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# Study of contaminants transported by microplastics in the Lebanese marine environment

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## Abstract

Anthropogenic activities are increasingly putting pressure on the environment of the Lebanese Mediterranean coast. One of the main emerging sources of pollution is plastics ending up in the marine environment and persisting as small (so-called microplastics, 1  $\mu\text{m}$  - 5 mm) particles which become a vector for the transport of a variety of contaminants. The assessment of microplastics-related environmental risks requires the development of multi-scope analytical approaches targeting different classes of organic and inorganic pollutants.

A comprehensive study of microplastic pollution of the Lebanese Mediterranean coast was performed. The samples were collected from the shoreline in 2020-2021, sieved and sorted into different sizes. The nature of the microplastics was investigated by Fourier Transform Infrared Spectroscopy (FTIR) revealing the predominant presence of polyethylene and polypropylene. For the study of adsorbed organic pollutants, solid-liquid extraction (leaching) procedures targeting polar and non-polar compounds were optimized. Metals were analyzed after the complete microwave assisted digestion of samples.

Prior to quantitative analysis, the organic pollutants were screened according to their accurate mass, chromatographic behavior and fragmentation. In this way, the lists of compounds for the subsequent targeted analysis were established.

This study produced the first ever LC-MS/MS and GC-MS data on microplastics-adsorbed organic pollutants present on Lebanese Mediterranean coast and demonstrated the persistency of several legacy pesticides, such as DDT prohibited for use more than 20 years ago and chlorpyrifos that was banned for use in Lebanon several years ago. Also, the presence of personal care products and pharmaceuticals, such as phenacetin and minoxidil, polycyclic aromatic hydrocarbons (PAH), different polychlorinated biphenyl (PCB) congeners prohibited long time ago due to their toxic effect on human health, and different additives incorporated in plastics was demonstrated. The quantification of metals was carried out by ICP-MS. The obtained data were discussed in the context of their possible environmental and anthropogenic sources and also their presence in pigments and additives added to plastics during the manufacturing process.

The performed study clearly shows that microplastics are not only a source of pollution by themselves, but also transport organic and inorganic contaminants in the marine environment and therefore represent a threat to the marine organisms and as well as human health. It is therefore important to study different types of pollutants to have a global view on the harmful and oblivious effect of microplastics in the marine environment.

Moreover, as microplastics are becoming important targets of environmental studies, the perspectives for future green methodologies reducing the use of organic solvents in sample preparation were highlighted. For example, liquid-extraction surface analysis (LESA) was investigated for the screening of pollutants sorbed on the surface of microplastics.

## Résumé

Les activités anthropiques exercent une pression croissante sur l'environnement de la côte méditerranéenne libanaise. L'une des principales sources émergentes de pollution est le plastique qui se retrouve dans le milieu marin et persiste sous forme de petites particules (appelées microplastiques, 1  $\mu\text{m}$  - 5 mm) qui deviennent un vecteur pour le transport d'une variété de contaminants. L'évaluation des risques environnementaux liés aux microplastiques nécessite le développement d'approches analytiques multi techniques ciblant différentes classes de polluants organiques et inorganiques.

Une étude approfondie de la pollution microplastique de la côte méditerranéenne libanaise a été réalisée. Les échantillons ont été prélevés sur le rivage en 2020-2021, tamisés et triés en différentes tailles. La nature des microplastiques a été étudiée par spectroscopie infrarouge à transformée de Fourier (FTIR) révélant la présence prédominante de polyéthylène et de polypropylène. Pour l'étude des polluants organiques adsorbés, les procédures d'extraction solide-liquide (Lessivage) ciblant les composés polaires et non polaires ont été optimisées. Les métaux ont été analysés après une digestion complète des échantillons par micro-ondes.

Avant l'analyse quantitative, les polluants organiques ont été sélectionnés selon leur masse précise, de leur comportement chromatographique et de leur fragmentation et les listes de composés pour une analyse ciblée ultérieure ont été établies.

Cette étude a produit toutes les premières données LC-MS/MS et GC-MS sur les polluants organiques adsorbés par les microplastiques présents sur la côte méditerranéenne libanaise qui démontrent la persistance de plusieurs pesticides tels que le DDT interdit d'utilisation il y a plus de 20 ans et le Chlorpyrifos qui a été interdit d'utilisation au Liban il y a plusieurs années. Aussi, la présence de produits de soins personnels et pharmaceutiques, tels que la phenacetin et le minoxidil, les hydrocarbures aromatiques polycycliques (HAP), différents congénères de biphényles polychlorés (PCB) interdits depuis longtemps en raison de leur effet toxique sur la santé humaine, et la présence de différents additifs incorporés dans les plastiques a été démontré. La quantification des métaux a été réalisée par ICP-MS. Les données obtenues ont été discutées dans le contexte de leurs sources environnementales et anthropiques possibles et aussi de leur présence dans les pigments et les additifs ajoutés aux plastiques au cours du processus de fabrication.

L'étude réalisée montre clairement que les microplastiques ne sont pas seulement une source de pollution en eux-mêmes, mais transportent également des contaminants organiques et inorganiques dans le milieu marin et donc représente une menace pour les organismes marins et ainsi que pour la santé humaine. Il est donc important d'étudier différents types de polluants pour avoir une vision globale de l'effet nocif et inédit des microplastiques dans le milieu marin.

De plus, comme les microplastiques deviennent des cibles importantes des études environnementales, les perspectives de futures méthodologies vertes réduisant l'utilisation de solvants organiques dans la préparation des échantillons ont été mises en évidence, par exemple l'analyse de surface par extraction liquide (LESA), a été étudiée pour le dépistage des polluants adsorbés à la surface des microplastiques.

## Résumé détaillé de la thèse

### Introduction

Au fil des ans, la demande de matières plastiques a augmenté en raison de leur faible coût, de leur flexibilité et de leur durabilité, tout comme leur production. Les plastiques, constitués de longues chaînes polymères mélangées à des additifs, sont très utilisés en raison de leur durabilité et de leur haute résistance.

Depuis quelques années, les « microplastiques », les nouveaux polluants émergents, sont à l'honneur. Les microplastiques peuvent pénétrer directement dans l'environnement marin sous forme de particules de petite taille appelées microplastiques primaires, tels que les granulés vierges utilisés pour la fabrication du plastique. De plus, leur présence peut résulter de la fragmentation et de la dégradation des gros plastiques, principalement par photo-oxydation des rayons UV, et on les appelle alors microplastiques secondaires. La taille la plus courante des microplastiques est de 1  $\mu\text{m}$  à 5 mm (An et al., 2020). Cependant, la présence de plastiques et de leurs additifs (stabilisants, retardateurs de flamme et pigments à base de métaux) n'est pas la seule préoccupation en milieu marin. De plus, lorsqu'ils pénètrent dans le milieu marin, les microplastiques ont tendance à adsorber les polluants organiques et inorganiques de l'eau et peuvent ainsi être considérés comme des vecteurs et des concentrateurs de polluants (Camacho et al., 2019 ; Catrouillet et al., 2021 ; Lionetto, 2021 ; Van et al., 2012). Ce processus est amplifié par la surface globale élevée de la charge microplastique (Teuten et al., 2009). L'accélération de l'industrialisation et de l'urbanisation a conduit à la production massive d'une grande variété de composés chimiques que l'on retrouve dans les systèmes aquatiques et qui peuvent potentiellement être adsorbés et transportés par les microplastiques et ainsi persister dans le milieu marin.

Les polluants organiques hydrophobes, tels que les biphényles polychlorés, les hydrocarbures aromatiques polycycliques et les pesticides, ont tendance à avoir une affinité plus élevée avec les plastiques qu'avec les sédiments ou l'eau (Teuten, 2016).

En fonction de leur densité, les microplastiques peuvent flotter à la surface de la mer et être emportés vers le rivage ou coulés dans les sédiments des profondeurs marines. Les microplastiques de surface de la mer sont les plus disponibles pour être ingérés par les organismes marins, depuis le bas de la chaîne alimentaire jusqu'à l'homme et il a récemment été démontré qu'ils se trouvaient dans le placenta (Ragusa et al., 2021). Un grand nombre d'organismes marins ont été étudiés pour la présence de microplastiques (Kosore et al., 2018 ; Provencher, 2019 ; Steer, Cole, 2017). La principale préoccupation est donc le transport des polluants des microplastiques vers l'eau de mer et le biote. Dans ce cas, les contaminants sont lessivés des plastiques pour se bioaccumuler dans les organismes marins et sont également rejetés dans l'eau et transportés dans le milieu marin. La persistance des microplastiques est une menace pour l'environnement marin, les organismes marins et en outre pour la santé humaine.

Ainsi, l'impact des microplastiques dans le milieu marin doit être considéré comme un effet combiné des particules de polymère (et éventuels additifs) et des polluants sorbés de l'environnement. Leur petite taille les rend plus facilement ingérables par les organismes et plus faciles à transporter dans le milieu marin.

Au cours des dernières années, de nombreuses études ont été menées pour étudier la présence de MP dans les compartiments du milieu marin et également dans d'autres matrices telles que le sol, la glace et les produits consommables. Considérées comme la demeure éternelle des plastiques, l'eau de mer, les sédiments et le biote contiennent une énorme quantité de plastiques de différents types et formes. Le

nombre de publications traitant de la pollution chimique liée aux MP a fortement augmenté ces derniers temps, passant de 1 publication il y a 10 ans à plus de 150 publications en 2022 selon Scopus.

De nombreuses études ont porté sur les polluants sorbés sur les MP environnementaux et même des études expérimentales ont été réalisées afin d'inspecter le comportement de sorption des microplastiques. Les études sur les polluants sorbés se sont principalement focalisées sur les HAP, PCB et OCP (Antunes, 2013 ; Camacho et al., 2019 ; Heskett et al., 2012 ; Mizukawa et al., 2013 ; Rios, 2007 ; Van et al., 2012) .

En tant que mer semi-fermée avec des échanges minimales avec son environnement, la mer Méditerranée est considérée comme l'un des points chauds de la pollution plastique et chimique. La côte libanaise, la Méditerranée orientale, comme d'autres milieux marins, sont menacées par différentes sources de pollution, des déchets marins gouvernés par le plastique aux polluants chimiques rejetés tout le long de la côte. Les microplastiques, considérés comme vecteur de transport des contaminants dans le milieu marin, il était important d'étudier les polluants chimiques transportés par les microplastiques.

## **Objectif de la thèse et résumé des travaux**

La présence de microplastiques sur la côte libanaise a été documentée pour la première fois en 1977 (Shiber, 1979). Cependant, depuis lors, seules quelques études récentes ont été menées afin d'identifier et de classer les microplastiques (Kazour et al., 2019 ; Jemaa et al., 2021). Aucune de ces études n'a cependant abordé le rôle des microplastiques en tant que vecteurs de pollution environnementale. De plus, à notre connaissance, ce sujet n'a pas été abordé non seulement au Liban, mais a à peine été abordé dans toute la mer Méditerranée. En effet, la plupart des études à ce jour concernaient les régions de l'Atlantique Nord et du Pacifique, et une seule classe particulière de polluants organiques était généralement abordée dans chacune des études (Antunes et al., 2013 ; Frias et al., 2010). Outre les polluants organiques, des études ont été menées pour inspecter la teneur en métaux des plastiques (Liu et al., 2022) et peu ont tenté de discriminer théoriquement les sources de métaux, qui proviennent soit d'additifs microplastiques, soit de sorption du système environnant (Catrouillet et al., 2021).

L'objectif de cette étude était d'étudier pour la première fois le rôle potentiel des microplastiques en tant que vecteurs des polluants sur la côte libanaise, en utilisant différentes approches analytiques pour couvrir différents types de contaminants, organiques et inorganiques.

Les objectifs de cette thèse comprenaient :

- Échantillonnage de plastiques de la côte libanaise et identification de la fraction de microplastiques,
- Un criblage non ciblé des composés faiblement polaires présents dans les microplastiques par GC-TOF-MS. Cela doit permettre d'identifier les contaminants et/ou polluants cibles les plus intéressants pour leur quantification ultérieure,
- Un criblage non ciblé de composés polaires dans des extraits de plastiques par MS2 dépendant des données HPLC permettant la sélection de cibles pour la quantification ultérieure par suivi de réactions multiples MS/MS,
- Etude du potentiel de développement de l'extraction de surface intégrée et de la spectrométrie de masse par LESA-MS,
- Analyse élémentaire par ICP MS afin de déterminer les concentrations totales de métaux dans les plastiques et discussion de leur origine putative.



## Echantillonnages et caractérisation du plastique

Des échantillons ont été collectés d'octobre 2020 à août 2021 sur 14 plages différentes de la côte libanaise entre Arida (S1) et Adloun (S14) avec un total de 21 lots d'échantillons de microplastiques. Les échantillons ont été prélevés sur les rives des plages de sable (sauf pour Amshit (S6) où les plastiques ont été collectés à la surface de la mer à l'aide d'un filet à main). Le matériel collecté a été transporté au laboratoire pour être séparés des autres déchets marins, du sable et de la matière organique. L'identification primaire des microplastiques a été effectuée par observation visuelle et ils ont été séparés des particules de sable grossières par des forceps. La taille des particules considérées dans cette recherche était comprise entre 0,2 mm et 5 mm.

2133 particules de plastiques ont été identifiées à l'aide de la spectroscopie infrarouge à réflexion totale atténuée (ATR), pour leur type de polymère afin d'avoir un aperçu général des types de plastique les plus couramment trouvés sur la côte libanaise. Les plastiques ont été choisis parmi différentes zones, tailles et apparences visuelles. Des macroplastiques, des mésoplastiques et des microplastiques ont été identifiés.

Parmi les mésoplastiques et macroplastiques identifiés, le PE et le PP étaient les types les plus abondants, suivis du PS. Certains fragments ont pu être identifiés comme du polyéthylène téréphtalate et de l'acrylonitrile butadiène styrène laissant 0,1 % de spectres non attribués.

Sur les 2133 particules de plastiques, 1213 d'entre elles étaient des microplastiques, seuls le polyéthylène (49%) et le polypropylène (45%) ou un mélange des deux polymères ont été identifiés dans les particules de microplastiques. Ceci est en accord avec les études précédentes.

Dans un point d'échantillonnage Tripoli 1 (S3) des dizaines de grammes de microplastiques ont été collectés. Il a été donc utilisé comme référence pour étudier la différence entre l'effet d'adsorption des microplastiques secondaires (microplastiques résultant de la fragmentation de plastiques plus gros) et des microplastiques primaires (granulés) et entre les PE et PP. Chaque type a ensuite été utilisé comme un échantillon complet pour la procédure d'extraction. S3 (Tripoli 1) a été échantillonné en novembre 2020, juin 2021 et août 2021.

Pour voir la disponibilité des polluants polaires dans l'eau de mer, 10 échantillons d'eau ont été prélevés sur les plages de la côte libanaise. 1 L d'eau de mer a été collecté sur chaque site en août 2021 et ils ont été filtré à travers un disque Atlantis SPE de 47 mm sous vide. Ensuite, les composés retenus ont été élués avec 40 mL de méthanol et ont été préconcentrés à l'aide d'un évaporateur rotatif et maintenus à 4°C en but de les cribler pour les composés polaires par LC-MS/MS.

## Préparation des échantillons et analyse des composés non polaire par GC-MS

Des échantillons (1 g), additionnés de PCB-30, PHE-d10 et CHL-d10 (Ils ont été utilisés pour vérifier, soit les performances de l'algorithme de data mining (PCB-30), soit comme étalons de substitution (SS) de composés halogénés (CHL-d10) et non halogénés (PHE-d10) pour estimer leurs concentrations dans le extrait final obtenu à partir des échantillons traités.), ont été extraits deux fois à l'aide de 6 ml d'un mélange 1: 1 de n-hexane: dichlorométhane pendant 24 h (après une étape d'ultra-sonication à 35 °C en début de procédé), sous agitation mécanique, suivie d'une troisième extraction avec le même volume d'isooctane. L'extrait combiné a été filtré à l'aide de filtres à seringue en microfibre de verre de 0,45 µm, évaporé à sec à l'aide d'un concentrateur rotavapor et reconstitué avec 1 ml d'isooctane. Avant l'analyse, les extraits ont été re-filtrés à l'aide d'un filtre à seringue de 0,22 µm de taille de pores.

Les composés volatils et semi-volatils dans les extraits de plastiques ont été déterminés par GC-MS, équipé d'une source d'ionisation électronique (EI). Les composés ont été séparés dans une colonne capillaire HP-5MS (30 m x 0,25 mm i.d., 0,25 µm d'épaisseur de film). Les paramètres d'acquisition dans l'instrument GC-QTOF-MS et le traitement des données ont été contrôlés à l'aide de différentes fonctions intégrées dans le logiciel MassHunter.

En premier lieu, les spectres déconvolutés ont été comparés à ceux existant dans la base de données basse résolution du NIST. Dans un deuxième temps, les spectres d'identifications provisoires ont été comparés soit avec ceux existant soit dans une base de données personnelle de composés (PCDL, acquise à l'aide du même instrument GC-TOF-MS) et avec une base de données précise EI-MS de pesticides fournie par Agilent. Une liste de plus de 100 composés a été faite, certains d'entre eux ont été vérifiés par des standards, parmi ces composés plus que 40 composés (les plus toxiques et les composés trouvés dans d'autres études) ont été quantifiés par comparaison avec des étalons à base de solvant préparés dans l'isooctane.

Les composés quantifiés ont été classés en cinq groupes : produits de soins personnels (PCP), pesticides, additifs de plastiques (plastifiants, retardateurs de flamme bromés et chlorés et absorbeurs d'UV), PCB et HAP.

Les absorbeurs d'UV de type benzotriazole, les tinuvin 326 et 327, étaient les polluants présentant les concentrations les plus élevées au sein du groupe des additifs de polymères. D'un point de vue écotoxicologique, les tinuvin sont considérées comme des polluants persistants, potentiellement bioaccumulatifs.

Au sein du groupe des PCP, le galaxolide et l'octocrylène (musc synthétique et filtre UV) représentaient plus de 60 % de la concentration totale de cette famille de composés dans 24 des 31 échantillons. Les deux sont des composés lipophiles et peu biodégradables, souvent présents dans les sédiments, y compris des échantillons obtenus dans l'estuaire de la rivière Kadicha au nord du Liban (Merhabi et al., 2021).

Le chlorpyrifos et la perméthrine représentaient également plus de 60 % de la concentration totale des pesticides sélectionnés dans plus de la moitié des échantillons. Le 1er insecticide était autorisé jusqu'à récemment dans l'espace économique de l'UE et pourrait rester dans les microplastiques issus de l'agriculture sous serre et des films de paillage, en plus d'être concentré dans cette matrice issue de l'environnement.

Six PCB, contenant entre 3 et 6 substituants chlorés, ont été inclus dans la liste des espèces quantifiées. La plupart d'entre eux ont été trouvés dans chaque extrait d'échantillon; cependant, leurs concentrations totales étaient relativement faibles (de 0,8 à 58,3 ng/g, rapportées à la matrice de microplastiques) par rapport à celles rapportées pour des échantillons obtenus dans d'autres parties du monde (W. Zhang et al., 2015).

Concernant le groupe des HAP quantifiés, leurs concentrations totales varient entre 187 et 430 ng/g, les niveaux les plus élevés correspondant au phénanthrène et au pyrène. Les HAP sont distribués de manière omniprésente dans tous les compartiments environnementaux, en raison de sources pyrogènes et pétrogéniques. Cela étant dit, certaines preuves ont souligné l'origine pétrogénique potentielle des HAP remarqués dans certains des microplastiques extraits. Par exemple, des ratios de concentration d'anthracène sur phénanthrène inférieurs à 10 % ont été corrélés à une origine pétrogénique des HAP (W. Zhang et al., 2015). Ce schéma a été observé dans 80 % des échantillons traités.

Concernant le site S3 (Tripoli 1), l'analyse a approuvé sur ce qui a été dit sur la section LC-MS/MS, que nous ne pouvons pas conclure le comportement d'adsorption de différentes formes de plastiques (fragments et

granulés) et types chimiques (polyéthylène et polypropylène). Les concentrations des composés dans ces différentes fractions ne représentaient aucun modèle spécifique.

### **Préparation des échantillons et analyse des composés polaire par LC-MS/MS**

Un échantillon de 1 g de microplastiques a été pesé, lavé quelques secondes à l'eau et mis dans des flacons en verre ambré. 6 ml du mélange méthanol/acetone de solvants ont été ajoutés et les échantillons ont été placés dans un bain à ultrasons pendant 30 min à 50 °C puis maintenus sous agitation sur un rotateur pendant 24 h. Après 24 h, les extraits ont été transférés dans un autre tube et la procédure d'extraction a été répétée 2 fois de plus en utilisant le même mélange de solvants. Après 72 h, le volume total de solvants est de 18 mL. Avant d'analyser les extraits sur LC-MS/MS, une étape de préconcentration doit être effectuée. Les extraits ont été préconcentrés par évaporation rotative à 1 ml. Les extraits sont conservés au congélateur jusqu'à l'analyse chimique. Avant LC-MS les extraits sont dilués avec la phase aqueuse et centrifugés à 1000 rpm pendant 10 min et prêts à être injectés.

Le dépistage non ciblé des extraits de microplastiques pour la présence de contaminants a été effectué par LC-MS/MS à l'aide d'un spectromètre de masse Q Exactive Plus fonctionnant en mode positif. La séparation des composés a été effectuée sur une colonne C18 en phase inverse. Un MS complet et un MS2 dépendant des données (Top 5) ont été réalisés pour le criblage du composé non ciblé.

L'acquisition des données a été réalisée à l'aide du logiciel Xcalibur et le traitement des données par Trace Finder et Compound Discoverer pour une recherche plus exhaustive. Une liste d'espèces candidates est alors faite. Ce choix s'est fait sur la base d'une bonne forme de pic chromatographique et la présence des fragments. La liste comprenait 19 composés (pesticides et pharmaceutiques), vérifiés par des standards analytiques et une méthode analytique a été ajustée pour chaque composé. Après avoir vérifié la présence de ces composés dans les échantillons de MPs et d'eau, ils ont été quantifiés par comparaison avec des étalons à base de solvants. La quantification a été effectuée en utilisant le fragment ionique le plus intense. L'identification positive était basée sur la présence de fragments et les temps de rétention exacts (moins de 0,1 min).

Après analyse de tous les échantillons, la présence de 9 des 19 composés a été confirmée dans les extraits de plastiques. Ces 9 composés ont été quantifiés, et 4 autres composés ont été trouvés et quantifiés dans les échantillons d'eau analysés. Les composés trouvés appartiennent à deux groupes différents, les pesticides et les produits pharmaceutiques.

Nous ne pouvons pas formuler de conclusion définitive selon laquelle les parties nord et médiane de la côte libanaise sont plus polluées que la partie sud, mais les résultats montrent la présence d'au moins 5 des composés quantifiés dans tous les échantillons du nord. S1 (Arida), S2 (Menye) S5 (Shekka), S6 (Amshit) et S7 (Jbeil) dans le Nord. S3 (Tripoli) est fortement pollué par les déchets mais présente un taux de pollution chimique plus faible par rapport aux autres sites.

Quant à S8 (Ramle), situé au milieu de la côte, près de Beyrouth, il a été échantillonné lors des trois campagnes et a montré le taux de pollution le plus élevé avec au moins 6 polluants trouvés sur 9. Quant à la variation mensuelle, on peut voir qu'en novembre 2020, juin et août 2021 nous avons 6 composés en commun retrouvés dans les extraits (phénacétine, pyroquilon, pyriméthanyl, kétoprofène, diazinon et chlorpyrifos). C'est une plage publique, voisine de Beyrouth, la capitale, la zone la plus peuplée du Liban et donc la pression anthropique est à son maximum dans cette zone. L'endroit est sujet aux rejets d'eaux usées provenant en masse des hôtels, restaurants et centres de villégiature. Il est également pollué par les

activités industrielles et les déchets ménagers. On peut noter également que le plus petit nombre de polluants a été détecté sur le site S13 (Sarafand).

Le chlorpyrifos représente plus de 60 % de la concentration totale des pesticides sélectionnés dans la plupart des échantillons. Ses concentrations variaient de 2,7 ng/g à 2500 ng/g. Sa présence dans les échantillons peut s'expliquer par sa présence dans l'eau mais aussi par son relargage à partir de certains plastiques utilisés en agriculture (Ramos, et al. 2015). Le chlorpyrifos a été suivi du diazinon trouvé dans plus de la moitié des échantillons tandis que les autres pesticides n'ont été trouvés que sur quelques sites. La persistance du chlorpyrifos et du diazinon dans les réseaux d'eau a été signalée ailleurs (Desbiolles et al., 2018; Hunt et al., 2003; Keller et al., 2005).

Concernant les produits pharmaceutiques trouvés, le kétoprofène a été trouvé dans 11 des échantillons analysés ; sa présence a été signalée dans d'autres études sur la mer Méditerranée (Desbiolles et al., 2018). La tripéennamine a été trouvée dans deux échantillons, et la phénacétine et le minoxidil dans cinq chacun.

Dans Cette étude, nous n'avons pas pu faire la différence entre les granulés et les fragments ni entre le polyéthylène et le polypropylène. En effet, pas de distinction claire entre les concentrations de polluants en fonction de la forme ou du type de plastiques. Cela peut être dû à la non-répétabilité dans les échantillons environnementaux car il n'est pas possible d'estimer le temps de contact entre le contaminant provenant de l'eau de mer et les microplastiques. Ainsi, aucune conclusion n'a pu être tirée concernant le comportement de sorption des différents types et formes de plastiques.

Contrairement aux échantillons de microplastiques, dans les échantillons d'eau, 11 des composés ont été trouvés présents. Une raison peut être qu'ils sont hydrophiles donc moins facilement adsorbés. 7 des composés trouvés sur les microplastiques ont été trouvés dans au moins un des échantillons d'eau. Seuls le pyroquilon et la tripéennamine n'étaient pas présents. La nicotine a été trouvée présente dans tous les échantillons à des intensités élevées, elle peut provenir de l'élimination des mégots de cigarettes qui se trouvent en grande quantité sur les plages. Dans le site S2 (Menye), trois composés supplémentaires ont été détectés. Premièrement, la cannabidivarine, présente dans le cannabis, qui n'a été trouvée qu'à cet endroit. Un pesticide pyréthrénoïde, la pyréthrine a été détectée mais était en dessous de la limite de quantification et, enfin, le testostérone cypionate. La présence de différents composés de testostérone a été mentionnée auparavant pour être présents en mer Méditerranée (Desbiolles et al., 2018).

Ces résultats soutiennent l'hypothèse selon laquelle plusieurs composés adsorbés sur les microplastiques proviennent de l'eau de mer. Cela fait des microplastiques un hôte pour l'adsorption et le transport de ce type de polluants et un échantillonneur passif pour étudier les polluants de l'eau.

### **Préparation des échantillons et analyse des métaux par ICP-MS**

Pour la digestion par micro-ondes, un échantillon de 200 à 300 mg de microplastiques a été pesé et 5 mL de conc. HNO<sub>3</sub> a été ajouté. Les échantillons sont exposés à une température et une pression élevées sous un flux d'azote gazeux, et conduit à une digestion totale des microplastiques. Un mode ajusté pour la digestion des polymères a été utilisé.

En guise d'évaluation préliminaire des métaux présents dans les échantillons, des échantillons digérés ont été dilués et injectés pour inspecter les éléments trouvés dans les échantillons. Après avoir choisi les éléments ciblés, un étalon multi-élémentaire a été préparé pour faire des courbes d'étalonnage et quantifier les 46 éléments qui ont été trouvés lors de notre premier dépistage.

Notez que la présence des métaux peut être due à leur utilisation comme additifs ou à l'adsorption chimique de l'eau. Dans notre travail nous n'avons pas été en mesure de discriminer clairement les parties ajoutées et adsorbées des métaux, cependant, les corrélations géographiques observées et la comparaison entre les plastiques secondaires (fragments) retrouvés et les plastiques primaires (granules translucides) (échantillons collectés de Tripoli 1 (S3) dans 3 différentes campagne d'échantillonnages) ont permis d'émettre quelques hypothèses.

Les éléments de terres rares, thorium et uranium. Les éléments de terres rares font partie de la croûte terrestre, mais plusieurs d'entre eux sont reconnus comme des éléments technologiquement critiques. L'origine naturelle de la présence des éléments de terres rares peut être facilement confirmée/infirmée en suivant la régularité de leur distribution (règle d'Oddo-Harkins). Les résultats montrent que les éléments de terres rares dans pratiquement tous les échantillons suivent le schéma de distribution de l'abondance des éléments de terres rares naturels, ce qui suggère leur origine naturelle. Elle montre également leur accumulation dans les plastiques d'un site particulier S14 (Adloun), le schéma d'accumulation qui est reproduit par U, Th et V ayant les mêmes propriétés, Pd, mais plus curieusement Li et Cs. A notre connaissance, aucun de ces métaux n'a été rapporté dans le cadre de la sorption sur plastiques, sauf U sur polyéthylène.

Bismuth, cadmium, chrome, cobalt, plomb et le sélénium. Plusieurs métaux toxiques sont employés dans les pigments et les stabilisants atteignant 25 g/kg de plastiques. Le sulfure et le séléniure de cadmium et le chromate et le molybdate de plomb sont couramment utilisés comme pigments rouges. Le  $\text{CrO}_3$  est également utilisé comme catalyseur dans la synthèse du polyéthylène. Bi est utilisé dans les pigments jaunes comme  $\text{BiVO}_4$  (Catrouillet et al., 2021).

La similarité de la répartition du Pb et du Cr peut être à cause de leur utilisation comme pigment « Chrome Orange »  $\text{PbCrO}_4$  utilisé seul ou en mélange avec du  $\text{PbO}$ . Les concentrations très élevées des deux éléments dans S13 indiquent que cette origine microplastique provient d'un pigment (blanc de plomb  $\text{PbCO}_3$ ) $_2$   $\text{Pb}(\text{OH})_2$  qui peut contribuer à une concentration inhabituellement élevée dans les microplastiques échantillonnés dans S4.

Mercure et étain, palladium. Le phénylmercure (1-3 g/kg) et les composés de dibutylétain, jusqu'à 10 g/kg, sont utilisés comme catalyseurs et stabilisants. Le Sn et de Pd sont présent à la fois dans les échantillons des fragments de plastiques et les granulés.

Arsenic et argent. L'arsenic sous forme de 10, 10' oxibisphéoxarsine et l'argent sous forme de nanoparticules sont ajoutés comme agents antibactériens et cela peut être la cause possible de leur présence dans les plastiques analysés

Autres éléments : B, Ba, Cs, Fe, Li, Mn, Ni, Ti et Zn. Ils sont présents à la fois dans les fragments et les pastilles translucides. Le sulfate de baryum est utilisé comme agent de remplissage utilisé pour durcir les plastiques (Turner & Filella, 2020). Même si certains de ces éléments sont utilisés comme pigments, leur présence en concentrations importante dans les granulés peut suggérer leur origine naturelle (procédé de fabrication, et mélange de sédiments) Les études de la géochimie de la Méditerranée orientale montrent son enrichissement en Fe, Mn et Ti à partir des éléments ici (Pruysers, et al., 1991) .

### **Analyse de surface par extraction liquide – spectrométrie de masse**

Le potentiel de la nouvelle méthode verte, LESA-MS été testé pour analyser le polluants sorbés sur la surface des plastiques. Après l'optimisation de différents paramètres, la méthode été testée sur des plastiques pollués et des plastiques dopés de standards.

La préparation des échantillons pour LESA-MS est minimale, les microplastiques doivent seulement être fixés sur la plaque d'échantillonnage. Les plastiques utilisés étaient du polystyrène expérimental et différents plastiques environnementaux collectés.

En théorie, LESA-MS devrait servir de méthode préliminaire pour le criblage des composés organiques sorbés sur les plastiques. Cependant, les limites de détection sont bien supérieures à celles de la méthode incluant l'extraction traditionnelle. Par conséquent, il était impossible de démontrer en pratique l'applicabilité de la méthode optimisée aux analyses des microplastiques étudiés dans ce travail.

L'applicabilité de la méthode serait limitée aux zones fortement polluées. Par exemple, il pourrait être utilisé pour le dépistage des polluants trouvés à proximité des enceintes d'eaux usées ou des usines de traitement des eaux usées. Une autre application potentielle pourrait être l'identification du type de polymère, en particulier dans le cas des plastiques environnementaux altérés qui échappent à la spectroscopie IR ATR.

## Conclusion

Les microplastiques ne sont pas seulement des polluants ubiquitaires en eux-mêmes mais aussi des vecteurs de contaminants toxiques : composés organiques dangereux non polaires et polaires et métaux. En transportant des contaminants dans l'écosystème marin, ils facilitent l'absorption et l'accumulation d'espèces toxiques tout au long de la chaîne alimentaire. L'importance des microplastiques est susceptible d'augmenter à mesure que la pollution plastique augmente, tout comme la quantité de leurs produits de dégradation environnementale : microplastiques et nanoplastiques. Dans une mer semi-fermée comme la mer Méditerranée, le cycle de pollution pourrait être à peine rompu en raison de l'échange minimal avec d'autres masses d'eau. L'importance de ce travail réside dans le fait qu'il s'agit de la première étude non ciblée des contaminants multiclassés associés aux microplastiques en mer Méditerranée.

Le polyéthylène et le polypropylène étaient les plus couramment trouvés car ce sont les types de plastiques les plus utilisés. La déconvolution des données d'analyse EI-MS précises a permis l'identification de plusieurs composés semi-volatils clairement récupérés par les microplastiques de l'environnement. Un nombre important de nouveaux composés, jusqu'à présent non pris en compte dans les méthodes GC-MS (MS) cibles, ont été identifiés dans les extraits de microplastiques. En plus des anciens polluants chlorés hautement toxiques, les microplastiques contiennent des niveaux pertinents d'autres polluants environnementaux bien connus, tels que les muscs, les filtres UV et les absorbeurs d'UV, qui pourraient représenter un danger pour les organismes marins si les microplastiques pénètrent dans leur système digestif. De même, un criblage LC MS non ciblé dépendant des données a montré que les polluants sorbés ne se limitent pas aux composés faiblement polaires. Le flux de travail d'identification des composés appliqués, combinant l'indice de rétention et les données spectrales, était particulièrement robuste vis-à-vis du signalement des faux positifs.

Il s'agit également de la première étude approfondie concernant les métaux véhiculés par les microplastiques en Méditerranée. Utilisés comme pigments, stabilisants ou catalyseurs, ils restent dans les microparticules résultant de la désintégration sans être rejetés de manière significative dans l'environnement sous des formes hydrosolubles. Par conséquent, le recyclage des plastiques, si leur contamination par les métaux n'est pas bien comprise, peut être un vecteur de propagation des polluants et peut être plus nocif s'il est recyclé que s'il est laissé dans l'environnement. Cela peut être le cas des bouteilles en plastique car des additifs entrent dans le processus de fabrication des plastiques et sont ajoutés à chaque recyclage.

S3 (Tripoli 1) s'est avéré être un site très pollué avec une grande quantité de plastiques de différentes formes et tailles malgré le fait qu'il s'agisse d'une plage publique donc beaucoup de gens entrent en contact avec cette pollution. Cette plage en particulier, devrait être nettoyée plus fréquemment car elle est non seulement un point chaud pour la pollution des plastiques par leurs additifs toxiques mais aussi pour les polluants toxiques qui s'y adsorbent.

Il convient également de noter que S8 (Ramle) est très préoccupant. Ces plages en particulier sont très polluées et publiques en même temps, de sorte que les gens sont en contact direct avec des polluants toxiques sans aucun contrôle.

La pollution ne peut pas être liée à une source ni à un site ou une région spécifique car nous ne pouvons pas confirmer l'origine des plastiques ou le temps qu'ils ont mis dans l'eau pour finalement arriver à terre. Mais on peut noter que ces polluants sont maintenant présents sur la côte libanaise et proviennent de l'eau et menacent le biote marin et les vies humaines. Ces plastiques peuvent également ne pas être encore dans leur destination finale et pourraient être ramenés en eau profonde par des vagues qui les emporteraient à nouveau du rivage.

Des recherches supplémentaires sont nécessaires pour comprendre les sources de pesticides non autorisés ou pour relier les microplastiques à des sources particulières, ce qui peut être fait en utilisant le modèle de concentration en métal. Des études plus systématiques permettraient également de mieux comprendre les variations temporelles, la discrimination entre l'absorption de composés du milieu aquatique et/ou d'évaluer si les microplastiques sont les véhicules transportant ces polluants depuis les sites d'application, c'est-à-dire les champs agricoles, vers les milieux marins est un autre objectif de perspective. .

La spectrométrie de masse joue un rôle fondamental dans l'analyse non ciblée et ciblée des contaminants associés aux microplastiques. Des procédures opérationnelles standardisées doivent être développées afin d'essayer de minimiser les erreurs et de pouvoir comparer et analyser les données provenant de différents emplacements. Une surveillance continue doit être mise en œuvre le long de la côte à différents moments avec des sites d'échantillonnage fixes pour suivre le schéma de pollution et comprendre les sources de pollution dans différents sites d'étude. Des approches multi-techniques couvrant différents types de polluants doivent être envisagées dans les études environnementales en général, pour essayer de couvrir le maximum de polluants. Approches non ciblées afin de sonder les nouveaux contaminants émergents.

Les procédures analytiques sont encore fastidieuses et nécessitent l'utilisation de quantités considérables de solvants et de main-d'œuvre lors de la récupération des polluants organiques des microplastiques. Par conséquent, le développement de méthodes directes économes en solvant telles que, par ex. LESA-MS devrait-on poursuivre. Nos résultats préliminaires ont montré que le LESA-MS pouvait être utilisé comme méthode de dépistage initial, du moins dans l'approche cible offrant des limites de détection basses.

Bien qu'il y ait eu beaucoup de suggestions et de méthodes pour nettoyer les océans de la pollution plastique, aucune solution réelle n'a été apportée pour traiter les plastiques qui seront nettoyés des plages. Il semble que la seule façon d'arrêter la pollution plastique est de réduire l'utilisation des plastiques, au moins le plastique à usage unique et d'essayer de les remplacer par des matériaux moins nocifs ou bien, des bioplastiques qui sont des alternatives aux plastiques fabriqués à partir de sources renouvelables provenant de sources naturelles.

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## List of abbreviations

ASE - accelerated solvent extraction

ATR - attenuated total reflectance

APCI - Atmospheric pressure chemical ionization

BDE - brominated diphenyl ethers

BPA - bisphenol A

CYX - cyclohexane

CHL-d<sub>10</sub> - labelled chlorpyrifos

DDD - dichlorodiphenyldichloroethane

DDE - dichlorodiphenyldichloroethylene

DDT- dichlorodiphenyltrichloroethane

DDA - data dependent analysis

DIA - data independent analysis

DCM - dichloromethane

ESI - electrospray ionization

EIC - extracted ion chromatogram

FTIR - Fourier transform infrared

FiSh - fragment ion searching

GC-MS - Gas chromatography mass spectrometry

HPL - High performance liquid chromatography

H<sub>2</sub>O<sub>2</sub> - hydrogen peroxide

HBCD - hexabromocyclododecane

HCH - hexachlorocyclohexane

HDPE - high density polyethylene

ICP-MS - Inductively coupled plasma-mass spectrometry

IPREM - Institute of Analytical Sciences and Physico-Chemistry for Environment and Materials

LC - Liquid Chromatography

LC-MS - Liquid chromatography mass spectrometry

LC-MS/MS - Liquid chromatography tandem mass spectrometry

LESA-MS - Liquid extraction surface analysis-mass spectrometry

LRI - linear retention index

LOQ - limit of quantification

LDPE - low density polyethylene

MP - microplastic

$m/z$  - mass to charge ratio

MS - mass spectrometry

MS/MS- tandem mass spectrometry

MS<sup>n</sup>- multistage mass spectrometry

MRM - multiple reaction monitoring

NP - nonylphenol

NCMS - National Center for Marine Sciences, Lebanon

Nd - not detected

OCP - organochlorine pesticides

OPE- OPFR- organophosphate ester

PE - polyethylene

PET - polyethylene terephthalate

PP - polypropylene

PS - polystyrene

PVC - polyvinyl chloride

PAH - polycyclic aromatic hydrocarbons

PCB - polychlorinated biphenyls

PCP - personal care products

PHCH - petroleum hydrocarbons

PRM - Parallel reaction monitoring

PHE-d<sub>10</sub> - labelled phenanthrene

Ppm - parts per million

Ppb - parts per billion

Q - quadrupole

REE - rare earth elements

RT- retention time

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## I. LITERATURE PART



## 1. Introduction

Over the years, the demand for plastic materials has been increasing due to their low cost, flexibility and durability, and so has been their production. Plastics, built of long polymeric chains mixed with additives, are highly used due to their durability and high resistance.

In the last few years, “microplastics”, the new emerging pollutants, have been in the spotlight. Microplastics can enter the marine environment directly as small-sized particles called primary microplastics, such as virgin pellets that are used for plastic manufacturing. Also, their presence can result from the fragmentation and degradation of large plastics, mainly by photo-oxidation from UV lights, and then they are called secondary microplastics. The most common size range of microplastics is 1  $\mu\text{m}$  – 5 mm (An et al., 2020). However, the presence of plastics and their additives (stabilizers, flame retardants and metal based pigments) are not the only concern in the marine environment. In addition, when entering the marine environment microplastics tend to adsorb organic and inorganic pollutants from water and thereby can be considered as vectors and concentrators of pollutants (Camacho et al., 2019; Catrouillet et al., 2021; Lionetto, 2021; Van et al., 2012). This process is amplified by the high overall surface of microplastic burden (Teuten et al., 2009). The acceleration of industrialization and urbanization has led to the massive production of a wide variety of chemical compounds that are found in aquatic systems and can potentially be adsorbed and transported by microplastics and thus persist in the marine environment.

The hydrophobic organic pollutants, such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and pesticides, tend to have an affinity to plastics higher than to sediments or water (Teuten, 2016).

As a function of their density, microplastics can be found floating on the sea surface and washed off to the shore or sank into the deep-sea sediments. Sea surface microplastics are the ones more available to be ingested by marine organisms, from the bottom of the food chain arriving to human and was recently shown to be in the placenta (Ragusa et al., 2021). A big number of marine organisms have been studied for the presence of microplastics (Kosore et al., 2018; Provencher, 2019; Steer, Cole, 2017). The main concern is thus the transport of pollutants from microplastics to seawater and biota. In this case, contaminants are leached from the plastics to bioaccumulate in marine organisms and are also released into the water and transported into the marine environment. The persistence of microplastics is a threat to the marine environment, marine organisms and furthermore to human health.

Thereby, the impact of microplastics in the marine environment should be considered as a combined effect of the polymer particles (and possible additives) and of pollutants sorbed from the environment. Their small size makes them more available to being ingested by organisms and easier to transport in the marine environment.

In the recent years, many studies have been conducted to study the occurrence of MPs in the marine environment compartments and also in other matrices such as soil, ice and consumable products. Considered as the forever final home of plastics, the marine water, sediments and biota, hold a huge amount of plastics of different types and forms. The number of publications discussing MPs-related chemical pollution has highly increased lately, from 1 publication 10 years ago to more than 150 publications in 2022 according to Scopus.

Many studies focused on the pollutants sorbed on environmental MPs and even experimental studies were done in order to inspect the sorption behavior of microplastics. Studies of sorbed pollutants were mainly



focused on PAHs, PCBs and OCPs(Antunes, 2013; Camacho et al., 2019; Heskett et al., 2012; Mizukawa et al., 2013; Rios, 2007; Van et al., 2012).

As a semi-enclosed sea with minimal exchanges with its surrounding, the Mediterranean Sea is considered to be one of the hotspots of plastic and chemical pollution. The Lebanese coast, Eastern Mediterranean, like other marine environments are being threatened by different sources of pollution, from marine litter governed by plastic to chemical pollutants discharged all along the coast. Microplastics, considered as a vector for the transport of contaminants in the marine environment, it was important to study chemical pollutants transported by microplastics.

## 2. Lebanese Mediterranean coast

“Mediterraneus” is a Latin word meaning Terra= land and Medius= middle. Hence, the name of the sea “Mediterranean” because it is located in the middle of the earth. The sea is bordered by Europe from the north and the west, Asia from the east, and Africa from its south. Mediterranean Sea is a semi-enclosed sea, the bordering continents are separated from each other by small straits: the Strait of Gibraltar, which separates Europe from Africa and separates the Mediterranean from the Atlantic Ocean by a distance of about 14 km. Asia is separated from Europe by the Dardanelles Strait which connects the Mediterranean with the Marmara sea, with a width of 1.2 km, and the Bosphorus strait which separates the Mediterranean from the Black Sea. Note that some consider Marmara and the Black Sea as the same entity. The Suez Canal separates Africa from Asia by hundreds of meters and connects the Mediterranean with the Red Sea (Coll et al., 2012).

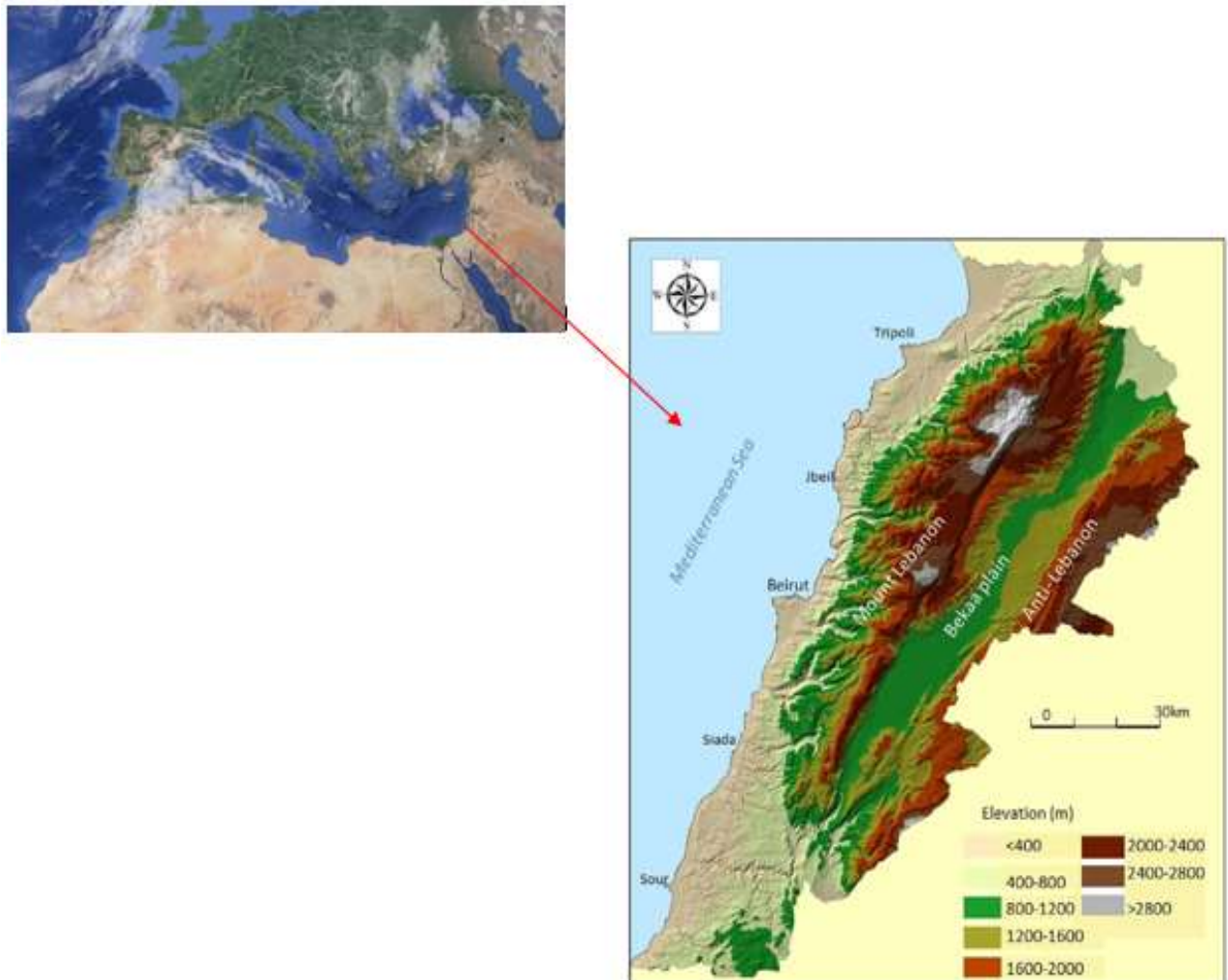


Figure 1. Map of Lebanon and its location on the Eastern Mediterranean (Google Earth & Asmar, 2011)

The Mediterranean Sea has an area of 2.5 million km<sup>2</sup>, some references may add to it the Black Sea with an area of 450 000 km<sup>2</sup>. Its length is about 3860 km, longing from the Strait of Gibraltar to the city of Iskenderun in Turkey, its maximum width is 1600 km between Libya and Slovenia and the average depth – 1500 m with

the deepest point of 5200 m in the Calypso Depth in the Ionian Sea. There are several extensions which are part of the Mediterranean Sea but as they occupy big areas, they are defined as seas apart. This is the case the Adriatic Sea in Eastern Italy, the Ionian in Southern Italy and the Aegean Sea between Turkey and Greece.

