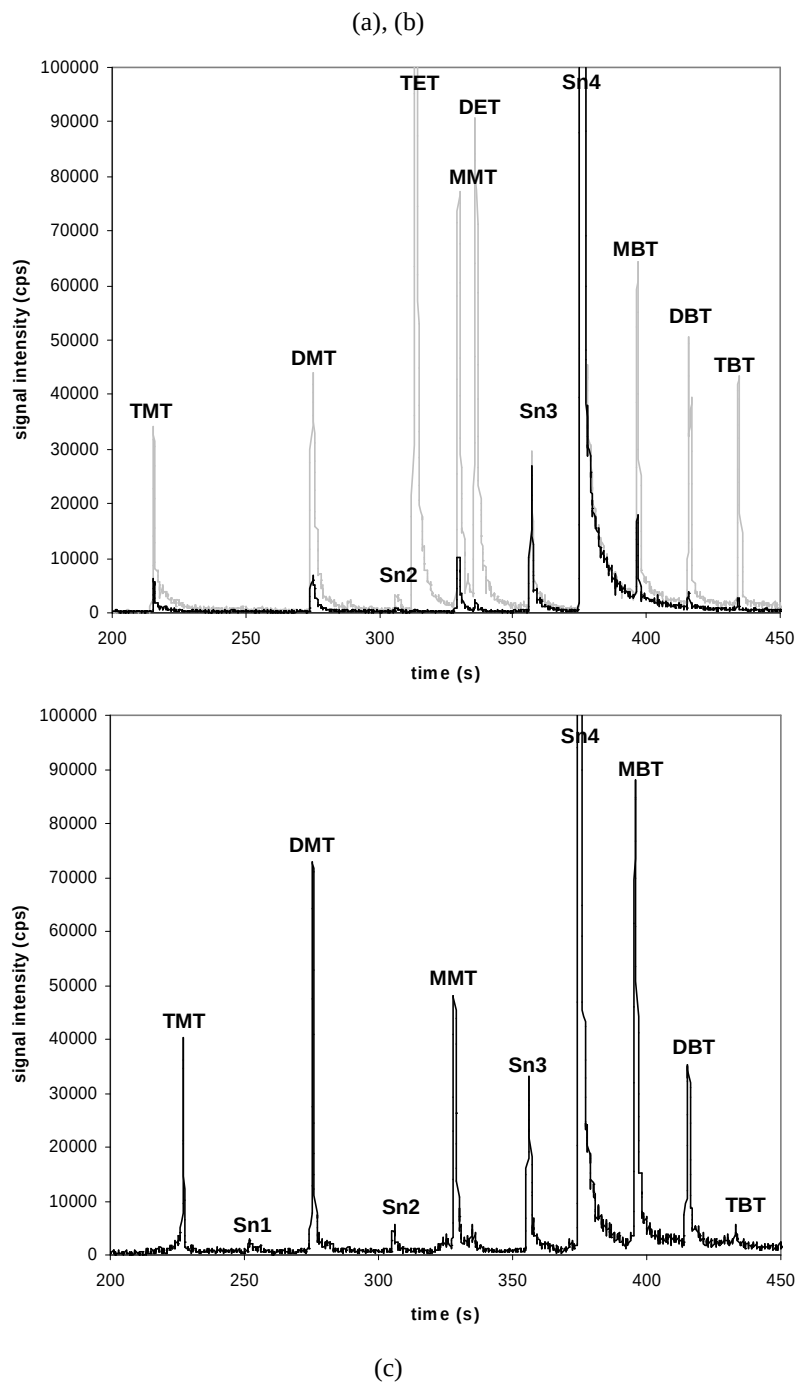


Figure IV.1.3 Chromatograms of microwave-extracted LB1 (a, in black) and this same sample fortified with standard addition at $1 \mu\text{g (Sn) L}^{-1}$ (b, in grey), and microwave extracted L.A (c)

Table IV.1.1 Identification of organotin species by the comparison of the boiling points (Bp) estimated using the experimental chromatographic data and estimated using the QSAR theory

Species	Retention time (s)	Chromatographic estimated Bp (°C)	Proposed derivatised species	QSAR estimated Bp (°C)	Corresponding identified species
Sn 1	244.0 ± 0.2	148 ± 1	SnEtMe ₂ Pr	149	SnEtMe ₂
Sn 2	301.0 ± 0.2	193 ± 1	SnMeEtPr ₂	192	SnMeEt
Sn 3	353.0 ± 0.3	233 ± 1	SnEtPr ₃	230	SnEt
Sn 4	375.0 ± 0.3	250 ± 1	SnPr ₄	248	Inorganic Sn

In order to identify such species, and following the methodology proposed in previous works [15,20], it was assumed that the chromatographic separation was only dependent on the boiling point of the tin compounds. In this way, a linear relationship between the boiling point and the retention time of standard solutions and samples was tested in this work obtaining a correlation factor of $R^2=0.996$. Therefore, a mathematic model (MpBpWin (v1.41)) developed by EPA was then used to estimate the boiling point (at 760 mm Hg) of the proposed species. The boiling point estimation methodology was based on the group contribution QSAR method (quantitative structure activity relationship) that calculates the boiling point of a given compound by adding group increment values according to equation [1]:

$$B_p(^{\circ}C) = -273.6 + 198.2 + \sum n_i \cdot g_i \quad [1]$$

where g_i is a group increment value and n_i is the number of times that such group occurs in the compound [21]. Table IV.1.1 shows the proposed alkyltin species and their boiling points obtained by this approach, named “QSAR estimated Bp”, in addition to their matching with boiling points estimated with the relationship between the boiling point and the retention time (“chromatographic estimated Bp”). As can be observed in the table, the experimental and the estimated values were good in agreement for the four species. Therefore, they were identified as dimethylethyltin, methylethyltin, ethyltin and the expected inorganic tin as Sn1, Sn2, Sn3 and Sn4 respectively. To the best of our knowledge, among the newly-identified species, it is the first time that two mixed methyl-ethyl species are identified in an environmental sample.

IV.1.3.2 Quantification of organotin compounds in landfill leachates

IV.1.3.2.1 Calculation of procedural detection limits

Detection limits were calculated as three times the standard deviation of procedural blanks by EC in which 5mL of the “landfill blank” followed all the sample preparation procedure. The corresponding detection limits were found to be 0.01, 0.02, 0.02, 0.02, 0.02, 0.03, 0.04 and 0.04 $\mu\text{g Sn L}^{-1}$ for TMT, DMT, MMT, TET, DET, MBT, DBT and TBT respectively. It is worth stressing that the detection limit of MET could not be calculated due to the unavailability of commercially available standards. Instrumental detection limits were comprised between 20 fg Sn for TMT and 60 fg Sn for DBT.

IV.1.3.2.2 Effect of microwave extraction

Landfill leachate samples are complex organic matrices. Therefore, in order to minimise possible matrix effects throughout the sample preparation procedure, a microwave assisted extraction was performed before derivatisation. In contrast to previous works in which the microwave assisted extraction was carried out employing acetic acid for the determination of butyltin compounds [22], nitric acid was selected in this work as it was found to provide a better average extraction of all the alkylated tin species. In addition, a final concentration of 20% of HNO_3 (v/v) was selected for the extraction as higher HNO_3 contents were found to suppress the extraction of TMT.

Table IV.1.2 Comparison of external calibration (EC) and species-specific isotope dilution analysis (SSIDA) for butyltin compounds in landfill leachate sample from L.A extracted or not under microwave with nitric acid

Leachate sample L.A	Species	Concentration ($\mu\text{g (Sn) L}^{-1}$)			
		EC		SSIDA	
Without extraction	MBT	0.08	± 0.01	0.32	± 0.03
	DBT	0.015	± 0.007	0.09	± 0.03
With extraction	MBT	0.46	± 0.02	0.32	± 0.03
	DBT	0.15	± 0.02	0.10	± 0.02

EC versus SSIDA for butyltin compounds: The influence of the microwave-assisted extraction step in terms of extraction yield, modification of the species repartition and matrix effects was studied. For this purpose the quantification of MBT and DBT in a leachate sample L.A with and without the application of a microwave assisted extraction step was evaluated using two

different calibration techniques: SSIDA and EC. The concentration values for TBT could not be obtained in this sample as they were below the method detection limit ($0.04 \mu\text{g Sn L}^{-1}$). As can be observed in Table IV.1.2 the results obtained for three independent aliquots of the leachate demonstrate that only when using the microwave assisted extractions both approaches provide similar concentration values. As expected, and in contrast to EC, SSIDA corrects for matrix effects and provides the same results with and without the extraction of the samples demonstrating that isotope equilibration is possible for butyltin species in this matrix even when no extraction procedure is applied. In the light of these results, we can conclude that EC is thus a suitable calibration technique only for extracted samples whereas for non-extracted samples, this calibration method provides a biased value of the species concentration. This comparison could not be achieved for methylated and ethylated species, as no enriched isotopic standards were available for this study. Therefore, taking into account the results obtained for MBT and DBT, it was assumed that for the rest of the alkyltin species, external calibration provides more accurate results for microwave assisted extracted samples than for non-extracted samples.

Recovery of methyltin compounds: The occurrence in the leachate of the three methylated tin species and the availability of their corresponding natural abundance standards allowed us to evaluate the efficiency of nitric acid extraction by calculating the recovery of such species in the leachate L.A. For this purpose, the three species were individually spiked to three different aliquots of the same sample before and after the nitric acid extraction and their concentrations were calculated by EC. Each addition of the methylated species was done in triplicate and the concentrations of the three species are reported on Table IV.1.3. The recoveries of MMT and DMT when the standards were added before extraction were found to be slightly lower than those obtained when they were added after extraction. However, a quantitative recovery for TMT was obtained when this species is added before the extraction ($95 \pm 10\%$) in comparison to that obtained when the addition is carried out after the extraction ($86 \pm 6\%$).

Conversion of spiked methyltin compounds: In order to study the occurrence of methylation reactions throughout the extraction procedure, the concentrations of the two unspiked species were also calculated. The Table IV.1.3 shows that when the addition of the natural abundance standards is carried out after the extraction there is not a significant methylation of the species. This is demonstrated with the quantitative recoveries obtained not only in the unspiked species but also in the sum of the methyltin species. However, when the addition of

the natural abundance standards is carried out before the extraction both a significant higher recovery for the unspiked TMT (as much as $138 \pm 6\%$) and a quantitative recovery for the sum of butyltin species are obtained. As the recovery obtained for TMT is quantitative when it is spiked before the extraction, those results clearly indicate the occurrence in this kind of complex matrix of a specific methylation which is only originated from the added DMT or MMT before the extraction. Therefore, these results demonstrate the risk of using standard addition approaches for calibration purposes in these samples, as there is a different behaviour of the added and the endogenous methyltin species occurring in the leachate during the extraction.

Table IV.1.3 Recovery tests of nitric acid microwave extraction on methylated species in a landfill leachate sample L.A

	Spiked species	Experimental spike / theoretical spike (%)		Unspiked species	Conc. in spiked sample/ Conc. in unspiked sample (%)		Recovery of the sum of methylated species (%)	
Spike before extraction	MMT	61	± 14	DMT	87	± 6	87	± 6
				TMT	123	± 8		
	DMT	87	± 5	MMT	93	± 5	101	± 5
				TMT	138	± 22		
	TMT	95	± 10	MMT	94	± 7	95	± 3
				DMT	90	± 16		
Spike after extraction	MMT	84	± 10	DMT	96	± 9	92	± 5
				TMT	90	± 7		
	DMT	95	± 3	MMT	96	± 6	98	± 1
				TMT	102	± 3		
	TMT	86	± 6	MMT	97	± 6	92	± 4
				DMT	92	± 7		

IV.1.3.2.3 Internal calibration (IC) for quantification of methyltin and ethyltin species

As reported above, SSIDA and EC can be used properly for quantification of MBT and DBT in the extracted samples but for the methyl- and ethyltin species, SSIDA can not be performed due to the lack of the corresponding isotopically enriched species. In addition, as explained above, propyltin species can not be used as internal standards since propylation is employed as derivatisation procedure. Therefore, in order to overcome these difficulties, isotopically

enriched butyltin species were tested as suitable internal standards for the other alkyltin species determination. For this purpose, the ^{119}Sn -enriched butyltin species was added to the samples at the beginning of the sample preparation procedure and the ^{119}Sn -enriched MBT was employed as internal standard. Then, the peak area obtained for the isotope 120 in each species was divided by that obtained for MBT for the isotope 119. It is worth stressing that the peak area obtained for the isotope 119 in MBT was corrected to subtract the contribution of the endogenous natural abundance MBT in the leachate, following the approach explained below. Accordingly, the peak areas of DBT and TBT for the mass 120 were also corrected in order to subtract the contribution of the added ^{119}Sn -enriched DBT and ^{119}Sn -enriched TBT to the mass 120.

Table IV.1.4 Comparison of external calibration (EC), internal calibration (IC), species-specific isotope dilution analysis (SSIDA) and species-unspecific isotope dilution calibration (SUIDC) for landfill leachate LB1

Concentrations and standard deviations in $\mu\text{g (Sn) L}^{-1}$ in leachate LB1						
	EC	IC	SSIDA	SUIDC with ^{119}MBT	SUIDC with ^{119}DBT	SUIDC with ^{119}TBT
MMT	0.14 $\pm$ 0.01	0.13 $\pm$ 0.01		0.18 $\pm$ 0.01	0.26 $\pm$ 0.01	0.86 $\pm$ 0.18
DMT	0.24 $\pm$ 0.01	0.27 $\pm$ 0.01		0.18 $\pm$ 0.01	0.26 $\pm$ 0.01	0.85 $\pm$ 0.13
TMT	0.41 $\pm$ 0.02	0.55 $\pm$ 0.07		0.16 $\pm$ 0.02	0.24 $\pm$ 0.03	0.77 $\pm$ 0.05
MET*				0.87 $\pm$ 0.05	1.28 $\pm$ 0.09	4.12 $\pm$ 0.56
DET	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01		0.03 $\pm$ 0.01	0.04 $\pm$ 0.01	0.13 $\pm$ 0.03
TET	n.d.	n.d.		n.d.	n.d.	n.d.
MBT	0.33 $\pm$ 0.05	0.32 $\pm$ 0.02	0.31 $\pm$ 0.02			
DBT	0.08 $\pm$ 0.01	0.09 $\pm$ 0.01	0.11 $\pm$ 0.01			
TBT	0.08 $\pm$ 0.01	0.09 $\pm$ 0.02	0.30 $\pm$ 0.04			

*identified species (Sn3)

The results obtained by such IC using ^{119}MBT for the alkyltin species were compared with those obtained by EC in the landfill leachate LB1 (Table IV.1.4). The quantification provided by this internal standard methodology was found to be in agreement with the results obtained by EC for all the methyl-, ethyl- and butyltin compounds, except for TBT where the results of EC and IC were not in agreement with SSIDA. This may indicate a serious matrix effect for TBT than for the rest of the species and could be explained by its lower polarity and thus higher affinity to the organic hydrophobic matrix. Finally, it can be highlighted that due to the absence of natural abundance standards for MET in this work, no concentration value could be obtained by EC or IC.

IV.1.3.2.4 Species unspecific isotope dilution calibration (SUIDC) for quantification of methyltin and ethyltin species

In the past, the method of unspecific spiking of isotopically enriched species has been employed for selenium compound with the use of selenomethionine for the purpose of quantification of selenocysteine [23]. In this work, in order to find more complementary calibration strategies for such complicated samples, a similar species-unspecific isotope dilution calibration consisting in using sensitivity factors obtained with three isotopically enriched species (MBT, DBT and TBT) was carried out for the evaluation of the concentrations of the tin species occurring in the leachates. For each of the three butylated species, a sensitivity factor was calculated as the ratio between the peak area of ^{120}Sn corresponding to the sample (I_s^{120}) and the concentration quantified by SSIDA. However, in order to consider only the peak area corresponding to the sample, the contribution of the isotopically enriched species to the ^{120}Sn has to be subtracted from the total peak area. This correction is performed by using a similar approach than that proposed by Hintelman *et al.* [24] in which the signals (peak areas) obtained for each isotope can be expressed as a linear combination of the different contributing sources. In this way the signals obtained in the particular case of MBT for the isotopes 120 (I^{120}) and 119 (I^{119}) can be expressed with equations 2 and 3:

$$^{MBT}I^{120} = ^{MBT}I_s^{120} + ^{MBT}I_{sp}^{120} \quad [2]$$

$$^{MBT}I^{119} = ^{MBT}I_s^{119} + ^{MBT}I_{sp}^{119} \quad [3]$$

Where $^{MBT}I_s^{120}$ and $^{MBT}I_s^{119}$ are the peak areas for the isotopes 120 and 119 originated from the endogenous species and $^{MBT}I_{sp}^{120}$ and $^{MBT}I_{sp}^{119}$ those originated from the isotopically enriched MBT.

