Emerging risks in recycling and waste: Perfluorinated compounds in plastic pellets and nanomaterials in contaminated soil

Damià Barceló, Naif Abdullah Al-Harbi, Hrissi K. Karapanagioti, Antoni Ginebreda,Marta Llorca, Josep Sanchís

Summary

Introduction

According to the **European Parliament over 1.8 billion tonnes of waste are generated each year in Europe** (3.5 tonnes per person) and less than a third of it is recycled.

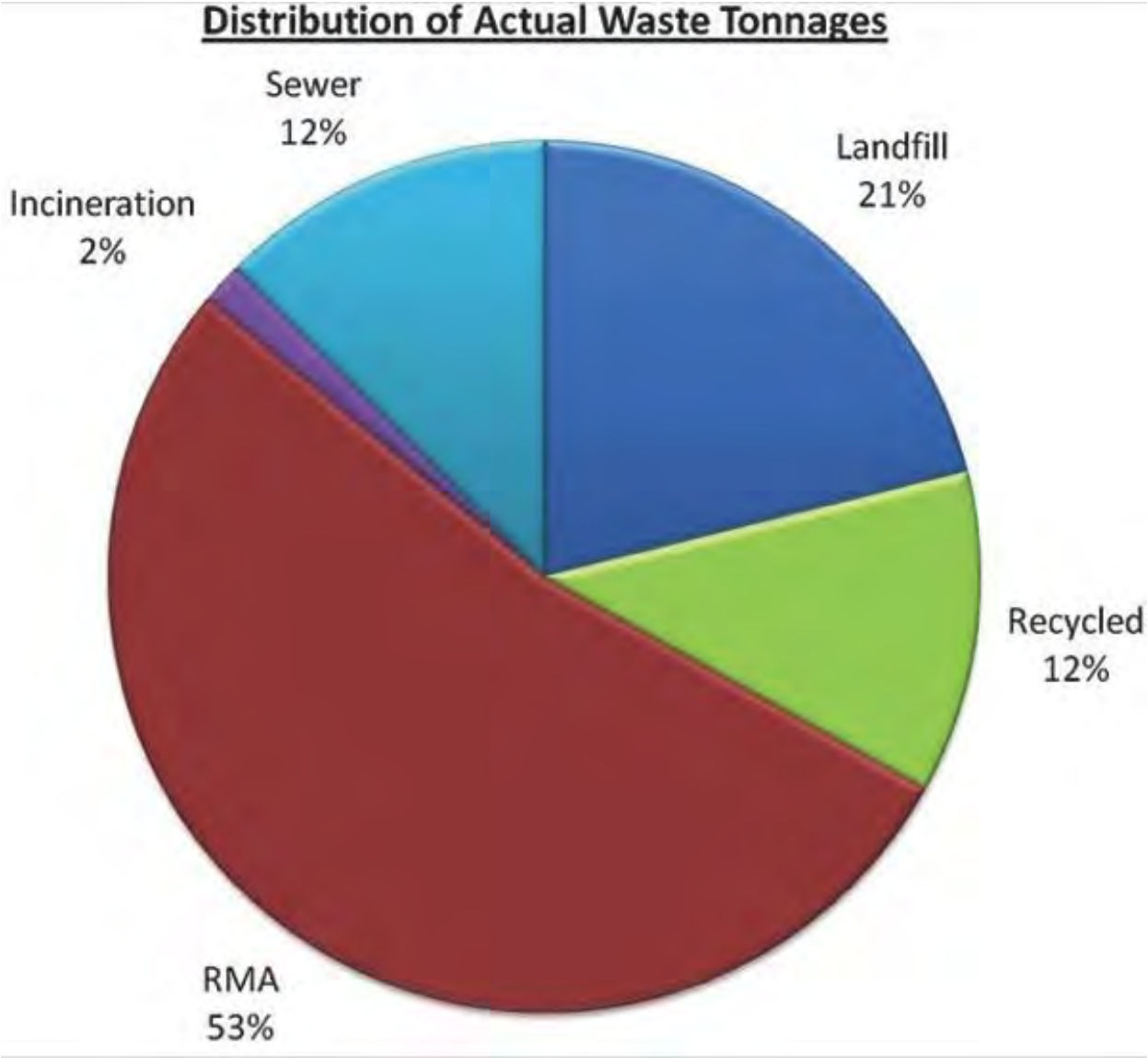
United States produces approximately 200 million tons of garbage each year, according to the Environmental Protection Agency.