The Mediterranean Sea can be roughly divided into two sub-basins, the Western and the Eastern Mediterranean (Amblàs, 2004). The characteristics of each of the sub-basins differ. The Lebanese coast, in the Eastern Mediterranean has been the area of interest in this study.

Lebanon is a small country situated in the Eastern shore of the Mediterranean Sea over 10 452 km<sup>2</sup>, between N 33°05'45.6" and 34°38'45.6" and E 35°06'10.8" and 35°58'37.2". The Lebanese coastal zone extends to 220 km of length, from the Arida on the north and El Nakoura on the south and an average width of 48 km. Pebble beaches and rocky coasts present 80% of the Lebanese coast with the rest being sandy beaches.

Lebanon is divided into 4 distinctive (Fig.1) areas with a variety of different features:

- Anti-Lebanon, the eastern mountain chain at the border of Lebanon with Syria at the east; its highest peak is 2600 m.
- The Bekaa Plain, located between the two mountain chains and is about 120 km from north to south and is a fertile land containing a variety of crops.
- Mount Lebanon, which is the other mountain chain that is parallel to Anti-Lebanon and to the sea.
- The coastal area that is aligned to the sea and is longed all over the 220 km

In general, the Mediterranean Sea is known for the diversity for biological life due to its connection with the Atlantic Ocean and the Red Sea that allows a variety of species to enter to its waters. Particularly, the Lebanese coast holds a wide range of marine species that are attracted by the climate and suitable environmental factors.

### **2.1. Topography and bathymetry**

The seabed structure is relatively poorly known; the seabed is uneven and has underwater canyons. (Stanley, 1969). In general, the continental shelf of the Levantine basin is narrow. In particular, along the Lebanese coast, the continental shelf is narrow (3-5 km on average) up to 200 m isobaths, it is 8 to 10 km in the south and 20 km in the north; the average depth of the shelf is between 20 and 40 m and the slope is parallel to the coast until 1100 to 1400 m deep 25-30 km from the coast before reaching the plain abyssal (Goedicke, 1972).

### **2.2. Weather conditions**

The climate in Lebanon contains 4 seasons. Winter is characterized by a high rate of precipitation accompanied by low temperatures (few degrees below 0 °C) and summer by high temperatures, above 35 °C and a very low rate of precipitation. Between these two seasons, autumn and spring are characterized by variable temperatures and precipitation rates.

Temperature and humidity are prone to vary between different regions. In the coastal zone, winter is relatively mild and the humidity is pretty high (reaching more than 80 % in the month of July and August), in comparison with winter in the other areas that have low temperatures. Also, summer is marked by very high humid air in the coastal zones with high temperatures around 35 °C that can reach 40 °C in extreme cases. Summer in the mountainous area is marked by high temperatures during the day and relatively low temperatures at night (Hayek et al., 2020).

### 2.3. Water circulation

The Mediterranean Sea is considered as a small-scale ocean system in which different spatial and temporal processes take place (El-Geziry & Bryden, 2010). Three water masses define the patterns of the movements: surface, Intermediate, and deep waters. A general surface current coming from the Atlantic Ocean via the Gibraltar Strait, moves to the Eastern part parallel to the North African coast and loses speed progressively, then turns and ends at the Lebanese coast. The volume of the water and the current's intensity depend on the flow of water coming from the Gibraltar Strait. Therefore, the dominant circulation along the Lebanese coast follows the counter-clockwise direction. Also, some clockwise small currents direct water masses. Thereby, suspended litters and matters arrive from all the neighboring countries to the Lebanese coast (El-Geziry & Bryden, 2010).

### 2.4. Coastal activities

#### 2.4.1. Urbanization

Lebanon has a high population density, around 496 person/km<sup>2</sup> (Khoury et al., 2020). Around 90 % of the population lives in urbanized areas and most of them are concentrated along the coast, putting on it an extra environmental pressure. It is estimated that the population is around 5 million of locals, in addition to approximately one million of foreigners and migrants. A large number of people tend to live on the coast due to job opportunities, big university campuses and growth of the industrial sector. Also, the commerce, agriculture, and tourism are active at the coastal area.

#### 2.4.2. Commercial and recreational activities

There are 5 commercial ports in Lebanon. The two main ones are Beirut and Tripoli. The port of Beirut is located in the capital and is considered the main port of the country. However, the explosion that occurred on the 4<sup>th</sup> of August 2020 decreased its capacity to import and was backed up by the port of Tripoli. It comes in the second place after the port of Beirut by the number of containers exported and imported.

The three other commercial ports are Saida, Tyr and Jounieh but they are considered more as fishing ports. There are also ports dedicated for fuel, oil and others such as El Zahrani, El jiye, Selaata, Dora and Zouk. In addition there are several private marinas and bays used for recreational activities along the coast. The overexploitation of the beaches is very clear; private resorts and hotels put severe environmental pressure on the coast which is a destination for tourists (Khoury et al., 2020).

#### 2.4.3. Industry and agriculture

The industrial sector in Lebanon plays an important role in the economy and it is one of the main sources of employment. Around 87 % of the industrial establishments operate in 10 major industrial sectors which are: food and beverages, non-metallic mineral products, electrical machinery and apparatus, furniture manufacturing, fabricated metal products, chemical and man-made fibers, printed material, paper and its products, rubber and plastic products and, finally, machinery and equipment (Programme & Union, 2015). This sector is a major pollution source in Lebanon, by dumping solid wastes and chemical products, untreated in most cases.

The different micro-climates present at different geomorphological zones of Lebanon are a cause for the variation of plants across Lebanon. 31 % of the total agricultural production are fruit trees, 23 % olives, 20 % cereals, 17 % vegetables and the rest are industrial crops. The most important fruit species grown in Lebanon are citrus, apricots, peaches, plums, cherries, grapes, almonds, apples and pears.

The coastal zone is known for the massive production of citrus and banana. Also, there is a lot of greenhouses along the coast with different types of crops. Thereby, agriculture contributes to solid waste pollution and chemical pollution coming mainly from pesticides (Programme & Union, 2015).

The urbanization and the growth of these diverse sectors, put more pressure on the coast. The origin of the coastal pollution is not only due to the direct dumping on the coast, but also comes from every region of Lebanon. Across Lebanon, 13 rivers end up in the Mediterranean Sea and contribute to the pollution of the coastal area and marine environment, by transporting waste from households, industry or agriculture.

The main sources of pollution affecting the Lebanese coast are discussed below.

#### **2.4.4. Waste disposal**

Lebanon has a solid waste crisis. Only few recycling plants are actually working, but recycling is difficult because the waste are not sorted at the source. Although the Lebanese authorities opened two dumpsites in the suburbs of Beirut, the Costa Brava and Bourj Hammoud, it is just a temporary solution to the waste treatment problem. In Lebanon, only few wastewater treatment plants are functional. Therefore, wastewater from households and different sector goes untreated to the sea causing organic, inorganic and bacteriological pollution all over the coast.

Each day, 6 500 tons of municipal solid waste are produced in Lebanon (Khoury et al., 2020). More than 50 % of the waste are organic, ca. 36 % are recyclable such as plastics and paper, and the rest is inert that cannot be treated, such as electronics. Although there are sanitary landfills, 50 % of the waste is directly disposed in illegal and uncontrollable dumpsites all over the coast.

In addition to municipal waste, 50 000 tons of hazardous solid wastes are generated in Lebanon each year (Khoury et al., 2020). Hazardous waste includes healthcare and medical wastes, electronic waste and batteries, chemical waste, and persistent organic pollutants from the energy sectors. The treatment of such type of waste does not exist so far in Lebanon, they are either stored, exported or dumped (Khoury et al., 2020).

#### **2.4.5. Oil spills**

Over the years, different oil spills threatened the Lebanese Mediterranean water and coast. The latest one occurred in 2021; it was an accidental leakage from a tanker of neighboring coast which left massive waves of tar and oils filled with organic pollutants of which hydrocarbons (García-Sánchez, 2022). Lumps of tar were transported and settled along the coast, it was first seen along the southern part all the way to Beirut and due to a coming storm, another wave of tar pollution invaded the coast and petroleum pollution was transported all the way through the northern part. These oil spills threaten the beaches affecting the marine biota, such as sea turtles and fish. Figure 2 shows an example of tar resulting from the oil spill of 2021, covering the beach.



Figure 2 Oil spill on the Lebanese coast-2021 (NCMS, 2021)

### 3. Microplastics-related chemical pollution of the aquatic environment

#### 3.1. Plastics – definition and classification

##### 3.1.1. Definition

Plastics are natural or synthetic materials that have different shapes and properties. From the chemical point of view they are polymers built of repeating units called monomers; those monomers originate from oil and gas. Copolymers are polymers deriving from more than one species of monomer. Plastics are synthetic polymers obtained by polymerization or polycondensation with possible addition of chemical additives improving their performance. Polymerization involves linking the monomers together, usually with a help of metal catalysts, to create a linear polymer chain. Polycondensation is the formation of polymers by combining different monomers with a release of low-molecular products such as, e.g. water (Fontanille, 2014).

Plastics production has extremely increased since the late nineties to reach globally, in 2019, 370 million tons (PlascticsEurope, 2020). Various materials are produced, with different properties to meet the demand. Packaging materials are the most produced plastics (39.6 %), followed by those used in building and construction (20.4 %), in automotive (9.6 %), and in other applications (16.7 %) (PlascticsEurope, 2020).

Plastics can be classified according to their physical and chemical properties, size and shape.

##### 3.1.2. Classification of plastics based on the physical properties

**Thermoplastics** are materials whose shape is reversible; they become malleable beyond a certain temperature, and regain their solidity below it, all thanks to the structure of the matrix where the molecules are separated one from the other and can therefore be moved at high temperatures.

**Thermoset** polymers are materials whose shape is obtained under the action of heat and is irreversible. Unlike thermoplastics, molecules of the matrix are linked together via additional bonds which creates an interconnected network. These polymers cannot therefore be reshaped at high temperature which would degrade them (Aucher, 2011).

**Elastomers** are polymers with elastic properties which support large deformations and can regain their shape after stretching. The most known elastomers are rubbers (Wang, 2002).

Each of these different classes with different physical properties include tens or hundreds of plastics divided according to the polymer chemical composition (Fig. 3)

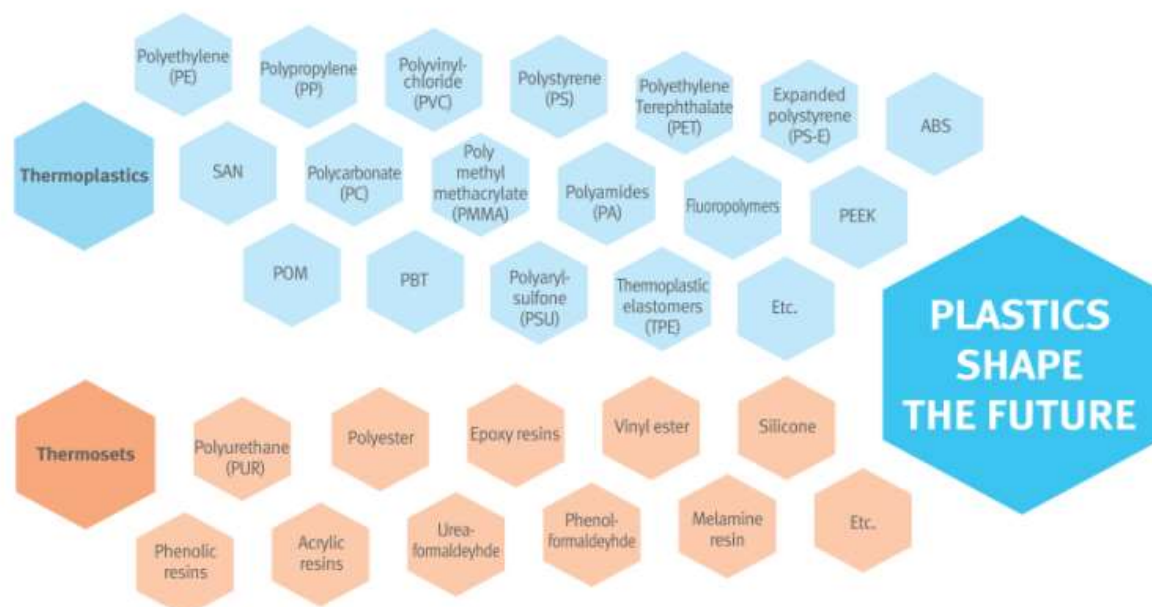


Figure 3 Different types of plastics(Plastics Europe & EPRO, 2016)

### 3.1.3. Classification based on the chemical properties

According to the monomer type and the polymerization process, we can find hundreds of plastics chemical types. Within those plastics, six are the most produced, used and somehow are capable of being recycled, they are known as “big six” and are indicated by numbers, from 1 to 6 on the packaging material. All other plastics are labelled under the number 7 on packaging materials. The “big six” are detailed below and figure 4 shows their chemical structure and density.

**Polyethylene (PE)** is classified into low density polyethylene (LDPE) and high density polyethylene (HDPE). It is obtained by polymerization of ethylene monomers. This type of plastic is the most manufactured among all plastics due to its very wide range of application such as, among others, plastic bags, food packaging and housewares (Andrady & Neal, 2009).

**Polyvinyl chloride (PVC)** is a synthetic resin coming from the polymerization of vinyl chloride monomer. It is used for manufacturing of, among others, pipes, window frames, and garden hoses (Endo, 2002).

**Polypropylene (PP)** results from the polymerization of propylene monomers in the presence of catalysts. This polymer comes in the second rank, in term of production, after the polyethylene. It is mainly used in the automotive sector and food packaging (Maddah, 2016).

**Polyethylene terephthalate (PET or PETE)** is obtained after the polycondensation of terephthalic acid with ethylene glycol. It is a polyester type plastic which has an ester group (-COO-) in its structure. It is used in the production of a wide range of products including mainly packagings, such as water bottles, food boxes and cleaner bottles (Lionetto, 2021).

**Polystyrene (PS)** is obtained by the polymerization of styrene monomers. It is the most common of the family of styrene polymers which contain various other copolymers such as styrene-butadiene (SB) or acrylonitrile butadiene styrene (ABS). Another form of the PS is the expanded polystyrene also known as



the polystyrene foam (EPS) used for the protection of electronic devices while transportation. Its high resistance comes from the small gas bubbles trapped with its structure (Andrady & Neal, 2009).

Number 7 refers to hundreds of other very different plastic from the six big plastics cited above and present in Fig. 4. For example, polycarbonate (PC) used for the manufacturing of baby bottles, polyamide (PA) for automotive applications, polyurethane (PU) are rigid foams such as car seats and foams between refrigerator walls, acrylonitrile butadiene styrene (ABS) such as pipes, and others (Europe, 2020).




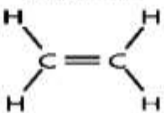

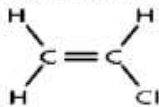

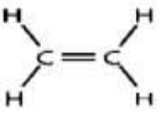

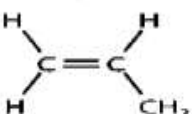

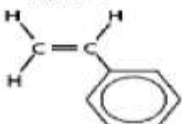
Polymer	Acronym and Number	Monomer	Density (g.cm <sup>-3</sup> )
<b>Polyethylene Terephthalate</b>	 PET	Ethylene glycol $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$ Terephthalic acid 	<b>1.37-1.45</b>
<b>High density Polyethylene</b>	 HDPE	Ethylene 	<b>0.94-0.97</b>
<b>Polyvinyl Chloride</b>	 PVC	Vinyl chloride 	<b>1.16-1.58</b>
<b>Low density Polyethylene</b>	 LDPE	Ethylene 	<b>0.91-0.93</b>
<b>Polypropylene</b>	 PP	Propylene 	<b>0.90-0.91</b>
<b>Polystyrene</b>	 PS	Styrene 	<b>1.04-1.10</b>

Figure 4 Big six plastics, their chemical structure and density (Jung et al., 2018)

### 3.1.4. Classification based on the size

Based on their size, plastics can be classified into macroplastic ( $\geq 25$  mm), mesoplastic ( $> 5$  mm and  $< 25$  mm), microplastic ( $> 1$   $\mu\text{m}$  and  $\leq 5$  mm) and nanoplastics ( $1\text{nm} - < 1$   $\mu\text{m}$ ) (Fig.5). Also, some researchers name plastics with a size larger than centimeters as megaplastics (Europe, 2018).



Figure 5 Different plastics size collected from the Lebanese coast (this work)

### 3.2. Microplastics and their sources

Microplastics can be classified into two main classes, primary and secondary MPs, according to their source. Plastics enter the marine environment either from land-based sources or sea-based sources, their exact origin is often difficult to be determined.

#### 3.2.1. Sources of microplastics

##### ***Municipal waste***

The majority of the plastics from municipal waste consists of plastic bags, bottles, packaging materials and disposable tableware. They are widely used due to their light weight, easy storage and most importantly low cost. In addition, packaging materials are used in all aspects of life, from food, to cloth, cosmetics, for transportation and so on.

The use of single-use plastic utensils and bags are being reduced or have been banned in many countries. The problem is not only in the consumer behavior but the plastic production is still raising and they are still present massively on all shelves of supermarkets. Producers are still taking advantages of low costs of plastics and thus using plastic bottles and wares to put their products. Also a lot of poor countries are still dependent on plastics in most of their packaging materials due to their low cost comparing to more eco-friendly packaging materials (An et al., 2020).

##### ***Agricultural waste***

In the agricultural field, different plastics material are used, especially plastic films are widely employed to increase the crop production. These films are mainly polyethylene of low and high densities. When left in

the environment, those agricultural plastics can be a vector of transport of pesticides and other organic pollutants.

### **Fishing and ship waste**

Fishing waste forms a significant source of MPs in the marine environment. Fishing gear and nets makes most of the sea-based pollution, more than 100,000 tons of fishing equipment are discarded in oceans every year (An et al., 2020). They include fishing nets, fishing lines cables and boxes. After entering the marine environment, the fishing nets and ropes sheds fibers that spread and are ingested by marine biota.

Other plastic waste resulting from aquaculture are polyethylene bags and Styrofoam used as floating devices. In addition, shipping, accidents lead to the entrance of plastic products to the ocean.

Figure 6 shows the different sources of plastics pollution and the ways by which they enter the marine environment. They enter the marine environment from the land by direct disposal from intentional or accidental dumping, waste water discharges, storm water runoffs or can be carried by wind. They also have sea-based sources, they are dropped from boats or sea-based platforms intentionally or by accident; there are also plastics debris resulting from aquatic farming.

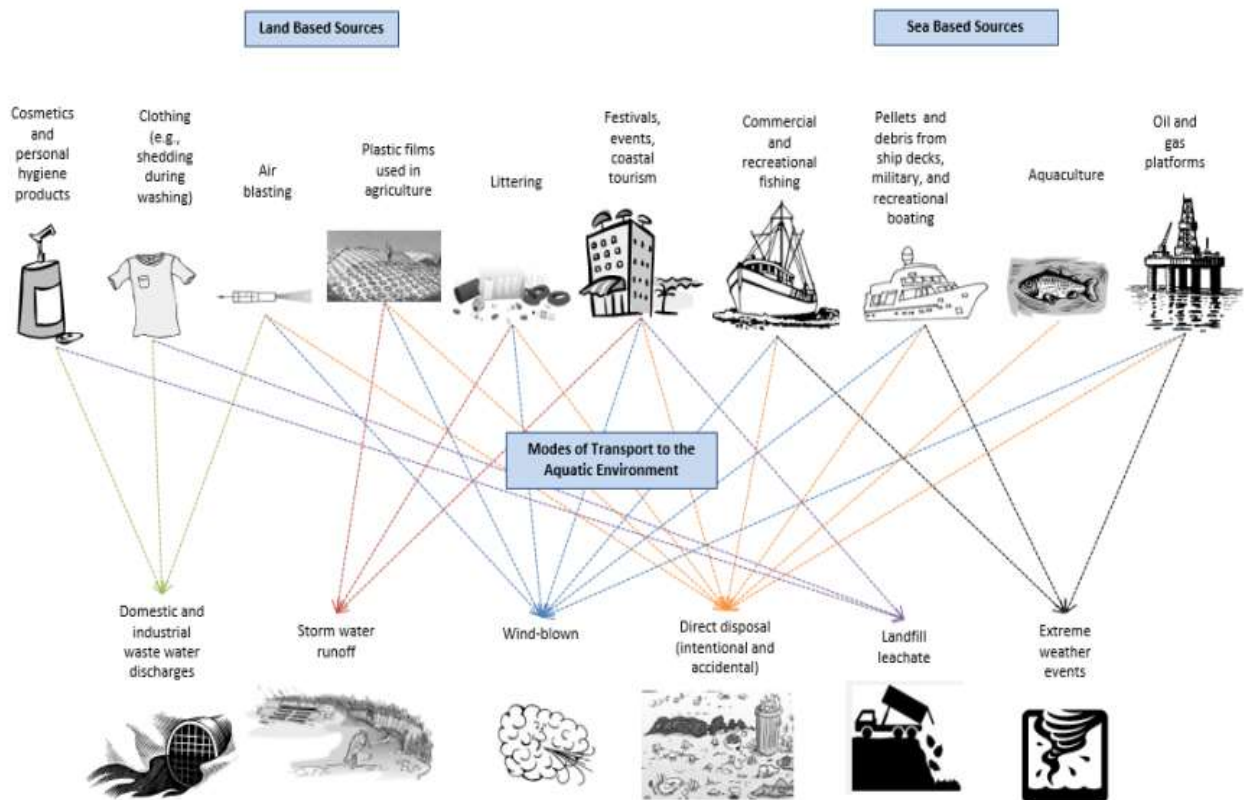


Figure 6 Sources of pollution and their mode of transport to the aquatic environment (States, 2016)

### 3.2.2. Primary microplastics

Primary MPs are the ones that are manufactured originally as small size plastics. They are found in different shapes and forms, such as plastic pellets, the raw materials that are used in the manufacturing of plastic products. They can also be found in household items and personal care and hygiene products such as exfoliating products or facial cleansers. Raw plastics pellets and personal care products are main contributors to the primary MPs. Also, some authors consider microscopic synthetic fibers, resulting from the degradation of textile wear released from washing machines as primary MPs while others consider them as secondary. Also, note that plastics used in paints, coatings, rubber tires and roads, washed off by industrial sewage or wastewater are considered as primary microplastics and contribute to the plastic pollution.

#### *Plastic pellets*

Plastic pellets are plastics of granular form, with a size ranging from 2 mm to 5mm (Fig.7). They are raw plastic materials used to make plastic products. The production of plastic pellets is expected to be increasing as there is a continuous demand of plastics. They may be accidentally dropped in the sea when transported by ships or from wastes of plastics manufacturing (An et al., 2020).

#### *Microbeads*

Tiny microplastics called microbeads are widely used in personal care products for cleansing, whitening and exfoliation. They are present in facial cleansers, sunscreens and toothpastes. They enter the marine environment through wastewater. More than 90 % of microbeads used in cosmetics are PE.



Figure 7 Plastic pellets collected from Tripoli beach-Lebanon (this work)

### 3.2.3. Secondary microplastics

Secondary microplastics are a result of the breakdown and degradation of larger plastic (Fig.8). In the environment, plastic is exposed to various biotic and abiotic factors that leads to its degradation.

**Photo-degradation** comes after the exposure of plastics to ultraviolet radiation, it leads to the oxidation of polymers and resulting in plastic fragmentation.

**Mechanical** processes, such as the abrasion of plastics due to waves and water movements and currents, have an important role in their degradation.

**Biological degradation** by microorganisms has a minimal role in the degradation process.

The speed of the degradation varies according to the polymer type and properties and to the environmental factors.

Secondary sources of microplastics are significant; they come primarily from municipal waste followed by agricultural and fishing wastes (fishing nets and fishing gear) with other plastics of various use and industrial sources (Andrady, 2011).



Figure 8 Plastic fragments collected from the Lebanese coast (this work)

### 3.3. Origins and impact of microplastics toxicity

The toxicity of microplastics can originate from the microplastic itself (and the presence of their constituents) or from the sorbed toxic compounds.

#### 3.3.1. Additives used in the manufacturing of plastics

In the manufacturing process of plastics, chemical additives are incorporated to raw polymers to improve their performance and to get specific properties for a desired product, e.g. to reduce their degradation, make them more resistant to high temperature or more malleable (Andrady & Neal, 2009) Also, residues of catalysts, such as metals, used in the manufacturing processes can be present in plastics. Additives are also used as plasticizers, flame retardants, antioxidants, acid scavengers, fillers, light and heat stabilizers, lubricants, pigments, antistatic agents, slip compounds and thermal stabilizers. The most commonly used additives are the following:

**Plasticizers**, such as phthalates and bisphenol A (BPA), are used to provide polymers with more flexibility and plasticity. These compounds accumulate in marine organisms and may affect reproduction and development in several biological organisms (Oehlmann et al., 2009).

**Flame retardants**, such as polybrominated biphenyl ethers (PBDEs), improve the resistance of polymers toward fire. It was shown that PBDEs are potential carcinogens, endocrine disruptors and neurotoxins (Wasnick et al., 2022).

**Heat stabilizers**, such as organotin, prevent thermal degradation of polymers when they are exposed to high temperatures (N.Hahladakis, 2018).

**Antioxidants** delay the oxidation of polymers exposed to sunlight (acrylamines and phenolics) (N.Hahladakis, 2018).

Metal-based additives are used in different pigments to give the different colors to plastics and as stabilizers and fillers (Murphy, 2001). Mineral fillers are used to increase the hardness, they include barium sulfate, calcium carbonate and hydrated magnesium silicate. The choice of pigments depends on the desired color, for example, white pigments contain ZnO and Sb<sub>2</sub>O<sub>3</sub>. Some pigments can also be used to add other properties to plastics such as flame retardation and stability.

In the marine environment, over time and under environmental conditions, those additives can leach from plastics to water and be harmful for marine biota and humans.

### 3.3.2. Organic pollutants sorbed on microplastics

Microplastics of different shapes and sizes can accumulate pollutants from the aquatic environment, especially after weathering, when their surface becomes more active and tends to sorb hydrophobic organic pollutants, such as pesticides, PAHs, PCBs or metal species. The rate with which those compounds are sorbed and desorbed from microplastics is dependent on different environmental factors, polymer characteristics and, furthermore, on the size of microplastics. When the size of plastics decrease, the sorption/desorption process is faster. The smaller the MPs size, the larger the relative surface area-to-volume ratio, and the greater relative adsorption and desorption (Teuten et al., 2009). For example, on thin (50 µm) polyethylene films PCB congener sorption took 50 days to reach equilibrium (Adams, 2007), whereas sorption of PCBs onto polyethylene pellets of 3 mm took approximately a year (Van et al., 2012).

In the marine environment, the surface properties of plastics change; as they weather they increase their polarity by oxidation (Mato et al., 2001) and increase their porosity and roughness (Artham et al., 2009) and therefore accumulate higher concentrations of chemical pollutants.

The industrial sector is one of the principal sources of pollution; industries release tons of toxic chemicals in rivers and oceans in countries that doesn't follow environmental plans. They also contribute to a massive atmosphere pollution that will, in turn, be reflected in aquatic ecosystem by the deposition (Lloyd-smith, 2018).

#### ***Polychlorinated biphenyls (PCB)***

Polychlorinated biphenyls (PCBs) are synthetic organic chemicals. Their molecules contain two benzene rings, in which hydrogens are replaced with chlorine; 2 to 10 chlorine atoms can be attached to biphenyl molecules (Fig. 9). The number of chlorine atoms and their locations in PCBs give up to 209 different PCBs congeners with different chemical and physical properties. Commercial PCBs are mixtures of different congeners (de Boer, 2004).

PCBs do not occur naturally, so when found in the environment they are attributed to anthropogenic sources (de Boer, 2004). PCBs are used for a variety of industrial uses including mainly electrical industry (in transformers and capacitors), in printing inks, carbonless copy paper and others.

PCBs are persistent contaminants, they are resistant to alteration and degradation in the environment. Polychlorinated biphenyls are lipophilic, they are found in low concentrations in water but they tend to adsorb to organic matter and suspended particulate matter and plastics. Furthermore, due to their lipophilic behavior, they tend to bioaccumulate in marine biota and pass into the food chain arriving to humans. They showed hepatotoxicity, developmental toxicity, endocrine disruption, immunosuppression and even carcinogenic effects (Immig, 2021).

PCBs are one of the world's worst toxic legacies. Their intentional producing was prohibited in 2001 according to the Stockholm convention (UNEP, 2009), but their use in electrical equipment is still allowed.

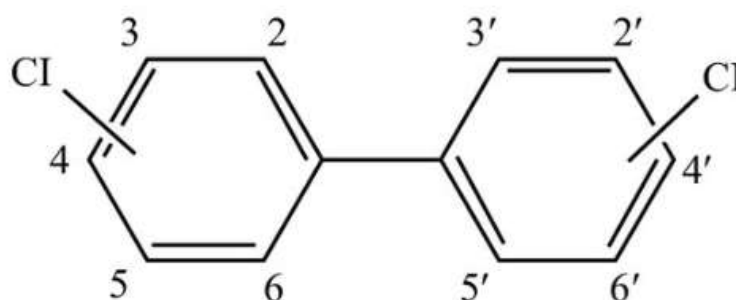


Figure 9 General structure of a polychlorinated biphenyl

### **Polycyclic aromatic hydrocarbons (PAHs)**

Polycyclic aromatic hydrocarbons (PAHs) consist solely of hydrogen and carbon atoms and have at least two benzene rings in different arrangements (linear, angular or cluster). They are formed during the maturation of crude oil. One of the major sources of petrogenic PAHs pollution is unintentional direct release in the environment, such as oil spills in oceans and seas or rivers and the release of gasoline and oils from the transportation sector (Lloyd-smith et al., 2018). They can also enter marine environments via industrial discharge, untreated waste disposal and most importantly from accidental leakage from ships or electricity plants. Oil related pollution is one of the major sources of threat to aquatic biota. Oil exposure can be so toxic it may cause death of fish and other marine biota in the case of longtime exposure (Kazlauskiene, 2008).

PAHs are highly hydrophobic. Their solubility in water is very low and they have a low vapor pressure that makes them semi-volatile. Those characteristics decrease with the increase of molecular weight. As the molecular weight of PAHs increases, their hydrophobicity increases, so their solubility in water and vapor pressure decrease and they become more resistant to degradation and thus persist longer in the marine environment (Who, 1999).

Different environmental agencies have created their priority PAHs lists specifying the species that are particularly toxic, have greater exposure and are found at high concentrations. The World Health Organization (WHO) (Who, 1999), and the United States Environmental Protection Agency (US-EPA) (United States National Academy, 1983) are examples of organizations which assembled priority PAHs lists according to their research objectives. Fig. 10 shows the 16 PAHs listed by the US EPA (Mastanjević et al., 2020).

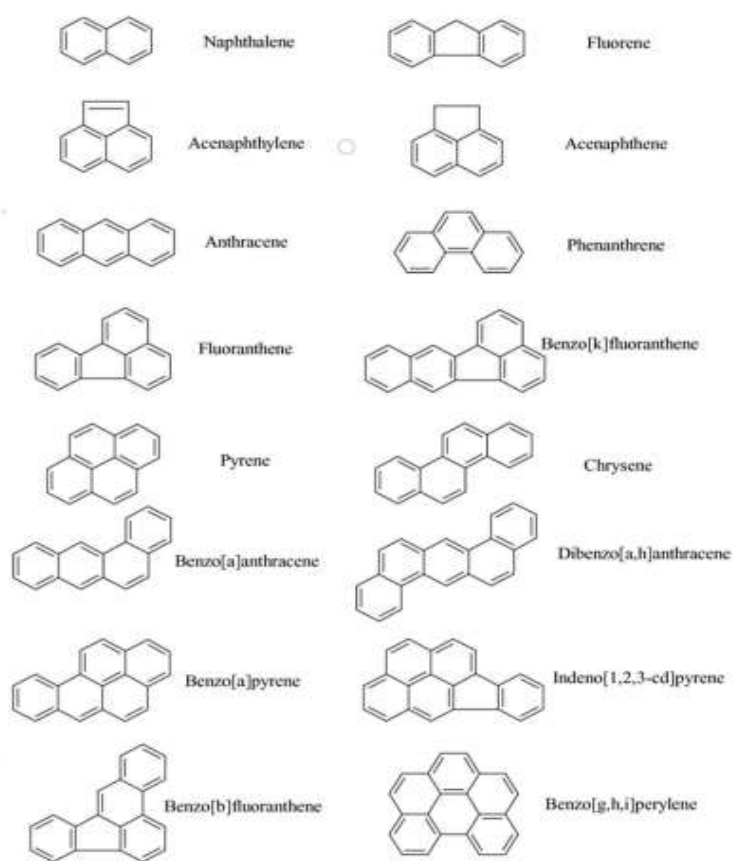


Figure 10 The 16 priority PAHs (Mastanjević et al., 2020)

### **Pesticides**

Pesticides, including fungicides, insecticides, herbicides and bactericides, are used in agriculture for pest control. They enter the marine environment as direct runoff from sprays drifting from agriculture, forestry, gardens of residential properties as well as from rivers and streams, storm water systems and wastewater treatment plants (Lloyd-smith et al., 2018). The most common classes of pesticides are organochlorine, organophosphate, carbamate and synthetic pyrethroid species (Fig.11) (Kaur, 2019).

Most of the pesticides have endocrine disrupting effects that can cause harmful effect to marine biota and humans by interfering with the body hormones. They can bind to cellular receptors and lead to unwanted responses or prevent the normal hormone from binding with the receptors and thus preventing normal body functions.

**Organochlorine pesticides** have low solubility in water and low volatility. This group of pesticides consists of polychlorinated biphenyls (DDT, dicofol), polychlorinated derivatives of cyclohexane (lindane) and polychlorinated cyclodiene (endosulfan). A number of those pesticides was banned from uses worldwide according to the Stockholm convention (UNEP, 2009). For example, DDT was used massively to control mosquitoes that spread malaria and was banned in the late nineties due to its high toxicity and persistence. After more than 20 years of the prohibition, organochlorine pesticides are still found in the marine environment (Hoffman et al., 2003).

**Organophosphorus pesticides** have high vapor pressure and their metabolism is usually fast, so it is necessary to study also their metabolites when controlling their presence and toxicity. The pesticides of



this class that are most commonly found in the marine environment and are harmful to humans are diazinon, dursban, malathion and chlorpyrifos (Hoffman et al., 2003). Chlorpyrifos was banned in most of the countries but is still found with its metabolites in the marine environment, it showed high toxicity toward marine animals, and can bioaccumulate in aquatic organisms such as fish; it also showed carcinogenic effects on humans (Hoffman et al., 2003).

**Carbamate pesticides** have very low water solubility. They generally have low and moderate toxicity but some exceptions are highly toxic such as carbofuran that acts as an endocrine disruptor and may be also cancerous if mixed with other chemicals (Hoffman et al., 2003).

**Synthetic pyrethroids** are synthetic derivatives of the naturally occurring pyrethrins extracted from chrysanthemum flowers. Pyrethrins showed that it has pesticidal activities but they were not so stable as pesticides, so similar more stable pyrethroids were chemically synthesized to obtain a better pesticidal effect (Wallace, 2013).

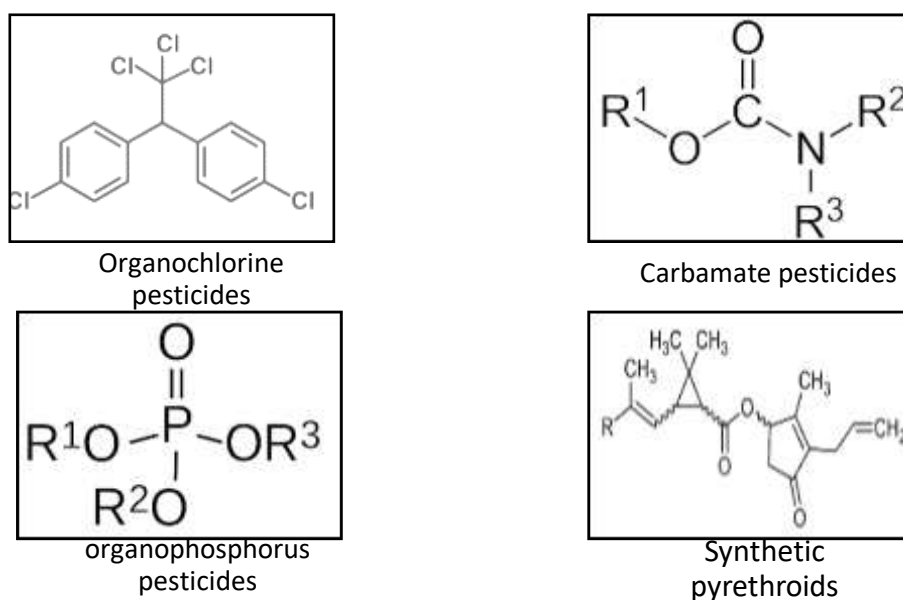


Figure 11 General chemical structures of different pesticides

### **Pharmaceutical and personal care products**

Pharmaceutical and personal care products (PCP) enter the environment in different ways. Urban and municipal wastes are their primary sources; drugs and their metabolites or degradation products excreted with urine and unused drugs trashed in through drains are carried with municipal waste water. In addition, hospital waste water may contain PCPs and drugs with no prior treatment. Consequently, they enter the marine environment and get adsorbed to sediment, litters and reach the marine biota.

Another significant source of pharmaceuticals in the marine environment are veterinary drugs that are excreted by animals, accumulate on the ground and are washed off by rain to nearby waters reservoirs or transported through the ground to groundwater. Also, they can be disposed in landfills (Lloyd-smith et al., 2018).

Pharmaceuticals are found in every water ecosystem because most of them could not be eliminated by conventional waste water treatment plants. More than 600 pharmaceutical product with their metabolites

and transformation products were found over 71 countries, including antibiotics, non-steroidal inflammatory drugs, hormones and many more. They can be harmful to aquatic organisms by causing metabolic and sex alterations and developing antibiotic resistance in aquatic microorganisms. In addition, some toxic ingredients in sunscreens and PCPs are toxic oxybenzone that is found in big quantities in the marine ecosystem can lead to the death of coral reefs by endocrine disrupting effect (Aus der Beek et al., 2016).

### 3.3.3. Metals and microplastics

Metals in aquatic systems can come from natural sources, such as weathering of rocks, soil erosion, and rainwater, but also from anthropogenic sources, mainly from industry and mining.

In general, metal compounds are used in the process of manufacturing plastics as additives, catalysts and pigments, so metals are found in newly manufactured plastics. Also, once in the sea plastics tend to sorb on their surface metals present in the marine environment.

In the aquatic environment, one of the parameters that effects the sorption of metals is pH. pH has significant influence on the process of adsorption/desorption because it determines the charge state and the reactivity of the polymer surface. In general, an increase in pH leads to a higher adsorption of metals. H<sup>+</sup> ions surround the surface of microplastics at a low water pH and promote the repulsion of metal cations which results in the decrease of adsorption and, at the same time, in an increase in the desorption of the metals already present on the surface of MPs (Tang, 2020).

Recently, several studies have been conducted in order to inspect metals sorbed on MPs surfaces and furthermore to discriminate the metals sorbed coming from the environment from those originating from additives incorporated in plastics (Catrouillet et al., 2021).

Table 1 shows different metals such as Al, Zn, Ba, Cu, Pb, Cd, Mn, and Cr present in additives and pigments. Leaching was done in order to recover the sorbed metals which are more bioavailable to be ingested by marine biota. Acid digestion was done to release metals used as additives and differentiating between plastics of different pigments. This table shows the discrimination of the source of Cd, As, Zn and Pb in different color plastics either coming from sorption or present as pigments.

Table 1 Different metals in different colored plastics (Catrouillet et al., 2021)

Color	Orange	White	Yellow	Blue	Beige	Green	Grey
<b>Cd</b>	Additive	Additive/ Sorbed	Additive/ Sorbed	Sorbed	Additive	Additive	Sorbed
<b>As</b>	Sorbed	Sorbed	Sorbed	Sorbed	Sorbed	Sorbed	Sorbed
<b>Zn</b>	Sorbed	Sorbed	Additive	Additive	Additive	Additive	Sorbed
<b>Pb</b>	Sorbed	Sorbed	Sorbed	Sorbed	Sorbed	Additive	Additive

Another study (El Hadri, 2020) discriminated additives from sorbed metals by laser ablation-ICP-MS. The authors found Pb, Cu and Sb originated from additives and Fe, Cu, Zn, As, Cd, Sn, Sb, Pb and U adsorbed to plastics. Cadmium, copper, iron, lead, chromium, cobalt, manganese, molybdenum, zinc, tin, uranium and antimony have been shown to sorb on environmental MPs from the aquatic environment (Ashton, 2010).

The sorption of metals increases with time, a study conducted for a whole year in the San Diego Bay showed that the concentrations of sorbed metals increased with exposure time (Rochman et al., 2014).

Table 2 shows different metal-containing pigments giving particular coloration to plastics (“Pigments by colour - ColourLex,” 2022).

Table 2 Different plastic colors with the metals entering in their pigmentations (“Pigments by colour - ColourLex,” 2022)

Colour	Name of the pigment	Composition
Blue	Han Blue	$YIn_{1-x}Mn_xO_3$
	Egyptian blue	$BaCuSi_2O_8$
	Blue Verditer	$CaCuSi_4O_{10}$
	Manganese Blue	$2CuCO_3 \cdot Cu(OH)_2$
	Vivianite	$BaMnO_4 \cdot BaSO_4$
	Cerulean Blue	$Fe_3(PO_4)_2 \cdot 8H_2O$
	Prussian Blue	$CoSnO_3$
	Smalt	$Fe_4[Fe(CN)_6]_3 \cdot xH_2O$
	Azurite	contain Co
	Cobalt Blue	$2CuCO_3 \cdot Cu(OH)_2$
	Ultramarine	$CoAl_2O_4$ $Na_7Al_5Si_3O_{24}S_3$
Red	Pompeian Red	Iron oxide + clay and quartz
	Chrome Red	$PbO \cdot PbCrO_4$
	Cadmium Red	$Cd(S,Se)$
	Red Lead	$Pb_3O_4$
	Red Ochre	Hematite (Iron oxide)
	Vermilion	$HgS$
Realgar	$As_2S_4$	
Yellow	Raw Sienna	Iron oxide + small amounts of Mn oxides
	Bismuth Vanadate	$BiVO_4$
	Yellow	$K_2O \cdot 4ZnCrO_4 \cdot (H_2O)_3$
	Zinc Yellow	$BaCrO_4$
	Lemon Yellow	$K_3[Co(NO_2)_6]$
	Cobalt Yellow	$Pb_3(SbO_4)_2$
	Naples Yellow	$CdS$
	Cadmium Yellow	Iron oxides
	Yellow Ochre	$As_2S_3$
	Orpiment	$PbCrO_4$
Chrome Yellow	$Pb_2SnO_4$	
Lead-Tin Yellow		
Green	Phthalocyanine Green	Cu organic complex
	Cobalt Titanate Green	$Co_2TiO_4$
	Verdigris	$Cu(CH_3COO)_2 \cdot H_2O$
	Green Earth	$K[(Al,Fe^{III}), (Fe^{II},Mg)(AlSi_3, Si_4)O_{10}(OH)_2]$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
	Viridian	$Cr_2O_3 \cdot 2 H_2O$
	Emerald Green	$3 Cu(AsO_4)_2 \cdot Cu(CH_3COO)_2$
Cadmium Green	mix of $CdS$ and $Cr_2O_3$	
Orange	Antimony Orange	$2 Sb_2S_3 \cdot Sb_2O_3$
	Cadmium Orange	$CdS$
	Chrome Orange	$PbO \cdot PbCrO_4$
	Orange Ochre	Iron oxides
	Realgar	$AsS_3$ , $As_2S_2$ or $As_4S_4$
Grey and Black	Spinel black	$MnFe_2O_4$
	Manganese Black	Manganese and Iron oxides
White	Titanium Dioxide White	$TiO_2$
	Calcite	$CaCO_3$
	Zinc White	$ZnO$
	Lead White	$2 PbCO_3 \cdot Pb(OH)_2$

### 3.3.5. Sorption dynamics of pollutants on microplastics

In order to understand the sorption/desorption behavior of contaminants on microplastics, a lot of model experimental studies have been conducted lately, however, real-world environmental processes are far more complex (Bakir et al., 2012; Lionetto et al., 2021; Qiu et al., 2019). The external parameters and the behavior of each particle of plastic is different depending on its type, physical properties, additives, the time spent in the marine ecosystem and many more. Therefore, it is difficult to mimic these processes experimentally or track their developments in the environment.

The residence time of microplastics in the marine environment plays a role in favor of the adsorption of contaminants. Over time, the surface of the plastic fragments is modified (it becomes less smooth) and pollutants will be able to be adsorbed more easily.

In addition, there are different external parameters affecting the sorption of pollutants on microplastics in the marine environment; they include

- The presence of other contaminants that can modify the adsorption process, e.g. DDT in a bi-solute system does not show significantly different adsorption behavior compared to a simple solute system. However, it was suggested that DDT acts as an antagonist by interfering with the adsorption of phenanthrene on microplastics (Bakir et al., 2012).
- The adsorption potential of a persistent organic pollutant is governed by its solubility, an increase in salinity reduces its solubility and is therefore likely to facilitate its association with sediments and microplastics. For example, PFOS adsorb easier on microplastics at high salt concentrations (Wang et al., 2015).
- An increase in suspended organic matter would promote the adsorption of contaminants on microplastics. For example, an increase in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  could cause the precipitation of dissolved organic matter and cover the sediments, which increases their organic matter content and therefore their capacity to adsorb persistent organic pollutants (Endo et al., 2013).