If the abundance ratios are defined as $R_1 = \frac{^{MBT}I_{sp}^{120}}{^{MBT}I_{sp}^{119}} = \frac{^{MBT}A_{sp}^{120}}{^{MBT}A_{sp}^{119}}$ and $R_2 = \frac{^{MBT}I_s^{119}}{^{MBT}I_s^{120}} = \frac{^{MBT}A_s^{119}}{^{MBT}A_s^{120}}$,

where $^{MBT}A_{sp}^{120}$ and $^{MBT}A_{sp}^{119}$ are the isotope abundances in the isotopically enriched spike and $^{MBT}A_s^{120}$ and $^{MBT}A_s^{119}$ those in the sample for the isotope 119 and 120 respectively, equations 2 and 3 can be expressed as follows:

$$^{MBT}I^{120} = ^{MBT}I_s^{120} + R_1 \cdot ^{MBT}I_{sp}^{119} \quad [4]$$

$$^{MBT}I^{119} = R_2 \cdot ^{MBT}I_s^{119} + ^{MBT}I_{sp}^{119} \quad [5]$$

Then, equations [4] and [5] provide a linear system with two equations and two unknowns that can be easily solved to obtain the intensity which is only coming from the endogenous MBT ($^{MBT}I_s^{120}$) in the corresponding chromatographic peak. In this way, a sensitivity factor for MBT can be calculated using the following expression

$$^{MBT}K = \frac{^{MBT}C_{SSID}}{^{MBT}I_s^{120}}$$

where $^{MBT}C_{SSID}$ is the concentration obtained by SSIDA in the same chromatographic run using the ^{119}Sn -enriched MBT. This set of equations can be written also for DBT and TBT. Therefore, three sensitivity factors can be calculated by dividing the corresponding corrected peak areas by the endogenous concentration obtained by SSIDA in each sample. Then each of these factors can be directly applied to quantify not only the methylated and ethylated species but also any unknown species or species from which no natural abundance standard is available.

The results of these three different quantifications are compared to EC, IC and SSIDA in Table IV.1.4. This table shows the results obtained in the landfill leachate LB1, which illustrates the general trend observed for the rest of the analysed landfill leachates. As can be observed, when using SUIDC with MBT, the results for MMT, DET, MET, MBT and DBT match the values quantified by EC, IC but not for DMT. On the other hand, when using SUIDC with DBT, the quantified values of the di-substituted species DMT were found to be in agreement with those evaluated by EC and IC. However for the mono-substituted species (MMT, MET and MBT), the results obtained by SUIDC using the ^{119}Sn -enriched DBT do not generally match those obtained with EC and IC.

On the other hand, in the case of TMT, the quantification with SUIDC using MBT and DBT was found to be always lower than that obtained by EC, IC and SUIDC with ^{119}Sn -enriched TBT. This indicates again a different behaviour of the tri-substituted species probably due to their higher affinity to the organic matrix. This is also reflected in the fact that the results obtained with SUIDC using ^{119}Sn -enriched TBT for all the species are not in agreement not

only with those obtained by SUIDC using MBT or DBT but also with those obtained by EC and IC, except for the case of TMT in some of the samples.

In the particular case of MET, no concentration values for EC and IC are presented in Table IV.1.4 due to the absence of natural abundance standards. When the average of the calibration slopes obtained for all the natural abundance standards is used to quantify such compound the results obtained by IC ($0.86 \pm 0.05 \mu\text{g Sn L}^{-1}$) are well in agreement with those obtained by SUIDC using the ^{119}Sn -enriched MBT ($0.87 \pm 0.05 \mu\text{g Sn L}^{-1}$).

According to these results its worth stressing that, except for TMT, concentration values in agreement with those obtained by EC and IC can be obtained for all the occurring species in the leachate samples with only one addition of the mixture of isotopically enriched butyltin species (and therefore one chromatographic run), without resorting to any external calibration or standard additions to the sample and hence minimising the total analysis time.

IV.1.3.3 Applicability to real samples

As a full validation of the ethyltin, methyltin and unknown tin species can not be performed due to the absence of specific isotopically enriched standards to perform SSIDA, the different calibration strategies proposed above were consider complementary in the case of landfill leachates. In this way, in order to cover the true values and to provide the most representative information, the final concentration values for the quantification of species in real samples were calculated as follows:

- for MMT, the average of EC, IC and SUIDC using ^{119}Sn -MBT.
- for DMT, the average of EC, IC and SUIDC using ^{119}Sn -DBT.
- for TMT, as there was no agreement between the proposed calibration strategies: the average of EC, IC, SUIDC using ^{119}Sn -MBT, SUIDC using ^{119}Sn -DBT and SUIDC using ^{119}Sn -TBT.
- for DET, the average of EC, IC, SUIDC using ^{119}Sn -MBT and SUIDC using ^{119}Sn -DBT.
- for MBT, DBT and TBT the values obtained by SSIDA.
- any unknown species or species in which there is any commercially available standards the value of SUIDC using ^{119}Sn -MBT.

Table IV.1.5 Organotin composition in $\mu\text{g Sn L}^{-1}$ of four landfill leachates (LB2, LB3, LC1 and LC2): mean values and standard deviations obtained using EC, IC, SSIDA and SUIDC

Concentrations and standard deviations in $\mu\text{g Sn L}^{-1}$ in four landfill leachates								
	LB2		LB3		LC1		LC2	
MMT	0.03	± 0.01	0.07	± 0.02	0.10	± 0.03	0.014	± 0.002
DMT	0.05	± 0.01	0.12	± 0.02	0.43	± 0.10	0.08	± 0.03
TMT	0.19	± 0.10	0.40	± 0.21	1.40	± 2.10	0.31	± 0.23
MET*	0.17	± 0.03	0.44	± 0.09	0.22	± 0.07	0.029	± 0.003
DET	0.009	± 0.003	0.02	± 0.01	n.d.		n.d.	
TET	n.d.		n.d.		n.d.		n.d.	
MBT	0.11	± 0.04	0.16	± 0.01	0.24	± 0.05	0.07	± 0.01
DBT	0.04	± 0.01	0.06	± 0.01	0.07	± 0.06	0.012	± 0.002
TBT	0.11	± 0.02	0.20	± 0.01	1.02	± 0.30	0.31	± 0.01

*identified species (Sn3)

According to this, the applicability of the entire developed methodology is illustrated in Table IV.1.5 with the determination of the alkyltin species concentrations in different leachates from L.B (LB2 and LB3) and L.C (LC1 and LC2). The majority of the concentration values of alkyltin compounds in these leachates are comprised between $0.02 \mu\text{g (Sn) L}^{-1}$ to $0.5 \mu\text{g (Sn) L}^{-1}$ (except two values for TMT and TBT for LC1). The high standard deviation of the TMT values in the sample LC1 corroborates the problematic determination of such species in the leachates as explained above. The concentration of the alkyltin species are in the same order of magnitude than the methylated and butylated tin compounds analysed by Mersiowsky *et al.* [5] except for MBT which is less concentrated here than in other European leachates. In comparison with waste water [14,25], the concentrations in the leachates are within the same order of magnitude. Ethylated species are reported for the first time in real landfill leachates as the seldom works using propylation are focused on butyltin species.

IV.1.4 Conclusions

The choice of different calibration strategies for the assessment of the quantification of all alkyltin species is explained by the fact that each method allows the correction of specific systematic errors. For example, as it was demonstrated for the case of methyltin compounds, there is a clear different behaviour between the added and the endogenous species during the extraction procedure. Therefore, other endogenous unspecific species already present in the

sample with similar polarity or affinity to the matrix are suspected to better correct for errors derived from this particular sample preparation step. On the other hand, other steps such as the derivatisation or the liquid-liquid extraction procedures may be better corrected by species-specific standards and hence, EC or IC can provide more realistic concentration values. The complementation of the different approaches is proposed in this work to overcome for the first time this complicated analytical problem. Additionally it is worth noting that the routine quantitative and semi-quantitative determination of all occurring alkyltin species (including unknown species) in any leachate can be performed in a single analysis by the addition of species-specific and species-unspecific isotopically enriched alkyltin species to the sample and hence drastically reducing the total analysis time.

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IV.2. Devenir des composés organostanniques dans les effluents de centres de stockage de déchets

Article en cours de soumission

Mobilisation and formation of organotin compounds in landfill leachates and biogases

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Abstract

The organotin compound potential release from municipal solid waste (MSW) disposal has been recently considered as a potential way of entering the environment. The determination of organotin species in leachates and biogases has been performed in this work to achieve the fate of organotin species in landfill. In leachates, methylated, ethylated, butylated and mixed methyl-ethylated tin compound concentrations are ranging from 0.01 $\mu\text{g (Sn)L}^{-1}$ to 6.5 $\mu\text{g(Sn)L}^{-1}$. In biogases, both methylated and ethylated volatile tin species occur with concentrations up to 25 $\mu\text{g(Sn)m}^{-3}$. The seasonal monitoring of landfill leachates has highlighted the influence of climatic conditions on the evolution of the composition of the leachates. The predominant phenomenon is waste leaching of anthropogenic species such as butyltin or some methyltin compounds during cold periods, and formation of new organotin compounds such as ethyltin compounds during hot periods. At larger time scale, the influence of waste degradation state on the alkyltin composition in the leachates and biogases has been also outlined. In this way, mobilisation and formation pathways have been proposed for the occurrence of the organotin compounds in both phases. Biogenic methylation and ethylation, are supposed to be the main mechanisms in leachates for the formation of trimethyltin, mixed methyl-ethyltin and ethyltin compounds. In the gaseous phase, permethylation and perethylation reactions have also been suggested. Although the estimation of emission factors has shown quantitatively low input from waste disposal, it is noteworthy that waste degradation has proved to induce the release in the environment of biologically harmful organotin species.

IV.2.1 Introduction

Even though municipal solid waste (MSW) disposal in landfill is one of the most common waste management pathway throughout the world, its potential release of major contaminants such as organotin compounds in both atmosphere and aquatic ecosystems is not documented. Some data of tin emissions are available for waste incineration but this atmospheric emission factor ranging between 1.0-10 g of tin per tons of incinerated MSW corresponds essentially to inorganic tin (1,2). Our recent work has pointed out tin as a main leachate contaminant among metals and metalloids (3, II p53) and the need of speciation analysis to assess its related environmental impact. The main sources of inorganic tin in MSW are manufactured products such as cans and containers. Additionally, the major anthropogenic applications that provide organotin compounds in wastes are PVC heat stabilizers, biocides, catalysts for polyurethane foam or silicones, agrochemicals and glass coatings (4-7). Thus MSW becomes a pool of different organotin compounds: tributyltin from agricultural products, monobutyl, dibutyltin, monomethyltin and dimethyltin from plastic formulations for food packaging (PVC, polyurethane, silicone), and monobutyltin and monomethyltin from glass coatings (4-7). The global tin content of MSW is scarcely documented as only compositions by waste categories are available. As an example, according to the French Agency for the Environment and Energy Management (ADEME) PVC wastes represent 1.5% of MSW humid mass and the concentrations of organotin compound in PVC are ranging from 100 to 5000 mg (Sn) kg⁻¹ (8). This example illustrates the potential contribution of organotin in MSW due to such particular source.

In this way, tin and organotin compounds could thus be mobilised and likely released in the environment by the percolation of water through the waste layers. These compounds can be also discharged through the gaseous phase in which volatile tin can be transferred. As reported by Hirner (9), landfill gathers the conditions enhancing the chemical and biological transformation of tin. Tin and organotin compounds present in the waste could thus be modified by hydridation, methylation, ethylation, dealkylation or transalkylation reactions with the consequence of generating new tin compounds in both liquid and gaseous phases (10). The potential impacts related to landfill leachates and biogases could thus change during the biodegradation of wastes. In fact, in contrast to dealkylation pathways which decrease the toxicity of the organotin compounds, the alkylation pathways enhance the mobility and the toxicity of the resultant compounds (7;10).

The combined liquid and gaseous organotin compounds determination appear thus to be necessary for the assessment of environmental and sanitary impacts of landfill. This kind of complete approach has only been proposed on simulated landfill by the examination of the fate of methyltin compounds in leachates and biogases (11). However, the scarce data on real landfills is only related to separated compartment studies. In these works, the occurrence of volatile hydride, methyl-, ethyl- and butyltin species has been described in landfill biogases with average concentrations ranging from less than $0.1 \mu\text{g (Sn) m}^{-3}$ to $35 \mu\text{g (Sn) m}^{-3}$ (12-13). In landfill leachates, mono- and dimethylated tin compounds in addition to the three substituted butylated tin compounds have been quantified with concentrations ranging from $0.1 \mu\text{g (Sn) L}^{-1}$ to $1 \mu\text{g (Sn) L}^{-1}$ (14).

The previous development of an organotin speciation analysis methodology in our laboratory especially adapted to landfill leachates is applied in this work (15, IV.1 p114). This methodology allows a reliable determination of methylated and butylated tin compounds in addition to ethylated and mixed methyl-ethylated tin compounds, whose expected occurrence has never been underlined before due to analytical limitations. The complete approach applied here combines the determination of dissolved ionic tin species in leachates and volatile tin species both in biogases and dissolved in leachates. The aim of this work is to propose possible sources and pathways to explain the occurrence of the identified species in landfill effluents. In this way, the main influent factors in the organotin composition evolution have been outlined by the monitoring of two landfills. Finally, the potential emissions of organotin compounds related to MSW disposal in landfill have been evaluated in a risk assessment point of view.

IV.2.2 Material and methods

IV.2.2.1 Sampling sites and procedures

IV.2.2.1.1 Landfill site description

Leachates and biogases were sampled in two different French landfills (Table IV.2.1).

The first landfill, named hereafter as L.A, has received 150000 tons of MSW per year and is composed of seven cells. The 1st cell has been filled from 1995 to 2000 (named hereafter LA¹) and each of the three following cells has been filled during one year until 2003 (named hereafter LA², LA³ and LA⁴). The second landfill, named hereafter as L.B, has been filled with 10000 tons of MSW per year from 1999 to 2002.

IV.2.2.1.2 *Leachate sampling*

In order to avoid the perturbation of the outflow no pumping was applied during sampling. In this way, the leachates were collected at the leachate pipe outflow and transported in 1L polyethylene bottle in ice-boxes at around 4°C. Within 2-5 hours, the leachates were transferred into 5mL polypropylene vials and frozen at -20°C until analysis. In all cases, the sampling bottles and the plastic ware used throughout this work were cleaned following a well-established protocol (15). The whole protocol from sampling to analysis was applied to one bottle filled with ultrapure water (18M Ω , Millipore USA) to constitute a “landfill blank”.

Table IV.2.1 Presentation of the sampling campaigns on the two landfills and the corresponding wet deposition

Landfill	Waste cells (cell filling period)	Leachate and biogas sampling campaigns					
		10/01/2005		04/07/2005		29/05/2006	
		Campaign A		Campaign B		Campaign C	
L.A.	LA ¹ (1995-2000)	LA ¹ _A		LA ¹ _B		BgA ¹ _C	LA ¹ _C
	LA ² (2000-2001)	LA ² _A		LA ² _B		BgA ² _C	LA ² _C
	LA ³ (2001-2002)	LA ³ _A		LA ³ _B		BgA ³ _C	LA ³ _C
	LA ⁴ (2002-2003)	LA ⁴ _A		LA ⁴ _B		BgA ⁴ _C	LA ⁴ _C
Wet deposition (mm)		63		40		51	
		12/10/2004	25/04/2005	11/07/2005	22/09/2005	06/12/2005	
		Campaign A	Campaign B	Campaign C	Campaign D	Campaign E	
L.B.	LB (1999-2002)	LB _A	LB _B	LB _C	BgB _C	LB _D	LB _E
Wet deposition (mm)		70	197	76		158	227

Duplicated leachates samples were collected three times in landfill L.A (10/01/2005; 04/07/2005; 29/05/2006) and five times in landfill L.B (12/10/2004; 25/04/2005; 11/07/2005; 22/09/2005; 06/12/2005). The corresponding leachate samples are LA¹_A to LA⁴_A for 10/01/2005, LA¹_B to LA⁴_B for 04/07/2005, LA¹_C to LA⁴_C for 29/05/2006 and LB_A, LB_B, LB_C, LB_D, LB_E for the five campaigns in L.B (Table IV.2.1).

The determination of dissolved volatile species was also performed in the leachates from L.A for the third campaign (29/05/2006). Additional leachate samples were thus collected in 1L thick polypropylene bottles, avoiding any head-space above the liquid phase.

IV.2.2.1.3 *Biogas sampling*

Both sampling sites are equipped with drain to collect and flare the landfill biogases. Biogases were sampled at the drain's bleed using ten-litres Tedlar bags. The bags were filled using a

laboratory-made box which provides a clean sampling as it is depressurised indirectly by a vacuum pump. After collection, bags were placed immediately in the dark to avoid photochemical degradations and kept at room temperature until pre-concentration step. For each sampling campaign, the last samples were collected in the ambient air above the landfill site.