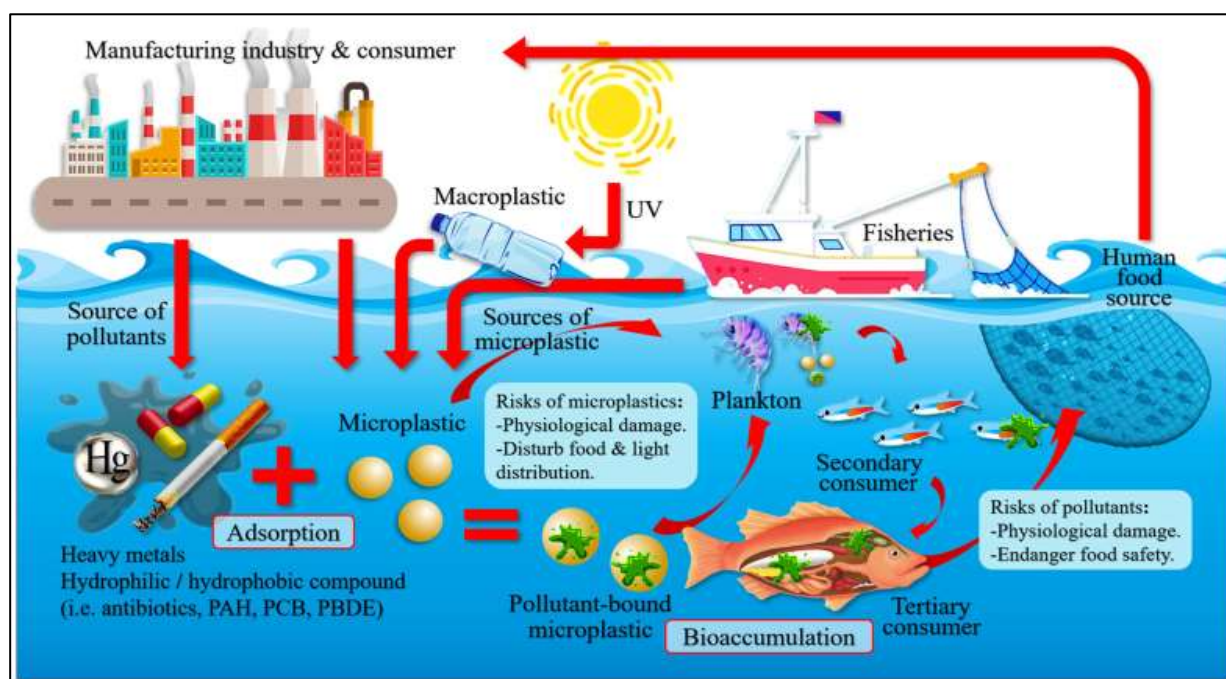


Figure 12 Illustration of the pathway of MPs in the marine environments and their impact on the marine ecosystem and organisms (Amelia et al., 2021)

Due to their composition and their sorption/desorption capacity, plastics will be able to transport organic contaminants over very long distances. Furthermore, when plastic debris break down to give MPs, living organisms are jointly exposed to MPs and organic contaminants. The ingestion of microplastics can lead to the desorption of the contaminants added in the polymer matrix during the design of the polymers but also of those adsorbed in the environmental matrices in which they have previously resided (Holmes et al., 2014; Mato et al., 2001; Teuten et al., 2009). MPs are therefore likely to play a role as a vector of contamination

for organism through ingestion or even by exposure, and represents a pathway for the transfer of contaminants to the food chain (Fig 12).

The species reported were PAHs, PCBs, pesticides and metals (Camacho et al., 2019; Catrouillet et al., 2021; Mizukawa et al., 2013; Rios, Jones, Moore, & Narayan, 2010). The degradation occurring over time in the aquatic environment increases the surface area-to-volume ratio of plastics and thus increases the concentration of pollutants sorbed on their surface and also facilitates the desorption of the sorbed and accumulated pollutants into the water (Adams et al., 2021). Microplastics were used as a passive sampler to assess the concentrations of hydrophobic compounds in environmental media (Adams, 2007).

Types and concentrations of pollutants sorbed to microplastics differ according to the geographical location of the sampled MPs due to different pollution sources. According to Hirai *et al.* (Hirai et al., 2011), samples from the Pacific Gyre, collected in the open ocean and urban beaches showed the presence of PCB congeners, PAHs, PBDE, alkylphenols, DDT and its metabolites and BPA ranging from 0.001 to 10 µg/g. PCBs were found in all plastic samples with concentrations ranging from 0.001 to 0.43 µg/g with the highest concentrations sorbed on polyethylene. PAHs concentrations ranged from 0.001 to 9.3 µg/g. It was also shown that PCBs and PAHs were more concentrated in plastics collected from urban beaches than the ones collected from open oceans due to land-based sources of those pollutants. DDTs (DDT, DDD and DDE) concentrations in fragments ranged from  $0.2 \times 10^{-3}$  to 0.12 µg/g. PBDEs were also found in concentrations ranging from  $2 \times 10^{-5}$  to 9.9 µg/g (Hirai et al., 2011).

Another study conducted by Camacho *et al.* (Camacho et al., 2019) in Canary Islands (Spain) showed a wide range of organic pollutants adsorbed on microplastic fragments and pellets. PAHs were found in high concentrations on pellets up to 17 µg/g and fragments up to 8 µg/g. The sums of PCB congeners concentrations were up to 0.28 µg/g in pellets and up to 0.77 µg/g in fragments. The organochlorine pesticides (DDT) summed with its metabolites ranged from  $0.4 \times 10^{-3}$  to 13 µg/g in pellets and  $0.4 \times 10^{-3}$ - 3.7 µg/g in fragments. The sum of other OCPs (HCB, heptachlor, dieldrin and mirex) ranged from  $0.9 \times 10^{-3}$  to 13.5 µg/g in pellets and  $0.7 \times 10^{-3}$  to 17.7 µg/g in fragments. The sum of UV-filters coming from personal care products mainly coming from sunscreens, was much higher in beaches frequently visited by tourists. They ranged from 0 to 37.7 µg/g and 0.003 to 2.1 µg/g in pellets and fragments respectively. The sum of brominated diphenyl ethers (BDE) attained 3.9 µg/g and organophosphorus flame retardants (OPFR) 7 µg/g in plastics fragments. Furthermore, chlorpyrifos pesticide was found in all plastic samples (Camacho et al., 2019).

A study conducted in different sites along the Portuguese coast by Mizukawa *et al.* (Mizukawa et al., 2013) analyzed organic pollutants sorbed on plastic pellets. This study showed the presence of PCBs (different congeners) in concentrations going up to 0.3 µg/g in Porto, a highly urbanized city. DDT concentrations went up to 0.04 µg/g, PAHs to 0.4 µg/g and hopane's concentrations ranged from 8.25 µg/g to 70.8 µg/g (Mizukawa et al., 2013).

### 3.3.6. Impact of microplastics on different trophic levels

Most of the studies conducted to inspect the ingestion of MPs by marine organisms were done under experimental conditions in order to control the external conditions, the exposure time, the type and number of microplastics.

Starting from the base of the food chain in the marine environment, **plankton**, studies showed that they were contaminated by MPs. A study showed a reduction in photosynthesis of microalgae when exposed to nanoplastics (Bhattacharya, 2010). In addition, many zooplankton species were found to ingest MPs. A

study of Cole *et al.* (Cole et al. 2013) showed that 13 taxa out of 15 studied had ingested MPs. Another study on copepods showed that the chronic exposure to small sized microbeads led to an infertility (Lee, 2013).

Going higher through the trophic chain, filter feeders such as **mussels** can filter up to few liters of water per hour and thus are prone to ingest more microplastics comparing to other marine organisms. Therefore, many studies were done on the mussel *Mytilus edulis* due to its economic importance (Karlsson et al., 2017; Wesch et al., 2016).

**Fish** can either ingest plastics from the marine environment or by ingesting species from lower levels, contaminated with MPs. Presence of microplastics in digestive tracts was reported in different studies. As examples, Lusher *et al.* (Lusher et al. 2013) examined 504 fish specimens collected from English Channel and found plastics ranging from 0.13 to 14.3 mm in size in 36.5 % of intestinal tracts, 92.4 % of them were microplastics. In 2019, a global assessment showed that MPs can be ingested by 427 different fish species, freshwater, estuarine and marine fish (Azevedo-Santos et al., 2019).

**Waterbirds**, collect their food from the water surfaces so they can ingest organisms contaminated with microplastics and ingest floating MPs. The ingested MPs are mainly retained in their gastrointestinal tracts (Brookson et al., 2019) Waterbirds can act as a vector for the transport of those plastics. The excretion of MPs in the faeces of waterbirds was recorded by (Provencher et al., 2019)

Many more species were shown to ingest microplastics and therefore MPs can be transported by the food chain. However, toxicological studies showing the effect of the exposure of plastics and plastic-associated contaminants are still scarce.

## 4. Analytical approaches

### 4.1. Sampling of microplastics present in different coastal compartments

In the marine environment, microplastics can be sampled from different compartments, from surface water, marine sediments, shorelines, and biota. They are rarely sampled from the water column that is considered only a transition media for plastics. Prior to sampling, it is essential to determine the aim of the study. To date, there is no standard method for microplastics sampling from the marine environment.

Documenting sampling campaigns remains a very important part. Photos of the area and sites serve as evidence of sampling besides noting the date, time, and coordinates of each sampling site. All sampled plastics should be preferably placed in a glass container to avoid contamination from plastic ones.

#### 4.1.1. Surface water

To collect plastics from the sea surface, nets are used. Most of the plastics found on the surface have a density below  $1 \text{ g/cm}^3$  (polyethylene, polypropylene, and polystyrene). Floating nets are used to collect microplastics from sea surface and hand nets are simply used to collect plastics from shallow water directly on a beach.

Different types of nets are used, the most commonly used is the Manta trawl (Fig. 13) followed by the Neuston net in several studies. The Manta net consists of a net fixed by a stainless steel or aluminum frame and ends in a collector (Pasquier et al., 2022a). From both sides of the frame lay the floaters that provide the stability and keep the Manta floating during the sampling. The dimension of the net and the mesh size differ from one study to another but the most widely mesh size used was 300 - 350  $\mu\text{m}$ .

The use of the Manta requires the use of a catamaran or any type of boat because the procedure consists of the deployment of the Manta net by cables or ropes from the side of the boat in a way that it doesn't get affected by the turbulent water movement caused by the boat motion. The net is towed horizontally against the current and dragged at a certain constant speed for a certain time. For most of the studies, the speed was below 3 knots and the dragging time ranged between 5 and 90 min with an average of 20 min in most of the publications (Pasquier et al., 2022a).

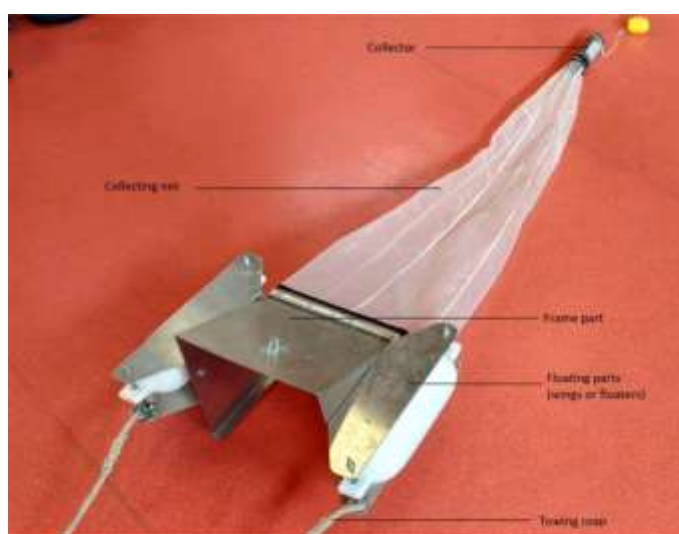


Figure 13 Manta trawl (Pasquier et al., 2022a)

The sampling is done as transects, and the coordinates of the starting and the endpoint are marked. The water volume is estimated using a flowmeter or calculated based on the distance traveled, known from the GPS coordinates and the width of the Manta net frame.

Winds and waves should be taken into consideration, and sampling is preferred to be done in calm sea conditions not to damage the net. Also, the net should be controlled regularly to make sure it is not clogged (Pasquier et al., 2022b).

The plastics sampled are then collected and separated by forceps from organic matter. Microplastics' minimum size is limited by the chosen mesh size.

#### 4.1.2. Sediments

##### Subtidal sediments

To collect seabed sediments, a grabber was used, most commonly a Van-Veen grab or simply any kind of corers. The microplastics are then extracted from the sediments, most commonly by density separation, using salt solutions such as zinc chloride and sodium iodide (Frias et al., 2018). The apparatus used for density separation can be a separatory funnel (Fig.14) or a glass beaker. The supernatants are filtered on glass fiber filters to be inspected by a stereomicroscope for counting and separation by size, shape, and color. Then, the microplastics are chemically characterized using different techniques discussed in the following chapters.



Figure 14 Separating microplastics by density separation in a separatory funnel

Some samples may also be treated with  $H_2O_2$  to eliminate the organic matter by oxidation. Those steps can be destructive so they are only used to classify and identify microplastics.

##### Shoreline samples

Waves coming from the sea usually form a line of litter on sandy beaches. This shoreline is the ideal place to collect plastics washed from the sea surface. Plastics are commonly collected based on the quadrat method, using square frames of different sizes, placed on the sand, and the first few centimeters of sediments are sieved and collected in glass jars. Sediments are dried, if wet, and microplastics are separated either manually by forceps or by density separation based on the purpose of the study and the size range of microplastics needed. The minimum size range here is limited by the pores of the sieves used. On rocky beaches, plastics can be collected manually (Frias et al., 2018).



### 4.1.3. Biota

Plastics ingested by different marine biota were recorded (Rezania et al., 2018) . Large organisms, such as fish were sampled by nets or traps (Lusher, 2017). Stranded and dead mammals, cetaceans, and seabirds are collected and dissected and the content of the digestive tract or the guts are needed for microplastics studies. In some studies, the excretions of living organisms are inspected (Avio et al., 2015; Patria et al., 2020).

In the case of mussels, snails, and worms they are collected by traps, nets, or hands and they are used as a whole. For the plankton, plankton nets are used to collect them and plastics are inspected under a microscope (Bergmann et al., 2015).

After plastics extraction from different compartments, plastics can be characterized based on different criteria.

## 4.2. Identification of microplastics

According to their visual appearance, plastics are separated from other organic or inorganic materials present in the sample and classified into different shapes, forms, and colors. The particles larger than 1 mm are usually sorted visually and the smaller ones are inspected under a stereomicroscope. (Hidalgo-Ruz, et al., 2012). They are classified mainly into foam, fibers, fragments, films, beads, and filaments, separated also by different colors and sizes.

It is always recommended to complement visual sorting with techniques to identify microplastics properly. Visual sorting can lead to erroneous results due to the difficulty to discriminate small plastic particles from other organic matter, sand granules, and diatom frustules. Furthermore, it is also limited by a certain particle size that requires high magnifications or cannot be managed even with high magnifications.

Different techniques are applied to identify the chemical types of plastics, there are the destructive techniques and the non-destructive techniques. The choice of the technique is based on the aim of the study. Raman and FTIR spectroscopies are the most commonly used techniques.

### 4.2.1. Attenuated total reflectance (ATR) Fourier –transform infrared spectroscopy

FTIR is the most commonly used technique nowadays for plastics identification and quantification. Visible microplastics can be identified by the conventional FTIR but for small sized and microscopic microplastics down to 10  $\mu\text{m}$ , a micro-FTIR equipped with a microscope is used to identify microplastics placed on filters. Plastics are identified according to their characteristic Infrared spectra.

The FTIR instrument is mainly constituted of 3 parts, a source, an interferometer and a detector.

- The source consists of a broadband infrared emitter that changes between equipment.
- The interferometer, it consists of a beam splitter, a stationary mirror, a moving mirror and a timing laser. First, the beam splitter splits the light coming from the source, half of the light goes to the stationary mirror and the other half to the moving mirror. Over the time, a constructive and destructive interference is caused by the difference in the path of the mirrors. A laser is used for determination of the position of the moving mirror by using its known wavelength.

- The light is then focused on the sample and directed to a detector that converts via a Fast Fourier Transform, the time domain signal into a frequency domain. Thereby, detectors convert photons into measurable electric signals and send them to computers.

There are four different types of sampling for FTIR spectroscopy, Attenuated total reflectance and transmissions are the ones usually used for plastics identification so they will be cited here. The other two are the specular reflectance and diffuse reflectance.

The transmission mode is the traditional FTIR mode and is a very effective method but it needs sample preparation and could be considered destructive so it was mainly replaced by ATR due to its analysis without prior sample preparation. For solid plastics samples, the sample is placed in a KBr pellet and pressed. The beam then passes through the sample and the transmitted radiation is measured. It is only used for thin particles.

**Attenuated total reflectance** is the most used FTIR, it is not destructive, gives high quality spectra and in few seconds and does not need sample preparation. The ATR technique is a fast technique, all it requires is placing the sample on the plate and applying pressure between the ATR crystal and the sample in order to make sure of a good contact between the sample and the crystal (Fig.15).

The ATR measures changes that happen in an internally reflected infrared beam when it comes into contact with the sample. The infrared beam is directed at a certain angle onto the crystal (ZnSe, Germanium or diamond) that has a high refractive index. The internal reflectance creates an evanescent wave that goes from the crystal to the sample and this wave will be attenuated and passes back to the Infrared beam and goes to the detector to finally obtain an Infrared spectrum (Subramanian & Rodriguez-saona, 2009).

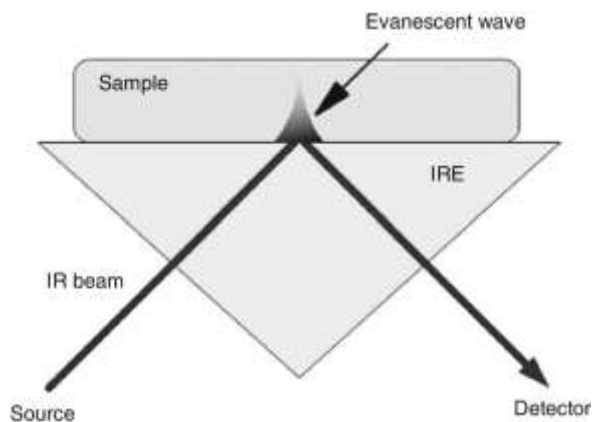


Figure 15 ATR-FTIR principle (Ruysschaert & Raussens, 2018)

#### 4.2.2. Raman spectroscopy

Raman spectroscopy is a commonly used technique for polymer identification. It is a non-destructive technique that allows the identification of small microplastics down to a few micrometers.

A Raman spectroscope consists of a light source, a sample holder and a detector. The technique is based on inelastic scattering of monochromatic light. Inelastic scattering is a phenomenon by which the frequency of photons changes when interacted with a sample. When a molecule is excited by photons coming from the light source it reemit photons, the frequency of the reemitted photons is shifted compared with the original monochromatic frequency, this shift of frequencies is unique for each molecule. This phenomenon is called the Raman Effect (Kim, 2015).

In Raman spectroscopy, a monochromatic laser source is focused toward the sample. The laser interacts with molecules and atoms and the difference between the frequency of the backscattered light and the laser frequency gives a substance-specific Raman spectra. A Raman spectrum is a result of the inelastic collision between incident monochromatic radiations and molecules. This radiation scatters in all direction: much of it constitutes Rayleigh scattering which is equal to the frequency of the incident radiation and a small fraction of radiation constitutes Raman scattering and have a different frequency than the incident radiation (Fig.16). Depending on the used system, wavelengths range between 500 and 800 nm (Kim, 2015).

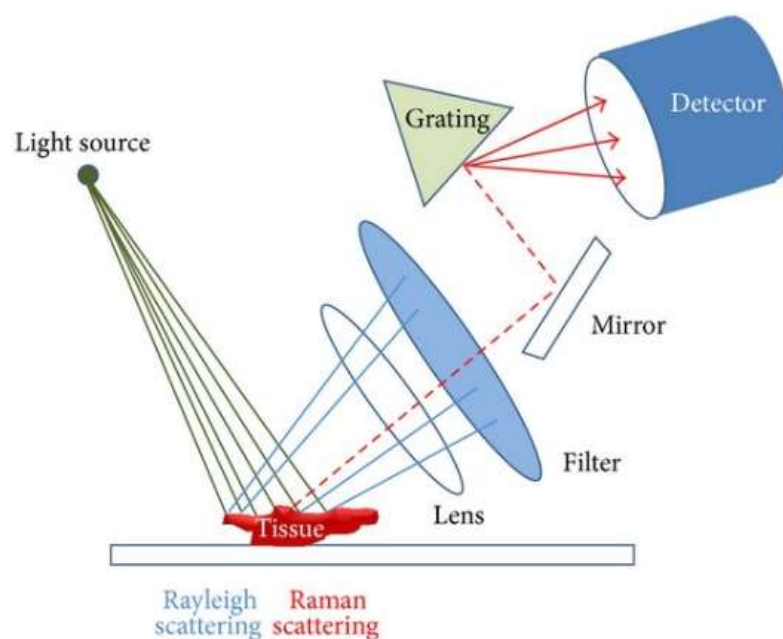


Figure 16 Raman spectroscopy principle (Kim, 2015)

Every plastic polymer has a Raman spectrum that characterizes it. A comparison with a reference spectrum allows the identification of plastics types within a few minutes. To facilitate the detection of small microplastics, a Raman spectroscope can be combined with a microscope.

#### 4.2.3. Pyrolysis - gas chromatography - mass spectrometry

In contrary to FTIR and Raman where only the surface is analyzed, by pyrolysis the sample is entirely analyzed. It is a destructive method where the sample is thermally decomposed at high temperature (> 400 °C) in an inert atmosphere to avoid the occurrence of chemical reactions such as oxidation. The decomposition creates different pyrolysis products that are smaller than the original microplastics. Knowing how polymers degrade and their degradation products help in their identification.

The reactions that mainly occur are the depolymerisation (decomposition to basic units), random excision (giving random small fragments), and the removal of side groups.

It is coupled with gas chromatography - mass spectrometry (GC-MS) for the separation and analysis of pyrolysis products of polymer degradation by identifying their chemical compositions (Fig.17). A lot of molecules are generated from the pyrolysis of polymers what make it difficult to use only mass spectrometry, this is why gas chromatography is used to separate molecules in addition to MS. Thus the coupling of GC-MS to pyrolysis improve the polymers identification (Dehault et al., 2022).

Therefore, the identification of polymer type is done based on characteristic pyrograms: chromatograms showing combustion products.

Pyrolysis-GC-MS is used for identification methods were developed for quantification of microplastics (Fischer & Scholz-böttcher, 2017). Recently studies were done for the quantification of microplastics in water (Fischer & Scholz-böttcher, 2017; Ter Halle et al., 2017) and sediment (Dierkes et al., 2019; Fischer & Scholz-böttcher, 2017).

Pyrolysis-GC-MS was also used to study additives incorporated in plastics (Akoueson et al., 2021). It is a good technique to surpass extensive sample preparations and losses of compounds in extractions steps and contamination resulting from solvents and laboratory material.

This technique is not suitable for direct identification of small-sized microplastics because samples should be placed manually in the pyrolysis tube.

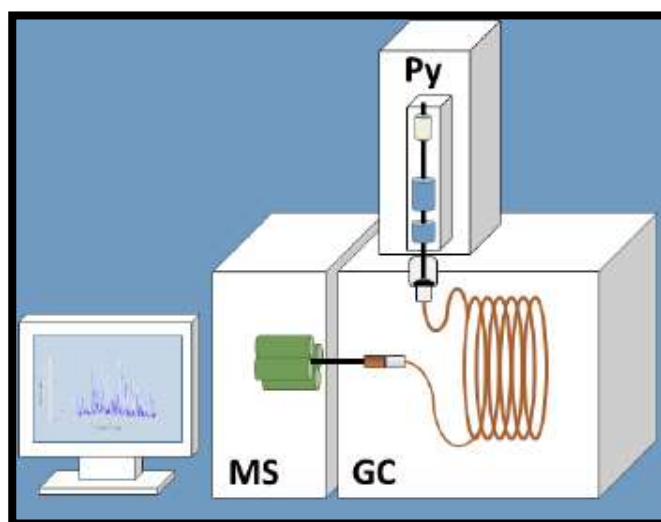


Figure 17 Pyrolysis-GC/MS apparatus (Picó & Barceló, 2020)

#### 4.3. Recovery of pollutants from microplastics

In order to study the pollutants adsorbed to the plastics or integrated into them, extraction should be done. The method and the solvent used are chosen according to the type of pollutants that will be studied and the equipment that will be used to detect the contaminants. Some methods are combined together.

##### 4.3.1. Maceration and solvent extraction

It is a simple procedure that consists of placing microplastics with the suitable solvent of choice starting from a few hours to 72 h. Solvents are chosen depending on the polarity of the targeted pollutants. The soaking is in most cases accompanied by shaking and the solvent is replaced by a new one every few hours (Bergmann et al., 2015).

The efficiency can be increased by using an ultrasound bath makes cavitation in the solvents which improves the extraction by increasing the diffusion and the dissolution of the solute. It can be done at room temperature or under heat.

#### 4.3.2. Soxhlet extraction

The apparatus for the Soxhlet extraction includes a distillation flask, a sample holder, a siphon, and a condenser (Fig.18). Several steps are required to carry out the extraction (López-Bascón et al., 2019).

- The sample should be first wrapped in filter paper and placed in the holder.
- Solvent placed in the flask starts to evaporate and pass through the part containing the sample that will be extracted and become a liquid in the condenser.
- When the solvent reaches the maximum level in the sample holder, the solvent carrying the extracted sample is aspirated and the liquid falls back into the flask.
- The solute is left in the flask and the solvents go up in contact again with the sample and the procedure repeats until the full extraction is done.

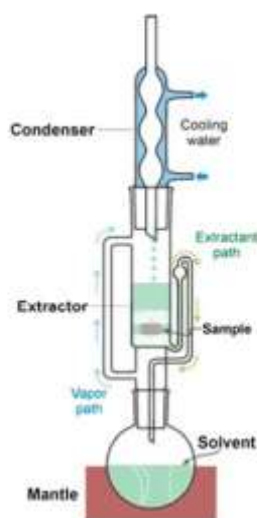


Figure 18 Soxhlet extraction apparatus (Dabbs, 2006)

#### 4.3.3. Accelerated solvent extraction

Accelerated solvent extraction is a technique used for the extraction of organic compounds from solid samples or semi-solid samples with liquid solvents. It is a fully automated technique. Compared to other extraction techniques, it allows to reduce extraction time and solvents used for extractions, but the equipment is of a very high cost. Note that the extraction time is short but the apparatus cleaning is time consuming and uses a large volume of solvents. A cleanup step of the extracts is also required before the chemical analysis.

The sample is enclosed in a cartridge filled with extraction fluid. Under elevated temperature (50-200 °C) and pressure (500-3000 psi), the sample is statically extracted. High temperature accelerates the kinetics of extraction and the high pressure maintains the solvent as a liquid above its boiling point (Fig.19) (Giergielewicz-Mozajska, 2001).

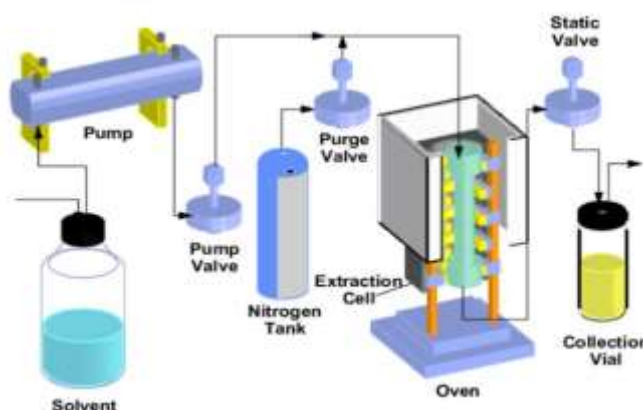


Figure 19 Accelerated solvent extraction apparatus (Maccioni et al. 1997)

#### 4.3.4. Microwave digestion

Microwave digestion is a sample preparation technique that digests solid samples producing a solution suitable for analysis by ICP-MS or other analytical techniques for elemental analysis. It is a fully automated procedure and each run digesting simultaneously several different samples takes less than one hour. In a microwave heating system, in closed containers, plastic samples should be digested using a liquid reagent, such as nitric or other acids to completely digest a sample. High temperatures are generated to accelerate the digestion process, accompanied by high pressures and samples are totally digested with no cleaning step prior to analysis (Fig.20) (Nóbrega et al., 2012).

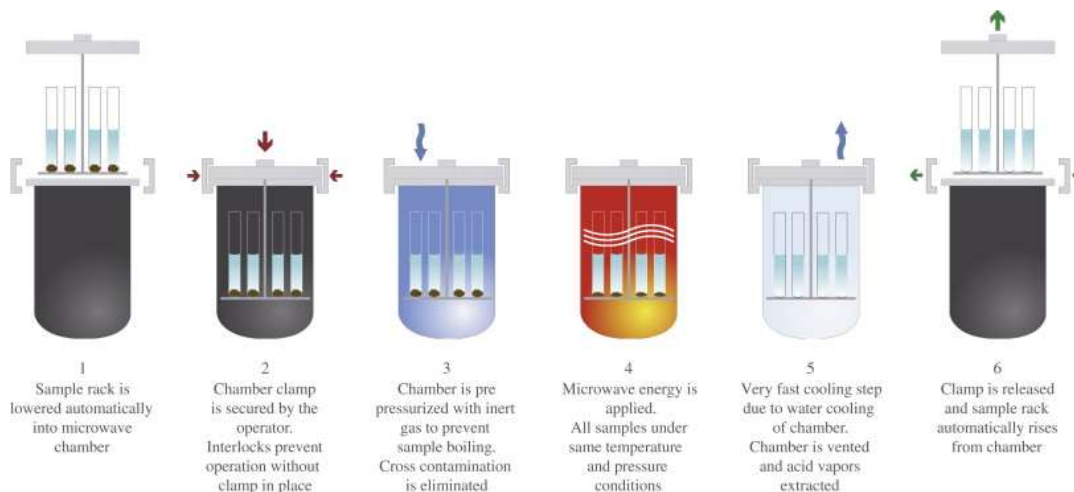


Figure 20 Process of Microwave digestion (Nóbrega et al., 2012)

### 4.4. Determination of organic pollutants

#### 4.4.1. High resolution accurate mass spectrometry

High resolution mass spectrometry (HRMS) is an analytical technique used for determining the exact molecular masses of compounds present in a sample (Marshall, 2008). The highly accurate nature of HRMS makes it ideal for identification of molecular structures, ranging from small organic molecules to large biological macromolecules. The two principal mass analyzers allowing the mass accuracy down to the ppm and resolution above 30,000 are time of flight mass analyzer and Orbitrap mass analyzer. Such a high mass accuracy and resolution allow the targeted identification of the compounds of interest.

### ***Time-of-flight mass analyzer***

In this system, the ions produced in the source of MS travel in a field-free region to reach the detector with a specific time. The flight time of each ion is different. With a specific applied energy, ions travel from the ion source, with a specific time, to reach the detector (Fig.21). At a given applied energy, smaller masses have larger velocities and larger masses have smaller velocities, thus ions with lower masses arrive to detector at first, followed by larger masses. The mass spectrum is therefore obtained by allowing time for all of the ions of interest to arrive to the detector (Salas-Tovar & Sepulveda, 2021).

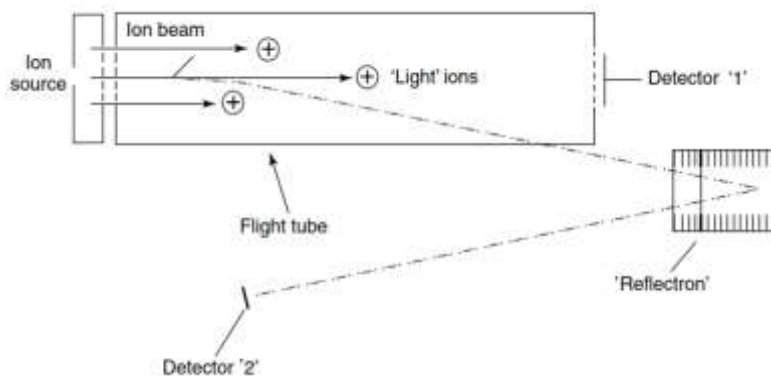


Figure 21 Time of flight mass analyzer(Salas-Tovar & Sepulveda, 2021)

### ***Orbitrap mass analyzer***

Orbitrap is a high resolution and high mass accuracy analyzer (Fig.22). It is accurate enough to allow the determination of monoisotopic mass and therefore is suitable for molecular formula determination. It is capable of producing mass spectra with an accuracy down to 1 ppm and a resolution higher than 250,000 in optimized conditions. This mass analyzer is therefore a high resolution analyzer allowing the determination of the empiric molecular formula of compounds (Zubarev & Makarov, 2013).

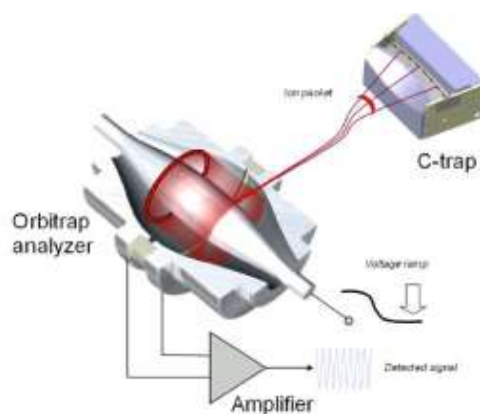


Figure 22 Orbitrap mass analyzer (Zubarev & Makarov, 2013)

#### 4.4.2 Tandem mass spectrometry

Tandem mass spectrometry is a technique known as MS/MS or MS<sup>2</sup>. It gives information about the structure of compounds. It uses two mass analyzers separated by a collision cell. The latter allows the fragmentation of precursor ions selected by a quadrupole filter into fragments specific to each of the targeted compounds. After the ionization, precursor ions of a specific  $m/z$  are selected (MS1) and are afterward the fragments are analyzed (MS2) to generate product ions to be detected. For example, the product ions from MS<sup>2</sup> could be fragmented to produce another group of product ions and so on.

The quadrupole analyzer consists of four parallel tubular rods. The opposite rods are connected electrically with a radio frequency (RF) and a direct-current (DC) applied between them. Ions of particular  $m/z$  will follow a stable trajectory through the rods, at a specific amplitude of voltage to reach the detector (Fig.23). Afterwards, a mass spectrum is produced by the variation in the RF and DC voltages in a way to bring ions to the detector. (Salas-Tovar & Sepulveda, 2021)

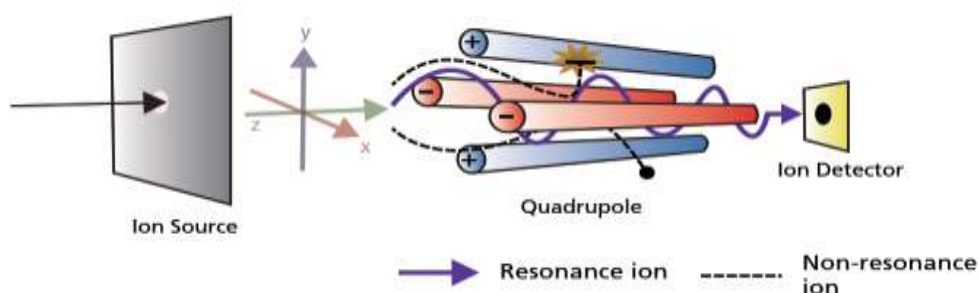


Figure 23 A quadrupole mass analyzer (“SHIMADZU,” 2022.)

The second mass analyzer can be another quadrupole (resulting in a triple quad configuration) or a high-resolution mass analyzer such as a TOF or orbitrap. The configurations are presented in Fig.24.

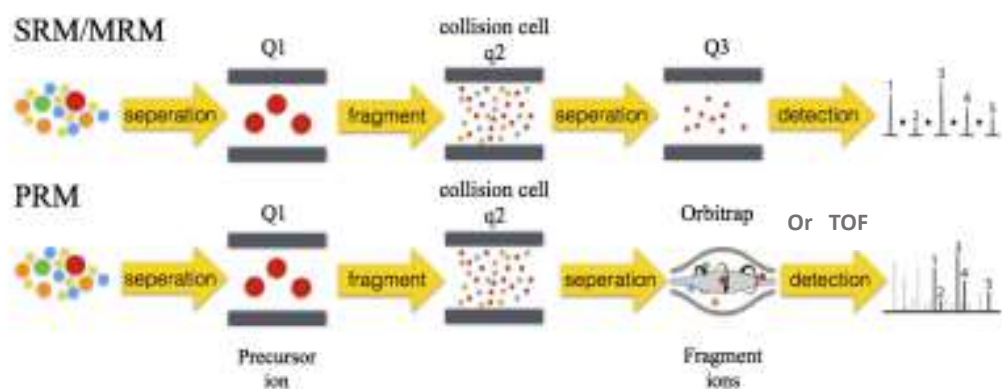


Figure 24 Configuration modes of tandem mass spectrometry (“Parallel Reaction Monitoring (PRM) Service - Creative Proteomics,” n.d.)



MRM/SRM mode monitors each precursor ion/product ion transition at a time, while PRM analyzes all product ions derived from a precursor ion with high resolution and mass accuracy. Both MRM/SRM and PRM allow relative and absolute quantification of compounds.

#### **4.4.3. Data acquisition: Targeted and untargeted approach**

Targeted studies are conducted widely in environment samples. Targeted compounds with known masses and molecular formula are inspected in the sample and suitable method developed based on known precursor ions and fragments to qualify and quantify them. The challenge here is to verify the identity of compounds in case of the absence of standards, but with high sensitivity mass spectrometers and MS<sup>n</sup> and with the help of libraries and databases this field is having a big step.

On the other hand, untargeted approaches are necessary in environmental field to investigate the types of pollution from a chosen environmental matrix. This will allow findings of unexpected and uncommon compounds found in the environment. The data acquisition could either be a data-independent acquisition (DIA) meaning that all the precursor ions in a selected *m/z* window are fragmented or data dependent (DDA) where only the most intense precursors are fragmented (Fernández-Costa et al., 2020).

Therefore, fragmenting a big number of precursor in DIA may be affecting the study negatively due to the risk of losing compounds from co-elution and matrix effect. It would be ideal to find all the compounds present in a given sample, but in fact, a trade-off is necessary. In DDA, some compounds of low intensity precursor will be neglected and also in DIA wrong identifications could result from co-elution.

In order to cover different types of pollutants a multi-technique approach should be applied. To study volatile and semi volatile / non-polar organic compounds adsorbed on microplastics, GC-MS is the most commonly used technique, whereas for non-volatile/polar compounds LC-MS is used. For elemental analysis of inorganic elements in plastics ICP-MS is used.

#### **4.4.4. Liquid Chromatography – MS/MS**

Liquid chromatography (LC) is a widely used technique for the separation of compounds from environmental samples. It is coupled with mass spectrometry as a detector in most cases. LC-MS/MS is used for the targeted and untargeted analysis of non-volatile compounds in different fields due to its high sensitivity and precision at a molecular level (Salas-Tovar & Sepulveda, 2021).

Separation of the compounds is done on the basis of their affinity toward a stationary phase. Reverse-phase chromatography is the most popular, the C18 columns are commonly used. The mobile phases are usually polar organic solvents mixed with water and slightly acidified for a better separation. In this type of studies methanol or acetonitrile are used as the organic phase and water as the aqueous phase, both could be acidified with 0.1 or 0.2 % of formic acid or others for a better ionization.

The ion sources that are most commonly used in LC-MS analysis are the electrospray (ESI) and the atmospheric pressure chemical ionization (Fig. 25).

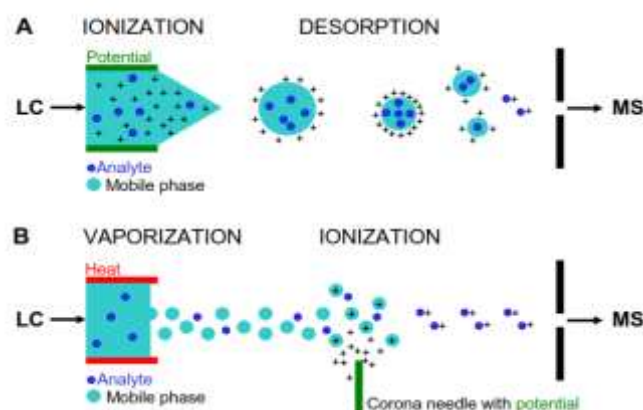


Figure 25 The difference between ESI and APCI. (A)ESI, (B) APCI (Verplaetse & Tytgat, 2014)

In ESI MS, sample extracts are pumped through a metal capillary and they are nebulized at its tip, forming a fine spray of charged droplets. Under the dry nitrogen stream and high temperatures, the electrical energy is used to assist the transfer of ions from the solution into the gaseous phase. The analytes are then transferred into the vacuum of the spectrometer. Thereby, the ions formed in the liquid phase are transferred to the gaseous phase (Ardrey et al., 2003).

In APCI, neutral analytes, in contrary of charged ones from ESI, are vaporized under a heated LC flow. The ionization consists of the transfer of charge between ion formed at the charged corona needle and a targeted ion. Thus, the ionization occurs in the gaseous phase. The number of ions generated by APCI is higher than ESI because they are formed redundantly (Ardrey et al., 2003).

While detecting and quantifying compounds, different criteria should be taken into consideration: the Retention time of each compound, their mass/charge ratios, and the fragmented ions in comparison with those of standards.

LC-MS is ideally suited for the detection of polar compounds. Thus it is necessary to use other techniques such as the GC-MS, which is used in most microplastic studies, to detect and quantify the adsorbed volatile and semi-volatile compounds and plastic additives. The studies showing different types of pollutants studied is shown in Table 3.

Table 3 Studies using LC-MS/MS to analyze different compounds

Origin of plastics	Plastic Characterization technique	Extraction technique/ time	Sample intake	Solvent used	Analyzed compounds	Reference
Experimental	-	Soaking/UAE/45 min	100 mg	Methanol/10 mL	Antibiotics	(Wang et al., 2020)
Water surface/ Manta trawls	ATR-FTIR	Soxhlet	-	Mixture of pentane: dichloromethane	PAHs, PCBs, PBDEs	(Chen et al., 2018)
Coast	FTIR	UAE/ 90 min	100 mg	DCM/ 4 mL	UVSs, antioxidants	(Rani et al., 2017)
Coast	Near infrared spectroscopy	UAE / 1 h	1 g	Methanol	PFASs	(Llorca et al., 2014)
Coast	-	Vortex/ 1 min	30 mg	DCM/4 mL	HBCD	(Jang et al., 2017)

#### 4.4.5. Gas chromatography – MS

Gas chromatography coupled with mass spectrometry (GC-MS) is a separation technique that separates analytes based on their retention time and molecular mass. GC-MS is commonly used to analyze volatile environmental pollutants (Kennedy & Huang, 2003).

GC works by vaporizing the sample, with a carrier gas, into gaseous compounds. The most commonly used carrier gas is helium. The separation of the compounds depends on two factors: the polarity which is based on the interaction of the compounds with the stationary phase of the GC column and the boiling point which means the volatility. The time taken for the compound to reach the detector is called retention time.

The retention time and chromatogram of a certain compound at the same parameters and column used should be the same. However, in reality, RT could be slightly different. So, in order to facilitate the work and obtain more accurate results by GC-MS, relative retention index is used for a better qualitative study. The relative retention depends on the ratio of the partition coefficient of the compound. It is calculated after injecting n-alkanes

Different types of column are used for the separation. Previously, packed columns were used but nowadays capillary columns are used for a more efficient separation. They give higher resolution, shorter run time and a small sample volume. Different injection modes: split, splitless, pulsed splitless can be used (Kennedy & Huang, 2003).

Mass spectrometry has been used for detection in most of the studies. Table 4 shows different compounds sorbed on plastics analyzed by GC-MS.

Table 4 Studies using GC-MS to analyze different compounds

Origin of plastics	Plastic Characterization technique	Extraction technique/ time	Sample intake	Solvent used	Analyzed compound	references
Experimental	-	ASE	-	Acetone : Toluene	PAHs	(Kleinteich et al., 2018)
Coast	-	ASE/ 5 min	1 g	Hexane: acetone	PAHs	(Antunes et al., 2013)
		Soxhlet/17 h	1 g	Hexane	PCBs, DDT	
Coast	FTIR	ASE/ 5 min	2 g	Hexane: acetone	PAHs	(Frias et al., 2010)
		Soxhlet/17 h			PCBs, DDTs	
Experimental	-	Maceration	2 g	Cyclohexane	Phenanthrene, tonalide, benzophenone	(Seidensticker et al., 2017)
Coast	-	Soaking	-	Hexane	Hopanes, PCBs, HCHs, DDTs, PAHs	(Mizukawa et al., 2013)
Coast	Near Infrared	Soaking	40 pellets	Hexane (100 mL)	PCBs	( Endo et al., 2013)
Beach	Near infrared	Soaking	-	Hexane	PCBs, DDE DDT,DDD,HCHs	(Heskett et al., 2012)
Experimental	-	Soxhlet/16 h	20 mg	Hexane :acetone	OPEs	(Chen et al., 2019)
Coast	ATR-FTIR	Soxhlet/16 h	0.01-0.5 g	Dichloromethane	OPEs, PAHs	( Zhang et al., 2018)
Coast	-	Soxhlet/8 h	1 g	DCM	PAHs	(Fisner et al., 2013)
Coast& Water surface / Neuston net	Near Infrared spectrometer	Soxhlet/18 h	-	DCM/150 mL	PCBs, DDTs, PAHs, PBDEs, Alkylphenols, BPA	(Hirai et al., 2011)
Surface water/ Hand net& Manta trawl	-	Soxhlet/24 h	1 g	DCM/150 mL	PCBs, PAHs, OCPs	(Rios et al., 2010)
Water surface and coast	FTIR	Soxhlet/12hours	1-2 g	Dichloromethane/ 150 mL	PCBs, PAHs, DDTs, pesticides	(Rios et al., 2007)
Water surface/ Plankton net	Micro-FTIR	UAE/ 10 min	2-3 g	Hexane/15 mL	PAHs	(Tan et al., 2019)
Coast	FTIR/Calorimetry	UAE/60 min	-	Cyclohexane: ethyl acetate/5 mL	OCPs, PCBs,PAHs, PBDEs, OPFRs	(Camacho et al., 2019)

Water surface/ Manta trawl	-	UAE/90 min	-	Hexane/20 mL	PAHs	(Mai et al., 2018)
Coast	-	UAE/ 60 min	1 g	Acetone :Hexane/10 mL	PAHs, PCBs, DDTs, Chlordanes	(Van et al., 2012)
Experimental	-	Wash	-	Hexane, Dichloromethane	PHCHs	(Qiu et al., 2019)
Water surface/ Manta trawls	ATR-FTIR	Soxhlet	-	Pentane : Dichloromethane	PAHs,PCBs,PBDEs	(Chen et al., 2018)

#### 4.4.6. Liquid extraction surface analysis-MS

Liquid extraction surface analysis mass spectrometry (LESA-MS) is a relatively novel, direct analysis technique. It was developed in 2010 by the Van Berkel group (Kertesz & Van Berkel, 2010). This technique is commercially available using a Triversa Nanomate from Advion (Ithaca, NY).

LESA-MS works using a robotic system, allowing the infusion by nanoelectrospray, of samples dissolved in solvents. The principle of the LESA-MS is shown in Fig. 26. The sample is placed on a plate. A micropipette sucks solvent from a solvent reservoir. The robot places then the pipette tip above the preselected sample position and drops the solvent to direct contact with the sample to extract it by creating a junction between the solvent droplet and the sample. The solvent with the extracted analytes is then retracted into the pipette tip and is finally delivered to a nano-ESI chip, to be analyzed by mass spectrometry.

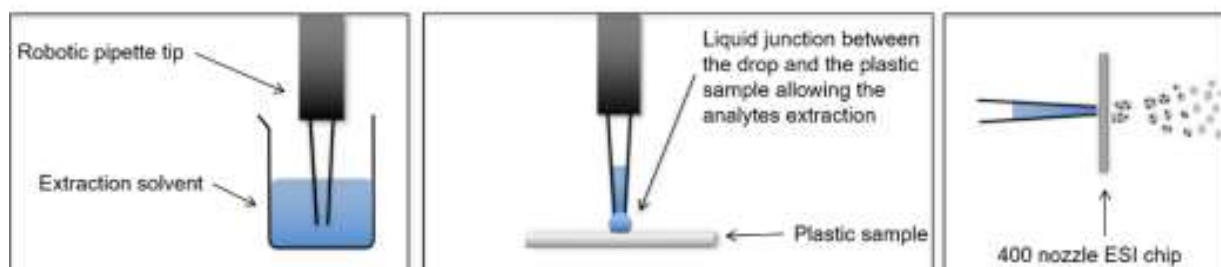


Figure 26 LESA-MS general principle (Issart et al., 2019)

The nano-ESI chip is a microfluidic silicon chip that is made of 400 nozzles. Those nozzles create an electrical field that leads to a good ionization with a stable spray. Thereby a very low solvent volume can be sprayed for more than 15 min.

This technique is a rapid, direct analysis method suitable for surface analysis. It is a green method that uses negligible volumes of solvents and doesn't require lengthy sample preparation procedures. This technique was applied in biological samples to study lipids, proteins, drugs, and carbohydrates, and was recently started to get applied in polymer sciences (Issart et al., 2019).

#### 4.5. Determination of metals by inductively coupled plasma – mass spectrometry (ICP MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique used for elemental and isotopic analysis, which provides information on the total metal content in a sample. It is a widely used technique in environmental studies allowing an accurate quantification of elements present in seawater, sediments and microplastics. ICP-MS is a powerful technique that analyzes most of the elements of the periodic table.

Typically, a liquid sample is delivered to the ICP-MS as an aerosol by passing through a pneumatic nebulizer under the effect of a carrier argon gas. Solid samples require a sample preparation step prior to analysis such as acid digestion in the case of metal analysis from microplastics.

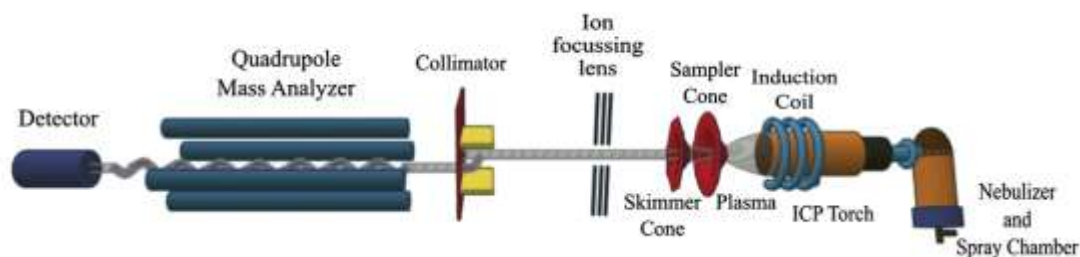


Figure 27 ICP-MS general equipment (Nageswaran, et al. 2017)

An ICP mass spectrometer consists of several parts (Fig.27):

**Sample introduction:** Liquid samples are transformed into an aerosol by pneumatic nebulization. The small droplets are directed into the central channel of the argon plasma and the larger aerosol droplets are removed by a spray chamber.

**Ion generation:** The aerosol droplets enter the plasma by the help of an argon flow contained in the torch (made from quartz). The quartz tube is located inside a copper coil through which a high frequency electric current passes and creates an intense magnetic field that causes collisions between argon atoms and the free atoms and produces ions and electrons until the formation of a high temperature and stable plasma. The aerosol droplets rapidly dry, are decomposed and vaporized and finally ionized.

**Plasma vacuum interface:** The ions formed in the plasma enter the vacuum through a pair of metallic cones.

**Ion focusing:** electrostatic lenses have the role of directing the ions as a compact ion beam, through the vacuum system to the mass spectrometer and the detector. The lenses have also an essential role in separating the ions from photons and other material.

**Mass spectrometer:** different types of mass analyzers are used with ICP-MS: quadrupole, time of flight and magnetic sector. The most used one is the quadrupole, which uses a combination of direct current and alternating current that separates ions based on their mass-to-charge ratio. Spectrum interpretation is simple because the  $m/z$  ratio is equal to the mass of a monocharged ion (Nageswaran et al., 2017).

Table 5 shows a number of publications where microplastics were analyzed for their metal content by ICP-MS. Those studies are model experimental studies where microplastics were soaked with metals and then analyzed or environmental studies such as (Catrouillet et al., 2021).

Table 5 Elemental analysis in microplastics by ICP-MS

Origin of plastics	Plastic Characterization technique	Sample preparation	Analyzed elements	references
Sediments	FTIR	Acid leaching & ultrawave digestion	Zn, Ba, Fe, Cu, Pb, Cd, Mn, Ni, Cr, As, V	(Catrouillet et al., 2021)
Sediments /Experimental	FTIR	Acid leaching	Cr, Co, Ni, Cu, Cd, Pb	(Holmes et al., 2012)
Sediments/ Experimental	FTIR		Cd, Co, Cr, Cu, Ni, Pb	(Holmes et al., 2014)
Sediments	-	Acid leaching	Al, Cr, Mg, Fe, Co, Ni, Zn, Cd, Pb	(Rochman et al., 2014)

Experimental	-	-	Si, Al, Fe, Mg, Cr and Ni	(Kedzierski et al., 2018)
Sediments	FTIR	Acid leaching	Ag, Cd, Co, Mo, Sn, Sb, U	(Ashton et al., 2010)
Sediments	Raman	Microwave digestion	Cr, Ni, Cu, Zn, Pb, As, Cd, Hg	(Deng et al., 2020)
Surface water/sediments	ATR-FTIR	Acid leaching	As, Cd, Cr, Cu, Ni, Pb, Zn	(Sarkar et al., 2021)
Sediments	$\mu$ -FTIR	Ultrasonic cleaning	Ni, Cd, Pb, Cu, Zn, Ti	(Wang et al., 2017)
Sediments	$\mu$ -FTIR	Microwave digestion	Cd, As, Cr, Zn, Cu, Ni, Pb, Mn, Fe, Al	(Xie et al., 2021)



## 5. Goals and objectives of the Project

The presence of microplastics on the Lebanese coast was first documented in 1977 (Shiber, 1979). However, since then, only few and recent studies were conducted in order to identify and classify microplastics. First, a study by Kazour *et al.* (Kazour et al., 2019), where microplastics were sampled from water surface and sediments, along the Lebanese coast. Water was found to be most contaminated in Sidon (Tyr), approximately 7 microplastics/m<sup>3</sup> while the highest microplastics contamination of sediments was observed in Tripoli approximately 5 microplastics/g. The second study published in 2021 by (Jemaa et al., 2021) was conducted to understand the spatio-temporal variation of macro and microplastics in the Lebanese coast and to determine the sources of pollution. It investigated the characteristics of plastic pollution in sea surface during the dry and wet season in different sites in Tyr and Beirut region. The results showed that the average concentration of MPs found were  $20.1 \pm 21.8$  and  $3.78 \pm 5.2$  MPs/m<sup>3</sup> in spring and fall respectively. The plastics visualized were mostly fragments and filaments. They classified MPs by color and the most dominant color was blue followed by black and white. They took a random subsample that represents 1% of the totality, 4 types of polymer were found, PE, PS, PP and PA. PP was the most abundant (48.5%) and only few particles of PA were found, representing 1.5% of the samples. The pollution load index showed a moderate contamination on the Lebanese coast except for several sites in Beirut.

None of these studies, however, discussed the role of microplastics as vectors of environmental pollution. Moreover, to our best knowledge this topic has not been addressed not only in Lebanon but has hardly been addressed in the entire Mediterranean Sea. Indeed, most to date studies concerned the north Atlantic and Pacific regions, and only one particular class of organic pollutants was usually addressed in each of the studies (Antunes et al., 2013; Frias et al., 2010). Beside organic pollutants, studies were conducted to inspect metal contents in plastics (Liu et al., 2022) and few tried to theoretically discriminate between sources of metals, that are either coming from microplastics additives or sorbed from the surrounding system (Catrouillet et al., 2021).

The goal of this study was to investigate for the first time the potential role of microplastics as vectors of the pollutants at the Lebanese coast, using different analytical approaches to cover different types of contaminants, organic and inorganic.

The objectives of this thesis included:

- i) Sampling of subsets of plastics from the Lebanese coast, and the identification of the microplastics fraction,
- ii) A non-targeted screening of weakly polar compounds present in microplastics by GC-TOF-MS. This should allow the identification of the most interesting target contaminants and/or pollutants for their subsequent quantification,
- iii) A non-targeted screening of polar compounds in plastics extracts by HPLC data-dependent MS2 allowing the selection of targets for the subsequent quantification by multiple reaction monitoring MS/MS
- iv) Investigation of the potential of development of integrated surface extraction and mass spectrometry by LESA-MS
- v) Elemental analysis by ICP MS in order to determine the total metal concentrations of metals in plastics and discussion of their putative origin.



## II. Experimental Part



## 6. Sampling

### 6.1. Plastics samples

Samples were collected from October 2020 to August 2021 from 14 different beaches on the Lebanese coast between Arida (S1) and Adloun (S14) with a total of 21 microplastic batches of samples. Samples were collected from shorelines of sandy beaches (except for Amshit (S6) where plastics were collected by hand net from the sea surface). Three random quadrats of 50 cm were chosen from each site and the first few centimeters of sands were sieved on site. The material collected was transported to the laboratory in glass jars and wet samples were dried at room temperature to be separated from other marine litter, sand, and organic matter. The primary identification of microplastics was done by visual observation and they were separated from coarse sand particles by forceps and preserved in the freezer until further analysis. The size of particles considered in this research was comprised of 0.2 mm to 5 mm.



Figure 28 Microplastics sampling points along the Lebanese coast

In some sampling points, plastic particles were sorted as polyethylene (PE) or polypropylene (PP) using attenuated total reflection (ATR) infrared spectroscopy. In other cases, the bulk sample of microplastics was employed for analysis.

Also, a number of plastic litter was identified for their polymer type to have a general look at the most commonly found plastic types on the Lebanese coast. Fig. 28 shows the different sampling points, and Table 6 compiles sampling dates and coordinates of each of the samples considered in the current research.

Table 6 Microplastics sampling points and their coordinates

Site code	Sampling site	Geographical coordinates	Sampling date
S1	Arida	34°33'47.04"N 35°59'33.09"E	10/08/2021
S2	Menye	34°29'3.95"N 35°55'28.42"E	10/08/2021 12/11/2020
S3	Tripoli 1	34°26'50.06"N 35°48'39.35"E	03/06/2021 10/08/2021
S4	Tripoli 2	34°25'44.76"N 35°48'52.67"E	03/06/2021
S5	Shekka	34°18'32.75"N 35°42'49.12"E	12/11/2020
S6	Amshit	34° 8'4.23"N 35°38'30.41"E	12/11/2020 20/10/2020
S7	Jbeil	34° 6'57.69"N 35°38'51.12"E	03/06/2021 13/11/2020
S8	Ramle	33°52'43.45"N 35°28'46.98"E	08/06/2021 23/08/2021
S9	Khalde	33°47'5.75"N 35°28'29.91"E	13/11/2020
S10	Saida	33°34'42.86"N 35°22'57.51"E	10/11/2020 08/06/2021
S11	Sour A	33°15'52.96"N 35°12'14.90"E	10/11/2020 08/06/2021
S12	Sour B	33°15'35.64"N 35°12'32.04"E	08/06/2021
S13	Sarafand	33°28'3.46"N 35°18'11.96"E	10/11/2020
S14	Adloun	33°24'46.57"N 35°16'1.20"E	10/11/2020

Initially, the idea was to collect microplastics from the water surface by the Manta trawl and deep-sea sediments by a grabber. The sampling was done at different points along the Lebanese coast, from North to South at the end of 2019 and 2020. The sediments were collected by a van-Veen grab from the scientific vessel the NCMS (CANa). The sea surface microplastics were collected on board of a catamaran and a zodiac inflatable boat. The manta net was deployed on the side of the boat to avoid the turbulence coming from the motor of the boat. In each different area, three different samples were taken by dragging the manta nets for 20 min in transects parallel to the shore, going from shallow water to deep sea. Fig. 29 shows pictures of small sized microplastics after filtration taken using on a stereomicroscope.

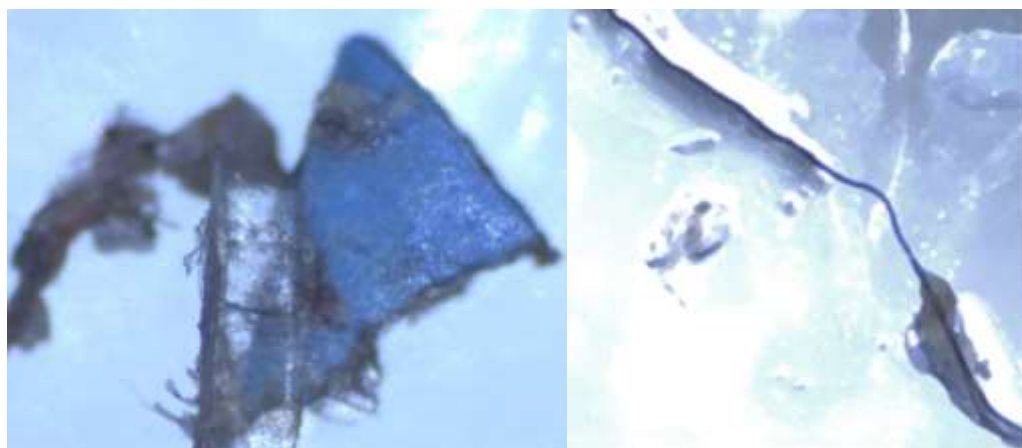


Figure 29 MP fragment (left) &amp; MP fiber under a stereomicroscope

However, only a few plastic particles with small size were recovered, and their amount was insufficient for the chemical analysis. Therefore, the material collected in this way was not used for analysis. Consequently, only shoreline plastics were investigated in this study.

The plastic debris coming from the sea formed a band from which microplastics were sampled. The sampling sites are chosen to cover all of the Lebanese coast and the sites are chosen to be sandy beaches and visually contain small-sized plastics. Samples were taken from the same sites on different months but not in every month microplastics were available. Only sites where microplastics could be sampled are mentioned table 6.

Note that the sampling approach was delayed due to Covid lockdown and the port of Beirut explosion but finally it could take place in October 2020. Few months before the second sampling campaign, there was an oil spill from neighboring country and most of the beaches along the shore were cleaned. This may be a cause of the decrease of the number of samples in June and August 2021.

## 6.2. Water samples

Water was sampled from some sites along the Lebanese coast in order to screen them for polar compounds by LC-MS/MS. 1 L of seawater was collected from each site in glass bottles in August 2021 and were transported in cold containers. The sampling points are shown in red in Fig 28 and their details are mentioned in table 7.

Table 7 Water samples collected (August 2021)

Site code	Sampling site	Geographical coordinates	Sampling date
<b>W1 (S1)</b>	Arida	34°33'47.04"N 35°59'33.09"E	10/08/2021
<b>W2 (S2)</b>	Menye	34°29'3.95"N 35°55'28.42"E	10/08/2021
<b>W3 (S3)</b>	Tripoli 1	34°26'50.06"N 35°48'39.35"E	10/08/2021
<b>W4 (S5)</b>	Shekka	34°18'32.75"N 35°42'49.12"E	10/08/2021
<b>W5</b>	Bouar	34° 2'47.94"N 35°37'52.68"E	17/08/2021
<b>W6</b>	Jounieh 1	34° 0'40.72"N 35°38'37.90"E	17/08/2021
<b>W7</b>	Jounieh 2	33°59'0.10"N 35°37'36.37"E	17/08/2021
<b>W8 (S8)</b>	Ramle	33°52'43.45"N 35°28'46.98"E	23/08/2021
<b>W9</b>	Ouzai	33°50'49.64"N 35°28'59.43"E	23/08/2021
<b>W10 (S9)</b>	Khalde	33°47'5.75"N 35°28'29.91"E	23/08/2021

## 7. Materials

### 7.1. Standards

For the analysis of polar organic compounds, 19 standards of pesticides and pharmaceuticals were purchased (Table 8). Except for cannabidivarin, bought as a solution, suitable solvents were used to make stock solutions of the standards. All the standards were purchased from Sigma-Aldrich with exception of pyrimethanil, pyrethrin, and the three testosterone standards from LGC standards.

For the non-polar compounds study, Standards of 2, 4, 6-trichloro biphenyl (PCB-30), phenanthrene d-10 (PHE-d<sub>10</sub>) and chlorpyrifos d-10 (CHL-d<sub>10</sub>) were obtained from Sigma Aldrich (St. Louis, MO). A solution of n-alkanes (C<sub>8</sub>-C<sub>40</sub>) in dichloromethane was purchased from Supelco (Bellefonte, PA). All other standards were mainly bought from Sigma-Aldrich and dissolved in Isooctane. The list of standards of the compounds are shown with their CAS number in Tables 18 and 19 in results section.

Monoelemental and multielemental standard solutions of 1000 mg L<sup>-1</sup> of the different metals were purchased from Plasma CAL standards (Teddington, UK).

For LESA, organic pollutants standards used were the same as the standards used for LC-MS analysis (chlorpyrifos, minoxidil, ketoprofen, diazinon, pyrimethanil, naphthalene acetamide, tripeleennamine, pyroquilon and phenacetin).

All standards and stock solutions should be kept at low temperatures between usages.

Table 8 Standards used for LC-MS & LESA-MS analysis

Standard	Molecular Formula	Molecular weight	CAS number	Dissolution solvent
Minoxidil	C <sub>9</sub> H <sub>15</sub> N <sub>5</sub> O	209.25	38304-91-5	Methanol
Nicotine	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub>	162.23	54-11-5	Methanol
Testosterone Cypionate	C <sub>27</sub> H <sub>40</sub> O <sub>3</sub>	412.60	58-20-8	Methanol
Testosterone Decanoate	C <sub>29</sub> H <sub>46</sub> O <sub>3</sub>	442.67	5721-91-5	Methanol
Testosterone Undecanoate	C <sub>30</sub> H <sub>48</sub> O <sub>3</sub>	456.70	5949-44-0	Methanol
Tridemorph	C <sub>19</sub> H <sub>39</sub> NO	297.52	24602-86-6	Methanol
Tripeleennamine	C <sub>16</sub> H <sub>21</sub> N <sub>3</sub>	291.82	154-69-8	Methanol
Norfenefrine	C <sub>8</sub> H <sub>11</sub> NO <sub>2</sub>	189.64	4779-94-6	Methanol
Pyrimethanil	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub>	199.25	53112-28-0	Methanol
Pyrethrins	C <sub>22</sub> H <sub>28</sub> O <sub>5</sub>	700.90	8003-34-7	Methanol
Diazinon	C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> PS	304.35	333-41-5	Methanol
Chlorpyrifos	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS	350.59	2921-88-2	Methanol
Phenacetin	C <sub>10</sub> H <sub>13</sub> NO <sub>2</sub>	179.22	62-44-2	Acetonitrile
Guaifenesin	C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>	198.22	93-14-1	Methanol
Menadione	C <sub>11</sub> H <sub>8</sub> O <sub>2</sub>	172.18	58-27-5	Methanol



Ketoprofen	C <sub>16</sub> H <sub>14</sub> O <sub>3</sub>	254.28	22071-15-4	Methanol
Naphthalene acetamide	C <sub>12</sub> H <sub>11</sub> NO	185.22	86-86-2	Acetone
Pyroquilon	C <sub>11</sub> H <sub>11</sub> NO	173.21	57369-32-1	Methanol
Cannabidivarin	C <sub>19</sub> H <sub>26</sub> O <sub>2</sub>	286.41	24274-48-4	Methanol

### 7.2. Solvents, acids, eluents

- LC-MS CHROMASOLV Hypergrade Acetonitrile, Sigma-Aldrich (Darmstadt, Germany)
- LC-MS CHROMASOLV Hypergrade Methanol, Sigma-Aldrich (Darmstadt, Germany)
- HPLC purity CHROMASOLV Acetone, Sigma-Aldrich
- Ultrapure (Type 1) water from a Direct-Q water purification system (18.2 MΩ / cm)
- High purity Formic acid (HCOOH), Optima LC/MS (Fisher scientific, USA)
- Dichloromethane HPLC Plus, For HPLC, GC, and residue analysis > 99.9%, containing 50-150 ppm amylene as a stabilizer From Sigma-Aldrich-For extraction
- n-Hexane reagent grade > 99%
- 2,2,4- Trimethylpentane (Isooctane) HPLC Plus, For HPLC, GC, and residue analysis > 99.5% From Sigma-Aldrich
- Ethyl acetate HPLC Plus, For HPLC, GC, and residue analysis > 99.9%, From Sigma Aldrich
- HPLC grade chloroform, Sigma-Aldrich (Darmstadt, Germany)
- Trace metal grade conc. nitric acid (67-70%) (SEASTAR CHEMICALS ULC, Canada)

### 7.3. Laboratory equipment

- Milli-Q water system (Ultrapure(type 1) water, Direct-Q-R 3 UV, France)
- Metler Toledo X 5105 Dual Range analytical balance (France)
- Orbital shaker (MS-Reciprocal shaker, Major Science, California)
- Microwave digester (Ultrasound Milestone, Shelton, CT)
- Centrifuge (5804R-Eppendorf, Hamburg, Germany)
- Rotary evaporator (Genavac, SP Scientific, England)
- pH meter from (Metler Toledo 7 compact pH meter, France)
- Ultrasound bath (Bandelin sonorex, Bandelin Electrical, Germany)
- Vortex-Genie 2 (Scientific Industries, France)

### 7.4. Glassware and general consumables

- 40 mL glass tubes
- 4 mL,10 mL amber glass vials
- 60 mL glass tubes for the evaporator
- 1.5 mL HPLC vials
- Glass inserts for 1 mL vials
- Glass beakers
- 500 mL , 1 L glass bottles
- Eppendorf Research plus pipette (0.5-5 mL) (Calibrated)
- Eppendorf Research plus pipette (100-1000 µL) (Calibrated)
- Eppendorf Research plus pipette (10-100 µL) (Calibrated)

- Eppendorf Research plus pipette (0.5-10  $\mu$ L) (Calibrated)
- Eppendorf Research plus pipette (0.1-2.5  $\mu$ L) (Calibrated)
- Volumetric flasks 10,25 mL
- Volumetric cylinders 100,250,500 mL
- 1.5 mL Eppendorf micro-centrifuge tubes
- Whatman 0.45  $\mu$ m glass fiber filters
- Glass vacuum filter device with holder for 47 mm filters
- Atlantic Discs C18 of 47 mm diameter from Biotage (Uppsala, Sweden)
- 5 mL B.Braun inject syringes
- Stainless steel tweezers
- Microwave glass tubes
- 50 mL plastic tubes
- 5 mL plastic tubes
- Graduated cylinder
- Separatory funnel

## 8. Instrumentation

### 8.1. Attenuated total reflectance-Infrared (ATR-IR) spectroscopy

In this study, an Agilent Cary 630 FTIR spectrometer was used to collect spectra from  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . The resolution was set to  $4\text{ cm}^{-1}$ . Samples were placed on a ZnSe crystal and pressed very well trying to fix only flat surfaces.



Figure 30 Agilent ATR-FTIR

### 8.2. Liquid Chromatography-tandem mass spectrometry (LC-MS/MS)

High-resolution mass spectrometry was used for the screening of non-volatile compounds and for the targeted approach afterward. A Thermo Fisher Scientific Q Exactive Plus mass spectrometer was used. Separation of compounds was performed by a Thermo Fisher Scientific Ultimate 3000 Rapid Separation LC pump. Data analysis for the detection, identification, and quantification of the compounds were performed using Xcalibur, Trace finder, and Compound discoverer software.



Figure 31 Quadrupole-Orbitrap Qexactive plus

### 8.3. Gas chromatography - mass spectrometry (GC-MS)

Volatile and semi-volatile compounds in plastic extracts were determined by GC-MS using a quadrupole time-of-flight (QTOF) type instrument, equipped with an electron ionization (EI) source, acquired from Agilent (Wilmington, DE). The GC-QTOF-MS system consisted of a 7890A gas chromatograph connected to a 7200 QTOF mass spectrometer.

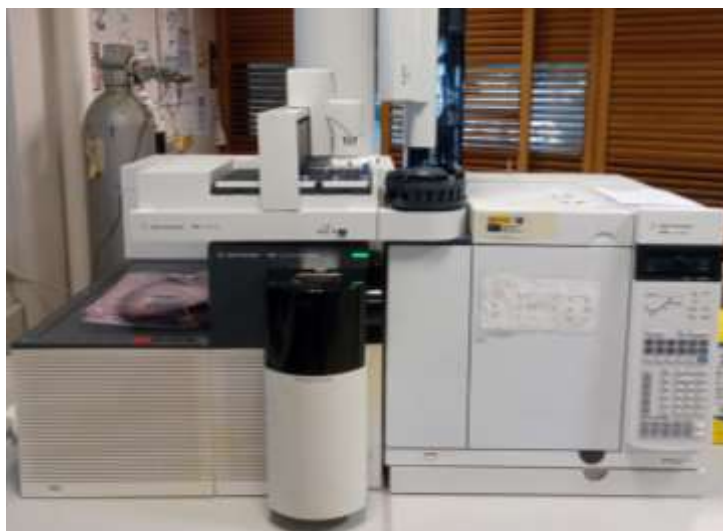


Figure 32 GC-Q-TOF-MS from Agilent

### 8.4. Inductively coupled plasma - mass spectrometry (ICP-MS)

An Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS) (Agilent, Tokyo, Japan) equipped with a collision cell with hydrogen/helium as collision gas, was used throughout the study. The sample introduction system consisted of a concentric nebulizer and a Scott spray chamber.



Figure 33 Agilent 7900 ICP-MS

### 8.5. Liquid extraction surface analysis- Mass spectrometry (LESA-MS)

A Triversa Nanomate from Advion was used, coupled with a high-resolution Thermo Fisher Scientific Orbitrap Fusion Lumos Tribid mass spectrometer. The nano-mate is operated by Chipsoft 8.3.1 software and the data analysis for the detection of found compounds was performed using Xcalibur for targeted compounds and Mass Frontier to compare fragmented compounds against a database as an untargeted approach.

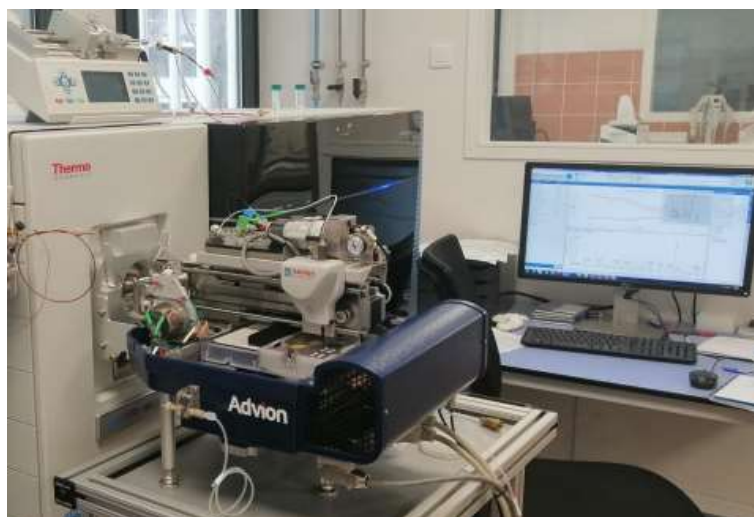


Figure 34 Triversa nanomate- Advion coupled with Orbitrap Fusion Lumos Tribid

## 9. Sample preparation procedures

### 9.1. Recovery of pollutants from microplastics

#### 9.1.1. For LC-MS/MS analysis

A sample of 1 g of microplastics was weighed, washed for a few seconds with water and put in amber glass vials. 6 mL of the mixture of solvents was added and the samples were put in an ultrasound bath for 30 min at 50 °C and then kept shaking on a rotator for 24 h. After 24 h, the extracts were moved to another tube and the extraction procedure was repeated 2 more times using the same mixture of solvents. After 72 h, the total volume of solvents is 18 mL. Before analyzing the extracts on LC-MS/MS, a preconcentration step should be done. Extracts were preconcentrated by rotary evaporation to 1 mL. Extracts are preserved in the freezer until chemical analysis. Before LC-MS extracts are diluted with the aquatic phase and centrifuged at 1000 rpm for 10 min and ready to be injected.

After extraction, and before the evaporation step, a filtration was attempted. However, as it added a very high background noise, it was not applied. The extracts were centrifuged to eliminate any particulate matter.

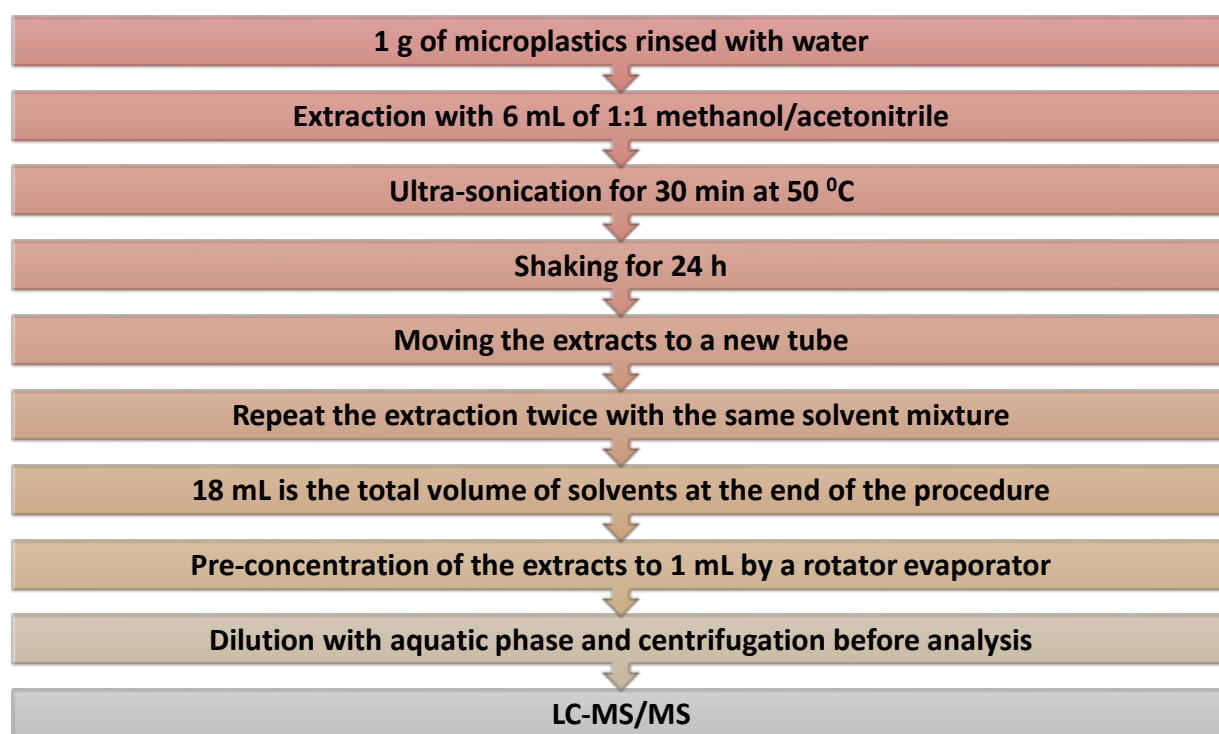


Figure 35 Workflow of the extraction of polar organic compounds

#### 9.1.2. For GC-MS analysis

Samples (1 g), spiked with PCB-30, PHE-d<sub>10</sub>, and CHL-d<sub>10</sub>, were extracted twice using 6 mL of a 1:1 mixture of n-hexane: dichloromethane for 24 h (following a step of ultra-sonication at 35<sup>o</sup> C at the beginning of the process), under using a mechanic shaking, followed by a third extraction with the same volume of isoctane. The combined extract was filtered using 0.45 μm glass microfiber syringe filters, evaporated to dryness, using a rotavapor concentrator, and reconstituted with 1 mL of isoctane. Before GC-MS analysis, extracts were re-filtered using a 0.22 μm pore size syringe filter.

Standards of 2,4,6-trichloro biphenyl (PCB-30), phenanthrene d-10 (PHE-d<sub>10</sub>) and chlorpyrifos d-10 (CHL-d<sub>10</sub>) were added to plastic samples (100 ng g<sup>-1</sup> for the deuterated species and 200 ng g<sup>-1</sup> in case of PCB-30) at

the beginning of the sample preparation procedure. They were employed to check, either the performance of the data mining algorithm (PCB-30), or as surrogate standards (SSs) of halogenated (CHL-d<sub>10</sub>) and non-halogenated compounds (PHE-d<sub>10</sub>) to estimate their concentrations in the final extract obtained from processed samples. A solution of n-alkanes (C<sub>8</sub>-C<sub>40</sub>) in dichloromethane was purchased from Supelco (Bellefonte, PA). A commercial stock (200 µg mL<sup>-1</sup> per compound) was diluted with dichloromethane to a concentration of 1 µg mL<sup>-1</sup> and injected in the GC-MS system under the same conditions as sample extracts. Retention times of the mixture of alkanes were employed to calculate the linear retention index (LRI) of every compound identified in sample extracts. This information was used to assist the identification process.

### 9.1.3. For ICP analysis

For microwave digestion, a sample of 200 - 300 mg of microplastics were weighed and 5 mL of conc. HNO<sub>3</sub> was added. The Milestone Ultrawave works by exposing samples to high temperature and pressure under a flow of nitrogen gas, and leads to a total digestion of microplastics. An adjusted mode for the digestion of polymers was used, it is a multistep procedure, 110 °C for 10 min, 180 °C for 10 min, 230 °C for 20 min and 230 °C for 5 min.

Each run included 15 samples, from each site three replicates were digested and blanks were included in every run. After the digestion, digests were diluted 10 times with water and kept at 4° before analysis by ICP-MS.



Figure 36 Samples after acid digestion

### 9.2. Solid-phase extraction for LC-MS/MS of seawater samples

To see the availability of polar pollutants in seawater, 10 water samples were collected from beaches across the Lebanese coast. A 1L of sample was filtered within 12 h through a 47 mm Atlantis SPE disk under vacuum. Thereafter, the retained compounds were eluted with 40 mL of methanol. The eluates were kept at 4 °C until their transfer to IPREM. They were preconcentrated using a rotary evaporator and kept at 4°C until analysis.



Figure 37 Glass vacuum filter device for SPE



## 10. Analytical procedures and experimental conditions

### 10.1. Identification of microplastics by attenuated total reflectance – infrared spectroscopy

To have a global view of plastic litter found on the Lebanese coast, a subset of 2133 plastics was identified for their polymeric composition using an Agilent Cary 630 FTIR spectrometer. Plastics were chosen from different areas, sizes, and visual appearances. Macroplastics, mesoplastics, and microplastics were identified.

ATR-FTIR is a non-destructive, quick, and cost-effective method that can be used for different types of samples and can be used to identify small microplastics down to less than 0.5 mm in size as observed in this analysis.

Spectra were collected from 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ . The resolution was set to 4  $\text{cm}^{-1}$ . Samples were placed on a ZnSe crystal and pressed to constitute a flat surface. The crystal was cleaned with 70 % ethanol between each sample, and a background scan was also done between each scan. Every sample was scanned 3 times to be sure of its identification. Spectra were obtained using MicroLab software and compared with spectra from literature (Jung et al., 2018). No library or plastic standards were used to identify plastics. The polymer positive identification was confirmed based on the presence of 4 minimum absorption bands.

In the case of S3 (Tripoli 1) dozens of grams of microplastics were collected. It was used as a reference to see the difference between the adsorption effect of secondary microplastics (microplastics resulting from fragmentation of bigger plastics) and primary microplastics (pellets). Each type was then used as a whole sample for the extraction procedure. S3 (Tripoli 1) was sampled in November 2020, June 2021 and August 2021.

### 10.2. Analysis of polar organic compounds by electrospray MS/MS

#### 10.2.1. Untargeted screening and choice of putative contaminants

Untargeted screening of microplastic extracts for the presence of contaminants was done by LC-MS/MS using a Q Exactive Plus mass spectrometer operated in positive mode. Compounds separation was performed on a reverse-phase, C18 column ACQUITY UPLC HSS C18 SB 1.8  $\mu\text{m}$  (2.1 x 100 mm, Waters, Ireland). 50  $\mu\text{L}$  of extracts were injected. The mobile phases were 0.1 % Formic acid (solvent A) and 0.1 % formic acid in methanol (solvent B). The elution gradient was: 0 -2min (10 % B), 20 min (90 % B), and 25 min. (10 % B). The flow rate was 0.4 mL/min with 20  $\mu\text{L}$  injection volume, the column temperature was set at 40  $^{\circ}\text{C}$ .

A full MS and a data-dependent  $\text{MS}^2$  were done for the screening of untargeted compound. The choice of the method properties was done based on an in-house method used. The extracts were injected in positive ion mode and the run time was 27 min. The full MS was done at a resolution of 70 000, 3e6 AGC target, the scan range was from  $m/z$  170 to 1000 and the maximum injection time was 240 ms. The dd- $\text{MS}^2$  was done at 35,000 resolution, 1e5 AGC target and the maximum injection time was 150 ms. The five highest intensity eligible precursors (Top 5) were selected  $m/z$  isolation window of 1 and the fixed first mass was 60  $m/z$ . In  $\text{MS}^2$ , previously fragmented precursors were excluded for a minimum of 20 s (dynamic exclusion).

The data acquisition was done using Xcalibur software and the data processing by Trace Finder (version 4.1 General Quan) and Compound Discoverer (version 3.2) for a more exhaustive search. The workflow followed to identify compounds existing was as follows.

First, using Trace Finder, the results were compared against different databases, EFS-HRAM, toxicology-HRAM and an in house library. The choice of candidate species was done on the basis of a good chromatographic peak shape, the presence of at least 2 isotopes, and the number of fragments above 2 taking into account their intensity.

In a second time, data were treated on Compound Discoverer. Masses were compared with those in *m/z* cloud, ChemSpider, and with the in-house mass lists, 5 ppm was the maximum *m/z* error. The fragmented spectra were compared to those existing in the mzCloud database. The low FISh scoring (Fragment Ion Search) didn't always mean a false identification, the intensity of the largest fragments was taken into consideration before excluding the compound from the list. The match confidence level was set at a minimum of 70 %. The compounds found in blanks, the naturally found compounds such as amino acids, proteins and nucleic acids and the compounds used in the manufacturing of plastics were excluded from the list.

For the targeted approach, the separation was done on the same reverse-phase, C18 column ACQUITY UPLC HSS C18 SB 1.8 $\mu$ m (2.1 x 100 mm, Waters, Ireland). Extracts were diluted 5 times with the mobile phase A. The mobile phases are 0.1 % formic acid (solvent A) and 0.1% formic acid in methanol (solvent B). The elution gradient is mentioned in the table 9. The flow rate was 0.4 mL/min with 20  $\mu$ L injection volume, the column temperature was set at 40 °C.

For mass spectrometry, the detection was carried out in parallel reaction monitor (PRM): the instrument was operated in positive ionization mode, the scan range from 100 to 1500, the spray voltage was 3.8 kV and the capillary temperature 350 °C. The MS<sup>2</sup> parameters are: an AGC target of 1e5, resolution of 35,000, the maximum injection time is 110 ms, the isolation window is 2 *m/z* and the normalized collision energy is 35.

Table 9 The elution gradient of the mobile phases injection

Time (mins)	Flow (ml/min)	%A	%B
0	0.4	80	20
2	0.4	80	20
15	0.4	10	90
18	0.4	10	90
19	0.4	80	20
20	End of the Run		

### 10.2.2. Quantitative analyses

The quantification of the polar compounds in the extracts was carried out by comparison with solvent-based standards prepared in methanol except naphthalene dissolved in acetone and phenacetin with acetonitrile. The quantification was done using the most intense ion fragment.

Positive identification was based on the presence of fragments and exact retention times (within 0.1 min). Calibration curves were built in the range of 0.005 ng.mL<sup>-1</sup> to 2.5 ng.mL<sup>-1</sup> or 5 ng.mL<sup>-1</sup> depending on the compound. For chlorpyrifos the upper calibration curve point was 25 ng.mL<sup>-1</sup>. Linearity was good with a coefficient of regression R<sup>2</sup> above 0.99 for all of the compounds. To validate the method and see the effect or the absence of effect of the matrix on the retention time, samples were spiked by standards.

### 10.3. Analysis of non-polar organic compounds by GC-MS

#### 10.3.1. Identification of the pollutants

Volatile and semi-volatile compounds in plastics extracts were determined by GC-MS, equipped with an electron ionization (EI) source. During the study, the system was operated in the single MS mode, at 2 GHz, offering a typical mass resolution of 6,000 (calculated as FWHM) at  $m/z$  131. EI-MS spectra were recorded in the profile mode, in the range of masses comprised between 40 and 700 Da. Each spectrum was the combination of 5427 transients, with 4 spectra recorded every second. The mass axis of the TOF analyzer was re-calibrated every 4 injections using perfluorotributyl amine (PFTBA).

Compounds were separated in a HP-5MS capillary column (30 m x 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) acquired from Agilent. Helium was used as carrier gas at a constant flow of 1 mL  $\text{min}^{-1}$ . The temperature of the column was programmed as follows: 65  $^{\circ}\text{C}$  (1 min), rated at 5  $^{\circ}\text{C min}^{-1}$  to 290  $^{\circ}\text{C}$  (8 min). The injector was set at 250  $^{\circ}\text{C}$  and the transfer line at 280  $^{\circ}\text{C}$ . The EI source and the quadrupole were maintained at 230  $^{\circ}\text{C}$  and 150  $^{\circ}\text{C}$ , respectively. The injection volume was 1  $\mu\text{L}$ . The pulsed splitless injection mode (25 PSI for 1.1 min, splitless time 1 min) was used during identification of compounds existing in sample extracts, and to estimate the concentrations of minor compounds (ca. those below 500-1000 ng  $\text{mL}^{-1}$ ). Thereafter, extracts were re-injected in the split mode (split ratio 10) to quantify the species noticed at higher concentrations in some samples, which produced saturated spectra in the pulsed splitless mode.

Acquisition parameters in the GC-QTOF-MS instrument and data processing were controlled using different functions integrated in MassHunter software. In particular, spectral deconvolution was performed using the Unknowns Analysis (UA) function (based on the SureMass algorithm), integrated in MassHunter Quantitative package (version B.10.02). Same software package was used to quantify the concentrations of selected compounds and to calculate their concentrations in sample extracts. MassHunter Qualitative software package (version B.08.00) was employed to revise the exact  $m/z$  ratio of ions associated to a given chromatographic peak. In this case, the average spectrum above 10 % of maximum peak height was considered. For saturated ions, the region above 30 % of the saturation threshold was also excluded from the average spectrum.

Calculated  $m/z$  values for ions with known structures in the nominal resolution NIST17 EI-MS database were obtained using the NIST-MS interpreter tool integrated in the MS Search software (version 2.3).

The workflow followed to identify compounds existing in the extracts from microplastics was adapted from previous studies (G. Castro, Rodríguez, Ramil, & Cela, 2019; Cobo-Golpe, Ramil, Cela, & Rodríguez, 2020). In first term, deconvoluted spectra were compared with those existing in the NIST low-resolution database. The comparison algorithm considered a hybrid between forward and reversed search modes (with a 70% contribution of the 1<sup>st</sup> mode) to generate a normalized score (0-100) representing the fitting between the deconvoluted spectrum and those compiled in the NIST low-resolution database. This score was combined with LRI values to build a list of suspected species. Compounds with normalized scores above 70, and differences between experimental and NIST LRI values lower than 50 units (absolute difference) were considered as tentative identifications. Any compound without LRI values in the NIST database was excluded from this list, regardless of the normalized spectral match score.

In a second step, the spectra of tentative identifications were compared either with those existing either in a personal compound database (PCDL, acquired using the same GC-TOF-MS instrument) and with an EI-MS accurate database of pesticides provided by Agilent. Together, these databases contain spectra for around 700 compounds. In some cases, tentative identifications were confirmed by injection of candidates, whose spectra were added to those existing in the customized PCDL.

For those compounds not compiled in the available accurate EI-MS database, tentative identifications derived from LRI and spectral match against the NIST low resolution database, were re-evaluated by comparison of experimental and calculated  $m/z$  values.

Whatever the source of accurate  $m/z$  values (experimental or calculated), positive identifications were based on mass differences below 50 ppm for at least two intense ions, between deconvoluted and accurate database spectra. This error is reduced to 25 ppm when using raw spectra before deconvolution. LRI differences should remain below 50 units.

### 10.3.2. Quantitative analyses

Quantification of compounds in the extracts from microplastics was carried out by comparison with solvent-based standards prepared in isooctane. Peak areas for the quantification ion (Q1) of each compound (mass extraction window 25 ppm) were corrected with that obtained for the associated SS (PHE-d<sub>10</sub> and CHL-d<sub>10</sub> for no-halogenated and halogenated compounds, respectively) and compared with those obtained for standards prepared in isooctane. Positive identifications were based on retention times and qualification (Q2) to Q1 ratios maximum differences of 0.1 min and  $\pm 30\%$ , respectively. It is worth noting that quantification was performed using raw spectra instead of the deconvoluted ones, and that the mass extraction window (25 ppm) for Q1 and Q2 ions was narrow than the maximum error allowed during compounds identification using deconvoluted spectra. In case of compounds presenting large differences among their concentration levels among samples, two different calibration curve ranges were built. The first range (from instrumental LOQs to 500 ng mL<sup>-1</sup>, depending on the compound) was obtained using pulsed splitless injection. A second calibration curve was built in the range from 500 to 20,000 ng mL<sup>-1</sup> using split injection.

## 10.4. Liquid extraction surface analysis – mass spectrometry

### 10.4.1. Sample preparation

Sample preparation for LESA-MS is minimal, microplastics need only to be fixed on the sampling plate. The used plastics were polystyrene bought from Goodfellow, UK, and different collected environmental plastics.

Plastics were put in normal river water and kept from 48 to 72 hours as well. The compounds were added at different concentrations, going from 1 to 50 ppb. Two pieces of 5 mm polystyrene were put with 3 mL of water in amber glass vials and kept shaking in the dark for 72 h. Plastics were then taken and dried to be analyzed by LESA-MS. For the untargeted study, plastics collected from the coast and plastics that were soaked in polluted river water were analyzed to screen the present compounds.

The measurements were done in the positive ionization mode with a scan range from 150 to 1100  $m/z$  at a resolution of 240000.

## 10.5. Determination of metals by ICP MS

### 10.5.1. Sample preparation

As a preliminary evaluation for the metals present in the samples, digested samples were diluted and injected to inspect the elements found in the samples. After choosing the targeted elements, a multi-elemental standard was prepared to make calibration curves and quantify the 46 elements that were found in our first screening. To overcome the interference of some elements, hydrogen gas was used.