One sampling campaign was done on each site (Table IV.2.1): for L.A, two Tedlar bags were used for each of the four cells sampled (29/05/2006): BgA¹_C, BgA²_C, BgA³_C and BgA⁴_C whereas for L.B, five Tedlar bags were filled on 11/07/2005 (BgB_C).

IV.2.2.1.4 *Cryogenic pre-concentration of volatile species*

Gaseous species. The principles of the operating cryogenic system is described elsewhere (16). Briefly, each Tedlar bag was directly connected via its valve to a cryogenic pre-concentration system within 2 hours after the on-site collection. The aspiration flow rate for the gas pumping was fixed at 800 mL min⁻¹. Gas samples were dried by passing through an empty U-shaped glass tube maintained at -20°C (mixture of ice and acetone) before being cryofocused at -80°C in glass wool quartz columns (i.d. 5mm, 17.5cm of length). This temperature was chosen to avoid the condensation of both carbon dioxide (Boiling point = -80°C) and methane (Boiling point = -164°C), which represent 50-80% of the total biogas content. For each Tedlar bags, three columns were used to pre-concentrate different volumes of biogas (four and two litres). For ambient air, the gas volume pre-concentrated was 8L. After cryofocusing, the cryotrap were closed with Teflon caps and immediately transferred to a dry atmosphere cryogenic container.

Dissolved volatile species. Volatile tin compounds were extracted from leachate samples using a purge system connected to the previously described cryogenic pre-concentration system. The principle of the purge is described elsewhere (17) and was directly done using the sampling polypropylene bottle. Only 500mL of leachate was kept in the bottle to avoid any problem of foaming. A modified cap equipped with a stem fitted with a glass frit was used to replace the initial cap of the bottle. A helium pressure allowing a flow rate of 250mL min⁻¹ was applied to the sampling bottle. Similarly to biogas samples, the column with the trapped-condensed species were closed with Teflon caps and immediately transferred to a dry atmosphere cryogenic container. Both storage (cryo-container) and purge blanks were performed (ultrapure water) to check for any contamination during sample treatment steps.

IV.2.2.2 Organotin speciation analyses by Gas Chromatography-Inductively Coupled Mass Spectrometry (GC-ICPMS) techniques

IV.2.2.2.1 Dissolved organotin species determination by GC-ICPMS analysis

The sample preparation procedure for the speciation analysis of organotin compounds in landfill leachates includes a soft nitric acid (J.T.Baker, Instra-Analyzed 70%, Atlantic Labo, France) extraction under microwave, a derivatization using NaBPr₄ (Galab, purity 98%, Geesthacht, Germany) and a liquid-liquid extraction with isooctane (Sigma-Aldrich, Seelze, Germany) (15). The speciation analysis is carried out by the coupling of a gas chromatograph Focus (Thermo Finnigan, Milan, Italy) equipped with a capillary column Tr-5 (Thermo Finnigan, San Jose, CAL, USA) and an X series inductively coupled plasma mass spectrometer (Thermo Electron Corp. Windsford, UK). The method allows the quantification of methyltin, ethyltin and butyltin species in landfill leachates. Previous screening using propylation showed that some ethyltin derivatives were detectable in landfill leachates. An approach using isotope dilution analyses (¹¹⁹Sn-enriched mixture of butyltin compounds, ISC-Science, Gijon, Spain) in the species-specific and species-unspecific spiking modes together with external calibration was validated in order to provide the most representative quantitative and semi-quantitative determination of all occurring alkyltin species in the landfill leachates (15).

IV.2.2.2.2 Dissolved total tin determination by ICPMS analysis

Total tin (Sn_T) concentrations are measured with an ICPMS (Agilent Technologies) after nitric acid microwave digestion (Ethos, Milestone) of the sample. The investigated protocol was presented elsewhere (3, II p53).

IV.2.2.2.3 Volatile organotin species determination by CT-GC-ICPMS analysis

The cryogenic trapping-gas chromatography (CT-GC) system is detailed elsewhere (16). The volatile species are thermally flash desorbed from the cryotrap into the chromatographic column (Chromosorb WHP, 60-80 mesh, 10% SP2100 Supelco) maintained at -196°C with nitrogen, and then subsequently eluted and separated in the column by heating up to 250°C. This cryogenic trapping system is hyphenated to an X series inductively coupled plasma mass spectrometer (Thermo Electron Corp).

The identification of tin volatile species is performed following the methodology proposed in previous works (12;18). The calibration method is provided by the simultaneous injection of liquid solutions and gases. Liquid internal standards are injected continuously during the analyses of the gas samples and the quantification is performed by injecting aqueous tin standard solutions (Analab, Bischeim, France) with the same plasma conditions. The detailed method has proved to be efficient for a semi-quantification of the species with less than 30% of error (19).

The concentrations of dissolved volatile species in landfill leachates were quantified similarly than the gaseous volatile species. It was not necessary to correct the quantified concentrations for the purge recovery as it was assumed to be efficient for each species in each sample for temperatures ranging between 10°C and 25°C, based on Henry's law constant equilibrium towards purging conditions (time, flow rate, temperature) (20).

IV.2.3 Results

IV.2.3.1 Occurrence of dissolved organotin species in landfill leachates

IV.2.3.1.1 Alkyl-group related distribution of organotins

The results of the three campaigns in landfill L.A and the five campaigns in landfill L.B are summarised in the Table IV.2.2 indicating the minimal and maximal concentration of each organotin species detected in the samples. The investigation of more than thirty samples has highlighted the occurrence of up to nine organotin compounds. Three families of alkylated tin compounds are detected in the samples such as methyltin (mono-, di- and tri-methyltin), ethyltin (mono- and di-ethyltin) and butyltin species (mono-, di- and tri-butyltin). In addition, a mixed methyl-ethyltin compound was found in some samples ($\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{X}$).

The presence of ethyltin compounds is reported here for the first time in landfill leachates. This particular occurrence is characterised by the predominance of monoethyltin and the absence of triethyltin in all the samples collected in the two investigated landfills. The contribution of ethyltin compounds in the total organotin content is in the same order of magnitude as methyltin and butyltin compounds for the leachates from L.B whereas this contribution is lower for all the leachates from L.A. The occurrence of methyltin and butyltin compounds was already observed in European landfills by Mersiowsky et al. (14). In this study, ethylation was used as derivatization procedure, avoiding thus any ethyltin species to be identified.

Table IV.2.2 Organotin composition of landfill leachates collected in the four cells of L.A during the three sampling campaigns and collected in L.B during the sampling five campaigns

Minimal and maximal concentrations of tin species ($\mu\text{g (Sn) L}^{-1}$)						
Species	Mean	LA ¹ _{A-C}	LA ² _{A-C}	LA ³ _{A-C}	LA ⁴ _{A-C}	LB _{A-E}
		min-max	min-max	min-max	min-max	min-max
	n : 34	n : 6	n : 6	n : 6	n : 6	n : 10
Sn(CH ₃)X ₃	0.04	0.02-0.04	0.01-0.03	0.01-0.02	0.07-0.10	0.02-0.15
Sn(CH ₃) ₂ X ₂	0.18	0.11-0.80	0.04-0.11	0.04-0.13	0.03-0.43	0.05-0.26
Sn(CH ₃) ₃ X	1.08	0.37-6.50	0.12-0.35	0.20-0.53	0.32-1.40	0.14-0.49
Sn(CH ₃) ₂ (C ₂ H ₅)X	0.02	<DL ^{**} -0.03	n.d ^{***}	n.d ^{***}	<DL ^{**}	n.d ^{***}
Sn(C ₂ H ₅)X ₃	0.14	0.02-0.07	0.01-0.06	0.03-0.04	0.10-0.21	0.05-0.87
Sn(C ₂ H ₅) ₂ X ₂	0.02	n.d ^{***}	n.d ^{***}	n.d ^{***}	n.d ^{***}	<DL ^{**} -0.03
Sn(C ₂ H ₅) ₃ X	n.d ^{***}	n.d ^{***}	n.d ^{***}	n.d ^{***}	n.d ^{***}	n.d ^{***}
Sn(C ₄ H ₉)X ₃	0.10	0.03-0.11	0.02-0.11	0.03-0.07	0.01-0.24	0.05-0.31
Sn(C ₄ H ₉) ₂ X ₂	0.03	0.01-0.05	<DL ^{***} -0.08	0.01-0.01	<DL ^{**} -0.06	0.01-0.11
Sn(C ₄ H ₉) ₃ X	0.33	0.12-0.26	0.08-0.33	0.10-0.38	0.08-1.36	0.10-0.30
Σ species (OTC)	1.9	0.7 - 7.8	0.3 - 1.1	0.4 - 1.2	0.5 - 3.5	0.4 - 2.5
total Sn (Sn _T)	61	12 - 22	3 - 42	2 - 23	1 - 95	11 - 355
OTC/ Sn _T (%)	11	3 - 49	3 - 4	4 - 18	3 - 38	1 - 4

n* number of samples; **<DL: below the detection limit (species detected but not quantified); *** n.d: not detected.

IV.2.3.1.2 Concentration related distribution of organotins

A screening of the samples from the two sites (Table IV.2.2) exhibits trimethyltin (Sn(CH₃)₃X) as the most abundant species with a mean value of 1.1 $\mu\text{g (Sn) L}^{-1}$ and concentrations ranging between 0.12 and 6.50 $\mu\text{g (Sn) L}^{-1}$. The three other predominant species were found to be tributyltin (0.08-1.36 $\mu\text{g (Sn) L}^{-1}$), monoethyltin (0.01-0.87 $\mu\text{g (Sn) L}^{-1}$) and dimethyltin (0.03-0.80 $\mu\text{g (Sn) L}^{-1}$). This was not the case in other European landfill leachates reported by Mersiowsky et al. in which monobutyltin was the major species with a mean value of 1.0 $\mu\text{g (Sn) L}^{-1}$ (14). Species concentrations obtained for the two studied landfills are comprised between 0.01 $\mu\text{g (Sn) L}^{-1}$ and more than 5 $\mu\text{g (Sn) L}^{-1}$. This range of concentration is in the same order of magnitude to that obtained by Mersiowsky et al. in other European landfill leachates in which the organotin concentrations ranged between 0.1 $\mu\text{g (Sn) L}^{-1}$ and 4.1 $\mu\text{g (Sn) L}^{-1}$ with a mean value around 0.3 $\mu\text{g (Sn) L}^{-1}$ except for monobutyltin (14). In comparison, the data for raw waste water (before treatment) obtained by Fent and Müller show a lower concentration range from 0.1 $\mu\text{g (Sn) L}^{-1}$ to 0.5 $\mu\text{g (Sn) L}^{-1}$ for butyltin

compounds (21). Considering the butyltin concentration in French river waters (lower than $0.03 \mu\text{g (Sn) L}^{-1}$), there is a clear need of a leachate treatment in order to remove or decrease the content of organotin compounds in landfill leachates (22).

Finally, the proportion of the total organic species content in relation with the total inorganic tin content (3) varies from 0.7% for LB_A to 49% for LA^1_C . Therefore, the high variability of the organotin proportion and its related potential toxicity highlights the need of an organotin composition assessment in landfill leachates.

IV.2.3.2 Occurrence of volatile organotin species in landfill effluents

IV.2.3.2.1 Gaseous volatile species in landfill biogases

In the two landfill sites, only methylated and ethylated volatile tin compounds were detected in biogases. The results of semi-quantification are presented in Table IV.2.3. Tetramethyltin is the predominant species in all the samples from the two landfills with concentration varying between $1 \mu\text{g (Sn) m}^{-3}$ and $20 \mu\text{g (Sn) m}^{-3}$, whereas tetraethyltin is only detected in small quantity ($0.01 \mu\text{g (Sn) m}^{-3}$) in biogas from L.B. On the other hand, mixed methyl-ethyl tin volatile compounds are detected in all the samples. In terms of quantification, the biogases BgA^1_C and BgB_C are less concentrated than the three other biogase from L.A (BgA^{2-4}_C). The concentrations of these species are consistent with three of four samples from other European landfills with the predominance of $\text{Sn}(\text{CH}_3)_4$ (in concentrations around $15 \mu\text{g (Sn) m}^{-3}$) (13). Ambient air mean concentrations from the two sites correspond to less than 10% of the biogas concentrations or the methyl- and methyl-ethyltin compounds. As a comparison, these ambient air samples collected above the landfills are however 1000 times more concentrated for $\text{Sn}(\text{CH}_3)_4$ than background site air samples collected at 100km far from the landfill site (16).

IV.2.3.2.2 Dissolved volatile species in landfill leachates

The concentrations of the dissolved volatile species are expressed in pg (Sn) L^{-1} of leachate. Tetramethyltin is the most abundant species with concentrations ranging from 3pg (Sn) L^{-1} to $150 \text{pg (Sn) L}^{-1}$ of leachate and the youngest leachate (LA^4_C) is the most concentrated one. Surprisingly, two species that were not present in the corresponding biogases are detected in the purged-leachate: tetraethyltin and methyltributyltin. In comparison with aquatic reference values measured in harbour and estuarine waters (14-15), SnMe_4 and SnMeBu_3 are 1000 times more concentrated in our landfill leachates.

Table IV.2.3 Volatile organotin species in landfill biogases from L.A and L.B and in landfill leachates from L.A

Volatile species	Sn(CH ₃) ₄	Sn(CH ₃) ₃ (C ₂ H ₅)	Sn(CH ₃) ₂ (C ₂ H ₅) ₂	Sn(CH ₃)(C ₂ H ₅) ₃	Sn(C ₂ H ₅) ₄	Sn(CH ₃)(C ₄ H ₉) ₃
Gaseous phase	Concentration (µg Sn m ⁻³)					
BgA ¹ _C	2.2 ± 1.6	0.12 ± 0.02	1.1 ± 0.1	0.50 ± 0.04	n.d.	n.d.
BgA ² _C	20.0 ± 3.1	0.90 ± 0.12	2.8 ± 0.4	0.74 ± 0.09	n.d.	n.d.
BgA ³ _C	16.2 ± 15.1	0.71 ± 0.11	3.6 ± 0.1	0.67 ± 0.06	n.d.	n.d.
BgA ⁴ _C	22.9 ± 7.9	0.90 ± 0.09	1.5 ± 0.1	0.28 ± 0.03	n.d.	n.d.
BgB _C	1.4 ± 0.4	0.15 ± 0.01	0.54 ± 0.06	0.15 ± 0.01	0.012 ± 0.004	n.d.
Ambient air (above landfill)	0.04 ± 0.02	0.010 ± 0.005	0.06 ± 0.03	0.026 ± 0.003	0.010 ± 0.07*	n.d.
Henry's law constant	6.5	8.6	11	15	20	83
Liquid phase	Concentration in pg (Sn) L ⁻¹					
LA ¹ _C	30 ± 20	0.3 ± 0.3	n.d.	0.2 ± 0.2	0.1 ± 0.1	1.3 ± 1.3
LA ² _C	14 ± 2	2.2 ± 1.0	2.5 ± 1.5	1.7 ± 0.9	0.3 ± 0.2	2.2 ± 0.2
LA ³ _C	3.5 ± 2.3	1.0 ± 0.1	n.d.	0.5 ± 0.1	0.2 ± 0.1	n.d.
LA ⁴ _C	153 ± 54	2.0 ± 1.9	36 ± 16	130 ± 61	17 ± 5	5 ± 0.2
Gas-Liquid system	Saturation ratio					
SRA ¹ _C	9%	4%	<0.1%	1%	≥100%	≥100%
SRA ² _C	0.5%	2%	1%	3%	≥100%	≥100%
SRA ³ _C	0.1%	1%	<0.1%	1%	≥100%	n.d.
SRA ⁴ _C	4%	5%	27%	711%	≥100%	≥100%

* only detected in ambient air from landfill L.B

IV.2.4 Discussion

IV.2.4.1 Landfill characteristics influencing organotin species concentrations in landfill effluents

IV.2.4.1.1 Seasonal evolution of organotin species concentration in landfill leachates

The five sampling campaigns performed on landfill L.B constitute a seasonal monitoring of the organotin compounds in leachates. As shown in Figure IV.2.1, the general evolution of the concentration of the sum of organotin compounds (OTC) follows the one of the total tin concentration. These two contents are inversely proportional to wet deposition. This illustrates the role of seasonal water precipitation influx in controlling the concentration levels of the organotin compounds in leachates.