The targeted isotopes were the following:  ${}^7\text{Li}$ ,  ${}^{11}\text{B}$ ,  ${}^{47}\text{Ti}$ ,  ${}^{51}\text{V}$ ,  ${}^{52}\text{Cr}$  ( $\text{H}_2$ ),  ${}^{55}\text{Mn}$ ,  ${}^{57}\text{Fe}$ ,  ${}^{59}\text{Co}$ ,  ${}^{58}\text{Ni}$  and  ${}^{60}\text{Ni}$  ( $\text{H}_2$ ),  ${}^{63}\text{Cu}$  and  ${}^{65}\text{Cu}$  ( $\text{H}_2$ ),  ${}^{64}\text{Zn}$  and  ${}^{66}\text{Zn}$  ( $\text{H}_2$ ),  ${}^{75}\text{As}$ ,  ${}^{78}\text{Se}$  and  ${}^{80}\text{Se}$  ( $\text{H}_2$ ),  ${}^{89}\text{Y}$ ,  ${}^{95}\text{Mo}$ ,  ${}^{105}\text{Pd}$ ,  ${}^{107}\text{Ag}$  and  ${}^{109}\text{Ag}$ ,  ${}^{112}\text{Cd}$  and  ${}^{114}\text{Cd}$ ,  ${}^{118}\text{Sn}$  and  ${}^{120}\text{Sn}$ ,  ${}^{121}\text{Sb}$  and  ${}^{123}\text{Sb}$ ,  ${}^{133}\text{Cs}$ ,  ${}^{138}\text{Ba}$ ,  ${}^{178}\text{Hf}$ ,  ${}^{182}\text{W}$ ,  ${}^{195}\text{Pt}$ ,  ${}^{197}\text{Au}$ ,  ${}^{201}\text{Hg}$  and  ${}^{202}\text{Hg}$ ,  ${}^{205}\text{Tl}$ ,  ${}^{206}\text{Pb}$  and  ${}^{208}\text{Pb}$ ,  ${}^{209}\text{Bi}$ ,  ${}^{139}\text{La}$ ,  ${}^{140}\text{Ce}$ ,  ${}^{141}\text{Pr}$ ,  ${}^{146}\text{Nd}$ ,  ${}^{147}\text{Sm}$ ,  ${}^{153}\text{Eu}$ ,  ${}^{157}\text{Gd}$  and  ${}^{158}\text{Gd}$ ,  ${}^{159}\text{Tb}$ ,  ${}^{163}\text{Dy}$ ,  ${}^{165}\text{Ho}$ ,  ${}^{166}\text{Er}$ ,  ${}^{169}\text{Tm}$ ,  ${}^{172}\text{Yb}$ ,  ${}^{175}\text{Lu}$ ,  ${}^{232}\text{Th}$ , and  ${}^{238}\text{U}$ .

#### 10.5.2. Quantitative analyses

A multi-elemental calibration curve was prepared daily. Calibration curves were built in the range of  $0.1 \text{ ng.mL}^{-1}$  to  $20 \text{ ng.mL}^{-1}$ . Linearity was good with a coefficient of correlation  $R^2$  above 0.99. Samples were diluted 100 times and thousand times based on the level of presence of the elements.



### III. Results and discussion





## 11.Characteristics of microplastics sampled on the Lebanese coast

### 11.1. Size, shape and color

Plastics found on the shoreline were of different sizes. Macroplastics, mesoplastics and microplastics of different forms and colors were collected from shorelines. Plastics found on beaches are affected by tides and environmental conditions and water movements. In the same site plastics may not have been present in different months; this was due to waves covering the line formed by plastics on beaches during the sampling time or due to water movements resulting in plastics not to be washed out on the beach in this particular time and area. Also, the absence of plastics in some sampling sites during 2021 can be attributed to the cleaning of beaches due to a previous oil spill.

Microplastics can be categorized into fragments, pellets, films, foams and fibers. Samples from all the sites showed a dominance of plastic fragments followed by pre-production pellets especially in S3 (Tripoli 1) where the presence of a massive amount of pellets was observed.

Floating plastics from S6 (Amshit) were mainly PE plastic bags and fragments of PS cups. In the other sites, there were plastics of different shape and size observed. Fishing nets and microplastics of few micrometers were found. The presence of plastics fragments shows that the rate of degraded of large plastics is significant. Concerning the pellets, they are considered as raw material used for plastic production. They either come from plastics processing plants next to the sampling site or they are transported from far distances by water movements, coming from other places or less likely from accident of ships containing pellets. Figure 38 shows different sizes, types, colors, and shapes of plastics collected from Adloun beach.

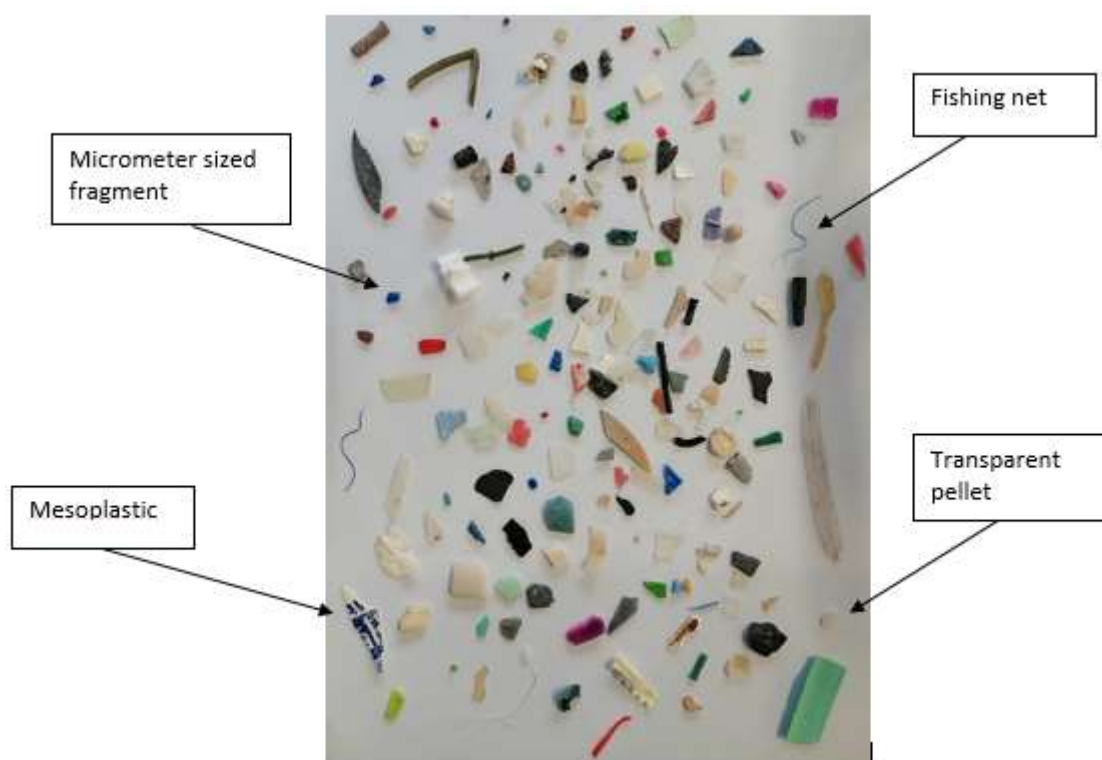


Figure 38 Different shapes, sizes and colors of sampled plastics-from S14 (Adloun)

## 11.2. Chemical composition

To have a global view on the plastic types found on the coast and, more precisely, on the most abundant types of microplastics, a number of pieces was submitted to ATR-FT IR analysis. At least 4 absorption bands were required to identify the polymer type (Fig. 41 and table 11). However, weathering and aging of plastics can affect the identification by modifying the spectral features of a certain type of plastics and also adsorbed compounds can add spectral bands that makes the identification process more difficult. Therefore, 3 particles were classified as unknowns.

A subset of 2133 particles of plastics was chosen for identification. The plastics were from the sampling of 2020 and chosen to be from sites present in northern, middle and southern part of the coast. All the plastics were collected from shore line except for S6 (Amshit), where a massive quantity of microplastics was observed. Small microplastics and really weathered plastics (18) could not be identified by FTIR so they were excluded from the counting.

The 2133 were chosen to be of different visual types, colors, shapes, and sizes. Plastics were chosen from different sites along the coast. In order to make samples more representative, sites containing a large mass of litter from different sizes were chosen for the identification, S3( Tripoli 1) for microplastics, S14 for microplastics and mesoplastics and S6 (Amshit) for macroplastics and the rest of the samples were chosen from random sites covering the coast and having different colors and shapes.

Of the identified mesoplastics and macroplastics, polyethylene and polypropylene were the most abundant type, followed by polystyrene, consisting of parts of plastic cups or utensils. Some fragments could be identified as polyethylene terephthalate and acrylonitrile butadiene styrene leaving 0.1 % of unattributed spectra (Fig. 39).

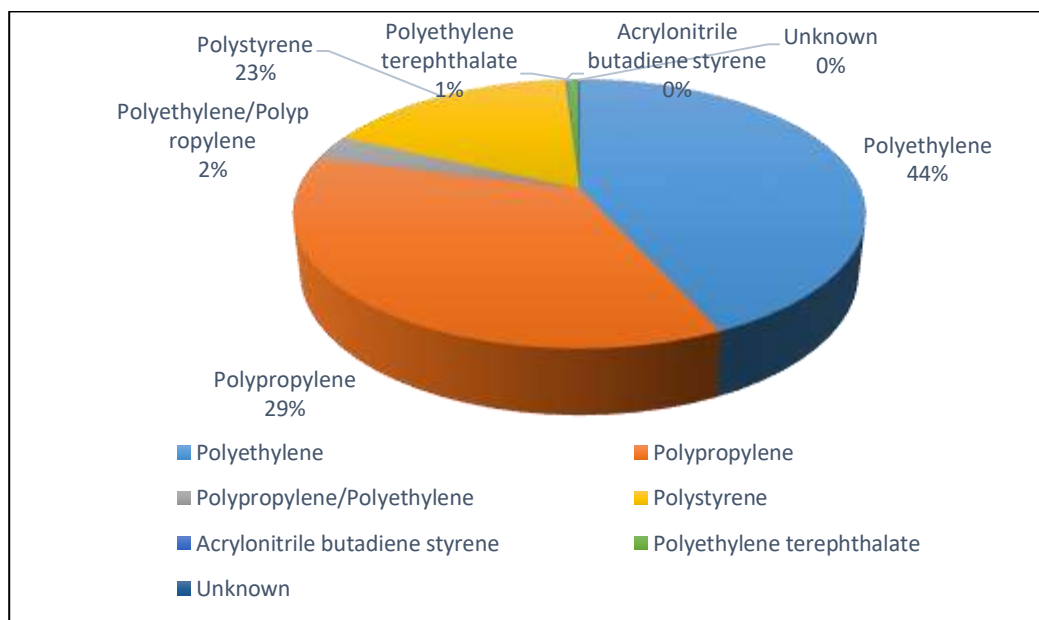


Figure 39 Distribution of plastics of all sizes based on their polymer types

Of the 2133 particles of plastics, 1213 of them were microplastics, only polyethylene and polypropylene or a mixture of both polymers were identified in microplastics particles (Figure 40). 45 % of microplastics were PP, 49 % PE and the rest 5.4 % is a mixture of both (Table 11). Polyethylene was taken as whole, there was no discrimination between polyethylene of low and high density. This is in agreement with the previous studies. According to Jemaa *et al.* (Jemaa *et al.*, 2021) four types of polymer were found on sea surface

across the Lebanese coast, PE, PS, PP and PA. PP was the most abundant (48.5 %) and only few particles of PA were found, representing 1.5 % of the samples. Edo *et al.* (Edo *et al.*, 2019) found 63 % PE, 32 % PP and 3 % PS from the total of 9149 plastic collected from beaches of Canary Islands.

Table 10 Plastics characterized by FTIR (micro stands for microplastics, macro for macroplastics and meso for mesoplastics)

	S3	S5	S6	S8	S9		S11	S14		Total	Total Micro
	Micro	Micro	Macro	Micro	Meso	Micro	Micro	Meso	Micro		
<b>Polypropylene</b>	185	12		43	42	7	5	149	301	744	553
<b>Polyethylene</b>	378	17	190	94	58	5	9	91	92	934	595
<b>Mix polyethylene/polypropylene</b>	41			10					14	65	65
<b>Polystyrene</b>			369							369	0
<b>Polyethylene terephthalate</b>			15							15	0
<b>Acrylonitrile butadiene styrene</b>			3							3	0
<b>Unknown</b>			3							3	0
<b>Total</b>	604	29	580	147	100	12	14	240	407	2133	1213

The public beach of Tripoli (S3) was found to be highly polluted with marine litter as also found elsewhere by Kazour *et al.* (Kazour *et al.*, 2019). Approximately 50 grams of microplastics were collected at each of the three different times. In our study, this site was also considered as a reference site for the difference in adsorption behavior between plastic fragments (secondary microplastics) and the weathered pre-production pellets (primary microplastics). Only particles with definitive identifications were used for the study of affinity of compounds to get adsorbed to particles.

This study shows the ability of ATR-FTIR to identify plastic types of small sizes going down to identifying some fibers from fishing net. This technique needs no prior sample preparation and was found to be fast and effective. The most important thing was to assure a good contact between the sample and the FTIR sampling plate.

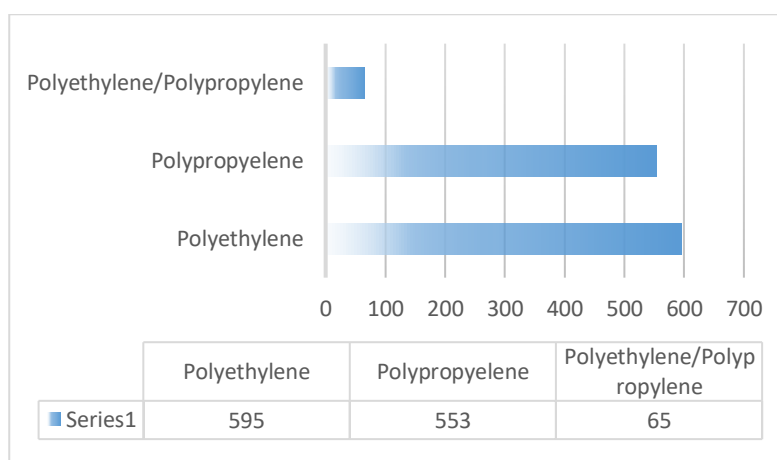


Figure 40 Distribution of MPs particles on different characterized types

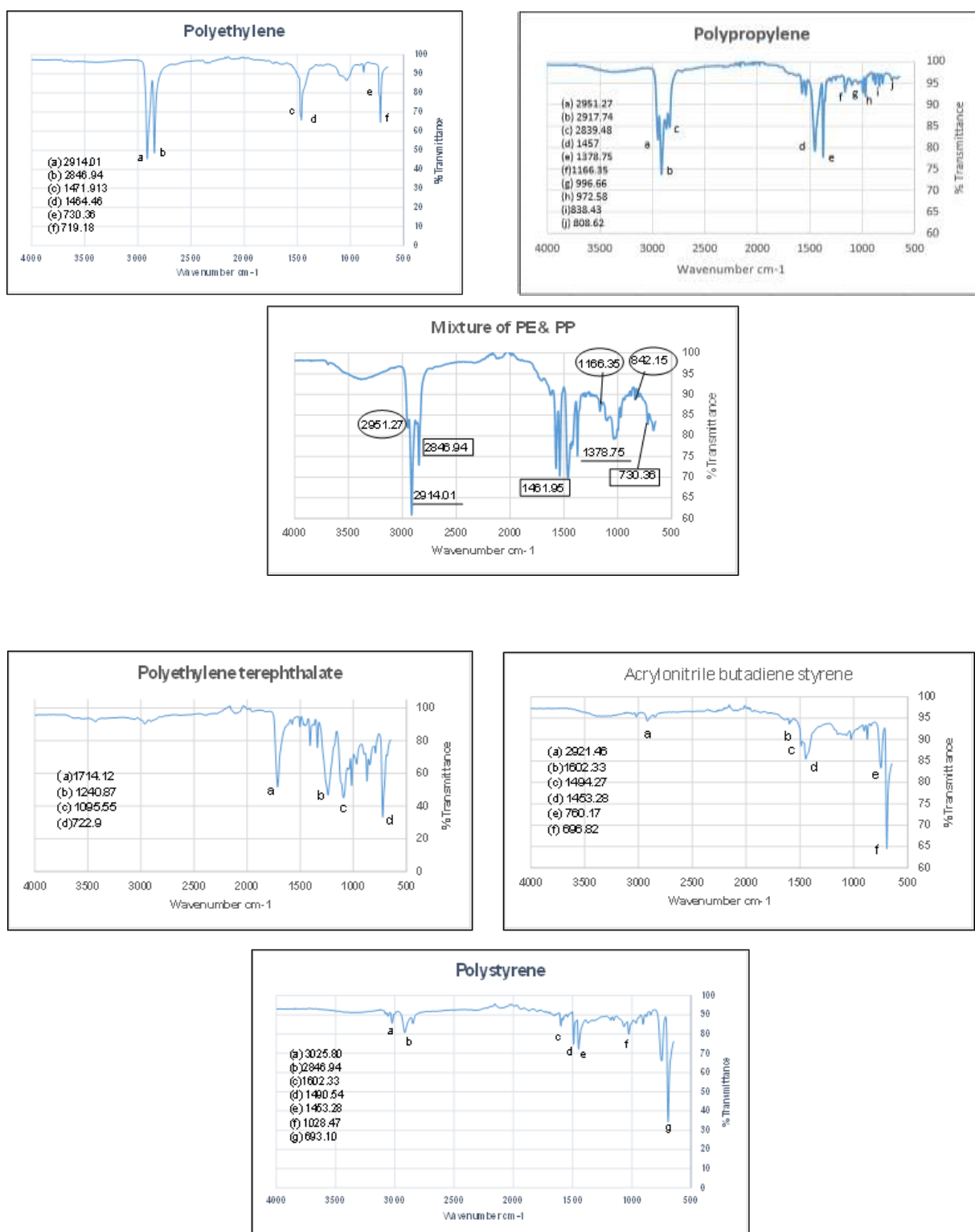
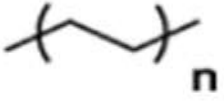
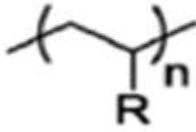
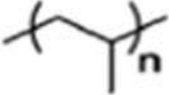
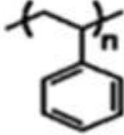
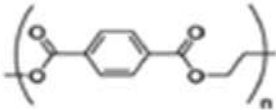
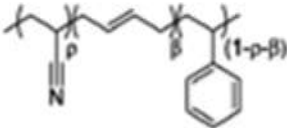


Figure 41 FTIR spectra of polyethylene, polypropylene, and mixture of polyethylene/polypropylene, polyethylene terephthalate, acrylonitrile butadiene styrene and polystyrene. For the mixture, the circled wavenumbers are the ones characteristic for PP, the squares are characteristics for PE and the underlined belong to both.

Table 11 Structure and Characteristic bands of the identified polymers(Jung et al., 2018)

Polymer	Chemical structure	Absorption bands	Assignment
Polyethylene (PE)		2915 (a) 2845(b) 1472(c) 1462(d) 730 (e) 717(f)	C-H stretch C-H stretch CH <sub>2</sub> bend CH <sub>2</sub> bend CH <sub>2</sub> rock CH <sub>2</sub> rock
	HDPE		
Polypropylene (PP)		2915(a) 2845(b) 1467(c) 1462(d) 1377(e) 730(f) 717(g)	C-H stretch C-H stretch CH <sub>2</sub> bend CH <sub>2</sub> bend CH <sub>3</sub> bend CH <sub>2</sub> rock CH <sub>2</sub> rock
	LDPE		
Polypropylene (PP)		2950 (a) 2915(b) 2838(c) 1455(d) 1166(e) 997(f) 972(g) 840(h) 808(i)	C-H stretch C-H stretch C-H stretch CH <sub>2</sub> bend CH bend, CH <sub>3</sub> rock, C-C stretch CH <sub>3</sub> rock, CH <sub>3</sub> bend, CH bend CH <sub>3</sub> rock, C-C stretch CH <sub>2</sub> rock, C-CH <sub>3</sub> stretch CH <sub>2</sub> rock, C-C stretch, C-CH stretch
Polystyrene (PS)		3024(a) 2847(b) 1601(c) 1492(d) 1451(e) 1027(f) 694(g)	Aromatic C-H stretch C-H stretch Aromatic ring stretch Aromatic ring stretch CH <sub>2</sub> bend Aromatic CH bend Aromatic CH out of plane bend
Polyethylene terephthalate (PET)		1713(a) 1241(b) 1094(c) 720(d)	C=O stretch C-O stretch C-O stretch Aromatic CH out of plane bend
Acrylonitrile butadiene styrene (ABS)		2922 (a) 1602 (b) 1494 (c) 1452 (d) 759 (e) 698 (f)	C-H stretch Aromatic ring stretch Aromatic ring stretch CH <sub>2</sub> bend Aromatic CH out-of-plane bend, =CH bend Aromatic CH out-of-plane bend

## 12. Polar organic compounds associated with microplastics sampled on the Lebanese coast

### 12.1. LC-MS/MS analysis

#### 12.1.1. Parameters optimization

In order to extract pollutants from plastics, solvents should be chosen on the basis of the polarity of the targeted compounds. Due to the lack of reference materials and the difference between environmental plastics and raw plastics, only the choice of extraction solvent could be optimized. A full optimization would require exposing plastics to environmental conditions for a long period and then spike them with standards prior to optimization.

For the extraction of polar compounds, polar solvents are used. Methanol, acetonitrile and chloroform were tried. Chloroform dissolves polystyrene and fragile plastics and thus was excluded. For methanol and acetonitrile, as shown in the figures 42 and 43, some compounds were extracted in both methanol and acetonitrile. The examples shown below concern two different samples from the same site, plastics were of the same type and size. The intensity for both diazinon and chlorpyrifos were slightly better in the samples extracted with methanol than in acetonitrile. However, some compounds were only seen when extracted with acetonitrile such as the phenacetin and pyroquilon (Fig. 44). Therefore, it was decided to use a mixture of methanol and acetonitrile to maximize the number of extracted compounds.

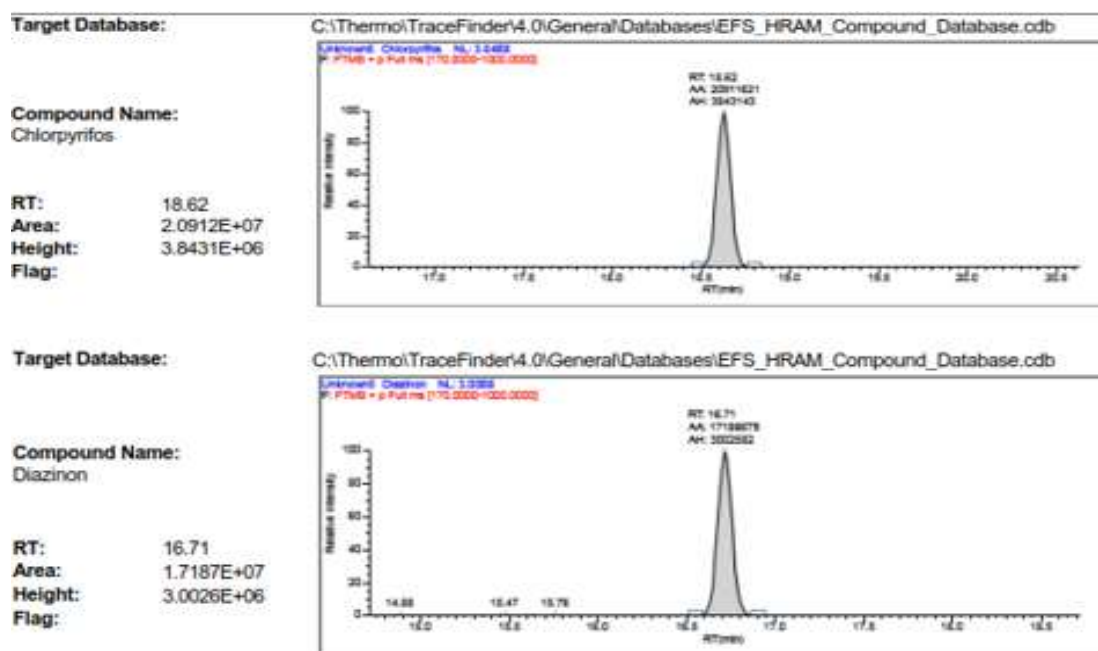


Figure 42 Chromatograms of chlorpyrifos and diazinon after the extraction with methanol

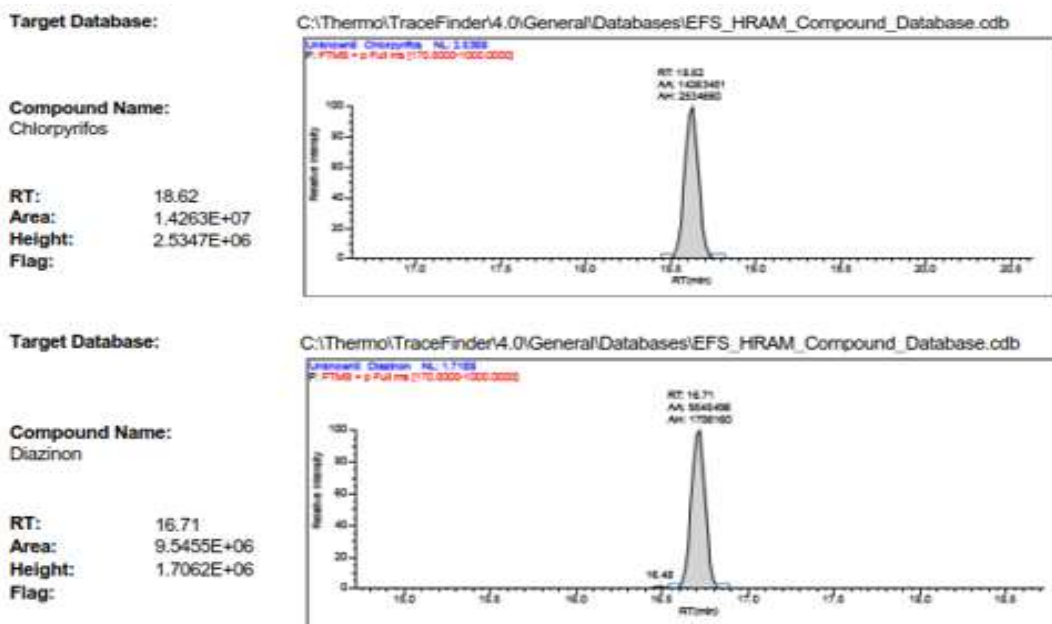


Figure 43 Chromatograms of chlorpyrifos and diazinon after the extraction with acetonitrile

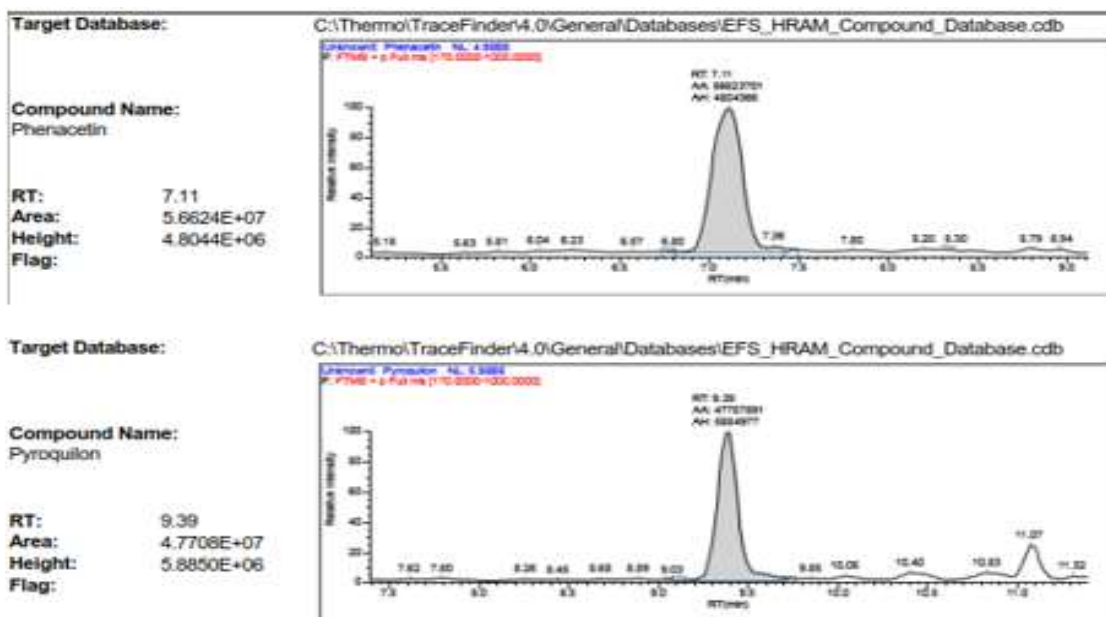


Figure 44 Chromatogram of phenacetin and pyroquilon only found in samples extracted with acetonitrile

Also, it was attempted to change solvent in each step of the extraction procedure and complete the sequence (third step) with the mixture. As no difference was observed in terms of recoveries in comparison when all three steps were carried out with the mixture, it was decided to carry out a three step sequential extraction using the methanol-acetonitrile (1:1) mixture.

### Identification of the candidate compounds

To confirm the identity of the compounds, they were compared against analytical standards. An analytical method was then executed for the targeted compounds. Some parameters were optimized to have better detection.

### Mobile phase optimization

Initially, 0.1 % formic acid acetonitrile as the organic phase and 0.1 % formic acid as the aqueous phase to compose the mobile phase but it resulted in a high background noise. It was considerably reduced when acetonitrile was replaced by methanol. The next step was to choose in which ratio the starting elution point of compounds was the best. At 8:2 aqueous / organic phase and 9:1 aqueous / organic phase, the chromatographic separation was the best.

### Collision energy and S-Lens optimization

All the standards were injected using the 8:2 aqueous/organic phase ratio. Full MS and MS/MS spectra were acquired for each of the compounds to identify their retention times and the fragments. The standards were also injected in infusion mode to track the best energy of collision for the fragmentation of each compound and the S-Lens. Figure 45 shows an example of the optimization done for one of the compounds, diazinon. The upper panel shows how the signal varies with the increase in S-Lens (radio frequency device that captures and focuses the ions in a tight beam). The intensity reaches a maximum plateau above 60. The same procedure was done for all compounds and a suitable S-Lens value of 60 was adjusted for all compounds.

Figure 45 (bottom panel) shows in green the precursor ion and blue and red are the most intense fragments, starting from approximately 5 %, and the fragmentation of diazinon starts. The best collision energy here is 40, when the precursor is being fragmented and the fragments are in higher intensities. The same type of optimization was carried out for the other compounds.

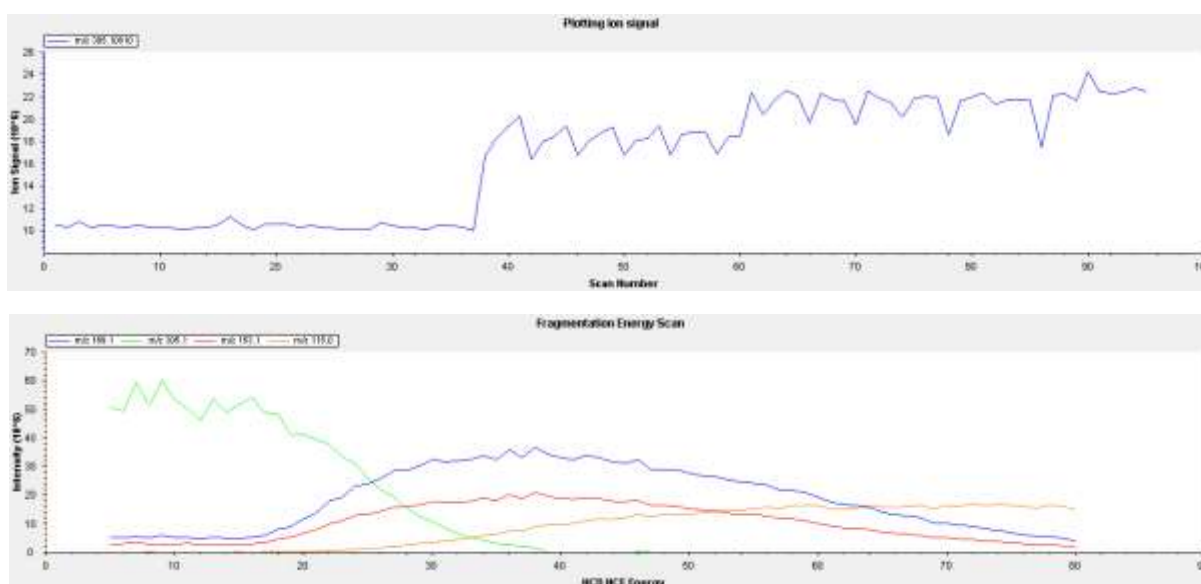


Figure 45 Optimization of S-Lens and energy of collision- diazinon example- The upper part showing the S-Lens variation and the lower part the fragmentation energy



**12.1.2. Development of the analytical method**

In order to validate the method and check the matrix effect, samples containing compounds were spiked with standards and the responses were checked. First, according to retention times, there was a slight shift in the case of ketoprofen, diazinon, and phenacetin, but after injecting the standards it was confirmed that those were the correct compounds. The retention times of all other compounds were the same as the standards (Fig. 46).

The chromatograms in Fig. 46 indicate the risk of overestimation and underestimation for some of the compounds if the method of standard addition is not used for quantification. For example, for minoxidil, naphthalene acetamide and tripeleminamine the signal intensity of the spiked sample is higher than the signal of the standard added to the signal of the compound in the extract.

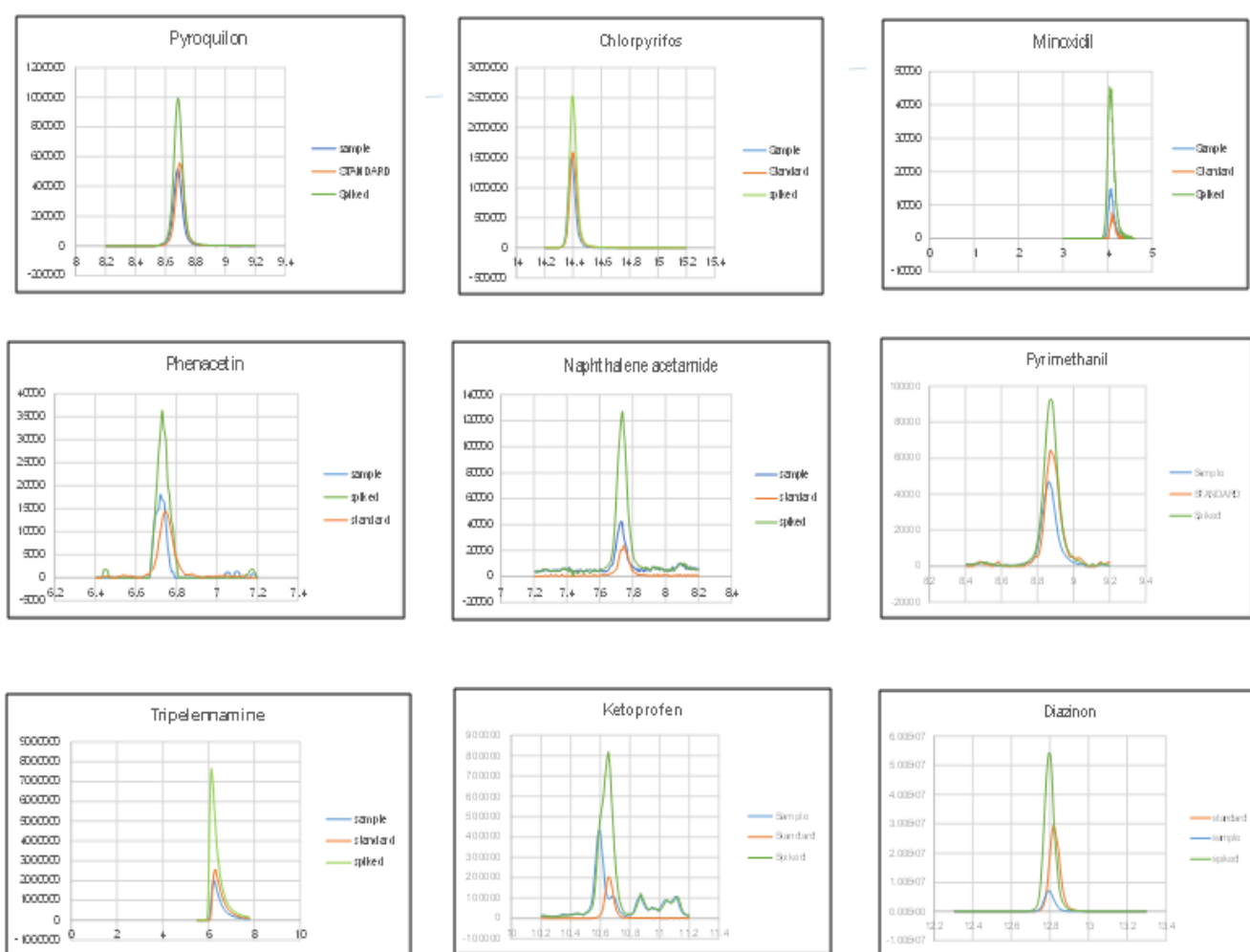


Figure 46 Chromatograph showing spiked compounds

### 12.1.3. Screening of polar organic compounds in microplastics extracts

After screening, Trace Finder and Compound Discoverer software packages were used to compare the found compounds with compounds from different databases. The identification was done in terms of: the chromatographic peak shape, the exact mass, the isotopes, and the fragmentation. The data were at first treated using Trace Finder and compared against some in-house libraries and pharmaceutical and pesticide libraries (Fig.47) (EFS\_HRAM, toxicology-HRAM).

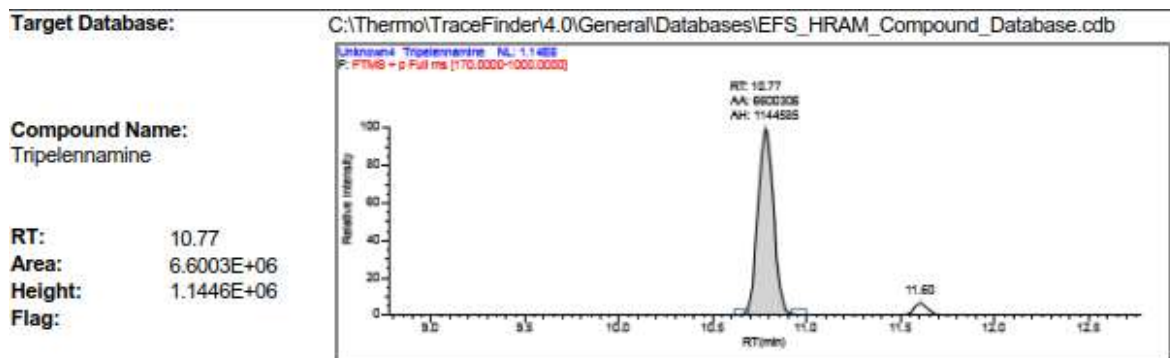


Figure 47 Tripelennamine found based on EFS-HRAM database using Trace Finder

In Compound Discoverer, few parameters were set in order to create a list of tentative compounds. mzCloud was the main library used to identify compounds. Mass error was set to less than 5 ppm, compounds found in procedural blanks or mobile phase blanks were excluded and the mzCloud best confidence match was set to equal or exceed 70. A good chromatographic peak shape was also taken into consideration (diazinon example, Fig. 48) and fragmentation was marked by FISh (Fragment ion searching) scoring, this score depends on the number of fragments in comparison with the library but not on the intensity of fragments; the higher the number of fragments in common with the library the highest the score. On one hand, we can have a very high FISh score by having a full match on very few fragments (which means poor level of confidence). On the other hand, we can have several fragments in the MS<sup>2</sup> spectrum but only 10 % of them may belong to the compound (matrix component co-isolation); in such case FISh score will be low since Compound Discoverer cannot assign most of the fragments, but we may still have a positive identification.

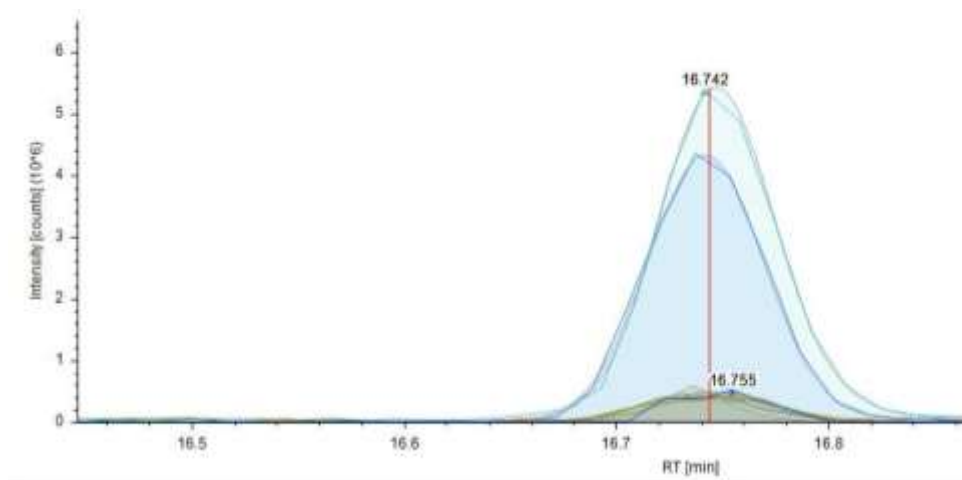


Figure 48 Chromatographic shape of diazinon- from Compound Discoverer

#### 12.1.4. Targeted analysis

After setting the parameters needed (mass error below 5 ppm, confidence match  $\geq 70$ , good Gaussian peak, good fragmentation with at least two fragments compared with the database and at least two matching isotopes), a list of 19 compounds could be established that were chosen for the targeted analysis (Table 12). Compounds found in nature, such as compounds produced by living organisms, and the compounds known as plastic additives, were excluded.

To confirm the identity of the 19 compounds, they were matched with standards. Each of the standards was injected and the retention time,  $m/z$  and the fragments obtained were compared. 19 compounds listed in Table 12 were analyzed by LC-MS (Fig. 50) and then in direct infusion mode to adjust the analytical method. Energy of collision were optimized for each of the compounds and fragments were noted.

Figure 50 shows spectrum of chlorpyrifos found in one of the sample (down) in comparison with the analytical standard (up), showing a very high compatibility with a pretty similar profile.

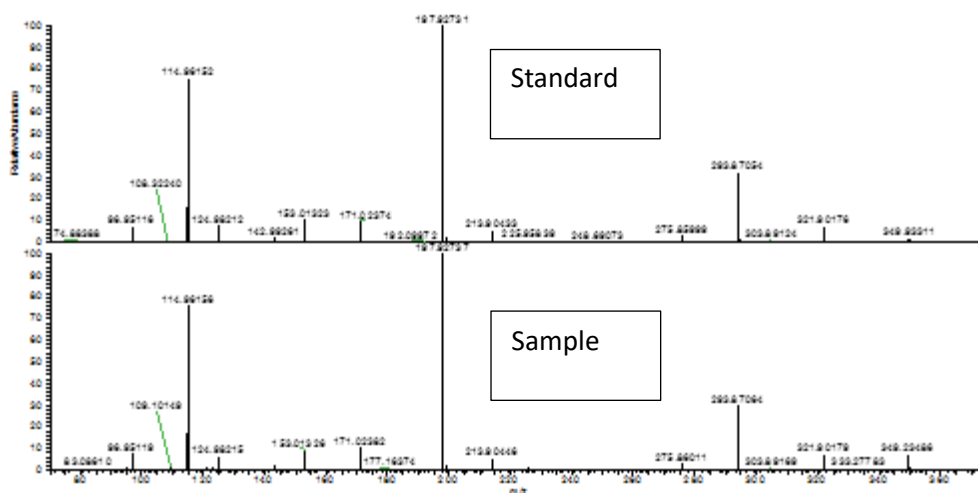


Figure 49 Spectrum of chlorpyrifos found in a sample (down) in comparison with the standard (up)

After analyzing all the samples, the presence of 9 out of the 19 compounds were confirmed in plastics extracts. These 9 compounds were quantified (Fig. 51), and an additional 4 compounds were found and quantified in the analyzed water samples. The confirmed and quantified compounds were marked in Table 12 by one asterisk for the compounds found in plastics extracts and by two asterisks for the compounds only found in water samples.

Table 12 List of targeted compounds

Compounds	Formula	Theoretical m/z ([M+H] <sup>+</sup> )	Fragmentation	RT (min)	Energy of collision
Norfenefrine	C <sub>8</sub> H <sub>11</sub> NO <sub>2</sub>	154.09	119.0491 136.0756 91.0542	0.78	10
Nicotine**	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub>	163.12	132.0793 106.0651 84.0807	1.06	70
Minoxidil*	C <sub>9</sub> H <sub>15</sub> N <sub>5</sub> O	210.13	164.0929 84.08131 193.1321	4.04	50
Guaifenesin	C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>	199.10	125.0597 151.0753	4.87	10
Tripeleennamine*	C <sub>16</sub> H <sub>21</sub> N <sub>3</sub>	256.18	211.1229 91.0544 119.0603	5.89	30
Phenacetin*	C <sub>10</sub> H <sub>13</sub> NO <sub>2</sub>	180.10	110.0602 138.0912 92.0494	6.76	60
Naphthalene acetamide *	C <sub>12</sub> H <sub>11</sub> NO	186.09	141.0697 115.0542 91.0542	7.71	40
Pyroquilon*	C <sub>11</sub> H <sub>11</sub> NO	174.09	132.0807 117.0574 55.0178	8.69	40
Pyrimethanil*	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub>	200.12	80.0500 82.0656 168.0682	8.97	80
Menadione	C <sub>11</sub> H <sub>8</sub> O <sub>2</sub>	173.06	105.0334 145.0647 117.0698	9.59	70
Ketoprofen*	C <sub>16</sub> H <sub>14</sub> O <sub>3</sub>	255.10	105.0334 209.1015	10.63	40
Tridemorph	C <sub>19</sub> H <sub>39</sub> NO	298.31	98.0968	12.37	60
Diazinon*	C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> PS	305.11	169.0792 153.10214 114.96153	12.81	40
Cannabidivarin**	C <sub>19</sub> H <sub>26</sub> O <sub>2</sub>	287.20	165.0908 231.1379 135.1168	13.32	50

<b>Pyrethrin**</b>	$C_{22}H_{28}O_5$	373.20	161.0960 133.1011 69.0334	13.87	10
<b>Chlorpyrifos*</b>	$C_9H_{11}Cl_3NO_3PS$	349.93	197.9273 114.9615 96.9511	14.42	25
<b>Testosterone Cypionate**</b>	$C_{27}H_{40}O_3$	413.31	107.0855 97.0647 109.0647	16.81	35
<b>Testosterone Decanoate</b>	$C_{29}H_{46}O_3$	443.35	97.0647 109.0647 175.1481	18.11	30
<b>Testosterone Undecanoate</b>	$C_{30}H_{48}O_3$	457.37	97.0647 109.0647 95.0855	18.74	30

The compounds found are used for different purposes and comes from different origins. They are of two different groups, pesticides and pharmaceuticals. In total five pesticides and four pharmaceuticals were identified, and a few more in the water samples.

Minoxidil is a medication used for hair growth purposes (Gupta, et al. 2022). Ketoprofen is a non-steroidal anti-inflammatory to treat pains. It is widely used and sold under different brand names. It was detected before in many studies (Desbiolles, et al. 2018; Weigel, et al 2002). Phenacetin was used as analgesic and fever reducing drug, but was withdrawn from medicinal use in the late nineties due to its kidney damaging and carcinogenic effects (Piper, et al. 1985).

It was also used as stabilizer for hydrogen peroxide in hair-bleaching products and some other hair products (Leino, et al. 1999) which explains its presence in most of our samples. It was also reported to be used as a cutting agent, added to drugs to increase their weight (Fiorentin, et al. 2019). The last compound belonging to the pharmaceuticals group detected is tripeleminamine, an anti-histaminic and anti-puritic, mostly used to prevent vomiting of animals (Papich, 2016).

Regarding pesticides, naphthalene acetamide is a synthetic auxin still used and authorized for use in agriculture as a rooting hormone (Kemper, 1985). Pyroquilon is a fungicide that was banned few years ago by the European Union but no data showed that it was banned in Lebanon (Aamir, 2018). Diazinon is an organophosphate pesticide used to control pests and insects in vegetable, fruit, and ornamental trees. It was used in households to control flies and cockroaches until it was banned by the EPA in 2004 for other uses than agriculture due to its high toxicity (Keller, 2005). Chlorpyrifos, banned few years ago, was found in each of the extracted samples and in high concentrations (Hunt et al., 2003). Those results were supported also by the results of the chlorpyrifos analyzed by GC-MS and shown later. The last pesticide, is the pyrimethanil, authorized for use, as a fungicide to control mold and commonly used to control fungus in grapes for winemaking (Saladin, 2003).

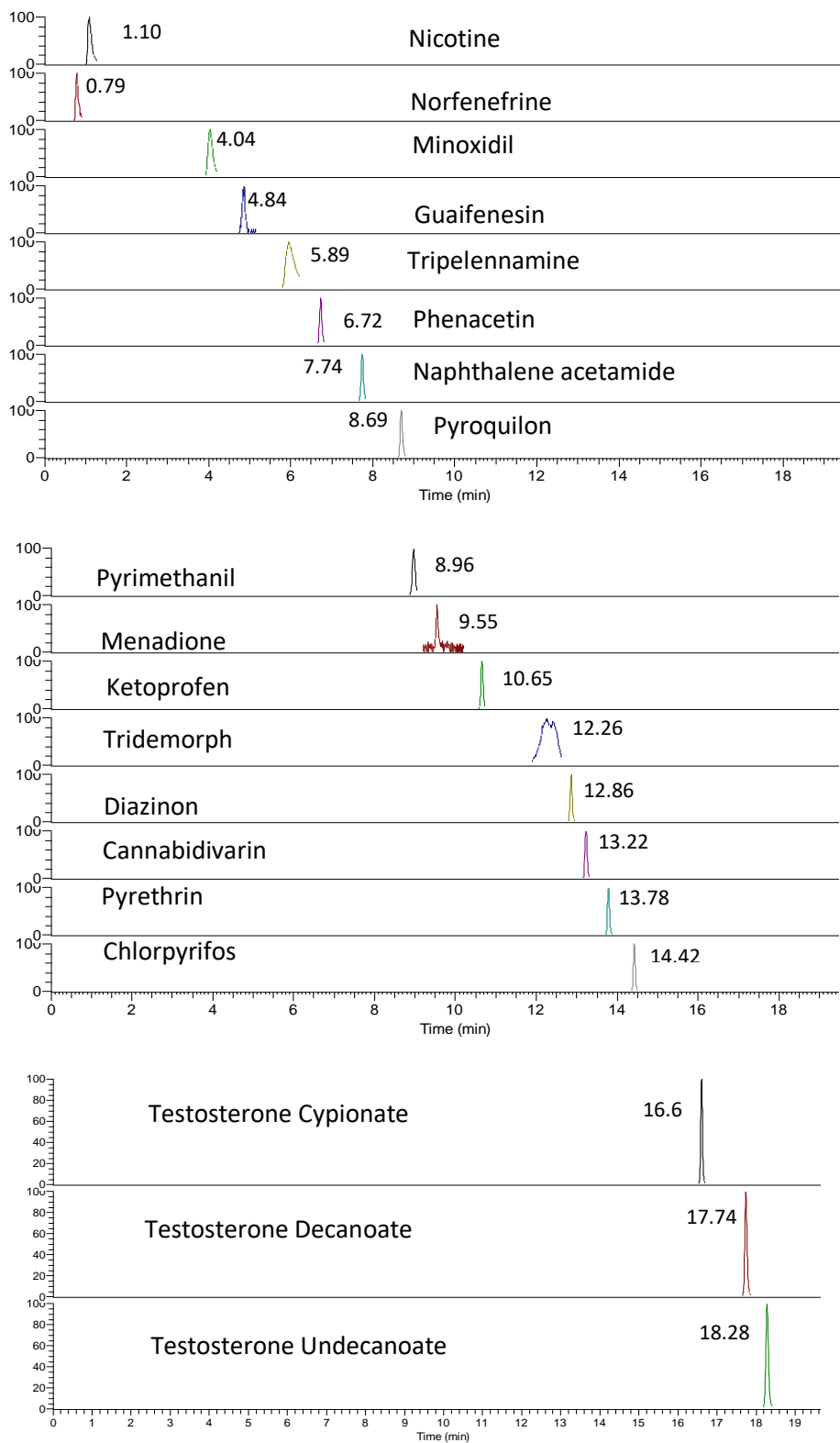


Figure 50 Chromatograms of the 19 targeted compounds- Analytical standards

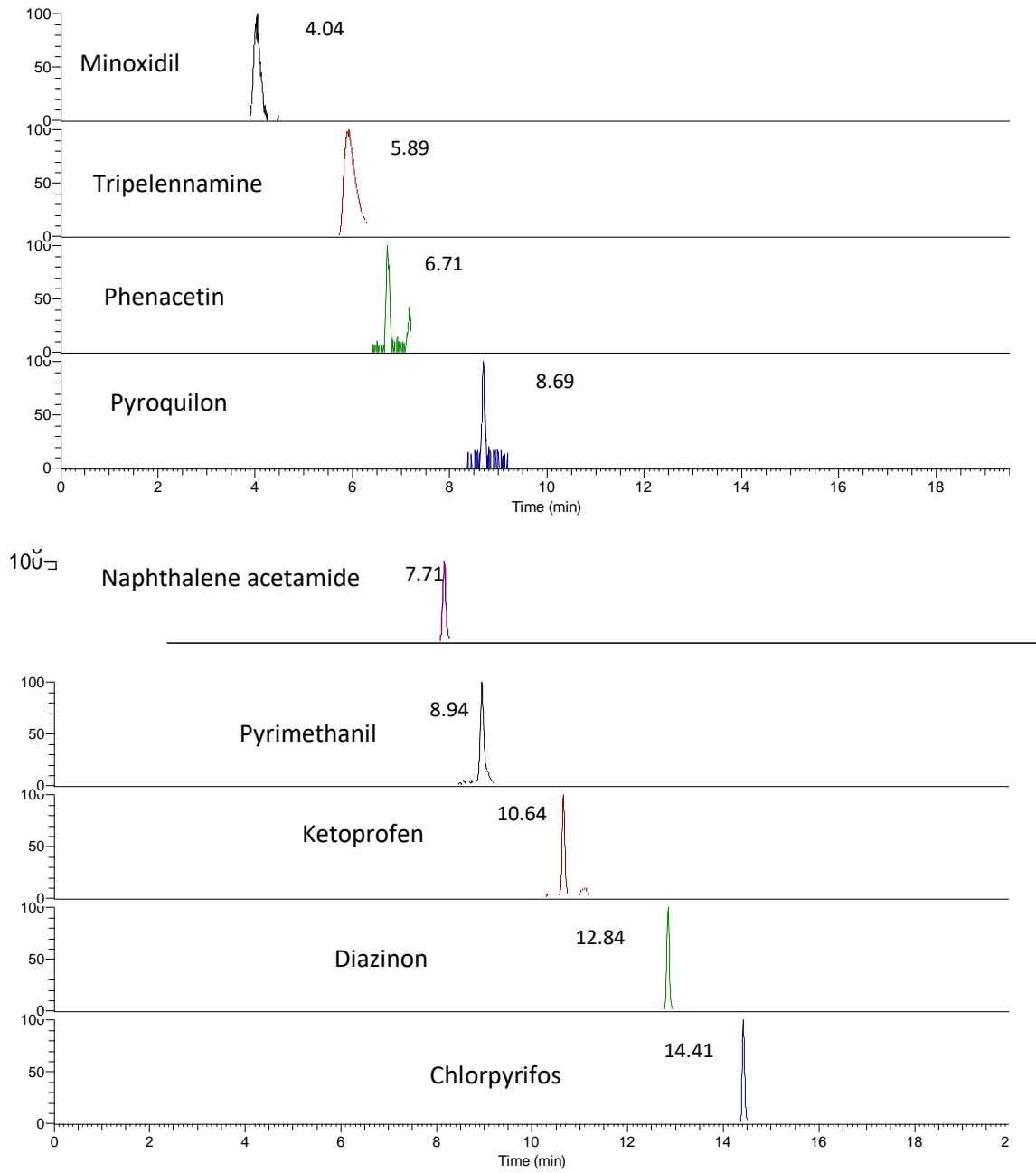


Figure 51 Chromatograms of the 9 compounds found in plastic extracts

### 12.1.5. Concentrations found

Tables 13 and 14 summarize the concentrations of those 9 compounds from plastic extracts. We cannot formulate a definitive conclusion that the Northern and Middle part of the Lebanese coast are more polluted than the southern part, but the results show the occurrence of at least 5 of the quantified compounds in all of the samples in the North. S1 (Arida), S2 (Menye) S5 (Shekka), S6 (Amshit), and S7 (Jbeil) in the North. S3 (Tripoli) is highly polluted by litter but shows a lower chemical pollution rate in comparison with other sites.

As for S8 (Ramle), located in the middle of the coast, near Beirut, it was sampled in all the three campaigns and showed the highest pollution rate with at least 6 pollutants found out of 9. As for the monthly variation, we can see that in November 2020, June and August 2021 we have 6 compounds in common found in the extracts (phenacetin, pyroquilon, pyrimethanil, ketoprofen, diazinon and chlorpyrifos). Note that the concentrations were the highest in August 2021, followed by November 2020 and finally June 2021. It is a public beach, neighboring Beirut, the capital, the most populated area in Lebanon and thus the anthropogenic pressure is at its peak in this area. The place is prone to wastewater discharges coming in masses from hotels, restaurants and resorts. It is also polluted by industrial activities and household waste. We can note also that the least number of pollutants was detected on the S13 site (Sarafand). Figure 52 shows the distribution of the 9 quantified compounds in all the extracted samples.

As it is mentioned above, S3 (Tripoli 1) is a site highly polluted by microplastics, it was sampled in November, June and August and was separated into pellets and fragments, and each of them was separated into PP and PE. This was done in a purpose to see the adsorption performance of pellets and fragments and different chemical types. Those experiments were done in a number of previous studies but they were done with controlled conditions under experimental parameters and non-environmental plastics or environmental plastics but without mimicking environmental factors.

In this study we could not tell the difference between pellets and fragments nor between polyethylene and polypropylene. Indeed, Fig. 53 shows no clear distinction between the pollutants concentrations as a function of the shape or type of plastics. This may be due to the non-repeatability in environmental samples because it is not possible to estimate the contact time between contaminant coming from seawater and microplastics. Thereby, no conclusion could be drawn concerning the sorption behavior of different types and shapes of plastics.

From the histogram in Fig. 53 we can note a monthly variation in terms of the number and concentrations of the compounds found. In November more compounds were detected and chlorpyrifos concentrations were much higher than samples of 2021. A future idea is to get newly manufactured microplastics from different shapes and sizes and to put them in seawater by hanging them in some sort of apparatus. Using this method we would be able to confirm the sorption behaviors of different plastics under real environmental conditions.

Note that we cannot talk of a proper seasonal or monthly variation in this case because we cannot tell for how long those plastics were on the shore and how long they spent in sea water. But in November, we noted higher concentrations and occurrence of the pollutants especially the chlorpyrifos concentration. This may be caused by the use, a couple of months earlier, of chlorpyrifos for agricultural purposes, on citrus trees that are planted along the coast.



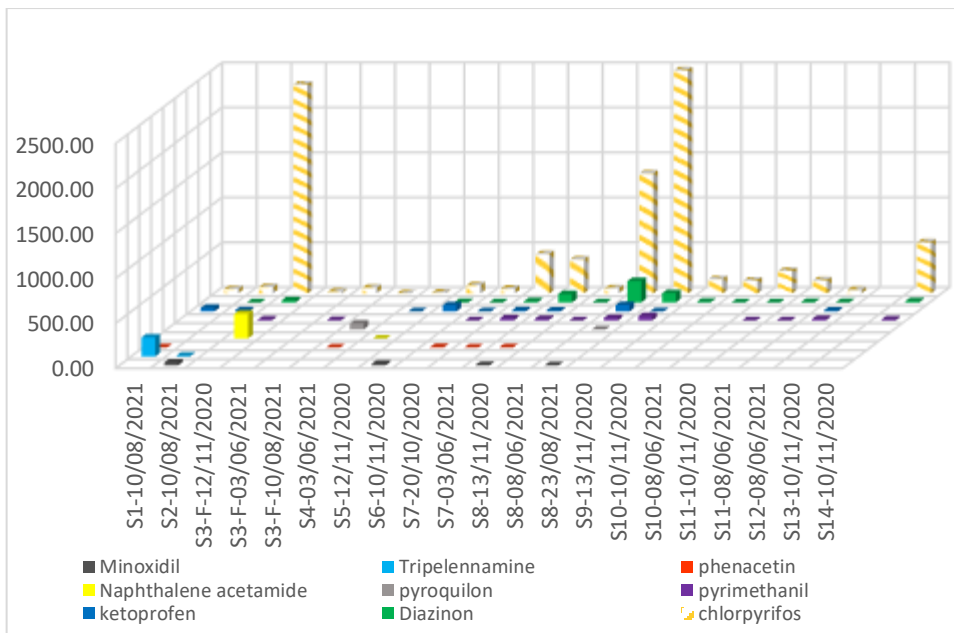


Figure 52 Histogram showing the distribution of the quantified compounds in the samples

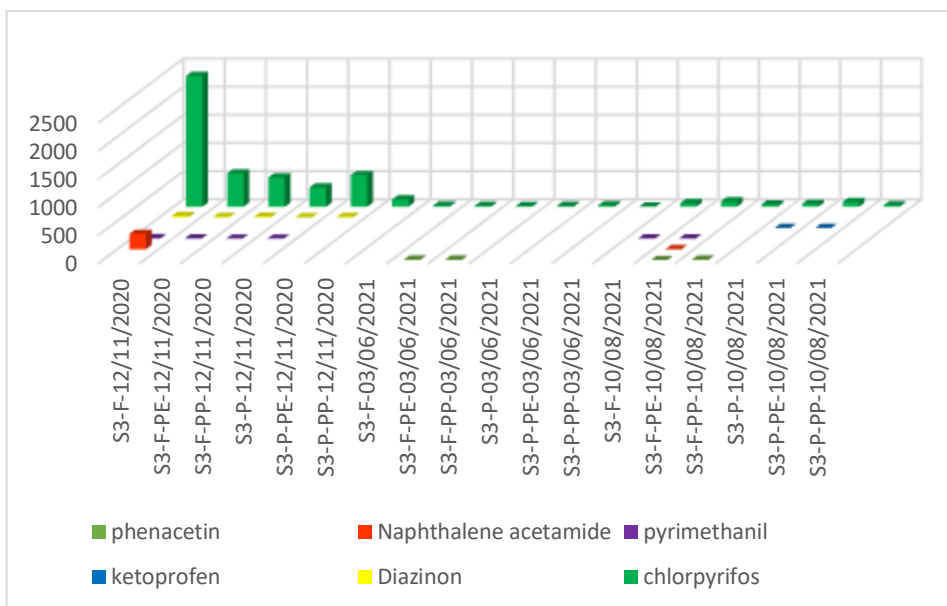


Figure 53 Histogram showing the distribution of the quantified compounds in sample S3 from November 2020, June and August 2021 separated into pellets (P), fragments (F), and each separated into PE and PP

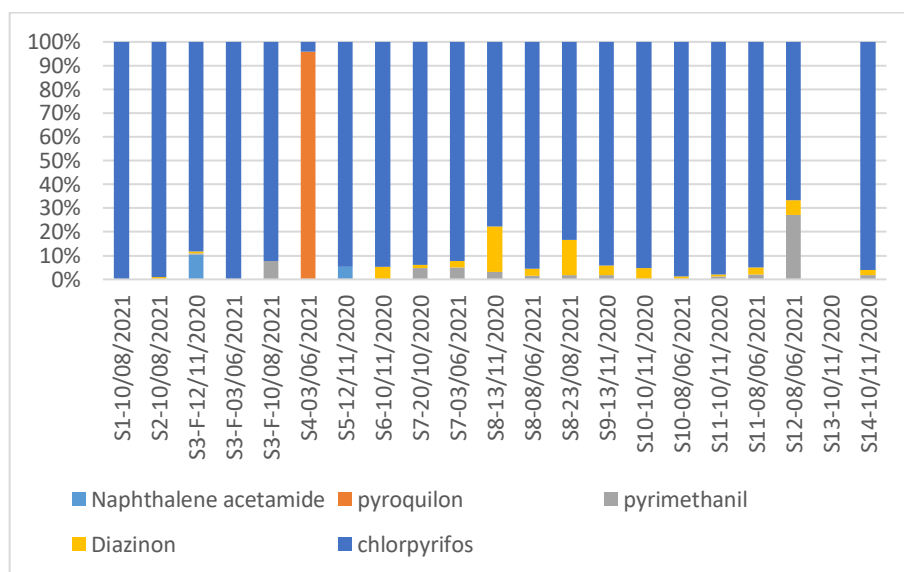


Figure 54 Percentual contribution of each of the found pesticides in samples

Figure 54 shows percent contribution of each of the found pesticides in plastics extracts. Chlorpyrifos represents more than 60 % of the total concentration of the selected pesticides in most of the samples. Its concentrations ranged from 2.7 ng/g up to 2500 ng/g. It is worth emphasizing that chlorpyrifos was banned in Lebanon a couple of years ago but it may be still used illegally. Its presence in the samples can be explained by its presence in water but also by its release from some plastics used in agriculture (Ramos, et al. 2015). Chlorpyrifos was followed by diazinon found in more than half of the samples while the other pesticides were found only at few sites. The persistence of chlorpyrifos and diazinon in water systems was reported elsewhere (Desbiolles et al., 2018; Hunt et al., 2003; Keller et al., 2005).

Regarding the found pharmaceuticals, ketoprofen was found in 11 of the analyzed samples; its occurrence was reported in other studies of the Mediterranean Sea (Desbiolles et al., 2018). Tripeleminamine was found in two samples, and phenacetin and minoxidil in five each.

The observed pollution cannot be related to a source nor to a specific site or region because we cannot confirm the origin of plastics or the time they spent in the water before arriving at the shore. However, we can state that these pollutants are now present at the Lebanese coast and represent a risk to marine biota. Also, these plastics may not have reached their final destination yet and can be taken again to deep water by waves washing them off from the shore.

Table 13 Compounds quantified from microplastic extracts by LC-MS/MS (ng/g of microplastics)

Sampling site	Sampling date	Minoxidil	Tripelennamine	Phenacetin	Naphthalene acetamide	Pyroquilon	Pyrimethanil	Ketoprofen	Diazinon	Chlorpyrifos
S1	10-08-21	<0.001	210 ±20	1.0 ± 0.09	<0.005	<0.005	<0.01	40 ±0.9	<0.005	49 ±0.81
S2	10-08-21	33± 0.36	7.9± 0.36	<0.005	<0.001	<0.005	<0.005	13 ±1.8	0.62 ±0.001	72 ±0.9
S3	12-11-20	<0.001	<0.01	<0.005	<0.001	<0.001	11 ±1.1	<0.001	23 ±0.5	2300 ±36
	03-06-21	<0.001	<0.01	<0.005	<0.001	<0.005	<0.005	<0.001	<0.005	21 ±0.7
S4	10-08-21	<0.001	<0.01	<0.005	<0.001	<0.005	5.2 ±0.4	<0.001	<0.005	63 ± 0.2
	03-06-21	<0.001	<0.01	0.48± 0.06	<0.001	66 ± 0.45	<0.01	<0.001	<0.005	2.7 ±0.09
S5	12-11-20	<0.001	<0.01	<0.005	0.56 ±0.09	<0.005	<0.01	0.75 ±0.09	<0.005	10± 0.36
S6	12-11-20	20± 0.09	<0.01	<0.005	<0.001	<0.001	<0.01	69 ±4.5	5.0± 0.54	91 ±0.09
S7	20-10-20	<0.001	<0.01	4.3 ± 0.18	<0.001	<0.005	2.6 ±0.18	0.75 ±0.09	0.81 ±0.09	54 ±0.45
	03-06-21	<0.001	<0.01	0.94± 0.09	<0.001	<0.005	24 ±0.27	13 ±0.9	12.6 ±0.09	440± 6.3
S8	13-11-20	6.5 ±0.09	<0.01	1.4± 0.09	<0.001	<0.005	16 ±0.54	10± 0.45	93 ±0.9	380 ±0.9
	08-06-21	<0.001	<0.01	<0.005	<0.001	<0.005	1.0 ±0.09	<0.005	1.76 ±0.03	58± 6.3
S9	23-08-21	1.9± 0.36	<0.01	<0.005	<0.001	0.50± 0.36	27± 1.8	72 ±2.16	240 ±18	1300 ±10.8
	13-11-20	<0.001	<0.01	<0.005	<0.001	<0.001	49 ±3.6	2.2 ±1.44	100 ±3.6	2500 ±72
S10	10-11-20	<0.001	<0.01	<0.005	<0.001	<0.001	<0.005	<0.005	7.8 ±0.36	160 ±3.6
	08-06-21	<0.001	<0.01	<0.005	<0.001	<0.001	<0.005	<0.001	1.9 ±0.36	140 ±2.16
S11	10-11-20	<0.001	<0.01	<0.005	<0.001	<0.001	3.0± 1.08	<0.001	2.4 ±0.072	250 ±10.8
	08-06-21	<0.001	<0.01	<0.005	<0.001	<0.001	3.1± 0.36	<0.001	4.5 ±0.36	150 ±1.8
S12	08-06-21	<0.001	<0.01	<0.005	<0.001	<0.001	16± 0.72	11 ±3.6	3.7 ±0.36	40 ±3.6
S13	10-11-20	<0.001	<0.01	<0.005	<0.001	<0.001	<0.005	<0.001	<0.005	<0.01
S14	10-11-20	<0.001	<0.01	<0.005	<0.001	<0.001	10± 0.36	<0.001	13 ±1.9	570 ±14.4

Table 14 Compounds quantified in extracts of different microplastic fractions by LC-MS/MS (ng/g of microplastics).  
 Sampling site: Tripoli 1 (S3). F - mixture of MP fragments, P- pellets, PP - polypropylene, PE - polyethylene

Sampling date	Fraction	Minoxidil	Tripelennamine	Phenacetin	Naphthalene acetamide	Pyroquilon	Pyrimethanil	Ketoprofen	Diazinon	Chlorpyrifos
12-11-20	F	<0.001	<0.01	<0.005	<0.001	<0.001	11 ±1.1	<0.001	23 ±0.5	2300 ±36
	F-PE	<0.001	<0.01	<0.005	<0.001	<0.001	4.7 ±1.1	<0.001	6.2 ±0.7	590 ±5.4
	F-PP	<0.001	<0.01	<0.005	<0.001	<0.001	1.0 ±0.9	<0.001	12 ±0.4	520 ±7.2
	P	<0.001	<0.01	<0.005	<0.005	<0.001	1.4 ±0.2	<0.001	1.1 ±0.1	340 ±7.2
	P-PE	<0.001	<0.01	<0.005	<0.001	<0.001	<0.005	<0.001	5.1 ±0.5	560 ±18
	P-PP	<0.001	<0.01	<0.005	<0.001	<0.001	<0.005	<0.001	<0.005	130 ± 1.8
3-06-21	F	<0.001	<0.01	<0.005	<0.001	<0.005	<0.005	<0.001	<0.005	21 ±0.7
	F-PE	<0.001	<0.01	7.1 ±0.2	<0.001	<0.001	<0.005	<0.001	<0.005	15 ± 1.8
	F-PP	<0.001	<0.01	6.1± 0.5	<0.001	<0.005	<0.01	<0.001	<0.005	12 ± 1.8
	P	<0.001	<0.01	<0.005	<0.001	<0.005	<0.01	<0.001	<0.005	14 ± 0.4
	P-PE	<0.001	<0.01	<0.005	<0.001	<0.005	<0.005	<0.001	<0.005	26 ± 1.1
	P-PP	<0.001	<0.01	<0.005	<0.001	<0.001	<0.005	<0.001	<0.005	5.3 ± 0.4
10-08-21	F	<0.001	<0.01	<0.005	<0.001	<0.005	5.2 ±0.4	<0.001	<0.005	63 ± 0.2
	F-PE	<0.001	<0.01	0.46± 0.1	2.8± 0.1	<0.005	2.9± 0.2	<0.001	<0.005	93 ± 1.8
	F-PP	<0.001	<0.01	7.1± 0.2	<0.001	<0.005	<0.005	<0.001	<0.005	40 ± 1.3
	P	<0.001	<0.01	<0.005	<0.005	<0.005	<0.005	0.79 ±0.2	<0.005	49 ± 1.6
	P-PE	<0.001	<0.01	<0.005	<0.001	<0.005	<0.005	0.52± 0.2	<0.005	83 ± 0.4
	P-PP	<0.001	<0.01	<0.005	<0.001	<0.005	<0.005	<0.005	<0.005	26 ± 1.3

The presence of these polar compounds was also investigated in water. A solid phase extraction was done for 10 water samples from the Lebanese offshore waters, some of the beaches were more polluted than others. The samples are then analyzed by LC-MS/MS for the 19 targeted compounds. Table 15 presents the 11 compounds found in water samples.

In contrast to the microplastics samples, in the water samples, 11 of the compounds were found present. A reason may be that they are hydrophilic so adsorbed less readily. 7 out of the compounds found on microplastics were found in at least one of the water samples. Only pyroquilon and tripeleminamine were not present. For most of the sites, the compounds found were below the limit of quantification but were clearly detectable. Nicotine was found present in all of the samples in high intensities, it can originate in the disposal of cigarette butts that are found in huge quantities over beaches.

In S2 site (Menye) three supplementary compounds were detected. First, cannabidivarin, present in cannabis, which was found only at this location. A pyrethroid pesticide, pyrethrin was detected but was below LOQ and, finally, testosterone cypionate, a medicine used usually for treatment of hypogonadism, but nowadays in supplements enhancing bodybuilding. The presence of different testosterone compounds were mentioned before to be present in the Mediterranean Sea (Desbiolles et al., 2018).

These findings support the hypothesis that several compounds adsorbed on microplastics come from seawater. This makes microplastics a host for the adsorption and transport of this types of pollutants and a passive sampler to study water pollutants.

Table 15 Compounds quantified in water samples (ng/L) collected in August 2021

	Nicotine	Minoxidil	Phenacetin	Naphthalene acetamide	Pyrimethanil	Ketoprofen	Diazinon	Cannabidivarin	Pyrethrin	Chlorpyrifos	Testosterone cypionate
<b>W1</b>	+	<0.005	<0.005	<0.001	<0.005	<0.005	<0.005	<0.001	<0.01	<0.005	<0.01
<b>W2</b>	+	<0.005	<0.005	<0.005	15±5.4	<0.005	<0.005	41 ± 7.8	<0.05	12 ±0.3	<0.05
<b>W3</b>	+	<0.005	<0.005	<0.001	<0.005	<0.001	<0.005	<0.001	<0.01	85±13	<0.01
<b>W4</b>	+	<0.005	<0.005	<0.001	<0.005	<0.005	<0.005	<0.001	<0.01	<0.005	<0.01
<b>W5</b>	+	<0.005	<0.005	<0.001	<0.005	<0.005	<0.005	<0.001	<0.01	<0.005	<0.01
<b>W6</b>	+	<0.005	<0.005	<0.001	<0.005	<0.005	<0.005	<0.001	<0.01	12 ±0.04	<0.01
<b>W7</b>	+	<0.005	<0.005	<0.005	<0.005	<0.001	<0.005	<0.001	<0.01	<0.005	<0.01
<b>W8</b>	+	420 ± 1	<0.005	<0.005	<0.005	<0.005	810 ±25	<0.001	<0.01	180 ± 4.8	<0.01
<b>W9</b>	+	<0.005	<0.005	<0.001	<0.005	<0.005	<0.005	<0.001	<0.01	<0.005	<0.01
<b>W10</b>	+	<0.005	104 ±5.2	<0.005	<0.005	<0.005	<0.005	<0.001	<0.01	<0.005	<0.01

## 12.2. Direct analysis by LESA-MS

For the parameter's optimization of LESA, PE plastic bags and PS plastics from Goodfellow were used. After being cut to 5 mm in size, the polymers were analyzed directly after being dried. The samples were put in the instrument holder, to adjust the parameters to be best for the analysis.

The most important thing to be considered in the LESA analysis is to create a good junction between the solvent and the sample surface. Thus, the parameters to be taken into consideration and optimized are the type of solvent and the shape of the drop. Other parameters include the extraction time and the number of extractions. For the purpose of optimization, a mix of organic standards were put on plastic particles and dried.

Different parameters are to be considered in order to extract best and analyze the compounds on microplastics:

- The junction between the tip of the micropipette and samples. For this, the surface of the sample should be more or less flat and as much homogeneous as possible. The tip height and the contact time between the solvent and the sample should be chosen to be the best
- The composition of the solvent used for the extraction and its aspired and dispensed volume
- The aspiration speed
- The number of repetitions of the extraction procedure, could go from 1 extraction to several respective extractions of the same point
- The voltage applied and the pressure during the spray (Issart et al., 2019).

### 12.2.1. Optimization of parameters

#### ***Solvent optimization***

Five solvents were tested according to the literature (Issart et al., 2019) in terms of their ability to create the junction between the solvent and the sample surface. They were methanol at different concentrations (50 % and 80 %), 30 % acetonitrile and methanol-chloroform (2:1). 0.1 % formic acid was added to enhance the ionization (0.2 % formic acid in 25 % methanol was also tested). Solvents containing chloroform were not suitable, chloroform was evaporating very fast. The solvent containing acetonitrile was dripping so no solvent was left to be delivered to the sample. Thereby these solvents were eliminated. The 1:1 ratio and 4:1 have the same result so we did a compromise between them and chose to use 0.1 % formic acid in 25 % methanol.

#### ***Contact time and number of extractions***

After choosing the best solvent, the second step was to adjust other parameters in order to obtain the best micro-junction. The solvent can be in contact with the sample for a maximum of 1 min. Choosing a long contact time can lead to two main issues, the spread of the solvents and thus the tip will not suck the totality of the solvents or the evaporation of the solvents and losing the volume dropped on the sample. Visually talking, above 3 s, the solvent starts to spread and/or evaporate so our chosen contact time was 3 s. 1 s was too fast to extract compounds and the background noise was too high.

As for the number of extractions, consecutive extractions could be done on the same sample. When detecting low analytes signal, we tried to repeat the extraction. Two consecutive extractions did not improve the signal but resulted in the presence of intense peaks resulting from the plastic material and masking the extracted compounds. Thereby, one extraction was judged to be sufficient.

The gas pressure and the voltage were chosen according to the response of the compounds standards injected. The gas pressure was set at 0.15 and the voltage at 1.35.

### 12.2.2. LESA MS of plastics

An untargeted screening was done on some samples kept in river water for a few days and on plastics collected from the Lebanese coast. Full MS and ddMS2 were carried out, a full mass spectrum was acquired and the most abundant ions were fragmented. The data were then compared against a library, using the Mass frontier program. No contaminants were found which may be due to the insufficient sensitivity of the procedure.

And for the targeted approach, a list of standards was injected at first on infusion mode to check the exact masses and see the fragments of each compound. A method was then created for the compounds after specifying the exact masses and the most intense fragment of each compound and the best energy of collision suitable for the fragmentation of each of the species. The data were treated on the Xcalibur program.

### Spiking of microplastics with target contaminants

Whereas for the extraction of the other organic pollutants, plastics were soaked with water spiked with 9 standards (the 9 compounds found in plastics extracts by LC-MS analysis) at different concentration, small signals were observed for some of the compounds without being fragmented and other compounds showed good signals and were even fragmented. Noting that the compounds are fragmented only when there is enough signal, the compounds found and fragmented were from samples soaked in 50 ppb standards solutions. Figure 55, 56 and 57 are examples of the compounds detected and fragmented by LESA-MS.

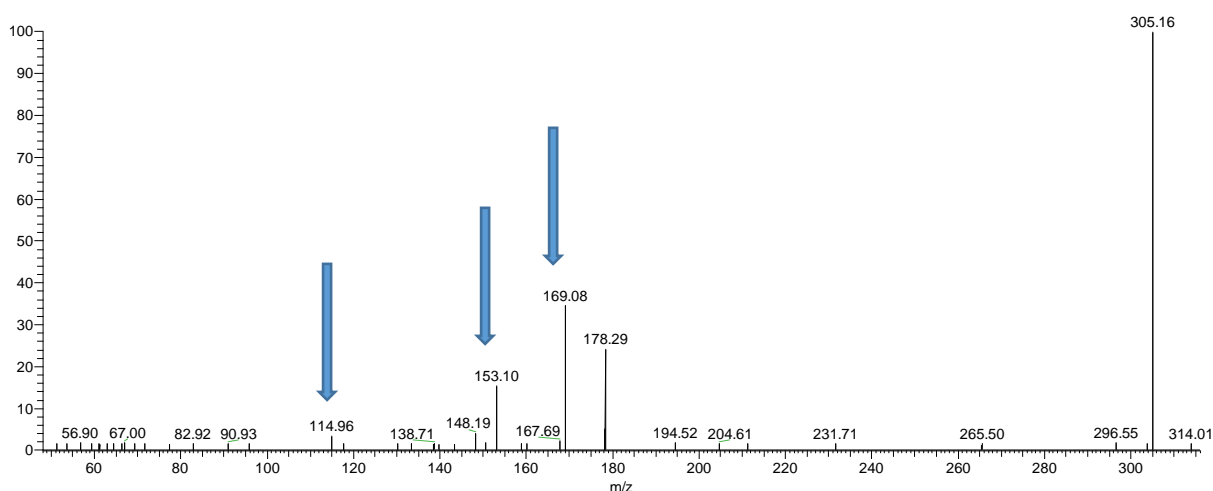


Figure 55 Spectra of fragmented diazinon from MPs soaked with 50 ppb standards, on LESA-MS

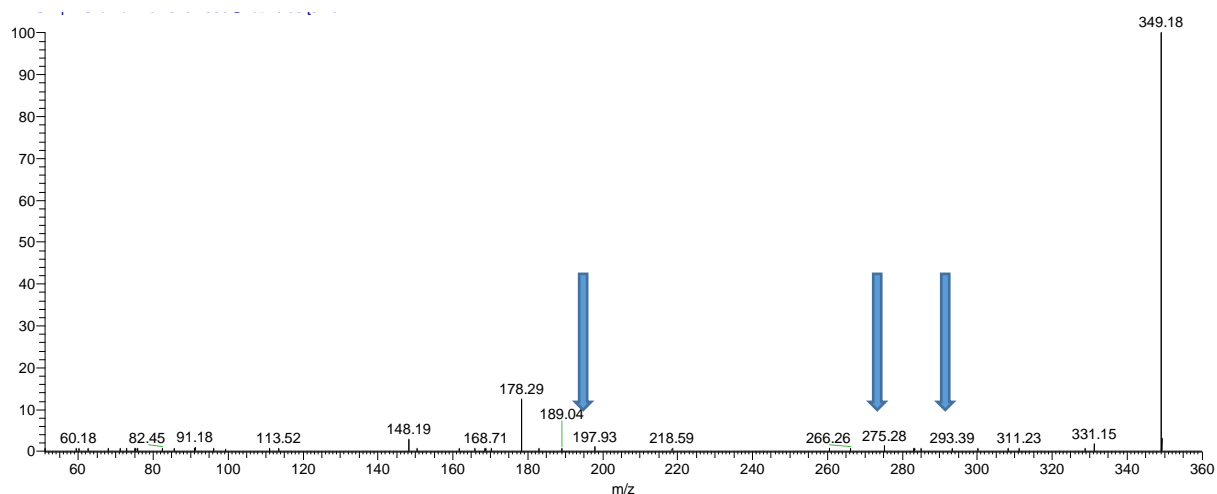


Figure 56 Spectra of fragmented chlorpyrifos from MPs soaked with 50 ppb standards, on LESA-MS

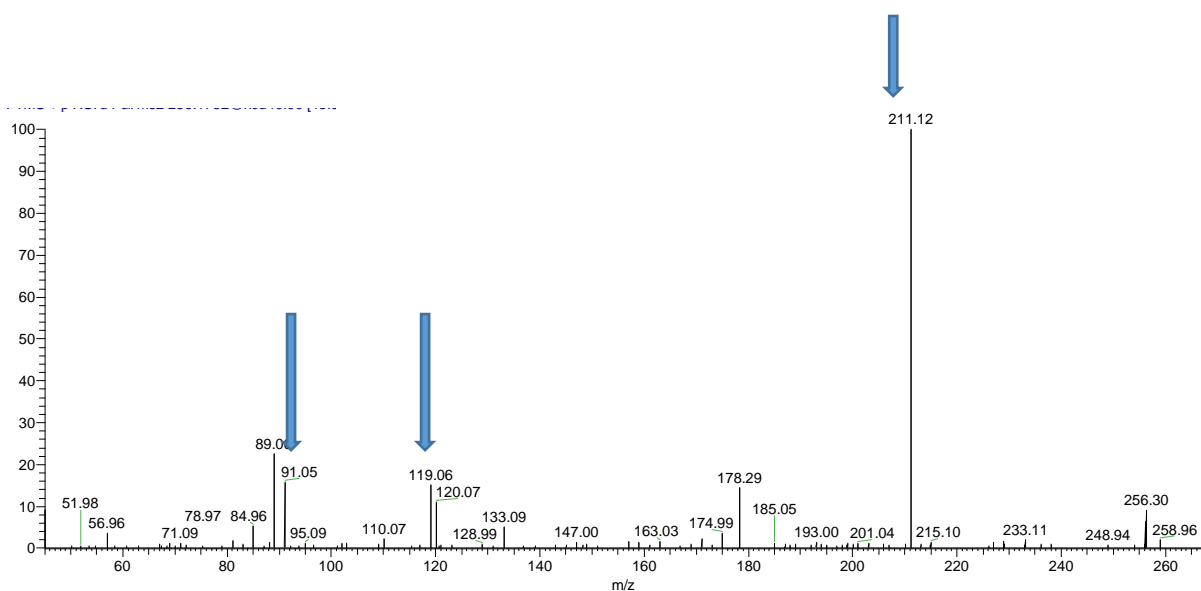


Figure 57 Spectra of fragmented tripeleminine from MPs soaked with 50 ppb standards, on LESA-MS

Those plastics were also extracted by methanol and analyzed by LC-MS/MS and all the compounds were extracted and found, chromatograms shown in Figure 58. So most probably, the high limit of detection is the cause of the lack of signals.



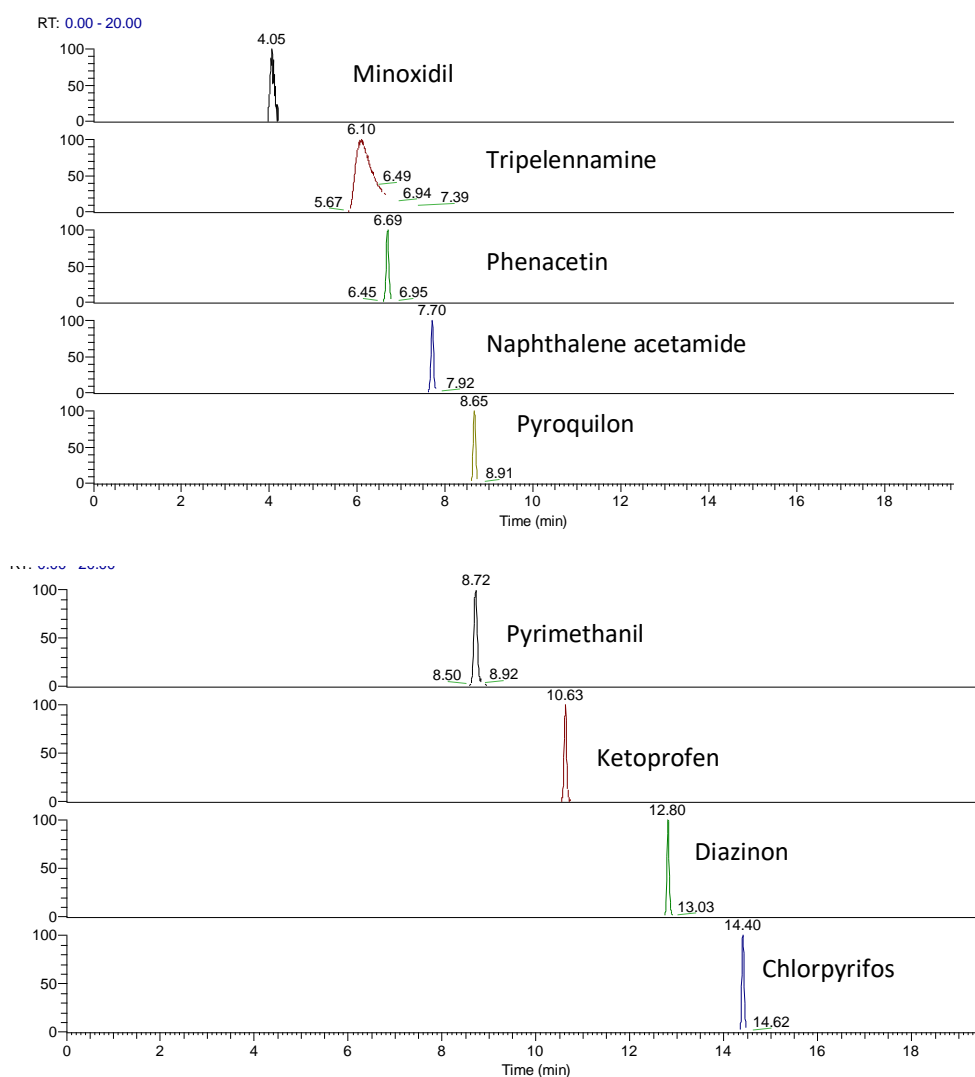


Figure 58 Chromatograms of all the 9 standards extracted from the replicates and analyzed by LC-MS, of plastics intended for LESA-MS analysis

### Feasibility of LESA to the analysis of pollutants sorbed on microplastics

In theory, LESA-MS should serve as an initial preliminary method for the screening of organic compounds sorbed on plastics, if only compared to compounds databases. However, the detection limits are much higher than those of the method including the traditional extraction. Consequently, it was impossible to demonstrate in practice the applicability of the optimized method to the analyses of any of the microplastics studied in this work.

The applicability of the method would be limited to highly polluted areas. For example, it could be used for the screening of pollutants found near wastewater enclosure or wastewater treatment plants. Another potential application could be the identification of polymer type, especially in the case of weathered environmental plastics which escape ATR IR spectroscopy.

## 13. Non-polar organic compounds associated with microplastics sampled on the Lebanese coast

### 13.1. GC-MS analysis

Usually, GC-MS is the most widely used technique to study the compounds adsorbed on microplastics with a main focus on PAHs and PCBs and OCPs (Camacho et al., 2019; Frias et al., 2010; Gorman et al., 2019; Tan et al., 2019). Considering the hydrophobicity of compounds detected by LC-MS, they are not adsorbed to plastics as other pollutants studied by GC-MS. To complement our study and cover a larger range of pollutants, a GC-MS analysis is developed afterward.

#### 13.1.1. Development of the analytical method

As a preliminary evaluation of the performance of the procedure (extraction and determination) employed to investigate the presence of organic pollutants associated to microplastic samples, the accuracy of  $m/z$  ratios measured for the most intense ions of a selection of compounds observed in sample extracts was evaluated.

Before choosing the solvents used for the extraction, some trials were done with different solvents. The solvents used for the extraction's trials were:

- 1- Isooctane
- 2- A mixture of 1:1 dichloromethane/ethyl acetate
- 3- A mixture of 1:1 dichloromethane/n-hexane for the first two extractions and isooctane for the last one

The mixture of dichloromethane/n-hexane and isooctane showed the best performance and extracted a larger number of compounds so this solvents combination was used for the extractions of all the samples analyzed by GC-MS.

Table 16 shows the results obtained for consecutive injections of 5 different microplastic extracts. The selection of compounds was made to cover different chromatographic regions, chemical families, and empirical formula. Mass errors varied in the range from 0.8 to 21 ppm, with standard deviations between 1.3 and 6.2 ppm. Considering that the interpolation performed by the Unknowns Analysis algorithm, to convert profile mode acquired data to deconvoluted centroid spectra, introduces a further bias of  $m/z$  values (Castro et al., 2022), the maximum error threshold, during comparison of deconvoluted spectra with those in accurate databases, and was set at 50 ppm. The short-term repeatability in the responses of the system was investigated, for same compounds, with 5 injections of the same microplastic extract. Relative standard deviations (RSDs, %) of peak areas for the quantification ion of above compounds, varied between 1 % and 20 %. The higher variability corresponded to compounds displaying low intensity peaks and/or eluting in a complex chromatographic region. The repeatability of the full analytical procedure, comprising extraction and determination steps, could not be evaluated directly due to the limited amount of each sample of microplastics. Instead, we calculated the variability in the responses of the deuterated compounds added to each sample. RSDs measured for PHE-d<sub>10</sub> and CHL-D<sub>10</sub>, corresponding to 31 different samples injected in duplicate during a one-week period were 25 % and 39 %, respectively.

Table 16 Mass accuracy assessment ( n=1 injection of 5 different extracts) and repeatability of the GC-TOF-MS response ( n=5 replicates of the same extracts)

Compound	Use	Retention time	Empirical formula	Extracted ion ( <i>m/z</i> )	Mass error (ppm)	SD mass error (ppm)	RSDs (peak area)
Cymene	Terpene	6.78	C10H14	119.0855	-12.3	1.3	6%
4-Ethylphenol	Phenol	10.32	C8H10O	107.0491	-12.0	1.3	20%
Benzothiazole	Plasticizer	11.89	C7H5NS	135.0137	-15.7	1.8	1%
Phenanthrene	PAH	25.18	C14H10	178.0777	-3.8	5.0	13%
TCPP	Flame retardant	25.69	C9H15Cl6O4P	277.0157	-0.7	3.1	7%
Galaxolide	Musk	26.77	C18H26O	243.1743	-1.5	2.9	9%
Dibutylphthalate	Plasticizer	27.016	C16H22O4	149.0233	-3.6	2.8	12%
Chlorpyrifos	Pesticide	29.64	C9H11Cl3NO3PS	313.9568	0.8	5.7	13%
Benzenesulfonanilide	Plasticizer	30.115	C12H11NO2S	233.0505	-2.4	5.2	9%
Pyrene	PAH	31.68	C16H10	202.0777	-1.5	3.9	4%
Triphenyl phosphate	Flame retardant	36.597	C18H15O4P	326.0702	-5.3	5.0	10%
Tinuvin 326	UV absorber	38.9	C17H18ClN3O	300.0898	-4.0	5.6	3%
Tinuvin 328	UV absorber	40.5	C22H29N3O	322.1913	1.6	6.2	10%
Tinuvin 327	UV absorber	40.671	C20H24ClN3O	342.1367	1.0	6.1	9%
Octocrylene	UV filter	40.805	C24H27NO2	360.2036	-20.5	6.2	16%

### 13.1.2. Screening of non-polar volatile and semi-volatile compounds in microplastic extracts and targeted analysis

Figure 59 illustrates the different steps leading to identification of lindane (gamma-hexachlorocyclohexane, HCH) and a dichlorinated biphenyl in the same microplastic extract. Fig. 59A and 59B show the raw and the deconvoluted GC-TOF-MS chromatograms in the region between 24 and 25.4 min. The 2<sup>nd</sup> plot (Fig. 59B) contains two small peaks at 24.79 and 24.84 min, whose spectra show several common ions to those in the NIST spectra for the isomers hexachlorocyclohexane (HCH) and a dichlorobiphenyl, Fig. 59C and 59D, respectively. In both cases, deconvoluted spectra (upper part of the figure) contained extra ions to those existing in the NIST database (lower part), so the spectral fitting is obviously not perfect. Their normalized scores (0-100 scale) were 70 and 84 for Fig. 59C and 59D respectively; moreover, the differences between NIST LRI values of HCH isomers and several dichlorinated PCBs and those for peaks at 24.79 and 24.84 min remained below 50 units. Compared to the accurate EI-MS spectrum of lindane (Fig. 59E), the deconvoluted spectra in Fig. 63C showed four common ions with relative mass errors between 4 and 10 ppm. Finally, the extracted ion chromatogram (EIC) plots (Fig. 59F) for a mixture of the four possible HCH isomers, a procedural blank, and the microplastic extracts, confirmed the identity of the suspected compound as lindane. In the particular case of the dichlorinated biphenyl, the exact identity of the observed congener was not confirmed given the number of potential congeners of dichlorinated PCBs.