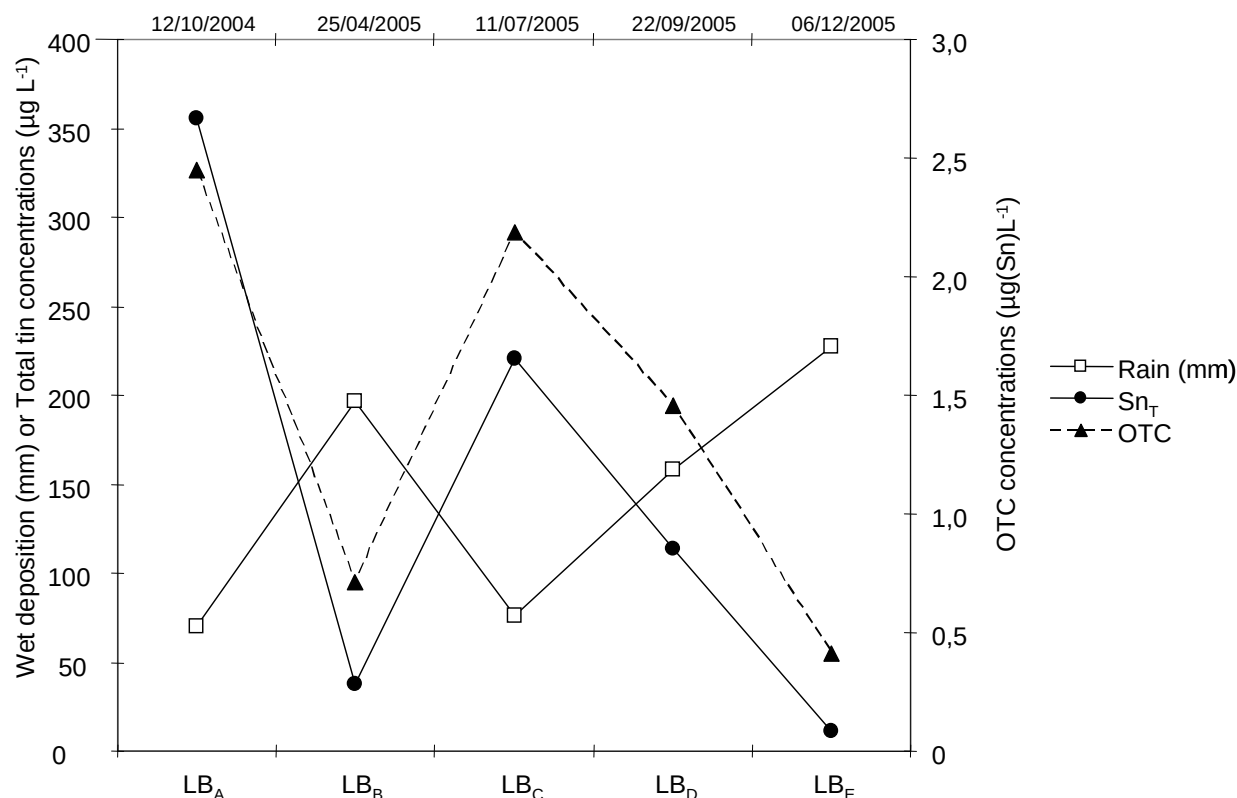


Figure IV.2.1 Wet deposition (mm) and concentrations of both total tin (Sn_T) and the sum of organotin compounds (OTC) in the five seasonal campaigns on landfill L.B

By taking into account the climatic conditions, two groups of data can be distinguished: on one hand LB_A and LB_C and on the other hand LB_B and LB_E which correspond respectively to dry season and wet season. The sampling campaign LB_D is a transition point between the two groups with middle concentrations. The Figure IV.2.2 represents the variation of alkyltin group (a) and substitution degree (b) of organotin compounds in relation with the total tin concentrations (Sn_T). On the Figure IV.2.2 (a), two linearity ranges appear for the three alkyltin group: for the lower values of Sn_T (from 10 $\mu\text{g L}^{-1}$ to 115 $\mu\text{g L}^{-1}$), the organotin compounds concentrations are proportional to total tin concentrations and for the higher values of Sn_T the organotin compounds concentrations tend to reach a steady state. The concentration relative proportion of the species varies also with the increasing total tin concentration. Whereas for the lower Sn_T concentrations, ethyltin compound concentrations are lower than methyltin and butyltin ones, these species are more concentrated for higher Sn_T concentrations. On the Figure IV.2.2 (b), a similar “two-stages” trend can also be outlined, especially for mono- and tri-alkylated tin compounds. For di-substituted compounds, which are always less abundant than the other compounds, there is no obvious slope break.

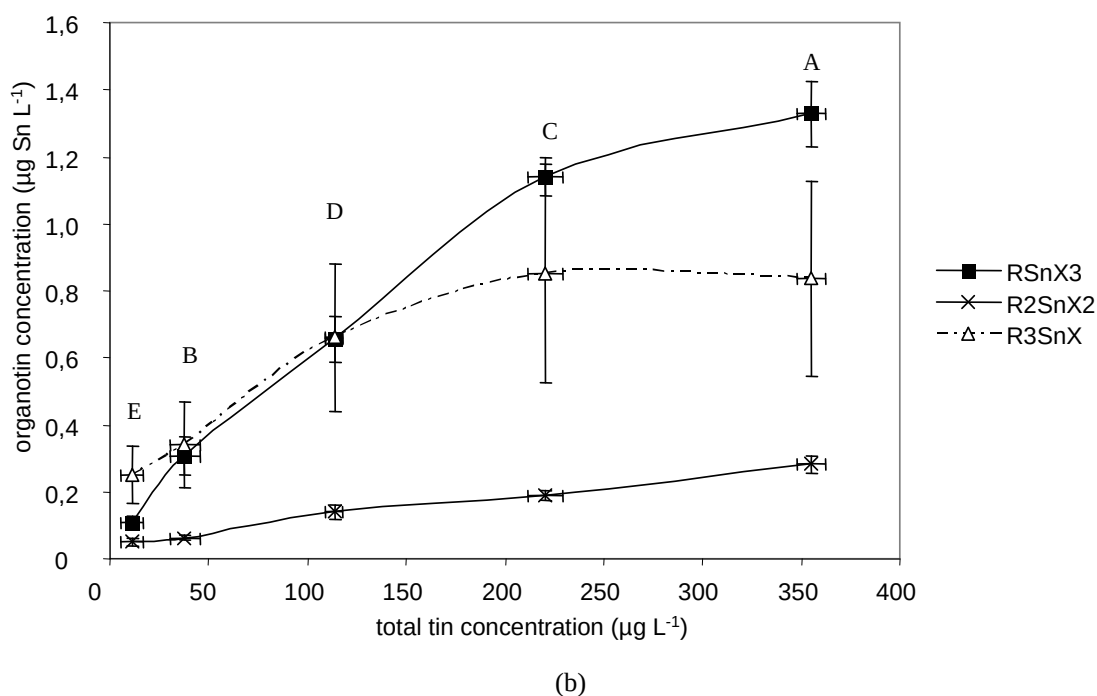
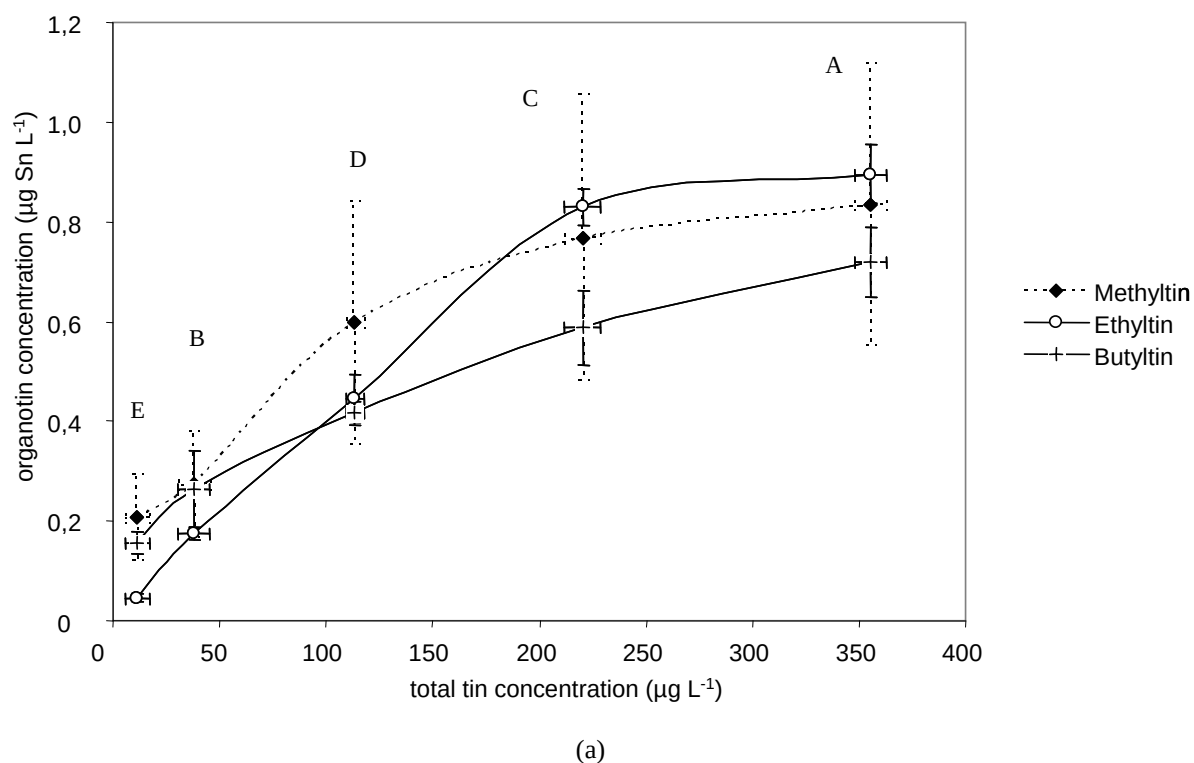


Figure IV.2.2 Variations of alkyltin group (a) and substitution degrees (b) in function of the total tin content for the 5 campaigns on landfill L.B (A: 12/10/2004, B: 25/04/2005, C: 11/07/2005; D: 22/09/2005, E: 06/12/2005).

These results suggest that, depending on climatic conditions, the behaviour of the organotin species is different. During wet and cold season (LB_B and LB_E), the proportionality between organotin compounds and total tin could be mainly related to the mobilisation and/or formation. During dry and hot season (LB_C and LB_A), a steady state equilibrium may occur

and reflect a balance between mobilisation and/or formation pathways and release and/or degradation pathways of the species.

IV.2.4.1.2 Landfill effluent organotin composition in relation to waste degradation state

The difficulty related to the understanding of landfill leachate composition is the influence of many parameters. The nature of the waste and its degradation state are supposed to be among the most influent factors determining the composition of the effluents.

Leachates. Taking into account the results obtained during the seasonal monitoring of landfill L.B, the evolution of organotin composition with the cell filling period was studied relatively to the total tin concentration. The linear correlations between alkyltin group concentration and total tin concentration were statistically evaluated by Bravais-Pearson tests and the corresponding slope and regression factors were also calculated (Table IV.2.4). The Bravais-Pearson correlation factor informs on the potential proportionality between alkyltin compounds and total tin concentrations. When the correlation is significant, organotin leaching and organotin formation are supposed to be dominant processes. In this case, the curve slope also the efficiency of such pathways in the landfill system.

Table IV.2.4 Linear correlation data (Bravais-Pearson tests, slopes and regression factors) for the alkyltin compound concentrations in relation with the total tin concentrations for the three campaigns on landfill L.A.

Alkyltin species		Landfill L.A cells			
		LA ¹ _{A-C}	LA ² _{A-C}	LA ³ _{A-C}	LA ⁴ _{A-C}
	Cell filling period	1995-2000	2000-2001	2001-2002	2002-2003
Butyltin	Bravais-Pearson test	-0.96	0.99	0.99	0.15
	(probability)	(<0.01)	(<0.05)	(<0.05)	(=0.8)
	Curve slope	-0.024	0.011	0.015	0.0022
	Curve regression factor	0.92	0.99	0.99	0.02
Methyltin	Bravais-Pearson test	-0.58	0.97	0.85	0.79
	(probability)	(=0.4)	(<0.05)	(=0.08)	(=0.1)
	Curve slope	-0.39	0.008	0.016	0.014
	Curve regression factor	0.33	0.95	0.72	0.62
Ethyltin	Bravais-Pearson test	-0.24	0.92	0.99	1.00
	(probability)	(=0.7)	(<0.05)	(<0.05)	(<0.05)
	Curve slope	-0.0013	0.0012	0.0017	0.0039
	Curve regression factor	0.05	0.84	0.99	1.00

For butyltin compounds, only the most recent cell (LA⁴) does not present a significant correlation between the organotin concentration and the total tin concentration. The oldest cell (LA¹) is characterised by a negative slope value (-0.024) indicating different processes than the two other cells in which positive value of the slopes was always obtained. For LA¹, LA² and LA³, slope values for butyltin compounds indicate that the leaching decreases with increasing degradation state. For methyltin compounds, no clear trend appears from the statistical data. Only the two middle aged cells (LA², LA³) present significant Bravais-Pearson factors (0.97 and 0.85) between the methyltin compound concentrations and the total tin concentration. For ethyltin compounds, a clear trend is obtained for the three more recent cells (LA², LA³ and LA⁴) for which the organotin concentrations are well correlated to the total tin concentration. The increasing slope values (0.0012, 0.0017, 0.0039) indicates that the younger the waste is, the more the ethyltin concentration increases.

Biogases.

The biogas sampling campaigns have been performed on the two landfills during hot and dry period (Table IV.2.1). The representation of the relative organotin composition of the biogases from L.A and L.B in relation with the cell filling period is shown in Figure IV.2.3.

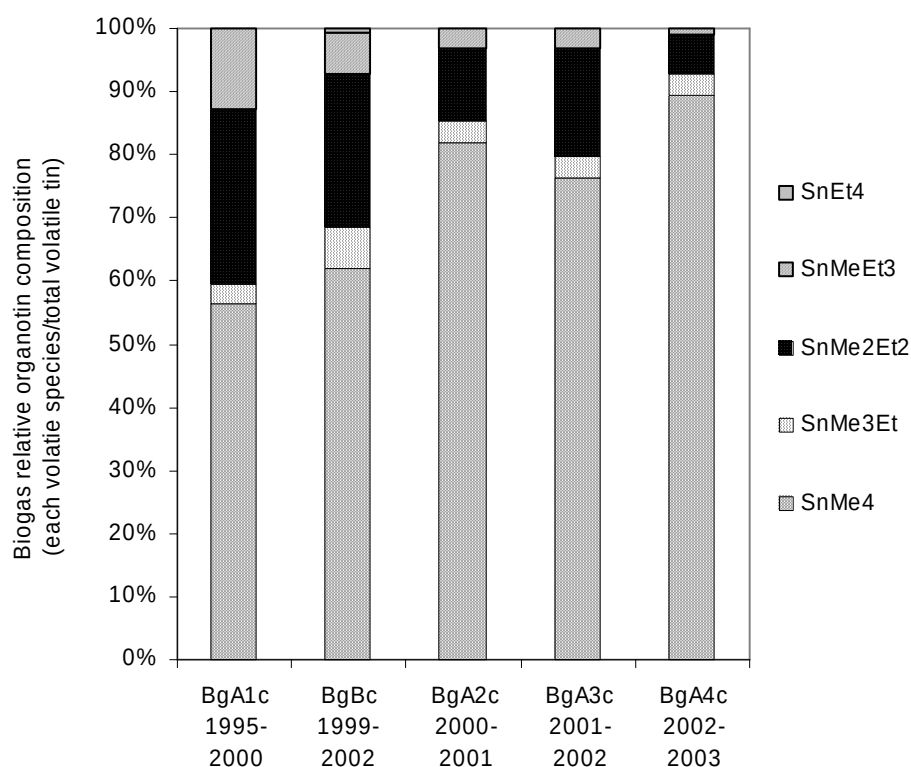


Figure IV.2.3 Relative composition of landfill biogases in function of the cell filling period

The degradation state of the waste is indicated by the period in which the cells were filled. The more the waste is degraded the lower $\text{Sn}(\text{CH}_3)_4$ content is and therefore the proportion di- and tri-ethylated compounds increases.

Figure IV.2.4 illustrates the particular case of $\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2$. The relative proportion of this species for each cell is represented in function of the period during which the cell has been filled. The correlation factor (Bravais-Pearson test: -0.80 , $p < 0.05$) indicates a trend between the waste degradation state and the relative content of $\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2$. It shows that the more the waste is degraded, the more the relative proportion of this species increases. The difference of reaction rates involved in the formation of the volatile compounds can be the origin of this phenomenon. Methylated volatile tin compounds seem thus to be more readily formed during the waste degradation processes than ethylated volatile tin compounds.

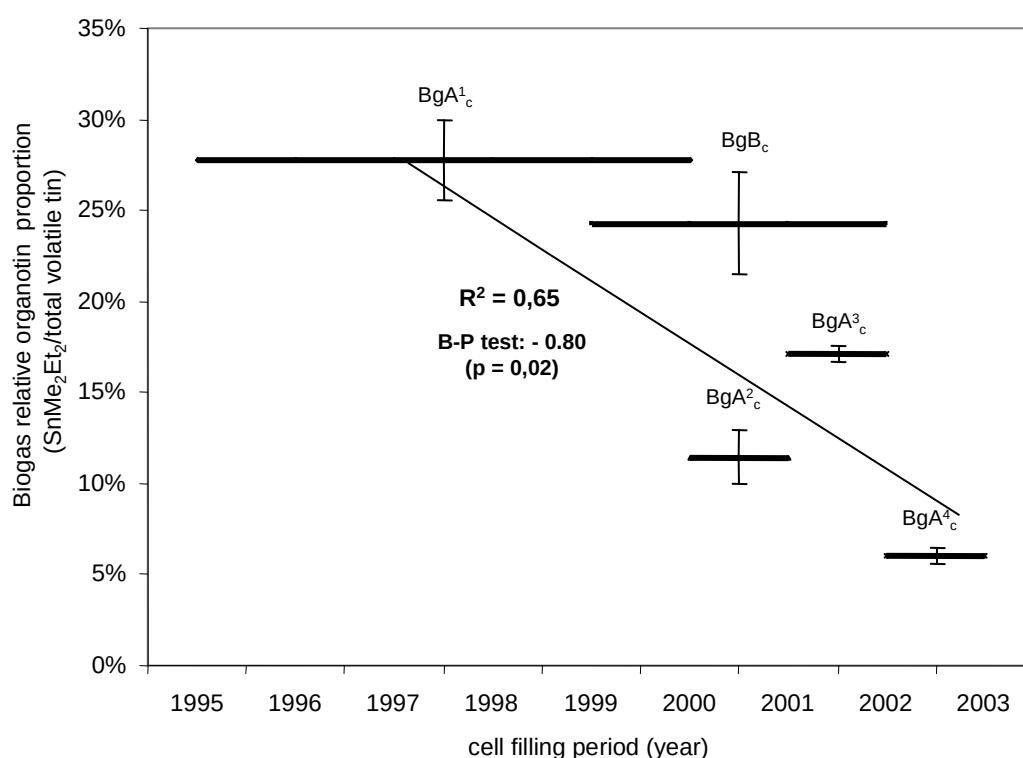


Figure IV.2.4 Variation of the relative proportion of SnMe_2Et_2 in function of the cell filling period

IV.2.4.2 Potential sources of the organotin species in landfill effluents

The Table IV.2.5 summarizes the possible sources and processes that can be proposed for the understanding of the effluent composition. The three compartments (waste, leachate and biogas) are in complete interaction and so the transfer of different species from one phase to another is likely to take place.

Table IV.2.5 Propositions of sources and processes for the organotin occurrence in waste, leachate and biogas

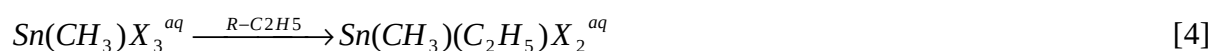
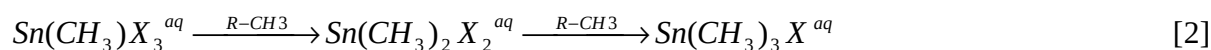
WASTE		LEACHATE			BIOGAS		
Species	Sources	Species	Sources	Processes	Species	Sources	Processes
$\text{Sn}(\text{C}_4\text{H}_9)_3\text{X}$	Biocides, agricultural chemicals	$\text{Sn}(\text{C}_4\text{H}_9)_3\text{X}$	Waste	Leaching	$\text{Sn}(\text{C}_4\text{H}_9)_3(\text{CH}_3)$	Leachate	Methylation
$\text{Sn}(\text{C}_4\text{H}_9)_2\text{X}_2$	Plasticizers	$\text{Sn}(\text{C}_4\text{H}_9)_2\text{X}_2$	Waste, Leachate	Leaching, Dealkylation			
$\text{Sn}(\text{C}_4\text{H}_9)\text{X}_3$		$\text{Sn}(\text{C}_4\text{H}_9)\text{X}_3$					
$\text{Sn}(\text{CH}_3)_3\text{X}_3$	Plasticizers, glass coatings	$\text{Sn}(\text{CH}_3)_3\text{X}_3$	Waste, Leachate	Leaching, Methylation	$\text{Sn}(\text{CH}_3)_4$	Leachate Biogas	Methylation
$\text{Sn}(\text{CH}_3)_2\text{X}_2$	Plasticizers	$\text{Sn}(\text{CH}_3)_2\text{X}_2$					
		$\text{Sn}(\text{CH}_3)_3\text{X}$	Leachate, Biogas	Methylation or dealkylation			
		$\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{X}$	Leachate, Biogas	Methylation or ethylation Dealkylation	$\text{Sn}(\text{CH}_3)_3(\text{C}_2\text{H}_5)$	Leachate Biogas	Methyl-or ethylatin
		$\text{Sn}(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{X}_2$			$\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2$		
		$\text{Sn}(\text{C}_2\text{H}_5)_3\text{X}_3$	Leachate, Biogas	Ethylation, or dealkylation	$\text{Sn}(\text{CH}_3)(\text{C}_2\text{H}_5)_3$	Leachate	Ethylation
		$\text{Sn}(\text{C}_2\text{H}_5)_2\text{X}_2$			$\text{Sn}(\text{C}_2\text{H}_5)_4$		

IV.2.4.2.1 *Anthropogenic species from municipal solid waste leaching*

Tin and organotin compounds known pools in wastes are metallic containers, glasses, plastic and agricultural products (4-7). Therefore waste degradation processes could be responsible of the direct mobilisation of anthropogenic-used compounds such as inorganic tin, mono-, di- and tributyltin compounds and mono- and dimethyltin compounds from the waste materials. An additional source of mono- and disubstituted butyltin and also methyltin in leachates could be the leaching of PVC pipes used in landfills to collect and drain the liquid effluent (23-24).

IV.2.4.2.2 *Neo-formed dissolved species by alkylation/dealkylation pathways*

The anthropogenic origin of organotin compounds in landfill leachates can not explain the occurrence of all the detected species, especially the ethyltin compounds. As described in Figure IV.2.2 and Table IV.2.4, the behaviour of ethyltin compounds has proved to be highly influenced by hydrological conditions and waste degradation state. This result suggests that ethyltin are formed within the landfill system, probably via biological pathways. During dry and hot season (campaigns A and C), the biological activity is enhanced and the proportion of ethyltin as well as methyltin rises (Figure IV.2.2). Biomethylation pathways [1] have already been reported in simulated landfills, especially to explain the occurrence of $\text{Sn}(\text{CH}_3)_3\text{X}$ [2] in leachates (11). Simultaneously to biomethylation, bioethylation mechanisms, such as reactions [3] and [4], could thus be hypothesized.



Biogenic formation of ethyltin species can also be similar to ethylation process of mercury which has been proposed to explain the occurrence of ethylmercury in sediments (25). Methanogenic bacteria have also shown their capability of producing ethane (26), confirming thus that biogenic ethyl transfer can be mediated by anaerobic bacteria.

In addition, both organic waste degradation and bacterial production can also lead to abiotic alkylation mechanisms. Halogenated compounds, dissolved components of organic matter such as fulvic and humic acids, which are known as methyl-donors (27-28), or other organometallic compounds could likewise be ethyl-donors under particular conditions. The

abiotic methylation with methyl donors such as methyl iodide was indeed already proposed for the explanation methyltin compound occurrence (29).

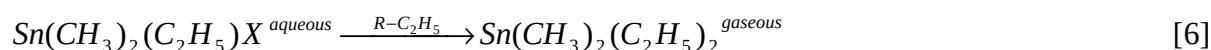
In addition, the process of dealkylation can induce the formation of di- or mono-substituted organotin compounds from tri- and di-substituted ones. Due to the potential sources of the less substituted species from waste leaching and/or from alkylation, the phenomenon of dealkylation can not be clearly observed but it is supposed to occur. The equilibrium between dealkylation and alkylation could also be responsible for the steady state reached by tri-substituted compounds (Figure IV.2.2).

IV.2.4.2.3 Neo-formed volatile species by peralkylation pathways

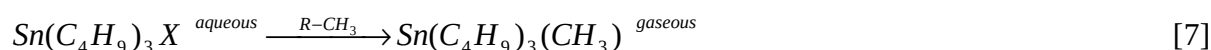
Formation. In biogases, the two major species are $\text{Sn}(\text{CH}_3)_4$ and $\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2$ whereas $\text{Sn}(\text{CH}_3)_3(\text{C}_2\text{H}_5)$ and $\text{Sn}(\text{CH}_3)(\text{C}_2\text{H}_5)_3$ are less abundant (Table IV.2.3). The presence of $\text{Sn}(\text{C}_2\text{H}_5)_4$ reported in landfill biogases for the first time, is quantitatively not significant. The occurrence of all these species illustrates the fact that methylation and ethylation mechanisms can be completed in landfill systems. Permethylation and perethylation have already been proposed in landfill to explain the occurrence of methylated and mixed methyl-ethyl species in biogases (12-13). The predominance of $\text{Sn}(\text{CH}_3)_4$ in biogases could be related to the high content of trimethyltin in leachates (Table IV.2.2) by the reaction [5], which completes the “aqueous” methylation mechanism [2].



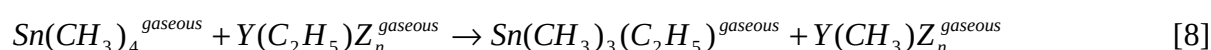
In the case of the second major gaseous species ($\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2$), two pathways can be proposed: methylation or ethylation of ionic species. As the presence of diethyltin is quantitatively insignificant in leachates (Table IV.2.2), the perethylation of methyltin compounds such as reaction [6] could be assumed as the main pathway for the mixed methylethyltin species formation.



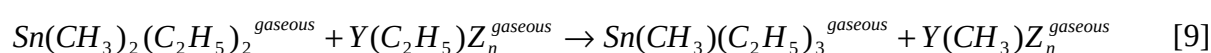
Additionally, volatile $\text{Sn}(\text{CH}_3)(\text{C}_4\text{H}_9)_3$ found in leachate confirms the aqueous methylation pathway of butyltin species [7] (18).



In both phases, specific volatile organotin species may also react under transalkylation mechanisms (10). For the five biogas samples (BgA¹⁻⁴_C and BgB_C), the Bravais-Pearson correlation factor between Sn(CH₃)₄ and Sn(CH₃)₃(C₂H₅) is 0.99 (p<0.05) indicating a close relationship between these two species. A chemical transalkylation such as reaction [8] could be proposed as a formation pathway for trimethyl-monoethyltin.



Similarly, the correlation factor between Sn(CH₃)₂(C₂H₅)₂ and Sn(CH₃)(C₂H₅)₃ is 0.84 (p<0.05). This statistical data is also highly significant for this kind of environmental samples. Chemical transalkylation reaction such as [9] can thus be suggested as a formation pathway.



This kind of chemical transalkylation pathways has already been assumed under heterogeneous mode to justify the ethylmercury occurrence in tetraethyllead contaminated site (30).

These mechanisms of peralkylation or transalkylation under biological or chemical routes allow the explanation of the occurrence in the biogases of all detected species. Nevertheless, these pathways are only suggested and need laboratory experimentations, such as those under simulated landfill conditions, to be confirmed.

Mobilisation. A better understanding of the fate of organotin volatile compounds in landfill effluents requires the knowledge of potential transfers between leachates and biogases. The evaluation of the dissolved volatile species content in leachate allows the assessment of an approximate partition between leachate and biogas. The calculations of saturation ratios were adapted to landfill effluents. The saturation ratio, which defines the deviation from the gas-liquid equilibrium, is defined by the formula [10] where C is the concentration of the species in each phase and H the Henry's Law constant (dimensionless). This constant defines especially the equilibrium gas-liquid partition and thus the volatility of the species. H has

been calculated at 20°C for each species (Table IV.2.3) by using a quantitative-structure-activity-relationship-based software provided by U.S.E.P.A. (HENRYWIN v1.90).

$$SR = \frac{C_{aqueous}}{C_{gaseous}} * H \quad [10]$$

The saturation ratios calculated for each species for the campaign in L.A (Table IV.2.3) can illustrate the potential phase transfer of these species. For each landfill cell, the low ratios ($SR \ll 1$) indicate the over-saturation of the biogas in relation to the leachate for $\text{Sn}(\text{CH}_3)_3(\text{C}_2\text{H}_5)$ and $\text{Sn}(\text{CH}_3)_4$. Several hypotheses can be proposed. These species could be formed in the gaseous phase or directly transferred to the gaseous phase after formation. Another possibility could be that these species are removed from leachates by biogas stripping. The cases of $\text{Sn}(\text{C}_2\text{H}_5)_4$ and $\text{Sn}(\text{CH}_3)(\text{C}_4\text{H}_9)_3$ are particular as these species are not detected in the gaseous samples but they are detected in the purges. Therefore, the approximate saturation ratios ($SR > 1$ or $=1$) are reflecting a better equilibration between the gaseous phase and the liquid phase. For these species, which have a higher molecular weight; their lower diffusivity may avoid effective transfer mechanism in both liquid and gaseous phases (18).

IV.2.4.3 Evaluation of potential emissions of organotin compounds from leachates and biogases

The risk assessment related to organotin compounds in the landfill system is contrasted. The biodegradation processes both produces less toxic species by dealkylation reactions but also more lipophilic and thus available species by alkylation reactions such as methylation or ethylation. The organotin speciation analysis in leachates is required to assess the contribution of the landfills towards the main organotin pollution sources.

Leachate and biogas average annual concentrations from the two landfills are used to evaluate the potential emissions due to waste disposal by taking into account the annual volume of leachates and biogases produced. The potential aquatic emissions extrapolated to the total MSW disposals in French landfills give a global quantity of 40 kg year⁻¹ for total tin and more especially 3.5 kg (Sn) year⁻¹ for organotin compounds. Similarly, extrapolated French atmospheric emissions from MSW landfills are 7 kg (Sn) year⁻¹ for volatile organotin compounds. These atmospheric emissions are relatively negligible compared to waste incineration emissions of tin which are estimated at 26 t (Sn) year⁻¹ in Europe (1-2). The corresponding atmospheric emission factor is 1.0 g (Sn) t⁻¹ of incinerated waste, and is

therefore 1000 times higher than the one calculated in our work ($0.001 \text{ g (organic Sn) t}^{-1}$ of disposed waste). For incineration, tin is emitted under inorganic forms, whereas for landfilling tin is under organic forms (before treatment). Although these estimations show a low input of organotin from waste disposals in the global mass balance of tin emissions, landfill effluents are contributing to the mobilisation of harmful organotin compounds both in biogases (100% of total tin) and in leachates (10% of total tin). However, this diffuse release of organotin compounds in the environment must be controlled towards to their extremely high toxicity. According to this, effluents treatment processes and the removal efficiency of organotin compounds from leachates and biogases require a special care.

IV.2.5 Acknowledgements

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IV.2.6 References

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La mise en œuvre des protocoles d'analyse de spéciation de l'étain dans les lixiviats et les biogaz a permis d'étudier le devenir des espèces organostanniques dans le système complexe constitué par les déchets, les lixiviats et les biogaz. Sur la Figure IV.2.5 sont indiquées les espèces organostanniques les plus abondantes dans les lixiviats (MBT, TBT, DMT, TMT, MET) et dans les biogaz (TeMT et DMDDET). Par ailleurs, cette figure illustre les phénomènes qui ont été proposés pour expliquer leur présence dans les deux effluents : d'une part la mobilisation à partir des déchets (espèces butylées et mono- et diméthylées) et d'autre part les mécanismes de méthylation et d'éthylation par voie biologique (espèces méthylées et éthylées ioniques et gazeuses).