Compounds identified in the extracts from microplastic samples are compiled in Table 17 (tentative identifications Table 18 (confirmed species). A number of aliphatic hydrocarbons (linear or branched) whose spectra contain just fragment ions at *m/z* ratios below 100, with nominal differences of 14 Da between consecutive fragment ions (losses of CH<sub>2</sub> moieties), were not included in any of these Tables given the poor specificity of such fragmentation pattern.

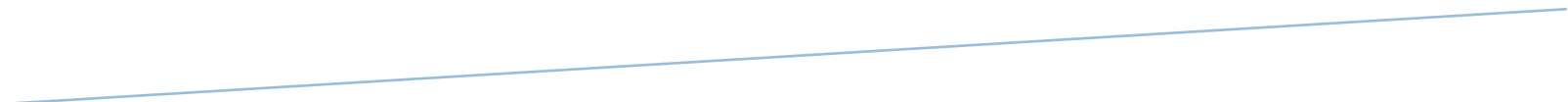
Species noticed at similar concentration levels in procedural blanks and samples extracts were also removed. The latter group comprised several phenolic antioxidants, with a chemical structure derived from that of di-tert-butyl phenol. Some plasticizers (i.e. phthalates), organophosphorous flame retardants (i.e. Tris(1-chloro-2-propyl) phosphate, TCPP) and UV absorbers were often noticed in procedural blanks; however, blank responses represented less than 10 % of those observed in the extracts from most microplastics. In these cases, they were considered as tentative or confirmed identifications.

Table 17 Summary of compounds tentatively identified in microplastic samples.

Compound	RT(m in)	CAS number	Base peak in EI spectra (a.m.u.)		Mass error (ppm)	LRI		LRI difference	Positive samples	Other ions	
			Experimen tal	Calculated		<sup>a</sup> Experimental	<sup>b</sup> Calculated			Ion 2	Ion 3
Propyl benzene	5.18	103-65-1	91.0534	91.0542	-8.8	969	953	-16	16	120.0859	
Benzaldehyde	5.29	100-52-7	105.0316	105.03349	-18.0	973	962	-11	14	78.0382	51.1147
Hexanoic acid	5.43	144-62-1	60.0201	60.0206	-8.3	977	990	13	25	73.0226	87.0373
Trimethylbenzene-1	5.48		105.0697	105.0698	-1.0	980	972-1013		29	120.0837	
Alpha-Phellandrene	5.60	99-83-2	93.0686	93.06988	-13.8	1005	985	-20	13	77.0308	136.1146
Aniline	5.61	62-53-3	93.0576	93.0573	3.2	985	977	-8	3	66.0398	
Trimethylbenzene-2	5.73		105.0696	105.0698	-1.9	990	972-1013		7	120.0870	91.0480
Furan, 2-pentyl	5.94	3777-69-3	81.0316	81.03349	-23.3	997	993	-4	6	138.0974	
2,3,6-Trimethyl pyridine	5.95	1462-84-6	121.0883	121.0886	-2.5	998	1003	5	24	79.0484	
Trimethylbenzene-3	6.03		105.0699	105.0698	1.0	1001	972-1013		28	120.0837	
D-Limonene	6.81	5989-27-5	93.0699	93.0698	1.1	1033	1018	-15	29	136.1164	121.0939
Benzyl alcohol	6.88	100-51-6	79.0532	79.05422	-12.9	1035	1036	1	1	108.0491	91.0470
Heptanoic acid	7.77	111-14-8	60.0198	60.0206	-13.3	1071	1078	7	22	73.0214	87.0364
p-Cresol	7.81	16-44-5	107.0484	107.0491	-6.5	1073	1077	4	4	77.0313	
2-Methyl benzaldehyde	8.09	529-20-4	119.0482	119.0491	-7.6	1084	1064	-20	8		

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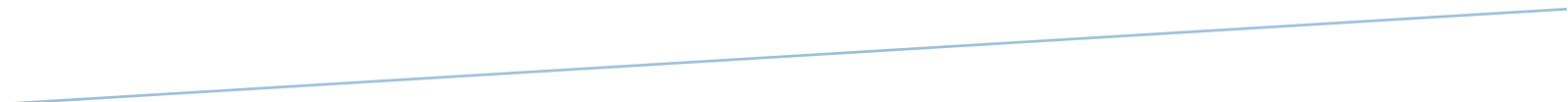
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<b>3-Acetyl-2,5-dimethyl furan</b>	8.34	10599-70-9	123.0446	123.044	4.9	1095	1099	4	25	138.0606	67.0481
<b>2-Cyclohexen-1-one, 4,4-dimethyl</b>	8.63	1073-13-8	82.0415	82.0413	2.4	1106	1101	-5	6	124.0794	95.0774
<b>Phorone</b>	8.91	504-20-1	123.0792	123.0804	-9.7	1117	1092	-25	10	138.0967	95.0773
<b>Benzoic acid</b>	10.00	65-85-0	105.0327	105.0334	-6.7	1158	1170	12	30	122.0292	77.0325
<b>Estragole</b>	11.14	140-67-0	148.0869	148.0882	-8.8	1201	1196	-5	1	147.074	131.078
<b>Benzaldehyde, 2,5-dimethyl</b>	11.59	5779-94-2	133.0645	133.0647	-1.5	1218	1208	-10	31	134.0635	105.0615
<b>Benzene, 1,3-terbutyl</b>	12.62	1014-60-4	175.1464	175.1481	-9.7	1257	1249	-8	19	190.1657	
<b>Anethole</b>	13.45	4180-23-8	148.0883	148.0882	0.7	1288	1284	-4	15	147.074	133.058
<b>Phenol, 2-methyl, 5-isopropyl</b>	13.82	499-75-2	135.0776	135.0804	-20.7	1303	1299	-4	4	150.0969	115.0478
<b>Naphthalene, 2-methyl</b>	14.12	91-57-6	142.0769	142.07775	-6.0	1314	1298	-16	15		
<b>Triacetin</b>	15.09	102-76-1	103.039	103.03897	0.3	1352	1344	-8	4	145.0414	116.0431
<b>n-decanoic acid</b>	15.46	334-48-5	129.09	129.091	-7.7	1366	1373	7	18	143.0962	73.0214
<b>Chloroxilenol</b>	15.96	88-04-0	121.0633	121.0647	-11.6	1386	1398	12	2	156.0256	158.0233
<b>Sulphur-6</b>	18.74	13798-23-7	191.8305	191.8318	-6.8	1498	1500	2	12	127.8801	63.9375
<b>Alpha Farnesene</b>	19.04	502-61-4	93.0701	93.06988	2.4	1511	1508	-3	1	107.0772	123.1084
<b>2,2'-Dimethylbiphenyl</b>	19.79	605-39-0	167.0834	167.0855	-12.6	1543	1546	3	4	182.1013	
<b>4,4'-Dimethyl biphenyl</b>	20.90	613-33-2	182.1076	182.109	-7.7	1590	1608	18	19	167.0795	
<b>3,5-Di-tert-Butyl-2-hydroxybenzaldehyde</b>	21.01	37942-07-7	219.1406	219.13796	12.0	1595	1621	26	16	234.1552	

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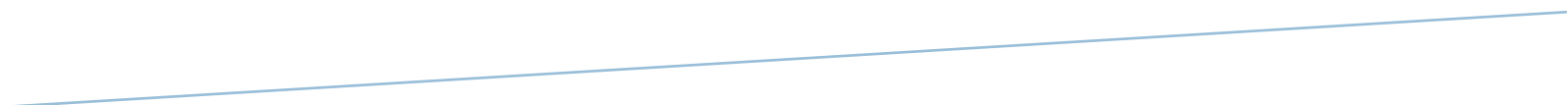
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<b>4-Propyl-1,1'-diphenyl</b>	22.71	10289-45-9	167.0845	167.0855	-6.0	1670	1679	9	6	196.1216	
<b>Dibenzothiophene</b>	24.54	132-65-0	184.0359	184.0341	9.8	1755	1766	11	7	139.0475	
<b>1,1'-Biphenyl, 3,3'-dichloro-</b>	24.83	2050-67-1	221.9981	221.999	-4.1	1770	1755	-15	13	223.9909	152.0554
<b>3,5-di-tert-Butyl-4-hydroxybenzaldehyde</b>	24.86	1620-98-0	219.1392	219.1379	5.9	1770	1772	2	26	191.1065	234.1631
<b>2,2',3-Trichloro-1,1'-biphenyl</b>	25.23	38444-78-9	255.9614	255.9607	2.7	1788	1811	23	2	220.987	186.0173
<b>2,4',6-Trichloro-1,1'-biphenyl</b>	26.00	38444-77-8	257.9588	257.9579	3.5	1825	1824	-1	1	255.9559	186.0173
<b>Methyl phenanthrene-1</b>	27.46		192.0924	192.09335	-4.9	1897	1890-1915		31	189.0693	
<b>Methyl phenanthrene-2</b>	27.58		192.093	192.09335	-1.8	1903	1890-1915		31	189.0694	
<b>Methyl phenanthrene-3</b>	27.96		192.0981	192.09335	24.7	1923	1890-1915		31	189.067	
<b>Dimethyldibenzo(b,d)thiophene-1</b>	28.64		212.0677	212.0654	10.8	1958	1947	-11	12	197.0359	178.0719
<b>Dimethyldibenzo(b,d)thiophene-2</b>	29.07		212.0648	212.0654	-2.8	1981	1947	-34	15	197.0382	178.0777
<b>Dimethyldibenzo(b,d)thiophene-3</b>	29.43		212.0636	212.0654	-8.5	2000	1947	-53	15		
<b>Dimethyl phenanthrene-1</b>	29.64		206.1099	206.10895	4.6	2010	2009-2051		31	191.0861	
<b>Dimethyldibenzo(b,d)thiophene-4</b>	29.80		212.0678	212.0654	11.3	2018	1947	-71	14		
<b>Dimethyl phenanthrene-2</b>	29.81		206.106	206.10895	-14.3	2020	2009-2051		31	191.0897	
<b>Dimethyl phenanthrene-3</b>	29.89		206.1097	206.10895	3.6	2023	2009-2051		31	191.0856	

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<b>Benzenesulfonanilide</b>	30.05	1678-25-7	233.0494	233.0505	-4.7	2032	2072	40	16	168.0806	140.9948
<b>Sulphur-8</b>	30.13	10544-50-0	159.86	159.8598	1.3	2036	2049	13	27	225.0904	159.858
<b>Dimethyl phenanthrene-4</b>	30.16		206.11	206.10895	5.1	2037	2009-2051		31	191.0856	
<b>Dimethyl phenanthrene-6</b>	30.39		206.1093	206.10895	1.7	2051	2009-2051		31	191.0852	
<b>Dimethyl phenanthrene-7</b>	30.51		206.1089	206.10895	-0.2	2060	2009-2051		31	191.0842	
<b>Dimethyl phenanthrene-8</b>	30.59		206.1093	206.10895	1.7	2066	2009-2051		31	191.0841	
<b>Tetrachloro biphenyl-1</b>	30.79		291.9159	291.9189	-10.3	2072	2082	10	1	219.98	
<b>Tetrachloro biphenyl-2</b>	31.52		291.915	291.9189	-13.4	2112	2094	-18	1	219.9777	
<b>Methyl stearate</b>	31.83	112-61-8	74.038	74.0362	24.3	2129	2128	-1	10	255.2247	298.2797
<b>Hexadecanamide</b>	32.81	629-54-9	59.0373	59.0365	13.6	2186	2184	-2	29	128.0957	212.1953
<b>Retene</b>	33.50	483-65-8	219.1192	219.1168	11.0	2223	2198	-25	1	2040891	234.1364
<b>Hexachloro biphenyl-1</b>	34.04		359.8417	359.841	1.9	2256	2250	-6	5	328.3126	301.2878
<b>Hexachloro biphenyl-2</b>	34.91		359.8412	359.841	0.6	2307	2345	38	7	324.8717	289.902
<b>Methyl dehydroabietate</b>	35.63	1235-74-1	239.1815	239.1794	8.8	2352	2336	-16	5	299.1995	314.2212
<b>Benz[a]anthracene, 2-methyl</b>	39.30	2498-76-2	242.1096	242.109	2.5	2586	2542	-44	28	119.5352	
<b>Terephthalic acid, bis(2-ethylhexyl) ester</b>	41.69	6422-86-2	261.1502	261.1485	6.5	2751	2766	15	31	167.0297	149.0197
<b>Perylene</b>	43.08	198-55-0	252.0949	252.09335	6.1	2851	2815	-36	24	125.039	
<b>Dinonyl phthalate</b>	43.49	84-76-4	149.021	149.0233	-15.4	2881	2880	-1	14	293.1769	

<sup>a</sup> $m/z$  values from profile spectra

<sup>b</sup>Calculated  $m/z$  from known fragment ions in the NIST database



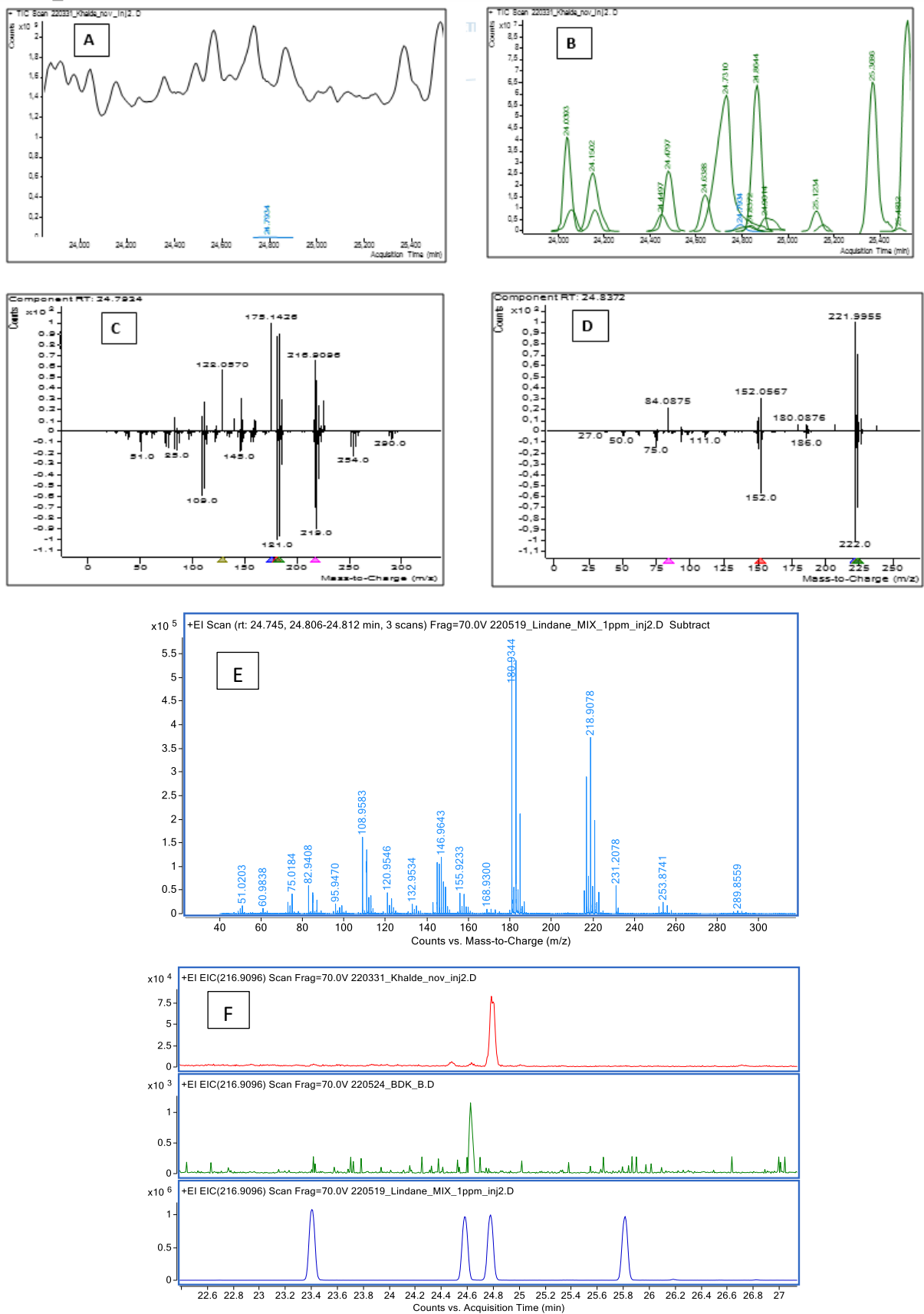


Figure 59 A, B, C, D, E, F Steps leading to the Identification of lindane

The reliability of the data mining strategy regarding false positives and false negatives was also evaluated. Spectral comparison against the NIST low resolution database combined with LRI match, (within limits defined in the Material and Methods section) led to a percentage of false positives below 2 %. Around 140 compounds fulfilling above criteria, only octyl benzene and 5-isopropyl-1H-1,2,4-triazole-3-amine were noticed as false identifications based on mass differences above 50 ppm between experimental  $m/z$  of most relevant ions in their deconvoluted spectra and those calculated from the NIST spectral database. In this vein, the use of accurate  $m/z$  ratios as additional confirmation, or exclusion, parameter represents a step ahead compared to previous screening approaches using nominal resolution mass analyzers (Ravit et al., 2019). On the other hand, the percentage of false negatives varied depending on the response intensity of each compound and the complexity of the chromatographic region around its retention time. Using PCB-30 as control species (added to samples at  $200 \text{ ng g}^{-1}$  before extraction) the compound was correctly identified in all samples; so, no false negatives were noticed. However, some compounds showing relatively low detection frequencies in Table 18, could be further quantified in a higher number of samples, tables 20-21. Some examples are octocrylene and galaxolide. Despite their relevant concentration levels in the extracts from microplastics, the UV filter, octocrylene, eluted in a complex chromatographic region and galaxolide presented a broad peak resulting from co-elution of both diastereomers. In summary, the data mining strategy was quite robust as regards the number of false positives, but underestimated the occurrence frequency of many compounds.

Table 18 Confirmed compounds identified in the extracts from microplastic samples-GC-MS

Compound	Use/type	Retention time (min)	CAS number	Base peak in EI spectra (a.m.u.)			LRI			Positive samples	Other ions	Other ions
				<sup>a</sup> Experimental (m/z)	<sup>b</sup> Database (m/z)	Mass error (ppm)	Experimental	Library	LRI difference		Ion 2	Ion 3
<b>o-Cymene</b>	Aromatic	6.72	527-84-4	119.0855	119.0855	0.0	1029	1022	-7	27	134.1047	91.0502
<b>Eucalyptol</b>	Terpene	6.90	470-82-6	139.1083	139.1117	-24.4	1036	1032	-4	4	154.1250	111.0784
<b>4-Ethyl phenol</b>	Aromatic	10.26	123-07-9	107.0491	107.0491	0.0	1168	1131	-37	22	122.0683	77.0353
<b>Octanoic acid</b>	Fatty acid	10.28	124-07-2	73.0281	73.0284	-4.1	1169	1180	11	30	115.0668	101.053
<b>Naphthalene</b>	PAH	10.76	91-20-3	128.0616	128.06205	-3.5	1187	1182	-5	13	102.0408	
<b>Alfa-Terpineol</b>	Terpene	10.94	98-55-5	93.07	93.0698	2.1	1194	1189	-5	4	136.1158	121.0927
<b>Benzothiazole</b>	Plasticizer	11.83	95-16-9	135.0134	135.0137	-2.2	1227	1229	2	27	107.9987	
<b>Nonanoic acid</b>	Carboxylic acid	12.86	112-05-0	73.02768	73.0284	-9.9	1266	1273	7	20	115.0668	129.0826
<b>Thymol</b>	Aromatic	13.56	89-83-8	135.0802	135.0804	-1.5	1293	1291	-2	4	150.0969	115.0478
<b>Phthalic anhydride</b>	Plasticizer	14.19	85-44-9	104.0249	104.0256	-6.7	1317	1316	-1	16	76.0253	
<b>Copaene</b>	Terpene	15.84	3856-25-5	161.1295	161.1324	-18.0	1381	1376	-5	4	204.1792	119.077
<b>Biphenyl</b>	Aromatic	15.86	92-52-4	154.0777	154.0777	0.0	1382	1381	-1	15		
<b>Methyleugenol</b>	Terpene	16.48	93-15-2	178.0971	178.09883	-9.7	1406	1402	-4	1	163.0666	147.0717
<b>Longifolene</b>	Terpene	16.63	475-20-7	161.1307	161.13248	-11.0	1413	1405	-8	2	204.181	189.1567
<b>Dimethyl phthalate</b>	Plasticizer	17.75	131-11-3	163.0395	163.0389	3.7	1458	1454	-4	10	133.0212	
<b>Phthalimide</b>	Pesticide	17.83	85-41-6	147.0316	147.0314	1.4	1461	1450	-11	2	104.0196	76.024
<b>2,5-Di-tert-Butyl-1,4-benzoquinone</b>	Antioxidant	18.08	2460-77-7	177.1275	177.1274	0.6	1471	1466	-5	7	220.1391	205.1153
<b>2,4,5-Trichloroaniline</b>	Pesticide	19.79	636-30-6	194.9378	194.9403	-12.8	1543	1554	11	2	196.9325	

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<b>Diethyl phthalate</b>	Plasticizer	21.09	84-66-2	149.0218	149.0233	-10.1	1598	1594	-4	11	177.0528	
<b>2,4,6-Tribromoanisole</b>	Pesticide	21.55	607-99-8	343.7868	343.7865	0.9	1618	1620	2	5	330.7581	
<b>Propylparaben</b>	PCP	21.69	94-13-3	121.0291	121.0284	5.8	1625	1632	7	1	138.0278	
<b>Benzophenone</b>	UV absorber	21.87	119-61-9	105.0315	105.0334	-18.1	1633	1635	2	12	182.0671	77.0332
<b>2,4,6-Tribromophenol</b>	Flame retardant	22.02	118-79-6	329.7745	329.7708	11.2	1640	1624	-16	1	331.7666	
<b>Hexachlorobenzene</b>	Pesticide	23.69	118-74-1	283.812	283.8096	8.5	1715	1707	-8	1	285.8047	281.8087
<b>Pentachloroanisole</b>	Pesticide	23.95	1825-21-4	264.8347	264.8357	-3.8	1727	1717	-10	1	279.859	281.8556
<b>Lindane</b>	Pesticide	24.79	58-89-9	180.9363	180.9373	-5.5	1767	1754	-13	1	216.9096	182.9294
<b>Phenanthrene</b>	PAH	25.14	85-01-8	178.0775	178.0777	-1.1	1782	1775	-7	31	152.0593	
<b>Pyrimethanil</b>	Pesticide	25.47	53112-28-0	198.1022	198.1026	-2.0	1799	1793	-6	1	199.1082	
<b>TCP</b>	Flame retardant	25.61	13674-84-5	124.9988	124.9998	-8.0	1806	1811	5	11	201.0091	277.019
<b>2-Ethylhexyl salicylate</b>	UV absorber	25.73	118-60-5	120.0208	120.0206	1.7	1811	1811	0	2	250.1579	138.0305
<b>Isopropyl myristate</b>	Natural product	26.06	110-27-0	60.0215	60.0206	15.0	1828	1827	-1	16	211.1984	228.1917
<b>Caffeine</b>	Natural product	26.49	58-08-2	194.0785	194.0798	-6.7	1849	1835	-14	1	137.0527	109.0854
<b>Galaxolide</b>	PCP	26.73	1222-05-5	243.1763	243.1743	8.2	1861	1851	-10	10	258.2013	213.1643
<b>Tonalide</b>	PCP	26.97	21145-77-7	243.1758	243.1743	6.2	1873	1843	-30	2	258.222	201.1235
<b>Prometryn</b>	Pesticide	28.06	7287-19-6	241.1368	241.1355	5.4	1928	1905	-23	1	184.0659	226.1224
<b>Dibutyl phthalate</b>	Plasticizer	28.81	84-74-2	149.023	149.0233	-2.0	1966	1965	-1	28	223.0981	
<b>Chlorpyrifos</b>	Pesticide	29.44	2921-88-2	196.9167	196.9196	-14.7	1998	1975	-23	19	313.9583	257.8941
<b>4,4'-dichlorobenzophenone</b>	Pesticide	29.49	90-98-2	138.9968	138.9946	15.8	1991	1981	-10	1	249.9982	251.9967
<b>Triadimefon</b>	Pesticide	29.55	43121-43-3	208.0282	208.0272	4.8	2005	1986	-19	1	181.014	127.9983
<b>Benzophenone-3</b>	UV filter	30.12	131-57-7	227.0714	227.0702	5.3	2035	2051	16	1	151.0366	
<b>Fluoranthene</b>	PAH	30.69	206-44-0	202.0772	202.0777	-2.5	2064	2054	-10	5	174.0464	100.0304


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<b>Drometrizole (Tinuvin P)</b>	UV absorber	30.74	2440-22-4	225.0904	225.0896	3.6	2069	2063	-6	1	168.0822	
<b>Pyrene</b>	PAH	31.63	129-00-0	202.0785	202.0777	4.0	2117	2093	-24	28		
<b>o,p'-DDE</b>	Pesticide	31.68	3424-82-6	246.0021	245.9998	9.3	2122	2097	-25	1	317.9253	
<b>p,p'-DDE</b>	Pesticide	32.88	72-55-9	245.9966	245.9997	-12.6	2188	2168	-20	2	315.9351	
<b>Mitotane (o,p')-DDD</b>	Pesticide	33.19	53-19-0	235.0099	235.0075	10.2	2206	2170	-36	2	165.0665	
<b>Tributyl acetyl citrate</b>	Plasticizer	34.29	77-90-7	185.0807	185.0808	-0.5	2270	2267	-3	20	129.0152	259.1543
<b>p,p'-DDD</b>	Pesticide	34.41	72-54-8	235.0065	235.0075	-4.3	2278	2257	-21	2	200.0417	165.0666
<b>2-Ethylhexyl-4-methoxycinnamate</b>	UV filter	35.19	5466-77-3	178.0647	178.0624	12.9	2325	2339	14	10	161.0548	133.0608
<b>4,4' DDT</b>	Pesticide	35.72	50-29-3	235.0069	235.0075	-2.6	2360	2343	-17	7	237.0047	
<b>Triphenyl phosphate</b>	Plasticizer, pesticide	36.54	115-86-6	326.0675	326.0702	-8.3	2407	2387	-20	10	325.0608	295.296
<b>Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-</b>	Antioxidant	36.89	119-47-1	177.13	177.1273	15.2	2427	2414	-13	27	340.2374	284.1722
<b>Chrysene</b>	PAH	37.45	218-01-9	228.0947	228.0933	6.1	2468	2437	-31	23	226.0724	
<b>BDE-47</b>	Flame retardant	38.38	5436-43-1	325.8781	325.876	6.4	2530	2530	0	2	485.71	
<b>Bis (2-ethylhexyl) phthalate</b>	Plasticizer	38.82	117-81-7	149.0243	149.0233	6.7	2554	2529	-25	27	167.0341	279.1646
<b>Tinuvin 326</b>	UV absorber	38.83	3896-11-5	300.0919	300.0898	7.0	2557	2577	20	2	315.1164	272.0612
<b>Tinuvin 329</b>	UV absorber	39.22	52188-76-8	252.1162	252.1131	12.3	2581	2601	20	2	323.2013	
<b>Tinuvin 328</b>	UV absorber	40.43	25973-55-1	322.1915	322.1913	0.6	2665	2665	0	19	351.2293	252.1092
<b>Tinuvin 327</b>	UV absorber	40.59	3864-99-1	342.1354	342.1367	-3.8	2674	2689	15	2	286.0729	357.1607
<b>Octocrylene</b>	UV filter	40.71	6197-30-4	248.0701	248.0706	-2.0	2682	2690	8	1	360.1951	232.0737
<b>Permethrin cis</b>	Pesticide	41.03	54774-45-7	183.0825	183.0804	11.5	2709	2706	-3	4	191.0842	
<b>Permethrin trans</b>	Pesticide	41.29	51877-74-8	183.0825	183.0804	11.5	2720	2706	-14	4	191.0842	

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<b>Octabenzone</b>	UV absorber	42.01	1843-05-6	213.055	213.0546	1.9	2774	2786	12	3	326.1855	137.0197
<b>BDE-99</b>	Flame retardant	42.25	60348-60-9	403.7876	403.7865	2.7	2790	2811	21	2	565.632	

Table 18 compiles spectral and chromatographic data for a list of 65 compounds (sorted attending to their increasing retention times) confirmed in the extracts from microplastic samples. In general, mass errors (calculated against the base peak in the spectra of verification standards) and LRI differences remained below 15 ppm and 20 units, respectively. Compounds in Table 18 have different origins and uses. Some of them are natural compounds, as it is the case of terpenes, fatty acids, and other low molecular weight phenolic species (i.e. methyl eugenol). Many of these species are employed as flavors and bactericides by food and cosmetic industry. So far, just one previous study highlighted the presence of this type of compounds in microplastics (Ravit et al., 2019).

A second group of compounds compiled in Table 18 corresponds to different kinds of additives in polymeric materials, from plasticizers (i.e. phthalates) to flame retardants (chlorinated and brominated), and UV absorbers (mainly benzotriazole derivatives) employed to enhance the photochemical stability of polymeric materials.

Some of the compounds included in this table are pesticides and/or their transformation products. Some are currently authorized pesticides (i.e. permethrin, triadimefon, pyrimethanil, prometryn). In other cases, their uses have been recently restricted (chlorpyrifos). Finally, some species are recognized as legacy pollutants (i.e. DDT and related species, hexachlorobenzene, pentachloroanisole, etc.), whose industrial production has been phased out by the end of the last century. The fungicides triadimefon and pyrimethanil, and the herbicide prometryn were identified in just one or two samples; however, they showed more intense signals than those of legacy pesticides. As example, prometryn was noticed in fragments of microplastics collected in S3-12/11/2020 (Tripoli 1), being absent in the rest of samples (18 samples) collected from same place during three sampling campaigns, Fig 60. It seems feasible that low occurrence pesticides are related with the former use of plastics, rather than with compounds uptake from the aquatic environment.

Table 17 compiles a list of 70 tentatively identified compounds, considering same thresholds as regards mass errors and LRI differences as for compounds in Table 18. In this case, their identities were not confirmed against authentic standards; thus, mass errors were estimated using the calculated  $m/z$  ratios of fragment ions with known empirical formulae in their NIST low resolution spectral database. Table 17 also includes several groups of congeners with identical EI-MS spectra and very close LRI values. Some examples are the methyl and di-methyl forms of phenanthrene, alkylated heterocyclic aromatic compounds (i.e. methylated dibenzothiophenes), and polychlorinated biphenyls (PCBs) with the same number of chlorine substituents. The latter represents a group of lipophilic and persistent pollutants, previously reported to be concentrated by microplastics; however, given the number of possible chlorination positions, their unambiguous identification is rather complex. For these groups of positional isomeric compounds, neither CAS numbers nor LRI have been included in Table 17

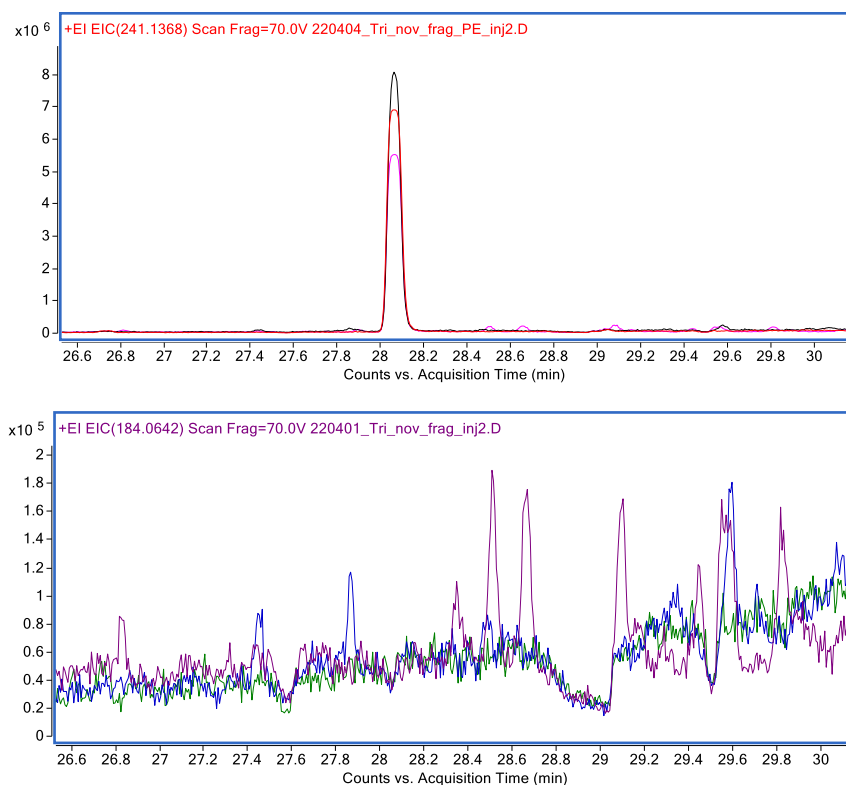


Figure 60 Overlay of EIC chromatograms for the most intense ions in the spectrum of prometryn in two different microplastic samples obtained in the same place ( above the contaminated sample and below a zoom on the area of RT of prometryn in a non contaminated sample)

### 6.1.1. Concentrations found

Tables 20 and 21 summarize the concentrations of 42 compounds in the extracts from microplastic samples. Quantification, qualification ions and linear responses range of the GC-QTOF-MS system for these compounds are provided in Table 22. The selection of compounds was made considering a number of variables: such as over the counter availability, detection frequency, ecotoxicity and previous studies reporting their presence in microplastics from other regions of the world (Capriotti et al., 2021; Fred-Ahmadu, et al., 2022; Frias et al., 2010; Gorman et al., 2019; Herrera et al., 2022).

In summary, the list of quantified pollutants includes several species from Table 19, a selection of six PCBs (usually found in environmental matrices), and a few additional compounds (i.e certain PAHs) not detected using the data mining approach defined in previous paragraphs, but with similar origin to those listed in Table 18.

Compounds in Tables 20 and 21 were sorted in five groups: personal care products (PCPs), pesticides, plastic additives (plasticizers, brominated and chlorinated flame retardants, and UV absorbers), PCBs and PAHs. In general, the percentage of extracts containing one of the target species above the instrumental LOQs (Tables 20-21) is higher than that obtained following the data mining approach (Table 18).



This is an expected result, considering that the success of data mining is affected by the efficiency of *SureMass* deconvolution algorithm, the chromatographic shape associated to each compound, the setting of minimum intensity threshold during the deconvolution process (in our case a minimum peak height of 50000 was established) and compounds misidentification (false negatives). The latter is rather common in case of species with same empirical formula and just subtle differences in their chemical structures, as well as for those showing only fragment ions at low  $m/z$  values.

Fig 61 shows the normalized contribution of each group of compounds in the processed samples, and Fig. 62 illustrates the relative concentrations of the two most abundant species within each group. The class showing the higher normalized concentration within each sample was that of polymer additives, followed by PCPs, PAHs, pesticides and finally PCBs.

The benzotriazole type UV absorbers, tinuvin 326 and 327 were the pollutants showing the higher concentrations within the group of polymer additives, Fig. 62. From an ecotoxicological perspective, tinuvin 328 has been pinpointed by the Stockholm convention as the only non-halogenated compound proposed for inclusion in the list of persistent organic pollutants (Karlsson, 2022). This latter compound was quantified in most samples, with a median concentration of  $130.5 \text{ ng g}^{-1}$ , Tables 20 and 21.

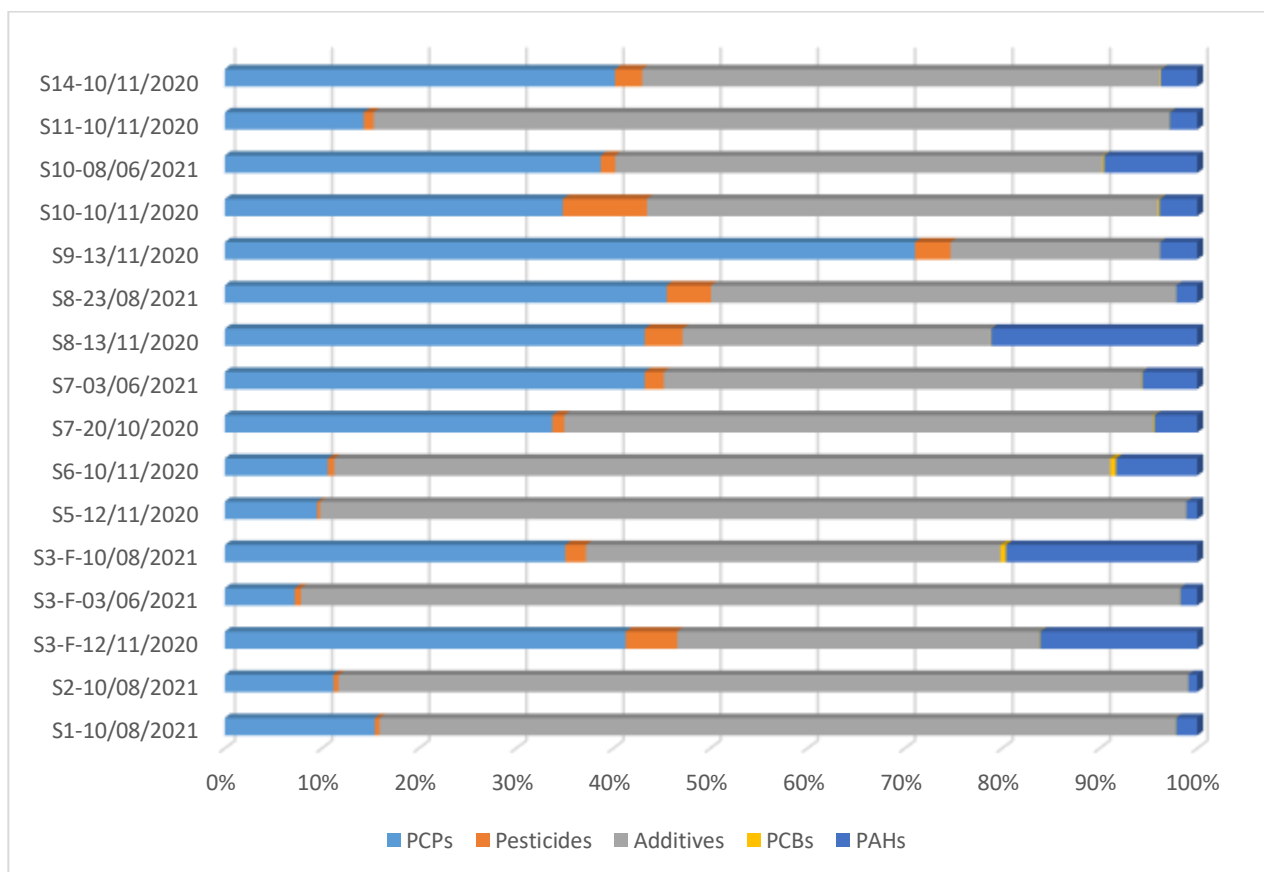


Figure 61 Normalized contribution of each family of compounds to the total compounds concentration measured in each sample

Table 19 Retention times, quantification and qualification ions, linearity and limits of quantification (LOQs) of the GC-QTOF-MS system for compound quantified in microplastic extracts

	Compound	Retention (min)	Quantification ion	Qualification ion 1	Qualification ion 2	Ratio 1	Ratio 2	R2, split (range ng mL-1)	R2, pulsed splitless (range ng mL-1)	LOQ (ng mL-1, splitless mode)
Personal care products (PCPs)	Galaxolide	26.69	243.1719	258.1947		0.15		0,993 (500-20000)	0,996 (3-500)	2
	Propylparaben	21.6	138.0308	121.0277		1.4			0,994 (10-1000)	3
	Benzophenone-3	30.09	227.0704	151.0365		0.4		0,995 (500-5000)	0,990 (10-500)	10
	EHMC	35.16	178.0596	290.1857		0.07		0,996 (500-5000)	0,999 (10-500)	5
	Octocrylene	40.67	360.1949	248.0706	232.0747	128	126	0,999 (500-5000)	0,990 (10-500)	5
Pesticides	Chlorpyrifos	29.39	313.9554	315.9458	196.9196	0.76	0.99		0,990 (5-1000)	4
	Triadimefon	29.51	208.0272	210.0245	293.0925	0.37	0.05		0,996 (10-2000)	8
	4,4'-DDT	35.72	235.0075	237.0048					0,990 (2-500)	1
	4,4'-DDE	32.86	317.9335	319.9312		0.49			0,995 (1-500)	1
	2,4'-DDE	31.67	317.9346	315.9372	245.9997	0.78	2.45		0,990 (1-500)	0.8
	4,4'-DDD	34.38	235.0062	237.0037		0.72			0,996 (1-500)	2
	4,4'-DDMU	31.5	281.9754	283.9724		0.95			0,997 (1-500)	2
	Permethrine 1	41.05	183.0785	163.0041		0.15			0,995 (2-1000)	2
	Permethrine 2	41.311	183.0785	163.0061		0.19			0,993 (2-1000)	2
	Hexachlorobenzene	23.6	283.7996	285.7967	281.8027	0.82	0.55		0,990 (1-100)	0.5
	1,4-Dichlorobenzene	6.42	145.968	147.9664		0.6			0,993 (1-500)	0.8
	4,4'-Dichlorobenzophenone	29.4	249.9924	138.9929		2			0,999 (1-500)	1
	Polymer additives	Pentachloroanisole	23.9	279.8592	281.8555	264.8362	0.66	1.06		0,999 (5-500)
TCPP		25.59	277.0043	124.9892	98.9747	4	3.5		0,990 (5-500)	5
Tinuvin P		30.68	225.0897	226.0926		0.15			0,999 (10-1000)	5
Tinuvin 320		37.79	323.2065	308.2202		2.1			0,999 (1-1000)	1
Tinuvin 326			300.0898	315.1153		0.5		0,991 (500-5000)	0,994 (10-500)	5
Tinuvin 327		40.55	342.1368	357.1602		0.23		0,995 (500-5000)	0,995 (10-500)	6

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	<b>Tinuvin 328</b>	40.4	322.1908	351.2299		0.12		0,991 (500-5000)	0,994 (10-500)	3
	<b>BDE 47 (2,2',4,4'-Tetrabromodiphenyl ether)</b>	38.33	485.7087	325.8742	487.7055	0.9	0.68		0,996 (4-200)	2
	<b>BDE 100 (2,2',4,4',6-Pentabromodiphenyl ether)</b>	41.38	565.6167	563.6187	403.7862	1.02	0.78		0,996 (1-50)	1
	<b>BDE 99 (2,2',4,4',5-Pentabromodiphenyl ether)</b>	42.22	565.6167	563.6187	403.7862	1.02	1.2		0,994 (4-200)	1
	<b>2,4,6-Tribromoanisole</b>	21.5	345.8025	343.8052	328.7526	0.97	0.097		0,998 (5-500)	2
	<b>2,4,6-Tribromophenol</b>	21.9	331.7673	329.7688		0.95			0,996 (10-500)	5
<b>PCBs</b>	<b>PCB28 (2,4,4'-Trichlorobiphenyl)</b>	27.08	255.9621	257.9593		0.98			0,999 (1-100)	0.5
	<b>PCB52 (2,2',5,5'-Tetrachlorobiphenyl)</b>	28.46	291.9203	289.9203		0.75			0,998 (1-100)	0.5
	<b>PCB101 (2,2',4,5,5'-Pentachlorobiphenyl)</b>	31.76	325.8807	323.8818	327.8763	0.66	0.68		0,998 (1-100)	0.7
	<b>PCB153 (2,2',4,4',5,5'-Hexachlorobiphenyl)</b>	34.88	359.8418	361.8392	357.8435	0.82	0.58		0,998 (1-100)	0.7
	<b>PCB138 (2,2',3,4,4',5'-Hexachlorobiphenyl)</b>	35.86	359.8418	361.8392	357.8435	0.82	0.58		0,997 (1-100)	0.8
	<b>PCB180 (2,2',3,4,4',5,5'-Heptachlorobiphenyl)</b>	38.24	393.8037	395.8008		0.99			0,998 (1-100)	0.6
<b>PAHs</b>	<b>Naphthalene</b>	10.76	128.0621	102.0464		0.086			0,996 (10-200)	2
	<b>Acenaphthene</b>	18.45	153.0699	154.0777		0.83			0,998 (10-500)	5
	<b>Phenanthrene</b>	25.1	178.0777	176.0621		0.23			0,998 (1-500)	0.5
	<b>Anthracene</b>	25.3	178.0777	176.0621		0.22			0,999 (1-500)	0.8
	<b>Fluoranthene</b>	30.62	202.0777	200.0621		0.23			0,993 (2-500)	1
	<b>Pyrene</b>	31.57	202.0777	200.0621		0.23			0,999 (1-500)	0.5
	<b>Chrysene</b>	37.44	228.0934	226.0777		0.3			0,998 (1-100)	1

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Table 20 Compounds quantified from microplastic extracts by GC-MS (ng/g) of microplastics

Sampling location	S1	S2	S3		S5		S6	S7		S8		S9	S10		S11	S14	Average	Frequency	Minimum	Median	Maximum
Sampling date	08/21	08/21	11/20	06/21	08/21	11/20	11/20	10/20	06/21	11/20	08/21	11/20	11/20	06/21	11/20	11/20					
<b>PAHs</b>																					
Naphthalene	170	82	120	54	270	22	190	20	78	280	160	16	35	70	17	31	101	100%	16	74	280
Acenaphthene			230	12		12	150	50	75	1900	130	81	88	49	31	48	220	81%	12	75	1900
Phenanthrene	54	45	330	160	58	44	240	69	270	960	230	180	170	77	84	57	189	100%	44	122	960
Anthracene		19				7	18	20				30	16				18	38%	7	18.5	30
Fluoranthene	54	23	95	42	56	15	40	61	130	310	117	79	110	29	28	53	78	100%	15	55	310
Pyrene	100	69	194	71	85	47	65	100	190	770	160	120	150	50	46	96	145	100%	46	98	770
Chrysene	75	45	86	67	160	41		79	134	130	65	39	40	45	29	45	72	94%	29	65	160
<b>PCBs</b>																					
PCB 28		1.3		0.7			15.5	4.5	0.9	1.5	2.1		2.9			1.3	3	56%	0.7	1.5	15.5
PCB 52		1	0.8	1.8	0.6		3.3	2.6	1.1	1.2	1.2	0.5	2.5			0.5	1	75%	0.5	1.15	3.3
PCB 101	0.9	1.4	1.6	2.0	1.6	0.8		1.8	2.4	1.3	1.5	0.9	3.5	1.4	0.9	0.9	2	94%	0.8	1.4	3.5
PCB 153	2.5	4.2		2.6	8.3	2.1	0.5	1.8	2.8	2.2	3.0	1.0	6.6	2.0	2.2	1.2	3	94%	0.5	2.2	8.3
PCB 138	1.3	1.8	1.1	1.2	1.8	1.1		1.1	1.5	2.8	2.9	0.9	3.1	1.1	1.2	0.9	2	94%	0.9	1.2	3.1
PCB 180	2.9	3.4	1.5	1.6	5.4	1.4	0.6	1.3	1.1	1.7	3.5	0.7	3.6	1.3	1.3	0.8	2	100%	0.6	1.45	5.4
<b>Pesticides</b>																					
Chlorpyrifos	43	107	240	38	31	10	7.5	33	200	190	1500	326	550	22	57	190	222	100%	7.5	82	1500
Triadimefon																					
4.4'-DDT	22		5.4	23		19	12	32	nd	34		8.8	30.8	5	5.5	7.4	17	75%	5	15.5	34
4.4'-DDE	14	7.4	9.7	12	10	11	2.2	10.1	6.3	4.3	18	4.4	23	4.9	1.7	4.5	9	100%	1.7	8.55	23
2.4'-DDE				1							2.3		2.2				2	19%	1	2.2	2.3
4.4'-DDD	2.5	6.1	7.1	21	8.3	3.9		5	8	17	14	8	12		1.2		9	81%	1.2	8	21
4.4'-DDMU								3.4	11								7	13%	3.4	7.2	11
Permethrin sum	20.4	40	43	46	20	4.8		25	79	500	250	171	730	17	17	47	134	94%	4.8	43	730
hexa-Cl-benzene	1.2	1	1.7	1.3	0.7	1.5	1	2.1	1.8	15	2.7	0.7	5.9	0.8	1.4	0.7	2	100%	0.7	1.35	15
1,4-diCl-benzene										4.5							5	6%	4.5	4.5	4.5
4,4 -diCl- benzophenone											4		2.9				3	13%	2.9	3.45	4
Penta-Cl-anisol			33	1				1.3		39		1.2	2.8				13	38%	1	2.05	39
<b>Additives</b>																					