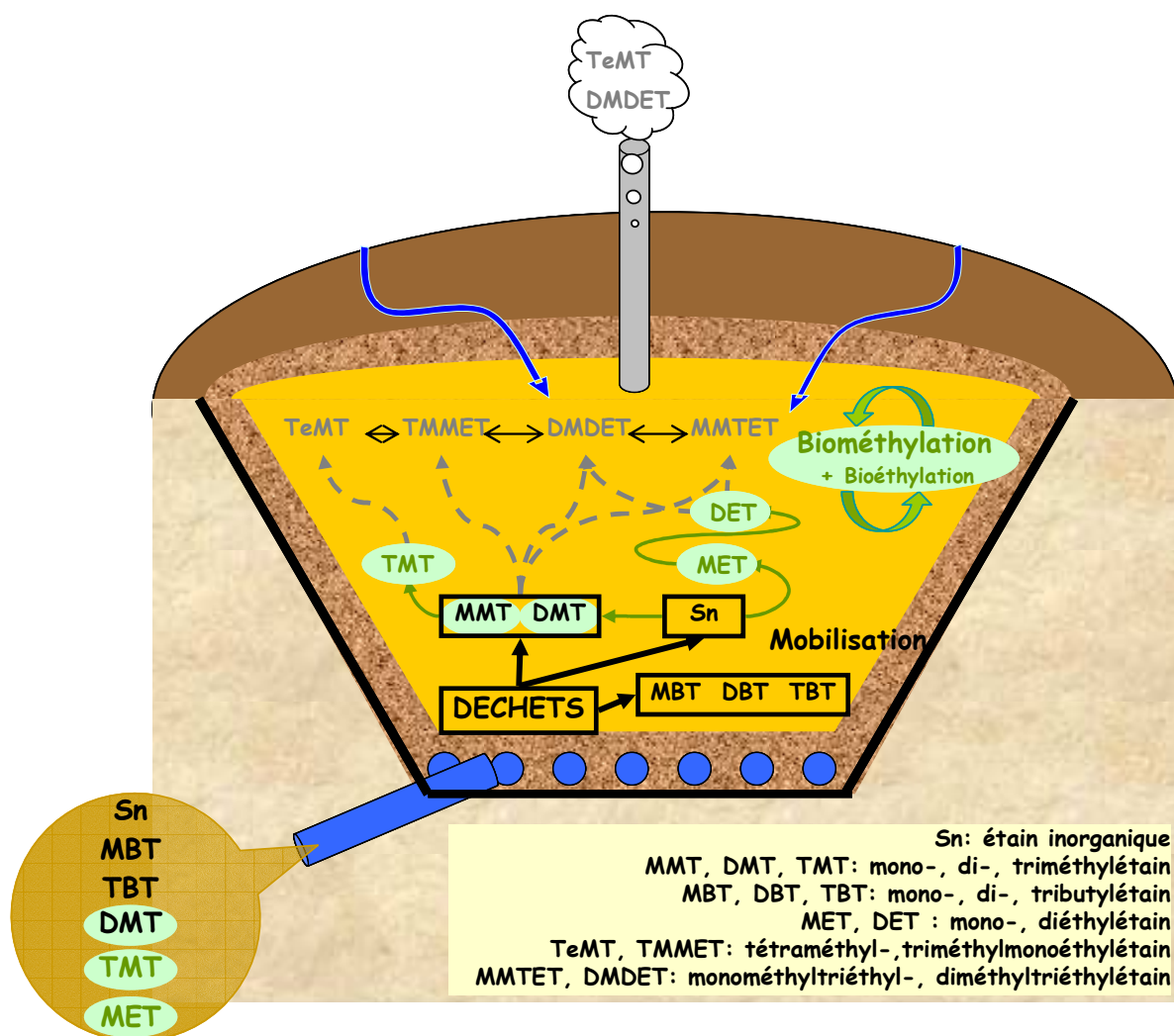


Figure IV.2.5 : Représentation schématique d'un CSD et des processus à l'origine de la présence des espèces organostanniques dans les lixiviats et les biogaz

CONCLUSION

Conclusion

L'objectif général de cette thèse était de caractériser qualitativement et quantitativement la présence et le devenir des métaux et des métalloïdes dans les effluents de centres de stockage de déchets (CSD) ménagers et assimilés. Deux étapes importantes ont été nécessaires pour atteindre cet objectif: le développement analytique et le suivi des sites d'étude.

La première étape a consisté à mettre au point les stratégies de préparation d'échantillons et d'analyse des métaux et métalloïdes dans les effluents de CSD. Les protocoles mis en œuvre sont représentés schématiquement dans le Schéma C.1. Les efforts ont été plus particulièrement concentrés sur les lixiviats car il n'existait pas de protocole spécifiquement adapté à ce type de matrice.

Les étapes du protocole de préparation des échantillons et d'analyse élémentaire des métaux et métalloïdes par spectrométrie de masse à plasma induit (ICPMS) ont été validées au moyen de la mise en place d'un lixiviat de référence de laboratoire évalué par un essai inter-laboratoire.

Les analyses de spéciation dans les lixiviats ont été focalisées sur la détermination des espèces de l'arsenic et de l'étain, deux contaminants majeurs des lixiviats dont la toxicité des espèces est variable. Alors que les espèces d'arsenic peuvent être séparées directement en phase aqueuse par la chromatographie en phase liquide (HPLC), les espèces d'étain nécessitent une étape de volatilisation par alkylation avant leur séparation par chromatographie en phase gazeuse (GC). Une attention toute particulière a été portée sur la préparation des échantillons afin de simplifier la matrice des lixiviats sans pour autant altérer les formes chimiques. La séparation de huit espèces d'arsenic a été réalisée sur une colonne échangeuse de cations (Hamilton PRP-X200). Alors que les pics correspondant à As III, AsV, MMA, DMA, TMA^s et AsB, sont bien résolus, ceux de TMAO et AsC se superposent en partie. Pour l'étain, la méthode développée par GC-ICPMS a permis la séparation de 9 composés connus (MMT, DMT, TMT, DET, TET, MBT, DBT, TBT) auxquels s'ajoute trois composés identifiés dans un deuxième temps : le monoéthylétain (MET) et deux composés mixtes méthyl-éthyl.

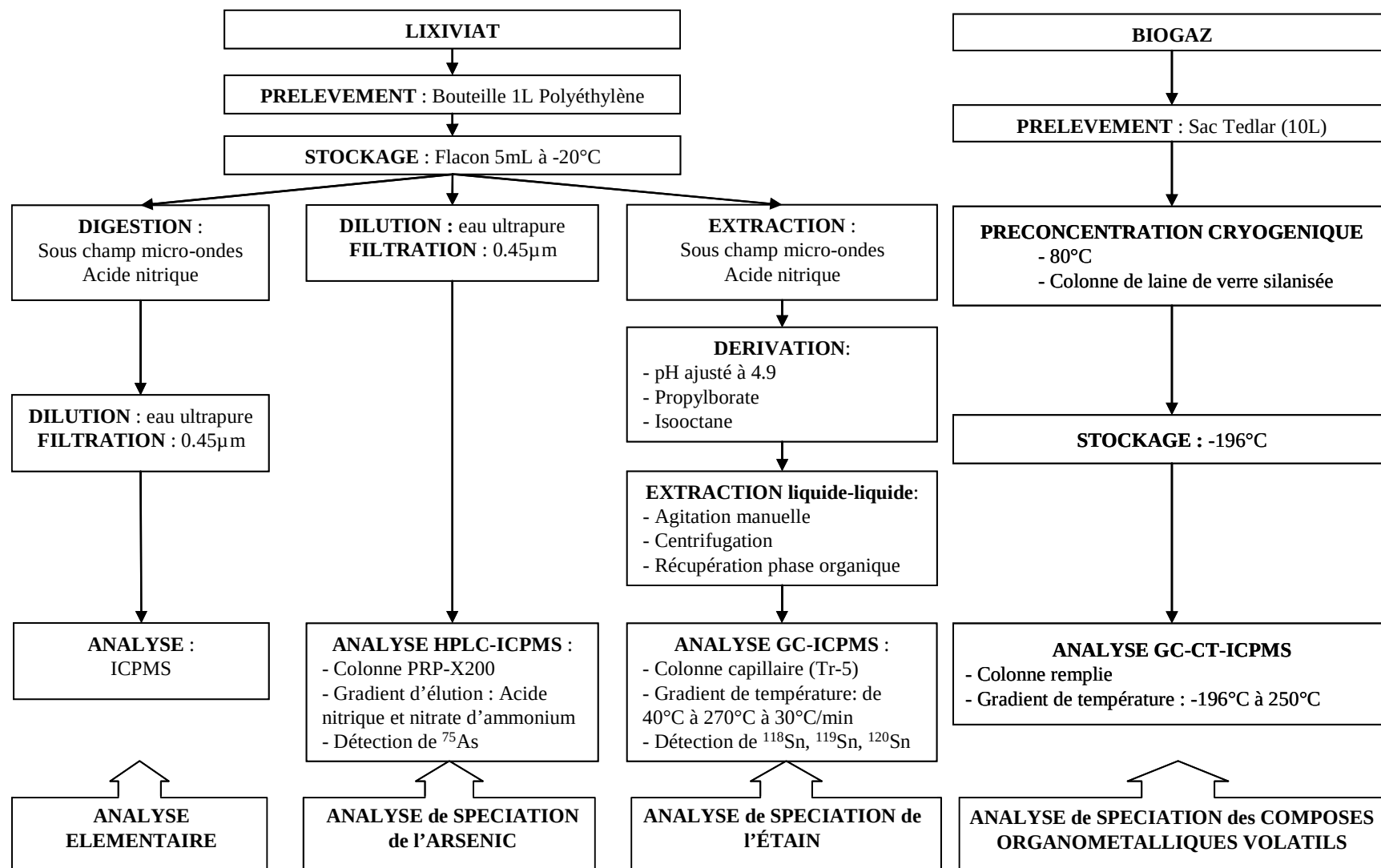


Schéma C.1 Synthèse des protocoles analytiques mis au point

Ces deux méthodes d'analyse de spéciation ont été validées par la comparaison des méthodes de quantification, à cause du manque de matériau de référence certifié adapté (matrice proche des lixiviats). Pour l'arsenic, la méthode par ajouts dosés a été utilisée en complément de la méthode d'étalonnage externe. Pour l'étain, son caractère multi-isotopique a permis de compléter les méthodes d'étalonnage externe et interne par la mise en place d'une méthode de dilution isotopique spécifique et non-spécifique.

Enfin, les compétences du laboratoire pour le prélèvement et l'analyse d'air ambiant et d'effluents gazeux ont été mise à profit dans le domaine des biogaz. La méthode de prélèvement dans les sacs Tedlar a été choisie pour sa simplicité de mise en œuvre. Le choix de la température de pré-concentration à -80°C a été guidé par les caractéristiques de la matrice, riche en méthane et en dioxyde de carbone. L'analyse par chromatographie en phase gazeuse avec piège cryogénique couplée à l'ICPMS a permis la détection, l'identification et la semi-quantification de nombreuses espèces méthylées et éthylées d'arsenic et d'étain simultanément.

Ainsi, cette première partie a abouti à la mise en place de méthodes et d'outils analytiques spécifiquement adaptés à l'analyse des métaux et métalloïdes dans les effluents de CSD. Tout au long du développement analytique, notamment pour la spéciation, une attention particulière a été portée sur la préservation de l'échantillon afin d'assurer la représentativité des résultats.

La deuxième étape de ces travaux a consisté à faire un suivi des métaux et métalloïdes dans les effluents de deux CSD aquitains. Deux échelles temporelles ont pu être considérées avec d'une part le suivi saisonnier et d'autre part le suivi pluri-annuel.

Cinq campagnes de prélèvement des lixiviats ont été réalisées durant l'année 2004-2005 sur un des deux CSD. L'évaluation de l'enrichissement relatif des lixiviats par rapport au bruit de fond hydrologique a mis en évidence quatre contaminants : l'arsenic, l'étain, l'antimoine et le chrome. Ces éléments se sont révélés présenter une caractéristique commune : leurs concentrations sont largement dépendantes des paramètres climatiques tels que les précipitations et les températures. L'étude plus approfondie des espèces de l'arsenic et de l'étain a permis de préciser leurs variations saisonnières. Comme l'illustre le Schéma C.2, il ne s'agit pas simplement d'une dilution ou d'une concentration des lixiviats au gré des conditions climatiques. Ce phénomène est en effet couplé à la formation d'espèces par des processus liés à l'activité biologique dans le massif de déchets. Les espèces supposées être

présentes dans les déchets sont, pour l'arsenic, les espèces inorganiques (As(OH) sur le Schéma C.2) et pour l'étain, les espèces butylées et certaines espèces méthylées (Sn(Bu) et Sn(Me)). Ainsi toutes les autres espèces détectées dans les lixiviats sont considérées comme nouvellement formées durant la dégradation des déchets. Il s'agit pour l'arsenic des espèces méthylées (As(Me)) et pour l'étain des espèces éthylées (Sn(Et)) et méthylées. Les proportions des espèces nouvellement formées par rapport aux espèces originelles (Schéma C.2) calculées lors des périodes climatiques chaudes sont toujours supérieures à celles calculées lors des périodes climatiques froides.

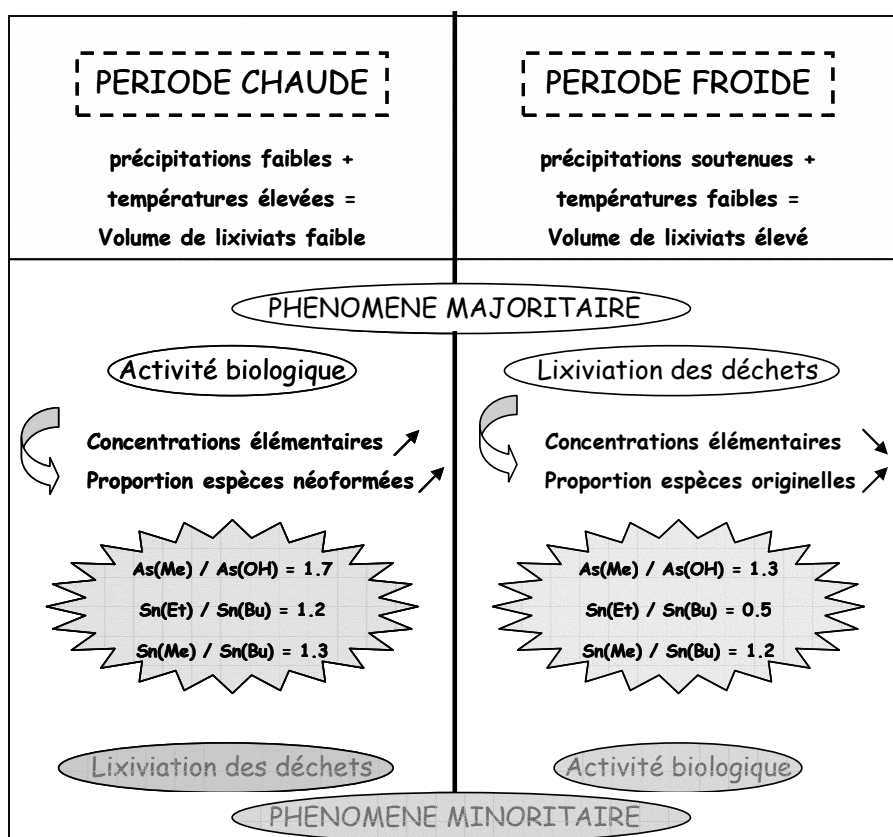


Schéma C.2 Représentation des variations saisonnières des métaux et métalloïdes dans les lixiviats

Le suivi combiné des espèces de l'arsenic et de l'étain dans les lixiviats a donc mis en exergue l'alternance de deux phénomènes liés aux conditions climatiques pour expliquer les variations des concentrations : lors des périodes chaudes c'est la formation d'espèces nouvelles régie par l'activité biologique qui est le phénomène prépondérant alors que lors des périodes froides c'est la lixiviation des déchets qui est le phénomène majoritaire.

Par ailleurs, l'approche complémentaire d'analyse de la spéciation des composés de l'arsenic et de l'étain à la fois dans les lixiviats et les biogaz a mis en évidence l'influence de l'état de dégradation des déchets sur la composition des effluents. Le Schéma C.3 représente l'évolution des lixiviats et des biogaz en fonction de la dégradation des déchets.

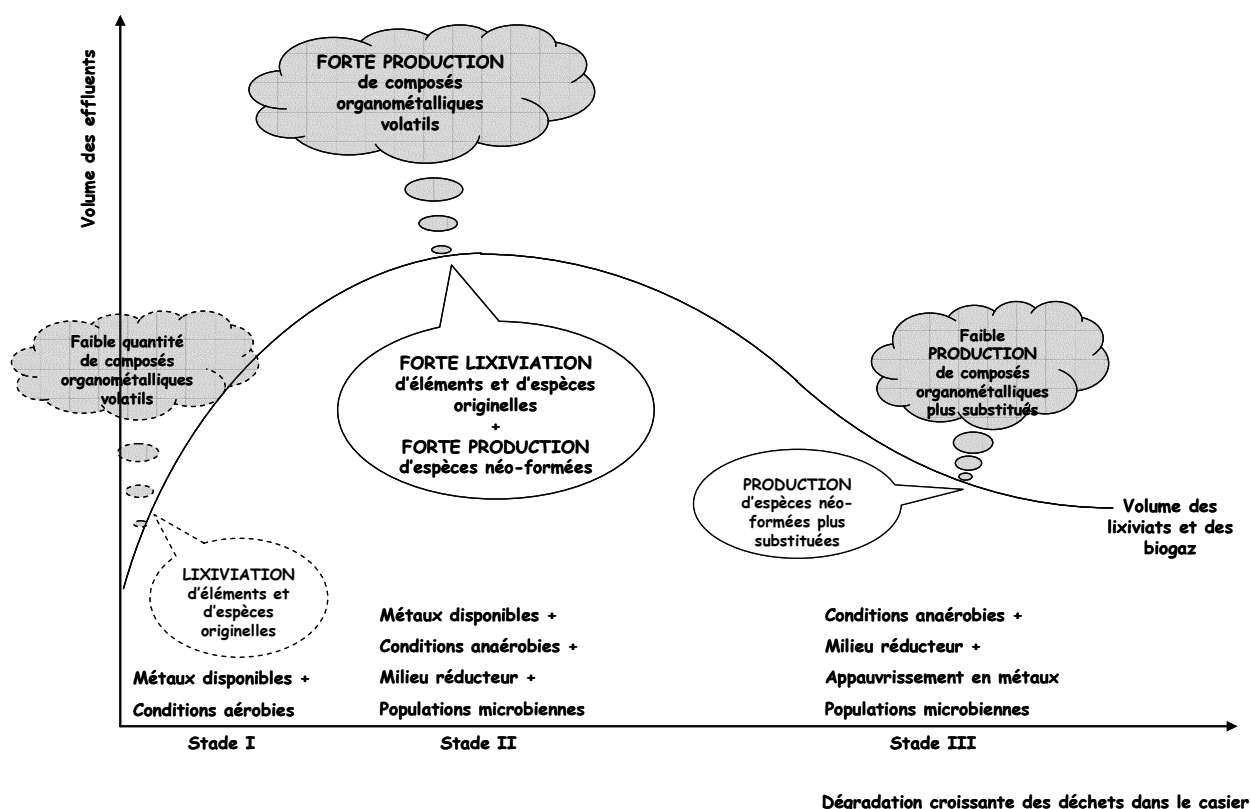


Schéma C.3 Représentation de l'évolution de la composition des lixiviats et des biogaz en fonction de l'état de dégradation des déchets

Les deux phénomènes décrits précédemment à l'échelle annuelle sont extrapolés ici sur la durée de vie d'un casier.