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TCPP	36	30.4	20	28			24	30	120	480	20.8	4200	43	46	21	392	81%	20	30.4	4200	
Tinuvin P	20.4						700				70			20		203	25%	20	45.2	700	
Tinuvin 320	26.5															27	6%	26.5	26.5	26.5	
Tinuvin 326	1200	1400	1700	5200	701	6900	90	3900	5600	3600	4600	2600	2200	190	6500	4000	3149	100%	90	3100	6900
Tinuvin 327	15000	25000	503	12000	360	6700	32	1200	270	560	2000	150	400	80	210	506	4061	100%	32	504.5	25000
Tinuvin 328	190	140	107	560	270	25	104	300	220	360	7000	120	200	1400	210	747	94%	25	210	7000	
Octabenzene				2500		1200	850		1400	1200	2700		1000			1550	44%	850	1200	2700	
BDE 47			4	6.7				12	3.7	6.2	7.7		12			7	44%	3.7	6.7	12	
BDE 100																					
BDE 99				5.2				4.7				4.3	13			7	25%	4.3	4.95	13	
2,4,6-tri-Br-anisol			16				2.5	10		89		30	76			37	38%	2.5	23	89	
2,4,6-tri-Br-phenol	30	25	48		23		980	21	62	487	2400	63.0	77		28	53	331	81%	21	53	2400
<b>Personal care products</b>																					
Galaxolide	2919	1443	2299	1074	880	749	116	838	3952	5964	6039	9457	4984	446	725	2150	2752	100%	116	1796.5	9457
Propyl paraben	5		75	415					9		198		11		4	102	44%	4	11	415	
Benzophenone-3		1229				506	100	1074			6227			717	238	860	1369	50%	100	788.5	6227
EHMC	29	63	74	32	99	16		88	476	609	2261	198	36	28	18	139	278	94%	16	74	2261
Octocrylene	238	736	238	135	153	313	150	1050	2246	2312	3620	459	421	100	205	401	799	100%	100	357	3620

Table 21 Compounds quantified in extracts of different microplastic fractions by GC-MS (ng/g of microplastics). Sampling site: Tripoli 1 (S3). F - mixture of MP fragments, P- pellets, PP - polypropylene, PE - polyethylene

Sampling date	12/11/2020						03/06/2021						10/08/2021						Average	Frequency	Minimum	Median	Maximum																				
Fraction	Fragments			Pellets			Fragments			Pellets			Fragments			Pellets																											
	F	F-PE	F-PP	P	P-PE	P-PP	F	F-PE	F-PP	P	P-PE	P-PP	F	F-PE	F-PP	P	P-PE	P-PP																									
<b>PAHs</b>																																											
Naphthalene	120	15	52	40	33	18	54	190	290	92	91	130	270	160	203	610	340	980	205	100%	15	125	980																				
Acenaphthene	230	180	140	340	410	46	12	16	10	21	28							60	124	67%	10	53	410																				
Phenanthrene	330	580	330	250	24	180	160	202	140	170	250	65	58	63	180	34	94	67	177	100%	24	165	580																				
Anthracene										26							20	nd	23	11%	20	23	26																				
Fluoranthene	95	115	67	166	190	23	42	74	25	44	64	18	56	29	35	33	51	17	64	100%	17	47.5	190																				
Pyrene	194	200	130	260	270	62	71	120	41	71	95	59	85	62	66	59	105	22	110	100%	22	78	270																				
Chrysene	86	93	40	290	83	30	67	140	45	54	62	64	160	71	102	106	109	38	91	100%	30	77	290																				
<b>PCBs</b>																																											
PCB 28				3.9			0.7	2.6			0.5	27.4						0.5	6	33%	0.5	1.65	27.4																				
PCB 52	0.8	2.1	3.7	4.4			1.8	0.5	1.0	0.5	0.7	7.1	0.6	0.5	0.7	0.6		0.5	2	83%	0.5	0.7	7.1																				
PCB 101	1.6	2.0	1.3	2.7	1.6	1.2	2.0	1.7	1.8	1.3	1.9	4.8	1.6	1.7	1.7	1.3	1.3	1.3	2	100%	1.2	1.65	4.8																				
PCB 153		6.1	1.4	2.2	5.7	1.9	2.6	4.5	2.2	6.4	4.0	10.8	8.3	3.8	2.2	3.9	3.3	3.2	4	94%	1.4	3.8	10.8																				
PCB 138	1.1	1.8	0.9	1.7	3.3	1.1	1.2	2.1	1.1	2.6	2.0	2.8	1.8	1.9	1.3	2.1	1.7	1.6	2	100%	0.9	1.75	3.3																				
PCB 180	1.5	3.7	1	1.5	6.4	1.8	1.6	3.4	1.2	4.2	4.6	5.3	5.4	2.4	1.6	7.7	3.4	4.3	3	100%	1	3.4	7.7																				

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Pesticides																								
Chlorpyrifos	240	140	220	96	99	19	38	15	9	5	13	5	30	25	60	19	33	8	60	100%	5	27.5	240	
Triadimefon		710																12	361	11%	12	361	710	
4.4'-DDT	5.4	120	8.2	19	nd	5	23	nd	33	17	71	120		97	nd	23	84	nd	48	72%	5	23	120	
4.4'-DDE	9.7	210	10	50	7.2	2	12	8.2	15	5.1	42	15	10	15	12	11	24	3.2	26	100%	2	11.5	210	
2.4'-DDE		22		2.3			1		1.3		6.4	4.6		1.3	1.2	1.1			5	50%	1	1.3	22	
4.4'-DDD	7.1	110	3.9	43		3	21	5.4	2.2		4.2	14	8.3	14	10			2.9	4	17	83%	2.2	7.1	110
4.4'-DDMU		54				3.1			4.9	2.2	3.7	6.2						2.7		11	39%	2.2	3.7	54
Permethrin sum	43	39	57	19	27	4.1	46	15	10	4.8	7.9	6.7	20	11	35	10	6.1	6.8	20	100%	4.1	13	57	
Hexachlorobenzene	1.7	1.2	1.8	1.0	0.5	0.7	1.3	0.8	1.3	0.5	0.7	11	0.7	0.8	1.8	0.9	1.2	0.8	2	100%	0.5	0.95	11	
1,4-di-Cl-benzene		130																	130	6%	130	130	130	
4,4-diCl-benzophenone		6.1						1.4	2.2			1.1		1.2	2.5				2	33%	1.1	1.8	6.1	
penta-Cl-anisol	33	203	2.8				1		1.5										48	28%	1	2.8	203	
Additives																								
TCPP	30.4	43	37	14		9.1	20	14	24			15	28	16	14	8.6		8.2	20	78%	8.2	15.5	43	
Tinuvin 320											17	61		3.2		570	19		134	28%	3.2	19	570	
Tinuvin 326	1700	11000	9500	5400	8300	490	5200	540	220	4300	440	240	700	1700	750	650	1700	410	2958	100%	220	1225	11000	
Tinuvin 327	500	290	56	190	850	140	12000	130	73	5600	6200	15000	360	510	420	29000	11000	510	4602	100%	56	505	29000	
Tinuvin 328	107	76	100	54	110	1000	560	130	62	56	190	71	270	130	105	66	340	31	192	100%	31	106	1000	
octabenzene				1600			2500			19000		8100			1000				6440	28%	1000	2500	19000	
BDE 47	4				5.7		6.7							10.7		11			8	28%	4	6.7	11	

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BDE 100																			2	11%	1.4	1.7	2
BDE 99							5.2												6	17%	5.2	5.9	6.3
2,4,6-tri-Br-anisol	16																		16	6%	16	16	16
2,4,6 -tri-Br-phenol	48	14	15	12	10.6													18	44%	10.4	13.5	48	
<b>Personal care products</b>																							
Galaxolide	2299	8550	4759	3400	3253	510	1074	503	275	246	969	98	880	505	834	426	2005	602	1733	100%	98	857	8550
Propyl paraben	75	120	109				415												180	22%	75	114.5	415
Benzophenone-3							243						221		1012				492	17%	221	243	1012
EHMC	74	38	68	49	41	13	32	21	17				99	24	50	29	17	15	39	83%	13	32	99
Octocrylene	238	350	400	79	115	49	135	65	102	52	48		153	132	272		57	34	143	89%	34	108.5	400



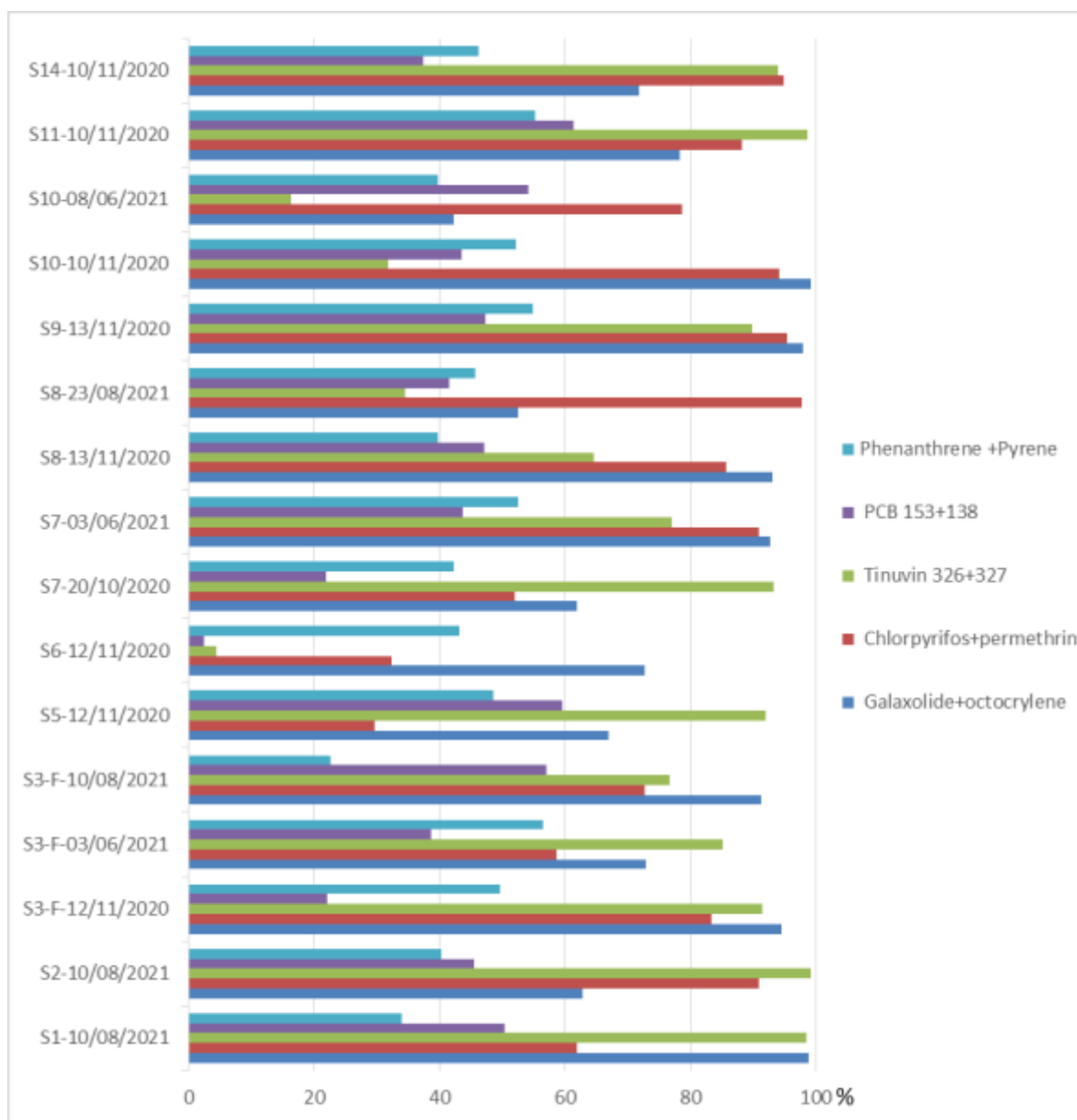


Figure 62 Percentual contribution of the two most relevant compounds to the total concentration per family

Within the group of PCPs, galaxolide and octocrylene (synthetic musk and UV-filter) represented more than 60% of the total concentration of this family of compounds in 24 out of 31 samples. Both are lipophilic, poorly biodegradable compounds, often found in sediments, including samples obtained in the estuarine of Kadicha river in the North of Lebanon (Merhabi et al., 2021). Galaxolide was recently identified in microplastic samples collected in East coast of North America (Ravit et al., 2019) but the authors did not report concentration data.

Several studies have reported the high affinity of synthetic musks, and particularly that of galaxolide, for different kinds of microplastics (Dong et al., 2019); so, the presence of this musk in marine microplastics is not surprising.

Moreover, galaxolide might be present in abrasion fragments arising from mechanical degradation of household and personal care plastic vessels.

Octocrylene was previously quantified in microplastics obtained from high-tourism pressure beaches in Canary islands at concentrations in the range from 11 to 4031 ng/g (Santana-Viera, et al., 2021), similar to that reported in this study (13- 3620 ng/g), Tables 20-21.

Chlorpyrifos and permethrin represented also above 60% of the total concentration of selected pesticides in more than half of samples. The 1<sup>st</sup> insecticide was authorized until recently in the EU economical area and might remain in microplastics arising from agriculture greenhouse and mulching films, apart from being concentrated in this matrix from the environment. In this regard, some studies have reported the preferential accumulation of pesticides in agriculture polyethylene film compared to agriculture soils (Ramos et al., 2015) Despite the high concentrations of chlorpyrifos found in microplastics, traces of its major transformation product trichloropyridinol were not found.

Six PCBs, containing between 3 and 6 chlorinated substituents, were included in the list of quantified species. Most of them were found in every sample extract; however, their total concentrations were relatively low (from 0.8 to 58.3 ng/g, referred to the matrix of microplastics) compared to those reported for samples obtained in other parts of the world (W. Zhang et al., 2015). As expected, the chromatographic profiles of PCBs in sample extracts were relatively complex, as correspond to former use of technical mixtures of these species (i.e. Arochlors) in industrial applications. Fig. 63 shows the profiles of tri- to heptachlorinated congeners in a microplastic sample (S3/06/2021 Tripoli 1 fragment PP) and those corresponding to two technical mixtures of PCBs (Aroclor 1242 and 1254) with different grades of chlorination. Apparently, the extract from the PP sample would match a combination of both arochlor mixtures, Fig. 63 In terms of measured residues, the hexachlorinated compounds (congeners 153 and 138) showed higher concentrations than the other PCBs quantified in this study, Tables 20 and 21.

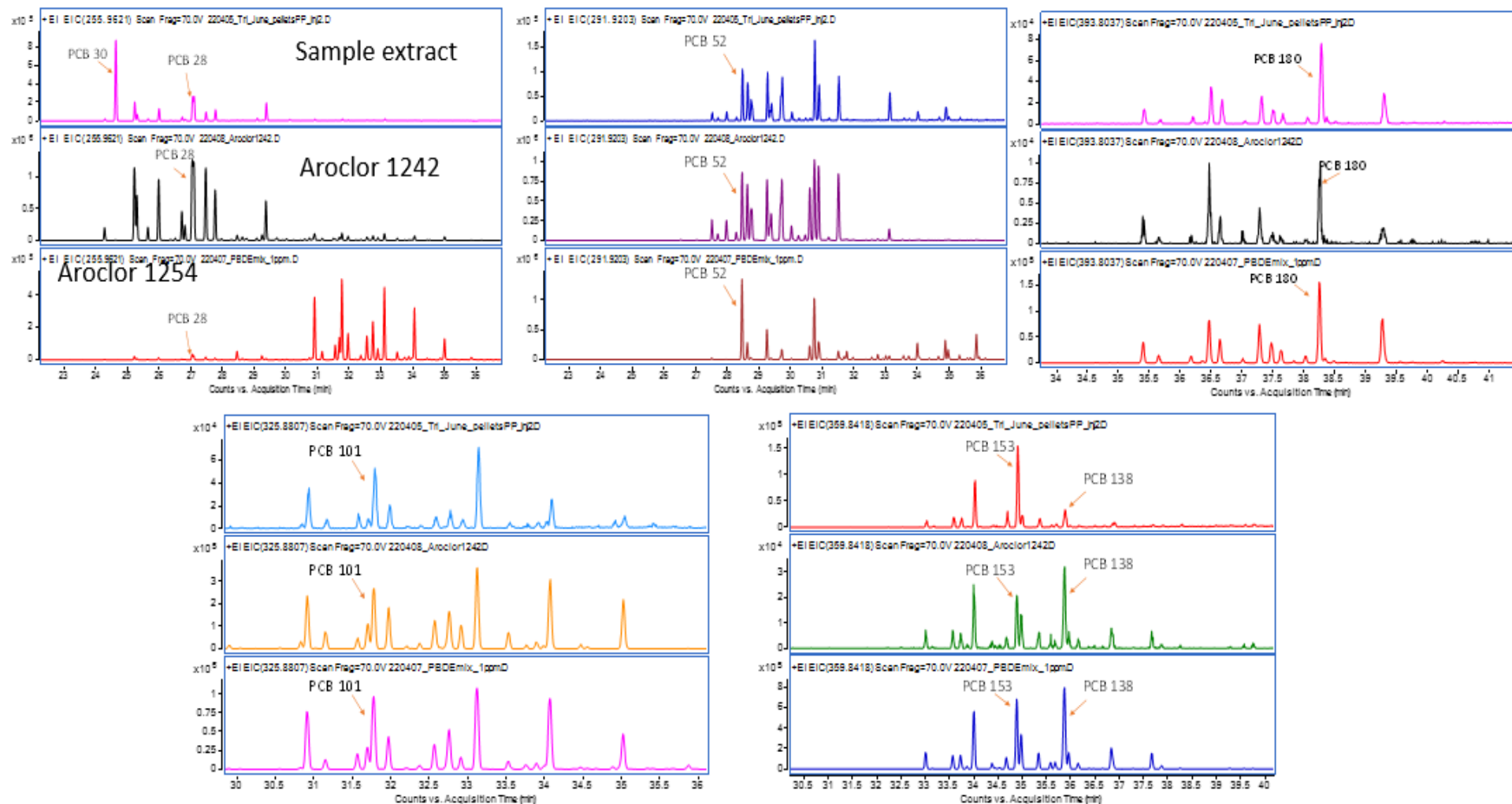


Figure 63 Chromatographic profiles of tri- to hepta-chlorinated PCBs in the extract from a MP sample and two commercial PCBs mixtures: Aroclor 1242 and Aroclor 1254. PCB30 is an internal standard (only added to microplastic samples).

Regarding the group of quantified PAHs, their total concentrations varied between 187 and 430 ng/g, with the higher levels corresponding to phenanthrene and pyrene. PAHs are ubiquitously distributed in all environmental compartments, as a result of pyrogenic and petrogenic sources. They have been also reported in new plastic items (Steinman et al., 2020), and formation during thermal extrusion of PE and PP polymers cannot be excluded. In fact, we have identified the presence of some PAHs in mulching agriculture films, Fig. 64.

That being said, some evidences pointed out the potential petrogenic origin of PAHs noticed in some of the extracted microplastics. As example, anthracene to phenanthrene concentration ratios below 10% have been correlated with a petrogenic origin of PAHs (W. Zhang et al., 2015). This pattern was observed in 80% of the processed samples, Tables 20-21. Moreover, the identification of alkylated (methyl and dimethyl) forms of phenanthrene in most of the samples supports the petrogenic origin of PAHs (Bateni, et al., 2022) in microplastic samples. Fig. 65 shows the response ratios between the sum of responses for the four methylated phenanthrene derivatives reported in Tables 20-21 and that of phenanthrene. Ratios above the unit were noticed in every sample.

Regarding the S3 site (Tripoli 1), the analysis approved on what was said on the LC-MS/MS section, that we cannot conclude the adsorption behavior of different plastics shape (fragments and pellets) and chemical types (polyethylene and polypropylene). The concentrations of compounds in those different fractions did not represent any specific pattern.

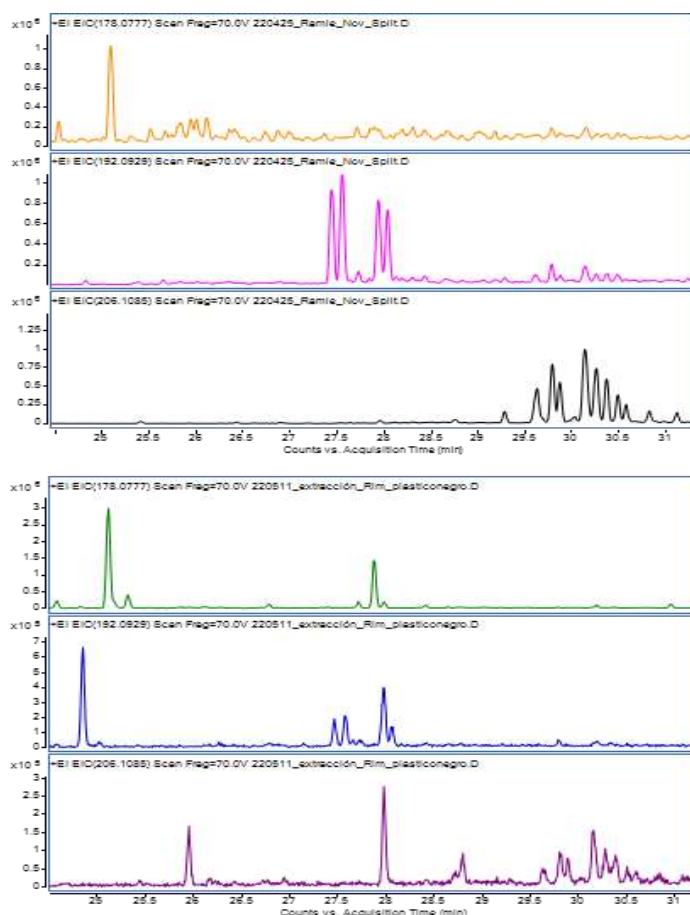


Figure 64 EIC chromatograms of phenanthrene and its methyl and dimethyl derivatives in microplastic (up) and a new polyethylene film for agriculture uses (down)

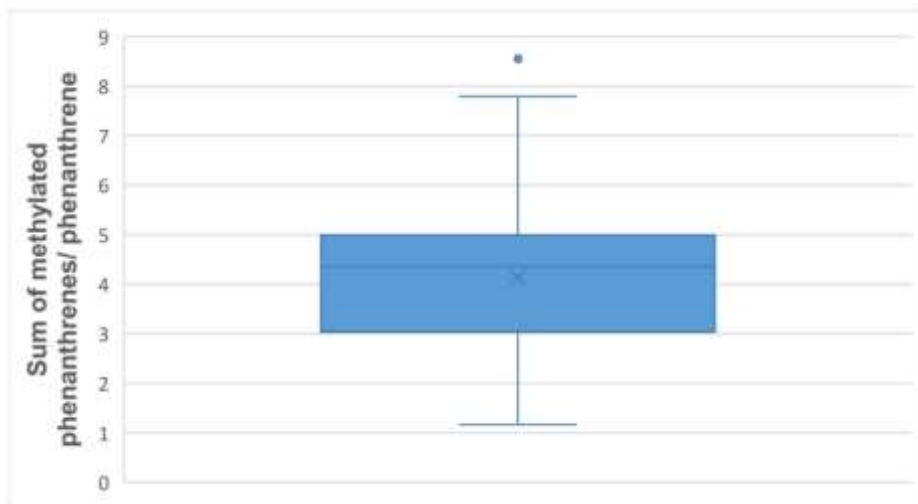


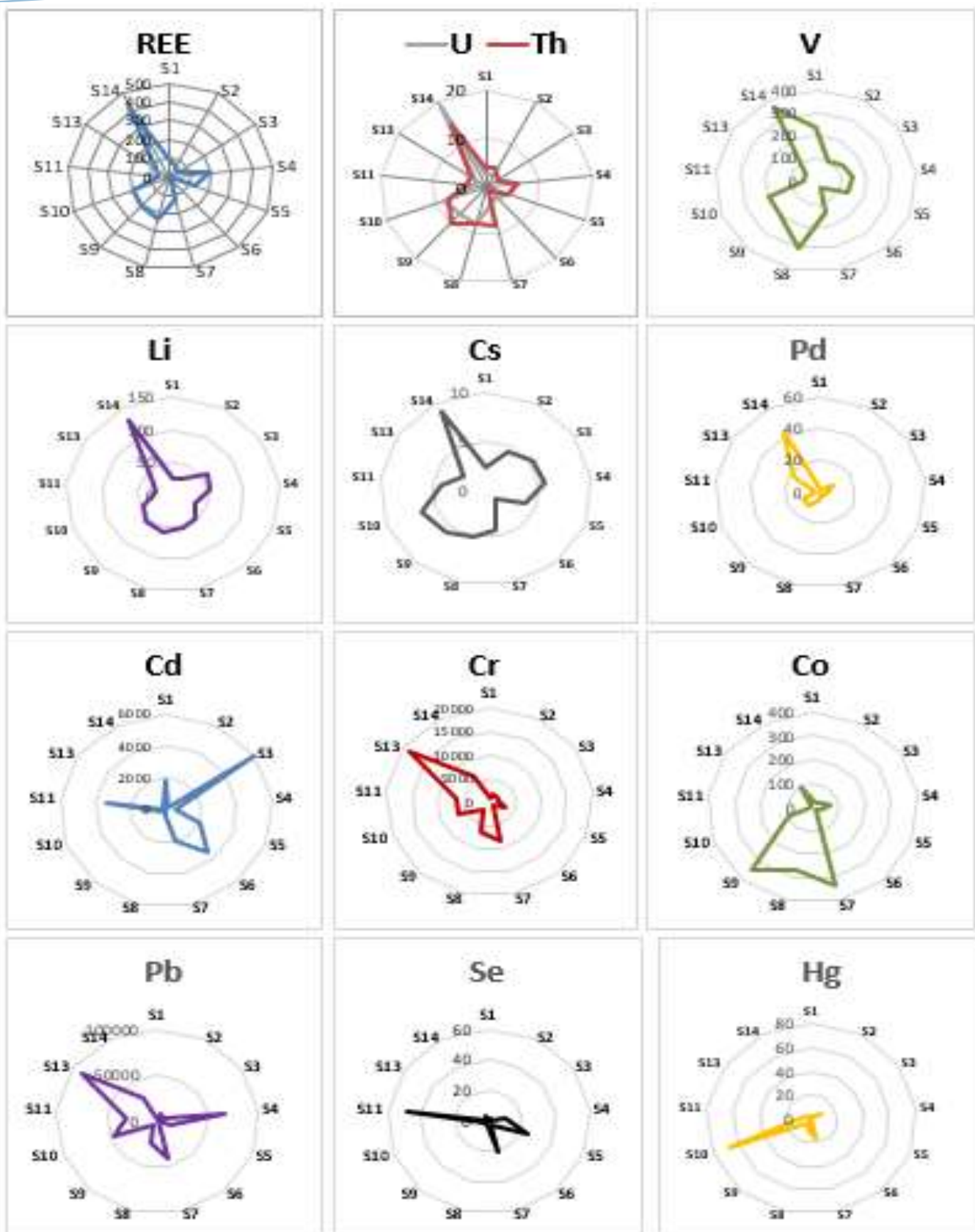
Figure 65 Box-Whisker plot showing the distribution of methylated phenanthrenes/phenanthrene

## 14. Metals associated with microplastics sampled on the Lebanese coast

### 14.1. Metals concentrations and distribution in microplastics from the Lebanese coast

The distribution of metals in the plastics sampled along the Lebanese coast is illustrated as radar plots in Figure 66. Even if there has been the discussion on the possible role of microplastics as vectors for metals sorbed on their surface (El Hadri, et al., 2020), the result strongly indicated that they act as vectors because of the presence of residues of metals used in pigments and catalysts, than from the metals taken up from the environment. Indeed, the leaching using acids is unable to discriminate between the sorbed plastics and leachable metals for microplastics sampled in the environment.

The radar plots usually suggest that there is a particular site that can be identified for a particular pollution by a given element, without that the global contamination by metals can be assigned to a particular site, despite the accumulation of plastic litter.



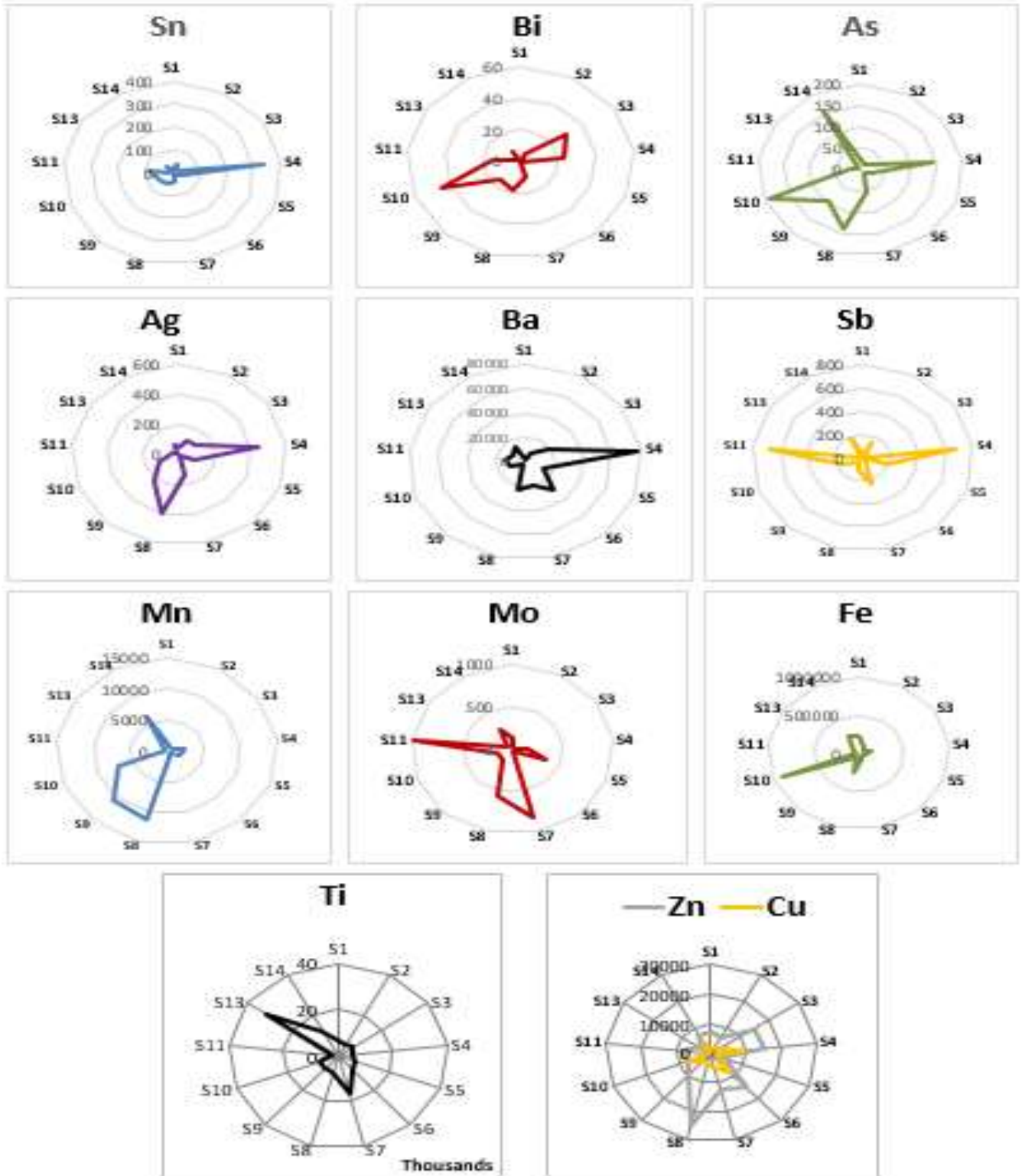


Figure 66 Radar plots of the distribution of metals in plastics sampled along the Lebanese coast



A good example is the case study of Tripoli 1 site (S3) which is, owing to the accumulation of litter, the only site in which the amount of collected microplastics was high enough to collect a sufficient amount of fragments (secondary) and translucent pellets (primary) of plastics at three different time points within 10 months. The results are summarized in Table 22.

Table 22 Total element concentrations (ng/g) in microplastic fragments in comparison to microplastic pellets (Tripoli site, S3)

Element	12-11-2020		3-06-2021		10-08-2021	
	Fragments	Pellets	Fragments	Pellets	Fragments	Pellets
<b>Ba</b>	7600	350	6900	330	41000	280
<b>Cs</b>	6.1	2.5	4.3	2.1	5.5	3.1
<b>Sb</b>	30.7	<0.03	<0.03	<0.03	13	<0.03
<b>Sn</b>	6.4	33	<0.04	<0.04	48	<0.04
<b>Ag</b>	150	<0.03	42	<0.03	140	16
<b>Pd</b>	22	0.4	1.4	<0.003	2.7	<0.003
<b>Mo</b>	62	31	<0.04	<0.04	27	<0.04
<b>Y</b>	16	5.6	6.3	<0.005	10.8	4.1
<b>Se</b>	2.6	1.3	0.7	<0.0008	1.4	<0.0008
<b>As</b>	35	13.2	12	<0.009	38	4.7
<b>Zn</b>	32000	10100	2700	6200	8700	12000
<b>Cu</b>	2700	<0.2	3300	<0.2	3700	140
<b>Co</b>	36	2.8	39	<0.01	29	<0.01
<b>Ni</b>	3700	1900	2000	590	2500	1300
<b>Ti</b>	6900	2300	6100	1600	7200	40000
<b>Mn</b>	770	310	410	200	670	310
<b>Cr</b>	2600	270	2200	21	640	76
<b>V</b>	150	72	130	31	100	53
<b>Fe</b>	9600	49000	5400	16000	69000	27000
<b>Bi</b>	83	<0.001	0.5	6	9	<0.001
<b>Pb</b>	9600	<0.2	10000	<0.2	15000	<0.2
<b>Hg</b>	21	<0.02	3	<0.02	<0.02	<0.02
<b>Cd</b>	92	<0.02	101	<0.02	70	9
<b>B</b>	5900	7500	8700	8500	8000	15000
<b>Li</b>	120	6.6	19	7.4	32	30

Note that the presence of the metals can be due to their use as additives or to the chemical adsorption from water. Indeed, a number of studies indicated that exposure of virgin polymers for a prolonged time in the environments resulted in the considerable absorption of Pb, Fe, M, Cu or Ag (Ashton et al., 2010; F. Gao et al., 2019; X. Gao, et al., 2021).

In our work we have been unable to clearly discriminate the added and adsorbed parts of metals, however, the observed geographical correlations and the comparison between the secondary plastics (fragments) found and the primary plastics (translucid pellets) allowed some hypotheses to be put forward.

*Rare earth elements, thorium and uranium.* Rare earth elements are a part of the earth’s crust but several of them are recognized as technologically critical elements. The natural origin of the presence of REEs can be readily confirmed/informed by following the regularity regarding their distribution (Oddo-Harkins rule) in which elements with an even atomic number (Ce, Nd, Sm, Gd, Dy, Er and Yb) are more abundant than elements with an odd atomic number (La, Pr, Eu, Tb, Ho, Tm and Lu), besides having decreasing contents with an increase in atomic mass. Fig 67 shows that the REEs in virtually all the samples follow the natural REEs abundance distribution pattern which would suggest their natural origin. It also shows their accumulation in plastics from one particular site S14 (Adloun), the accumulation pattern that is reproduced by U, Th and V having the same properties, Pd, but more curiously Li and Cs. To our knowledge, neither of these metals was reported in the context of sorption on plastics, except U on polyethylene.

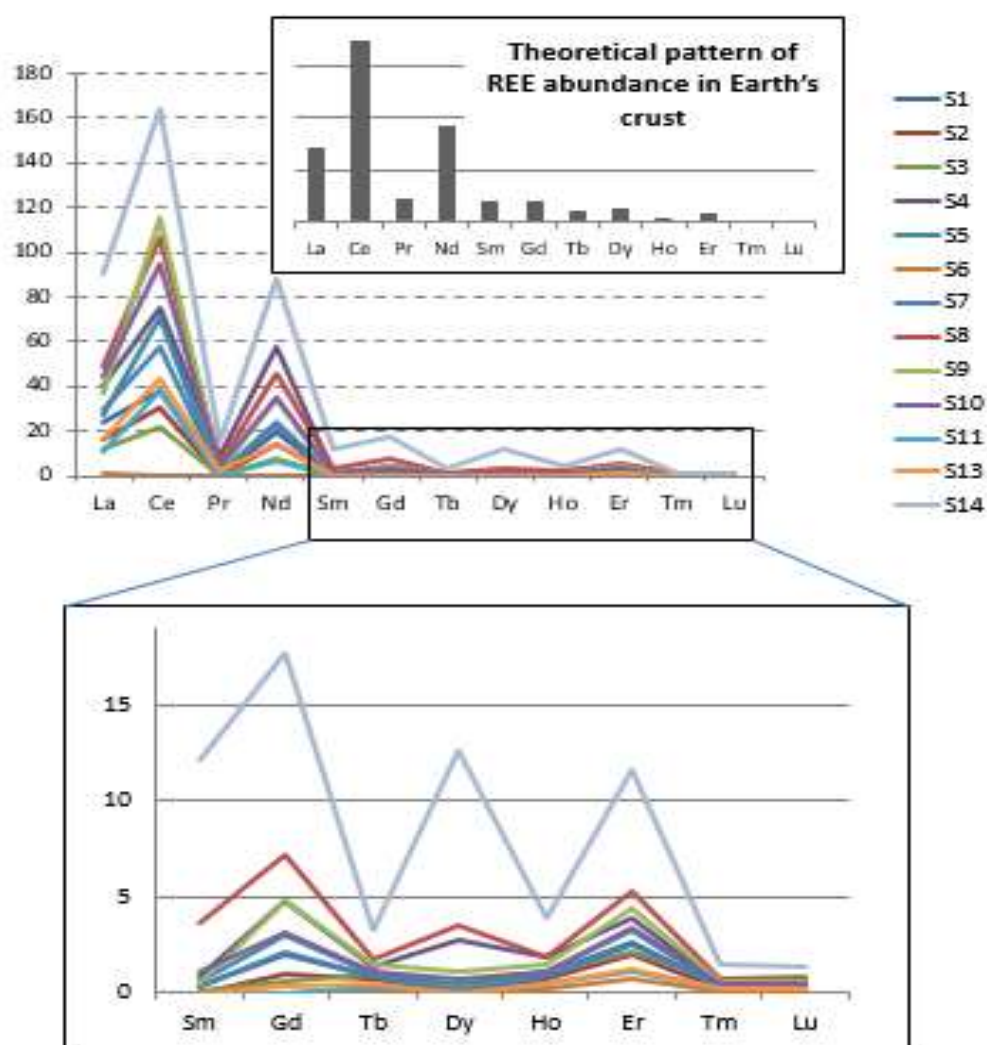


Figure 67 Distribution of REEs in microplastics as a function of sampling site

*Bismuth, cadmium, chromium, cobalt, lead and selenium.* Several toxic metals are employed in pigments, and stabilizers reaching 25 g/kg of plastics. Cadmium sulfide and selenide and lead chromate and molybdate are commonly used as red pigments. The maximum concentrations reported for lead exceeded 20 g/kg in beached plastic litter from Geneva lake (Turner & Filella, 2020) and Ookushi beach (Japan) (Nakashima, 2012) while those of chromium 6,7 g/kg (in Geneva lake). Concentrations between 2.5 and 5 g/kg were reported in SW England regalis for both beached microplastic pellets and fragments (Massos & Turner, 2017). CrO<sub>3</sub> is also used as catalyst in the synthesis of polyethylene. Bi is used in yellow pigments as BiVO<sub>4</sub> (Catrouillet et al., 2021).

The similarity of the distribution of Pb and Cr is very likely to result in their use as pigment "Chrome Orange" PbCrO<sub>4</sub> used alone or mixed with PbO. The very high concentrations of both elements in S13 point to this microplastic origin from pigment (lead white PbCO<sub>3</sub>)<sub>2</sub> Pb (OH)<sub>2</sub> that can contribute to unusually high concentration in microplastics sampled in S4.

*Mercury and tin, palladium.* Phenyl mercury (1-3 g/kg) and dibutyltin compounds, up to 10 g/kg are used as catalysts and stabilizers. The presence of Sn and Pd both on plastics and pellets (Table 22)

*Arsenic and silver.* Arsenic in the form of 10, 10' oxibisphoxarsine and silver in the form of nanoparticles is added as antibacterial agents and this maybe be the possible cause of their presence in plastics analyzed

*Other elements: B, Ba, Cs, Fe, Li, Mn, Ni, Ti, and Zn.* They are present in both the fragments and the translucent pellets. Barium sulfate is used as filler agents used to harden plastics (Turner & Filella, 2020) This is also the case of Cr which would suggest a CrO<sub>3</sub> common catalyst for the PE may be the major source. Even if some of these elements are used as pigments, their significant presence in pellets may suggest their natural origin (manufacturing process, and mixture of sediments) Studies of the geochemistry of the Eastern Mediterranean shows its enrichment in Fe, Mn and Ti from the analyzed elements here (Pruysers, et al., 1991) .

Studies have been focused lately on the interaction of plastics with heavy metals. Those studies showed that plastics are heavily loaded with heavy metals with increasing concentrations in more polluted places, here are few studies to compare our results with. According to (Xie et al., 2021), from expanded polystyrene collected from beaches of 5 islands in the Pearl river estuary, China, concentrations of heavy metals were as follow, Cd 270 ng/g, Cr 14900 ng/g, Cu 15000 ng/g, Ni 17200 ng/g, Pb 24800 ng/g, Mn 730000 ng/g and Fe 8340000 ng/g. Plastic debris collected from beach sediments on the Persian gulf (Dobaradaran et al., 2018) and analyzed for their heavy metals content, showed concentrations of Cd 35 ng/g, Cr 915 ng/g, Cu 3600 ng/g, Ni 2030 ng/g, Pb 4590 ng/g, Mn 32200 ng/g and Fe 531000 ng/g. Another study in the Mangrove wetland in China (Deng et al., 2020) showed concentrations of Cr ranging from 4790 to 15700 ng/g , Ni 2110-6000 ng/g, Cu 2420-23250 ng, Pb 13420-51580, Cd 20-780 ng/g and the concentrations of Hg ranged from 0 to 76 ng/g. In addition to those elements, two additional elements, As and Zn were analyzed in the study of (Sarkar et al., 2021) with ranges of concentrations of 1560-4510 ng/g and 1880-1 191520 ng/g respectively. Of all other elements, Arsenic was the only one that showed low concentrations in our samples in comparison with the one shown in the study of Sarkar *et al.* (Sarkar et al., 2021) with concentrations not exceeding 40 ng/g in our samples compared to more than thousands.

## Conclusions

Microplastics are not only ubiquitous pollutants by themselves but also vectors of toxic contaminants: non-polar and polar hazardous organic compounds and metals. By transporting contaminants in the marine ecosystem, they facilitate the intake and accumulation of toxic species all along the food chain. The importance of microplastics is likely to increase as the plastic pollution increases so is the amount of their environmental degradation products: microplastics and nanoplastics. In a semi-enclosed sea like the Mediterranean Sea, the cycle of pollution could be barely broken due to the minimum exchange with other water masses. The importance of this work is in its being the first untargeted study of multiclass contaminants associated with microplastics in the Mediterranean Sea.

Polyethylene and polypropylene were the most commonly found because they are the most used types of plastics. Deconvolution of accurate EI-MS scan data allowed the identification of several semi-volatile compounds clearly recovered by microplastics from the environment. A relevant number of new compounds, so far not considered on target GC-MS (MS) methods, were identified in the extracts from microplastics. In addition to legacy, highly toxic chlorinated pollutants, microplastics contain relevant levels of other well-known environmental pollutants, such as musks, UV filters and UV absorbers, which might represent a hazard for marine organisms if microplastics enter their digestive system. Similarly, a data-dependent not targeted LC MS screening showed that the sorbed pollutants are not limited to the low polar compounds. The applied compounds identification workflow, combining retention index and spectral data, was particularly robust towards the report of false positives.

This is also the first comprehensive study regarding the metals carried by microplastics in the Mediterranean. Used as pigments, stabilizers or catalysts, they stay in the microparticles resulting from the disintegration without being significantly released to the environment as water-soluble forms. Consequently, recycling plastics, if their contamination by metals is not well understood, can be a way of spreading pollutants and may be more harmful if recycled than when left in the environment. This can be the case of plastic bottles because additives enter in the manufacturing process of plastics and are added each time they are recycled.

S3 (Tripoli 1) was confirmed to be highly polluted site with a large amount of plastics of different shapes and sizes despite the fact that it is a public beach so a lot of people get in contact with this pollution. This beach in particular, should be cleaned more frequently because it is not only a hotspot for plastics pollution by their toxic additives but also to toxic pollutants adsorbed on them.

Also it is to be noted that S8 (Ramle) is of high concern. Those beaches in particular are highly polluted and public at the same time so people are in direct contact with toxic pollutants without any control.

The pollution cannot be related to a source nor to a specific site or region because we cannot confirm the origin of plastics or the time they took in the water to finally take end on shore. But we can note that those pollutants are now present in the Lebanese coast and comes from the water and are threatening marine biota and human lives. Those plastics also may not be in their final destination yet and could be taken again to deep water by waves washing them off again from the shore.

Further research is necessary to understand the sources of unauthorized pesticides or relating the microplastics to particular sources which can be done using the metal-concentration pattern. More systematic studies would also allow better understanding of the temporal variations, the discrimination between compounds uptake from the aquatic environment and/or assessing whether microplastics are the vehicles transporting these pollutants from application sites, i.e. agriculture fields, to the marine media is another perspective goal.

Mass spectrometry plays a fundamental role in non-targeted and targeted analysis for contaminants associated with microplastics. Standardized operational procedures should be developed in order to try and minimize error and be able to compare and analyze data from different locations. Continuous monitoring should be implemented along the coast in different times with fixed sampling sites to follow the pollution pattern and understand sources of pollution in different study sites. Multi-technique approaches covering different types of pollutants should be considered in environmental studies generally, to try cover the maximum of pollutants. Untargeted approaches in order to probe for new emerging contaminants.

Analytical procedures are still tedious and necessitate the use of considerable amounts of solvents and manpower during the recovery of organic pollutants from microplastics. Therefore, the development of direct, solvent-sparing methods such as, e.g. LESA-MS should be pursued. Our preliminary results showed that the LESA-MS could be used as an initial screening method, at least in the target approach offering lower detection limits.

Although there was a lot of suggestions and methods to clean oceans from plastic pollution but no real solutions were made to treat the plastics that will be cleaned from beaches. It seems that the only way to stop plastic pollution is by reducing the use of plastics, at least the single use plastic and try to replace them with less harmful material or else, bioplastics that are alternatives of plastics made with renewable sources that comes from natural sources.

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