- Stade I : parmi les casiers qui ont bénéficiés d'un suivi, aucun n'était à un stade initial de dégradation des déchets. Les processus majeurs intervenant lors de la formation des lixiviats et des biogaz n'ont donc pas été vérifiés par l'analyse de ces deux effluents. On peut supposer que comme les conditions anaérobies et réductrices ne sont pas atteintes à la fin du remplissage des casiers, la production d'espèces organométalliques dans les lixiviats comme dans les biogaz est un phénomène minoritaire.
- Stade II : une fois que les conditions anaérobies et réductrices sont réunies, les populations microbiennes susceptibles de produire des espèces organométalliques peuvent alors enrichir les effluents en espèces alkylées. Les mécanismes de biométhylation et de bioéthylation

permettent d'expliquer la présence de toutes les espèces qui ont été détectées dans les lixiviats et les biogaz. Le caractère « biologique » de ces mécanismes peut inclure de nombreux phénomènes comme le transfert d'alkyl intracellulaire ou bien l'alkylation par des composés biogènes provenant de l'activité bactérienne et/ou de la dégradation de la matière organique.

- Stade III : lorsque l'état de dégradation avance, la production de lixiviats et de biogaz diminuent graduellement et le massif de déchets s'appauvrit en métaux. Dans les effluents, la proportion des espèces plus substituées augmente. Il peut être suggéré que leur formation est favorisée du fait de l'augmentation du temps de résidence des espèces dans le massif de déchets.

Les émissions de composés organométalliques par les CSD lors de la phase intermédiaire de dégradation des déchets sont susceptibles d'être qualitativement importantes aussi bien dans les milieux aquatiques que dans l'atmosphère. Dans un contexte plus large de développement de nouvelles techniques comme le pré-traitement biologique ou la recirculation des lixiviats, on peut supposer que la dégradation des déchets accélérée par une activité biologique importante pourra engendrer une forte production de composés organométalliques. Selon l'élément considéré, cela pourra se traduire par une augmentation, comme pour l'étain, ou une diminution, comme pour l'arsenic, de la toxicité par la formation de nouvelles espèces.

Ces travaux de thèse novateurs dans le domaine du suivi des métaux et métalloïdes dans les effluents de CSD ouvrent un large champ de perspectives. Deux principaux axes de recherche pourraient être envisagés par la suite. Tout d'abord, les efforts pourraient porter sur le développement de l'analyse de spéciation de l'antimoine et du chrome dans les lixiviats. En effet, ces deux éléments présentent de fortes concentrations dans les lixiviats et, comme pour l'arsenic et l'étain, leurs formes chimiques sont caractérisées par de grandes différences de toxicité.

Dans un deuxième temps, la reproduction à l'échelle pilote des conditions de dégradation des déchets pourrait permettre de vérifier la validité des hypothèses proposées pour expliquer la présence des espèces organométalliques dans les deux effluents. L'utilisation de traceurs isotopiques, comme par exemple les espèces d'étain enrichies isotopiquement, serait particulièrement intéressante pour observer et préciser les voies de transfert des espèces entre les déchets, les lixiviats et les biogaz.

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ANNEXES

Annexes

Annexe 1 : Récapitulatif des campagnes de prélèvement sur les deux CSD **p174**

Annexe 2 : Concentrations élémentaires en $\mu\text{g L}^{-1}$ dans les lixiviats provenant des casiers de CSDA **p175**

Annexe 3 : Concentrations élémentaires en $\mu\text{g L}^{-1}$ dans les rejets au milieu naturel pour les deux CSD (campagnes de prélèvement de décembre 2005) **p177**

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Annexe 1 : Récapitulatif des campagnes de prélèvement sur les deux CSD

Campagnes de prélèvement et effluents prélevés (L : lixiviat, B :biogaz)							
CSDA		10/01/2005		04/07/2005		08/12/2005	29/05/2006
Casier	Remplissage						
LA1	1995-2000	L		L		L	L + B
LA2	2000-2001	L		L		L	L + B
LA3	2001-2002	L		L		L	L + B
LA4	2002-2003	L		L		L	L + B
LA5	2003-2004	L		L		L	
LA6	2004-2005			L		L	
CSDB		12/10/2004	25/04/2005	11/07/2005	22/09/2005	06/12/2005	
	1999-2002	L	L	L + B	L	L	

Annexe 2 : Concentrations élémentaires en $\mu\text{g L}^{-1}$ dans les lixiviats provenant des casiers de CSDA

Campagne du 10/01/2005	Casiers de CSDA									
	LA1		LA2		LA3		LA4		LA5	
Cd	0.04	±0.05			0.17	±0.03	0.17	±0.05	0.17	±0.09
Se	1.4	±0.09	0.5	±0.15	2.5	±0.1	1.7	±0.1	2.1	±0.1
Pb	2.4	±0.4	0.3	±1.2	6	±4	9	±1	3	±1
Sb	1.3	±0.1	0.7	±0.1	3	±1	5	±1	3.7	±0.4
Cu	5.5	±2.2	2.4	±2.0	11	±3	29	±12	11	±4
As	12.5	±0.1	10.8	±0.2	31.9	±0.5	50	±0.8	41	±1
Zn	12	±2	65	±51	62	±7	84	±3	34	±11
Mn	324	±7	641	±6	271	±8	341	±9	719	
Sn	21.6	±0.7	2.9	±0.9	20	±1	95	±2	16	±3
Cr	74	±4	42	±3	161	±7	500	±10	145	±5
Al	1404	±11	562		3610	±143	3112	±164	2169	±57
Sr	434	±6	1183	±16	1073	±36	1415	±26	1183	±12
Fe	26774	±260	6168		2899	±184	2695	±333	8144	±66

Campagne du 04/07/2005	Casiers de CSDA											
	LA1		LA2		LA3		LA4		LA5		LA6	
Cd	0.07	±0.02	1.4	±0.1	0.07	±0.01	0.03	±0.01	0.22	±0.03	0.07	±0.01
Se	2.6	±0.2	3.0	±0.2	1.1	±0.2	1.3	±0.2	4.3	±0.4	0.4	±0.4
Pb	2.9	±0.5	12	±1	2	±1	2	±1	6	±1	9	±2
Sb	72	±1	6.2	±0.4	1.00	±0.04	0.95	±0.01	8.8	±0.2	10.6	±0.2
Cu	30	±7	42	±27	6		7	±4	7.8	±0.4	120	±25
As	31.5	±0.4	35.34	±0.01	19	±1	17	±1	68	±2	5	±0.5
Zn	27	±16	124	±38	18	±22	14	±11	77	±35	333	±45
Mn	275	±8	450	±3	515	±3	291	±9	801	±5	1.58	±0.04
Sn	12	±3	42	±7	2	±1	1.2	±0.1	18	±1	0.9	±0.1
Cr	326	±9	383	±1	36.6	±0.1	17	±1	192	±2	3.2	±0.2
Al	1623	±41	3836	±42	434	±9	542	±326	2438	±47	31	±15
Sr	562	±11	1385	±3	1120	±7	840	±25	1177	±1	3	±1
Fe	1950	±23	15790	±22	14479	±12	1463	±5	51156	±9081	161	±52

Annexe 2 (suite)

Campagne du 08/12/2005	Casiers de CSDA											
	LA1		LA2		LA3		LA4		LA5		LA6	
Cd	0.22	±0.01	0.15	±0.01	0.25	±0.05	0.42	±0.06	0.30	±0.17	0.110	±0.001
Se	0.9	±0.1	0.55	±0.08	0.63	±0.01	3.7	±0.3	2.3	±0.1	0.12	±0.05
Pb	50	±3	10.1	±0.1	4	±1	8	±0	4	±1	63	±53
Sb	186	±6	2.8	±0.2	1.8	±0.1	8.7	±0.2	7.1	±0.1	35	±1
Cu	120	±1	10.6	±0.1	11.6	±0.4	19	±1	7.3	±0.2	525	±27
As	79	±4	13	±1	17	±1	89	±2	46	±1	4.7	±0.2
Zn	163	±6	27	±7	20	±4	132	±6	29.1	±0.2	130	±7
Mn	409	±3	671	±17	1198	±1	333	±2	850	±2	1.7	±0.2
Sn	21	±1	0.4	±0.1	0.6	±0.1	86	±2	9.9	±0.3	0.9	±0.1
Cr	203	±1	5	±3	6	±1	653	±2	109	±5	1.3	±0.7
Al	1139	±1	241	±1	526	±97	3469	±21	815	±14	40	±39
Sr	535	±1	355	±6	768	±16	1368	±4	1218	±3	1.1	±0.2
Fe	2595	±34	6122	±118	25808	±116	2133	±5	3156	±81	54	±24

Annexe 3 : Concentrations élémentaires en $\mu\text{g L}^{-1}$ dans les rejets au milieu naturel pour les deux CSD (campagnes de prélèvement de décembre 2005)

Rejet au milieu naturel après traitement sur site				
Site	CSDA		CSDB	
Traitement	osmose inverse		physico-chimique et biologique	
Cd	0.09	± 0.02	0.10	± 0.05
Se	0.2	± 0.1	0.35	± 0.02
Pb	7	± 3	2.5	± 0.1
Sb	1.2	± 0.1	2.3	± 0.1
Cu	1.5	± 1.2	8.1	± 1.0
As	0.6	± 0.1	8.3	± 0.4
Zn	9	± 3	16.6	± 1.9
Mn	3.5	± 0.1	518	± 11
Sn	0.3	± 0.2	1.4	± 0.2
Cr	0.7	± 0.1	17	± 1
Al	n.d		155	± 36
Sr	6.9	± 0.1	672	± 6
Fe	n.d		1069	± 167

Annexe 4 : Ordre de grandeurs des concentrations (ng m⁻³) en composés organo-métalliques volatils dans les biogaz provenant des deux CSD

Elément	Espèces proposées	Ordre de grandeur des concentrations (ng m ⁻³)				
		CSDA				CSDB
		LA1	LA2	LA3	LA4	
Se	SeMe ₂	~10	~200	~10	~1500	~50
	SeEtMe	n.d.	~50	~1	~100	n.d.
	SeEt ₂	n.d.	~10	~1	~50	n.d.
Sb	SbMe ₃	~1	~30000	~15000	~35000	~1
Bi	BiMe ₃	~0.5	~50	~10	~100	~0.1
Te	TeMe ₂	~1	~300	~100	~1000	n.d.
	TeMeEt	n.d.	~1	~1	~5	n.d.
Hg	Hg ^o	~10	~10	~50	~50	~5
	HgMe ₂	~0.5	~1	~1	~5	~1
Pb	PbMe ₄	~0.1	~0.5	~0.1	~0.1	~1
	PbMe ₃ Et	n.d.	~0.1	n.d.	~0.1	~0.1
	PbMe ₂ Et ₂	n.d.	n.d.	n.d.	n.d.	~0.1
	PbMeEt ₃	~0.1	~0.1	~0.1	n.d.	~0.5
	PbEt ₄	~0.5	~0.5	~0.5	~0.5	~5

Annexe 5 : Paramètres physico-chimiques des lixiviats provenant des casiers de CSDA

Campagne du 10/01/2005	Casiers de CSDA				
	LA1	LA2	LA3	LA4	LA5
pH	7.9	7.8	7.7	7.7	7.7
Carbone organique total (COT) (mgC L ⁻¹)	389	300	915	858	792
Carbone inorganique (CI) (mgC L ⁻¹)	833	564	1157	1227	836
Na ⁺ (mg L ⁻¹)	1263	725	1864	1586	1239
K ⁺ (mg L ⁻¹)	532	295	814	801	670
Cl ⁻ (mg L ⁻¹)	1514	599	2070	1880	1368
Br ⁻ (mg L ⁻¹)	15	4	8	7	7
F ⁻ (mg L ⁻¹)	2	0.3	1	1	n.d
SO ₄ ²⁻ (mg L ⁻¹)	33	n.d	16	33	48
NO ₃ ⁻ (mg L ⁻¹)	1	11	n.d	2	n.d
ΣPO ₄ ³⁻ (mg L ⁻¹)	n.d	n.d	n.d	26	n.d

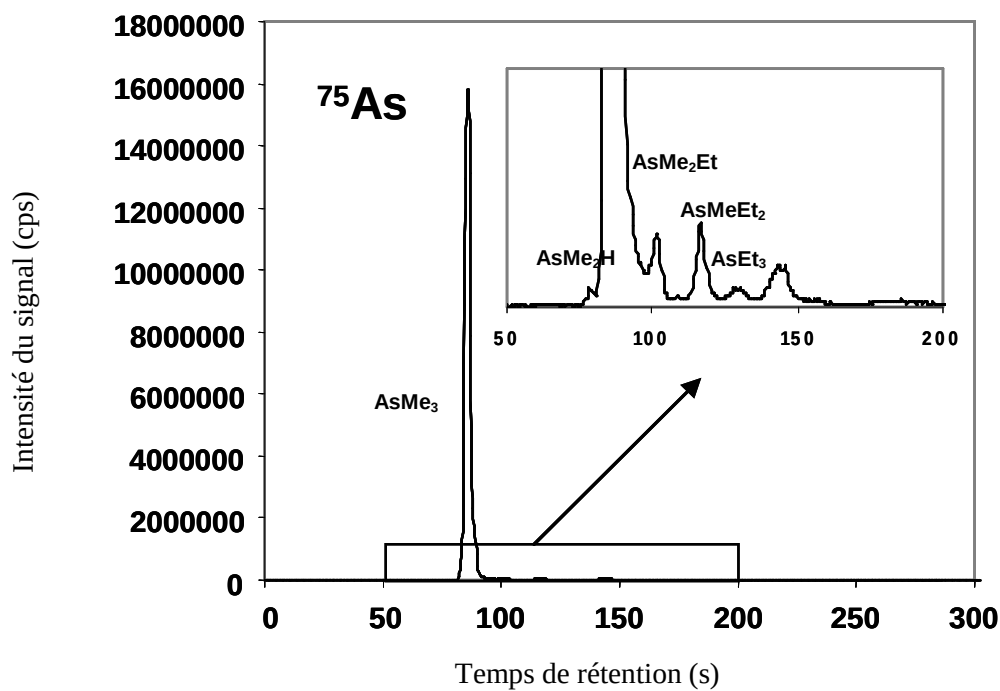
Campagne du 04/07/2005	Casiers de CSDA					
	LA1	LA2	LA3	LA4	LA5	LA6
pH	8.6	7.7	7.5	7.7	7.7	7.6
COT (mgC L ⁻¹)	1763	1914	1395	1385	807	3778
CI (mgC L ⁻¹)	691	743	292	378	879	59
Na ⁺ (mg L ⁻¹)	929	862	294	392	938	33
K ⁺ (mg L ⁻¹)	785	740	337	426	1127	4
Cl ⁻ (mg L ⁻¹)	1430	1132	230	348	1463	9
Br ⁻ (mg L ⁻¹)	12	4	1	2	7	n.d
F ⁻ (mg L ⁻¹)	0,3	0,3	n.d	n.d	1	27
SO ₄ ²⁻ (mg L ⁻¹)	106	65	16	21	145	8
NO ₃ ⁻ (mg L ⁻¹)	2	2	n.d	n.d	2	3
ΣPO ₄ ³⁻ (mg L ⁻¹)	n.d	5	n.d	n.d	n.d	n.d

Annexe 5 (suite)

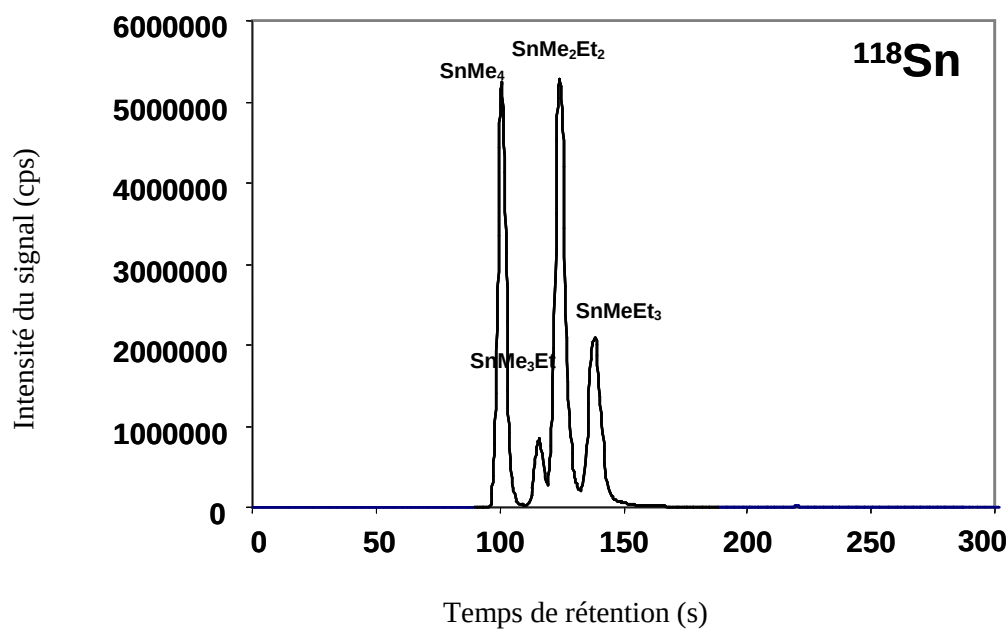
Campagne du	Casiers de CSDA					
08/12/2005	LA1	LA2	LA3	LA4	LA5	LA6
pH	7.7	6.9	6.6	7.8	7.3	7.6
COT (mgC L ⁻¹)	1000	1285	1247	2198	1560	1690
CI (mgC L ⁻¹)	347	120	196	1520	752	315
Na ⁺ (mg L ⁻¹)	359	63	98	1258	710	16
K ⁺ (mg L ⁻¹)	316	80	134	1403	797	4
Cl ⁻ (mg L ⁻¹)	393	54	64	2186	926	5
Br ⁻ (mg L ⁻¹)	1	n.d	n.d	7	5	n.d
F ⁻ (mg L ⁻¹)	n.d	n.d	n.d	1	0,3	8
SO ₄ ²⁻ (mg L ⁻¹)	224	54	323	35	44	7
NO ₃ ⁻ (mg L ⁻¹)	n.d	18	n.d	5	2	3
ΣPO ₄ ³⁻ (mg L ⁻¹)	5	n.d	n.d	46	7	n.d

Annexe 6 : Exemples de chromatogrammes des composés organométalliques dans les biogaz

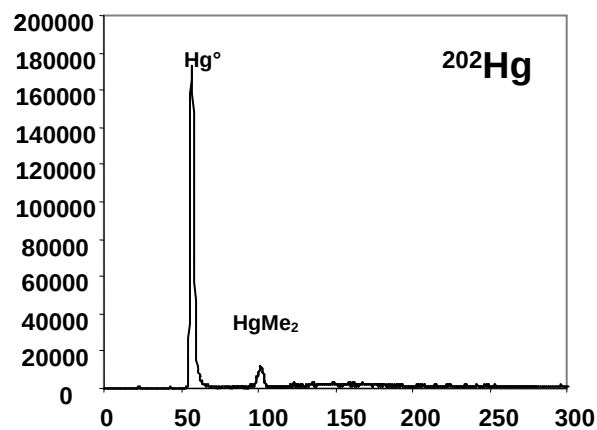
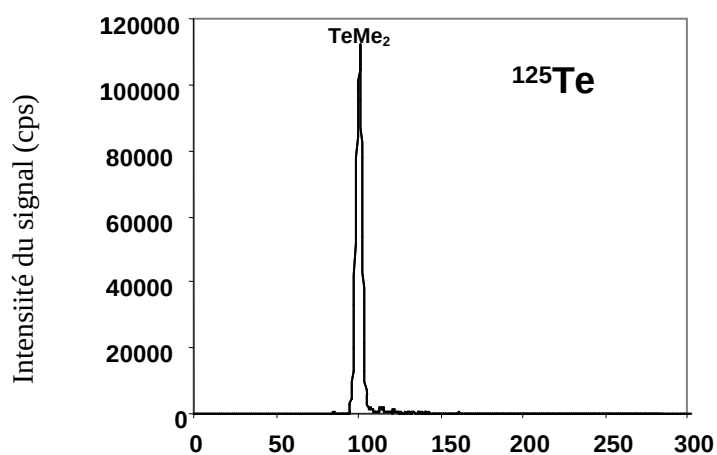
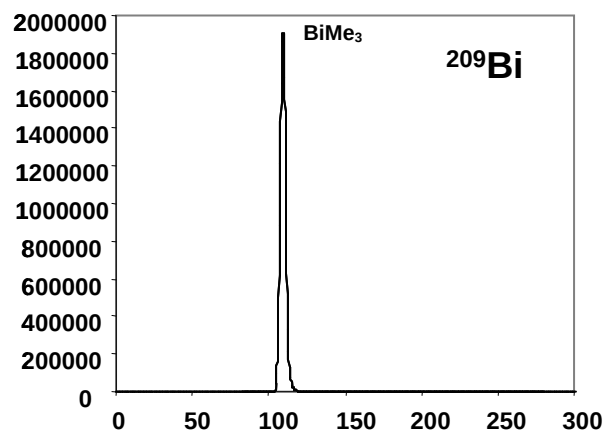
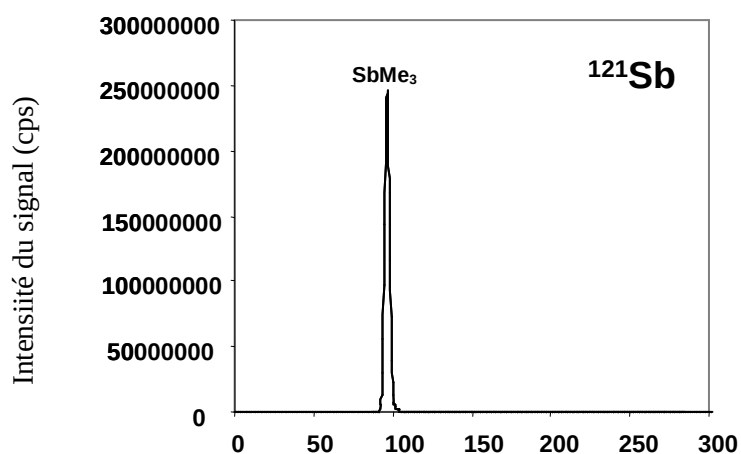
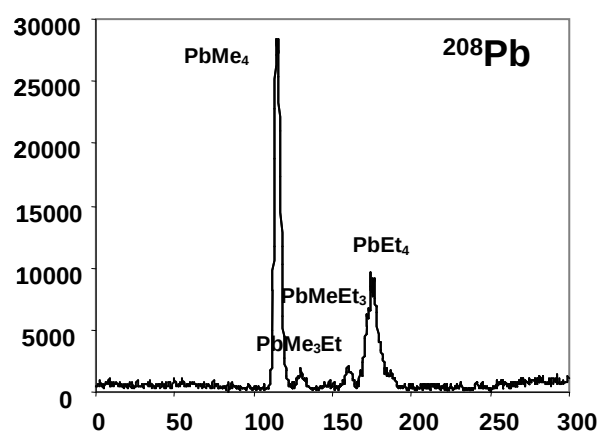
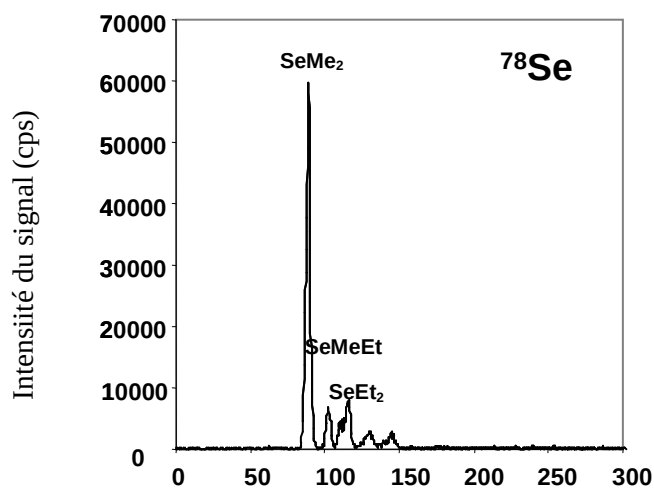
CSDA casier 1



CSDA Casier 4



CSDA Casier 4



Temps de rétention (s)

Temps de rétention (s)

PUBLICATIONS ET COMMUNICATIONS

Publications et communications

Publications

- Evaluation of analytical strategies for the determination of metal concentrations to assess landfill leachate contamination

P. Pinel-Raffaitin, M. Ponthieu, I. Le Hécho, D. Amouroux, L. Mazéas, O.F.X. Donard, M. Potin-Gautier

Publiée dans Journal of Environmental Monitoring, 2006, 8, 1069–1077

- Présence de métaux et d'organométalliques dans les effluents des centres de stockage des déchets

M. Ponthieu, P. Pinel-Raffaitin, L. Mazéas, I. Le Hécho, D. Amouroux, O. F.X. Donard, M. Potin-Gautier

Publication soumise à Déchets, sciences et techniques

- Arsenic speciation analysis in landfill leachate

M. Ponthieu, P. Pinel-Raffaitin, L. Mazéas, I. Le Hécho, D. Amouroux, O. F.X. Donard, M. Potin-Gautier

Publication soumise à Water Research

- Determination of alkylated tin compounds in landfill leachates using isotopically enriched tin species with GC-ICP-MS detection

P. Pinel-Raffaitin, P. Rodriguez-Gonzalez, M. Ponthieu, D. Amouroux, I. Le Hécho, L. Mazéas, O.F.X. Donard, M. Potin-Gautier

Publication acceptée dans Journal of Analytical Atomic Spectrometry

- Distribution and fate of inorganic and organic arsenic species in landfill leachates and biogases

P. Pinel-Raffaitin, I. Le Hécho, D. Amouroux, M. Potin-Gautier

Publication soumise à Environmental Science and Technology

- Mobilisation and formation of organotin compounds in landfill leachates and biogases

P. Pinel-Raffaitin, D. Amouroux, I. Le Hécho, P. Rodríguez-Gonzalez, M. Potin-Gautier

Publication soumise à Environmental Science and Technology

Communications orales

- Importance of metals and organometals speciation analysis to evaluate environmental impacts of landfill leachate and biogas

P. Pinel, I. Le Hécho, D. Amouroux, O.F.X Donard, M. Potin-Gautier

Sardinia 2005-10th International Waste Management and Landfill Symposium (Octobre 2005, Cagliari, Italy);

Publication in Proceedings (7p)

- Influence of sample processing on metals and metalloids partitioning and speciation in landfill leachates

P. Pinel, D. Amouroux, I. Le Hécho, O.F.X Donard, M. Potin-Gautier

Sardinia 2005-10th International Waste Management and Landfill Symposium (Octobre 2005, Cagliari, Italy); Publication in Proceedings (7p)

- Validation of metal analysis in bulk and filtered landfill leachate using an internal reference leachate material

P. Pinel, M. Ponthieu, I. Le Hécho, D. Amouroux, L. Mazéas, O.F.X Donard, M. Potin-Gautier

Sardinia 2005-10th International Waste Management and Landfill Symposium (Octobre 2005, Cagliari, Italy); Publication in Proceedings (7p)

- Speciation of alkylated tin compounds in landfill leachates by GC-ICPMS

P. Pinel-Raffaitin, P. Rodriguez-Gonzalez, D. Amouroux, I. Le Hécho, O.F.X Donard, M. Potin-Gautier

4th International Franco-Spanish Workshop on Bio-inorganic Analytical Chemistry (Octobre 2006, Pau, France)

Communications par affiches

- Sampling and sample processing development for the analysis of metals and metalloids in municipal landfill leachates.

P. Pinel, I. Le Hécho, D. Amouroux, O.F.X Donard, M. Potin-Gautier

9^{ème} Conférence FECS Chimie et Environnement (Septembre 2004, Bordeaux, France)

- Protocol set-up for speciation analysis of trace elements in landfill effluents

I. Le Hécho, P. Pinel, D. Amouroux, O.F.X. Donard, M. Potin-Gautier

8th ICOBTE Conference (Avril 2005, Adelaïde, Australia)

- Analyse de spéciation des métaux et métalloïdes dans les lixiviats de centres de stockage de déchets ménagers

P. Pinel, I. Le Hécho, D. Amouroux, M. Potin-Gautier

Spectratom 2005 (Avril 2005, Pau, France)

- Validation d'un protocole d'analyse de lixiviats issus de centres de stockage de déchets ménagers : mise en place d'un matériel de référence interne

M. Ponthieu, P. Pinel-Raffaitin, L. Mazéas, I. Le Hécho, D. Amouroux, O. F.X. Donard, M. Potin-Gautier

Spectratom 2005 (Avril 2005, Pau, France)

- Occurrence of organoarsenic and organotin species in landfill effluents

P. Pinel-Raffaitin, M. Ponthieu, I. Le Hécho, D. Amouroux, L. Mazéas, O.F.X. Donard, M. Potin-Gautier

ISSEBETS 2006 (Juin 2006, Bialowieza, Pologne)

Suivi des métaux et métalloïdes dans les effluents de centres de stockage de déchets : spéciation et devenir des composés de l'arsenic et de l'étain dans les lixiviats et les biogaz

Résumé :

Les centres de stockage de déchets (CSD) ménagers et assimilés constituent encore une filière de gestion très répandue. Ce sont de véritables « boîtes noires » dans lesquelles des phénomènes physiques, chimiques et biologiques interviennent simultanément. Deux effluents sont produits au cours de la dégradation des déchets : les lixiviats et les biogaz. Même si le contact entre les effluents et le système environnant est limité, leur suivi est nécessaire pour améliorer leur traitement et prévenir les risques sanitaires et environnementaux. Ce travail a eu pour objectif de mettre en place des méthodologies analytiques adaptées aux métaux et métalloïdes afin d'étudier leur devenir dans les effluents de CSD. L'étude approfondie de l'arsenic (As) et de l'étain (Sn) a été motivée par leur présence dans les déchets (verres, composants métalliques, plastiques), par leur existence sous forme de nombreuses espèces et par la toxicité avérée de certaines de leurs formes chimiques. L'optimisation des protocoles d'analyse de spéciation de As et Sn dans les deux matrices complexes a permis leur suivi au sein des CSD en intégrant les caractéristiques des sites et les données climatiques. La répartition des espèces a été examinée en tenant compte de leur occurrence initiale dans les déchets. Des processus de formation et de mobilisation ont été proposés pour expliquer leur présence dans les deux effluents : d'une part la mobilisation à partir des déchets (espèces inorganiques de As et Sn, espèces butylées et mono- et diméthylées de Sn) et d'autre part la méthylation et l'éthylation par voie biologique (espèces méthylées de As et espèces méthylées et éthylées de Sn, ioniques et gazeuses).

Mots-clés : Arsenic - Etain - Lixiviat - Biogaz- Déchets- Méthylation – Ethylation.

Metal and metalloid monitoring in landfill effluents: speciation and fate of arsenic and tin species in leachates and biogases.

Abstract:

Landfilling is still nowadays the most used way of municipal solid waste (MSW) management with incineration. MSW landfills remain « black boxes » in which physical, chemical and biological phenomena interact simultaneously. Two effluents are produced during the waste degradation: leachates and biogases. Even if there are limited contact between effluents and the surrounding ecosystem, effluent monitoring is required to improve their treatments and to prevent sanitary and environmental risks. The aim of this work was to develop the methodologies to analyse metals and metalloids in order to assess their fate in landfill effluents. The focus on arsenic (As) and tin (Sn) was motivated by their presence in the municipal solid wastes (glasses, metals, plastics) and in the effluents, and by the difference of toxicity between their species. The development of speciation analysis protocols for As and Sn in the two complex matrices has aimed to their monitoring in the effluents by integrating landfill characteristics and climatic conditions. The occurrence of the species has been examined by taking into account their potential presence in the wastes. Formation and mobilisation processes were proposed to explain their occurrence in the two effluents: first, mobilisation from the waste (inorganic species of As and Sn, butylated and methylated Sn), then methylation and ethylation reactions through biological pathway (methylated As and Sn, ethylated Sn, ionic and gaseous).

Key-words: Arsenic - Tin - Leachate- Biogas- Waste- Methylation – Ethylation.