Chemicals

Plastic wastes

e-Wastes

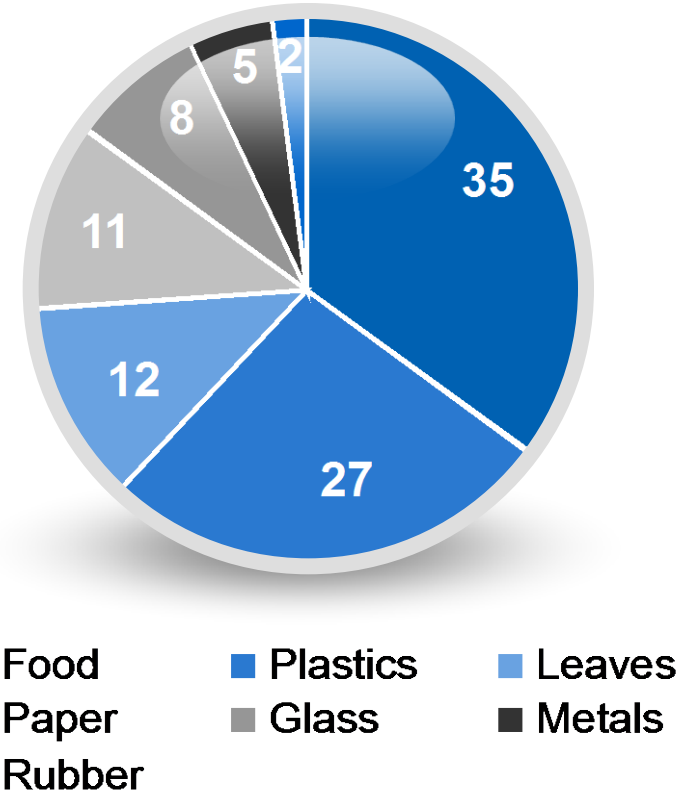
Introduction



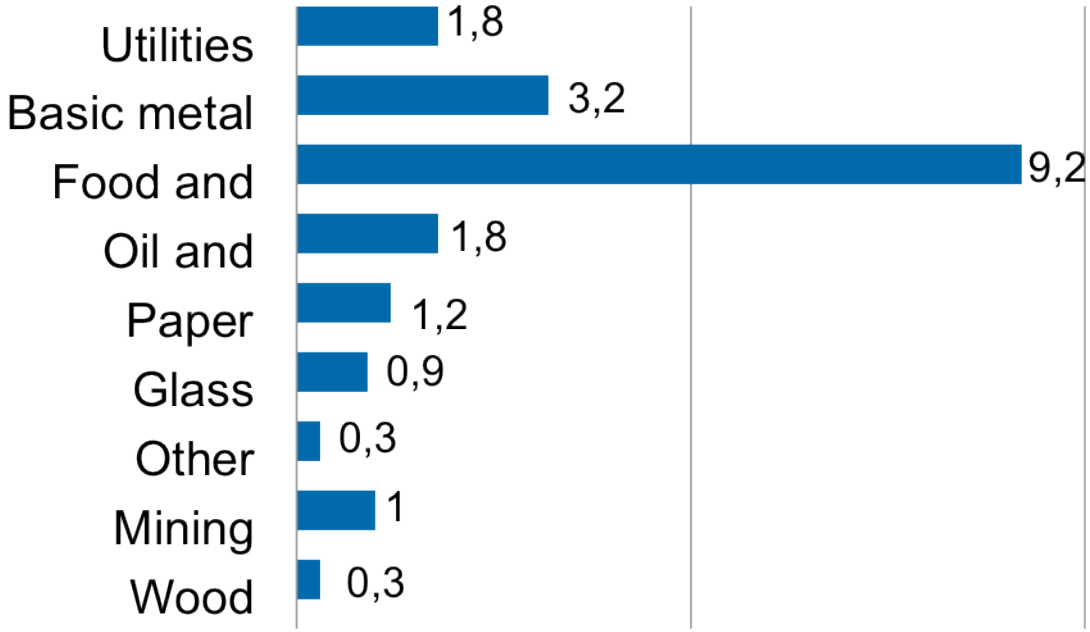
Introduction

Composition of solid urban wastes vs. Industrial wastes

Distribution in percentage of URBAN wastes in EU



INDUSTRIAL wastes in million tonnes (Source CBS) in EU



Case study presentation

The lack of recycling constitutes a new source of emerging contaminants to the environment and some materials could act as adsorbents able to stabilize and transport persistent organic pollutants.

Two case studies will be presented

- Perfluorinated compounds in sea plastic pellets
- Occurrence of nanomaterials in contaminated soil

Objectives

- **To develop analytical methods for their determination in environmental samples based on liquid chromatography and tandem mass spectrometry**
- **To assess their occurrence in the environment in order to create enough data to create the basis of a future risk assessment**

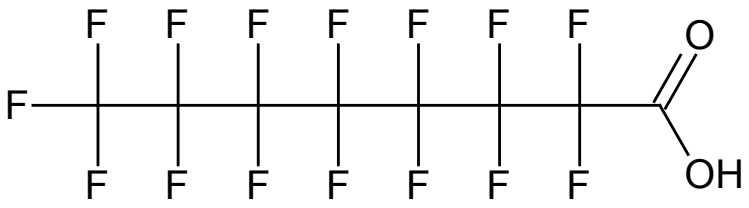
Case study I

Perfluorinated compounds in sea plastic pellets

Perfluorinated compounds in sea plastic pellets

Perfluoroalkyl substances (PFASs) or perfluorinated compounds (PFCs)

Perfluorinated = fully fluorinated



Ex. Perfluorooctanoic acid (PFOA , C-8)

Very stable (C-F bond energy 485 kJ/mol)

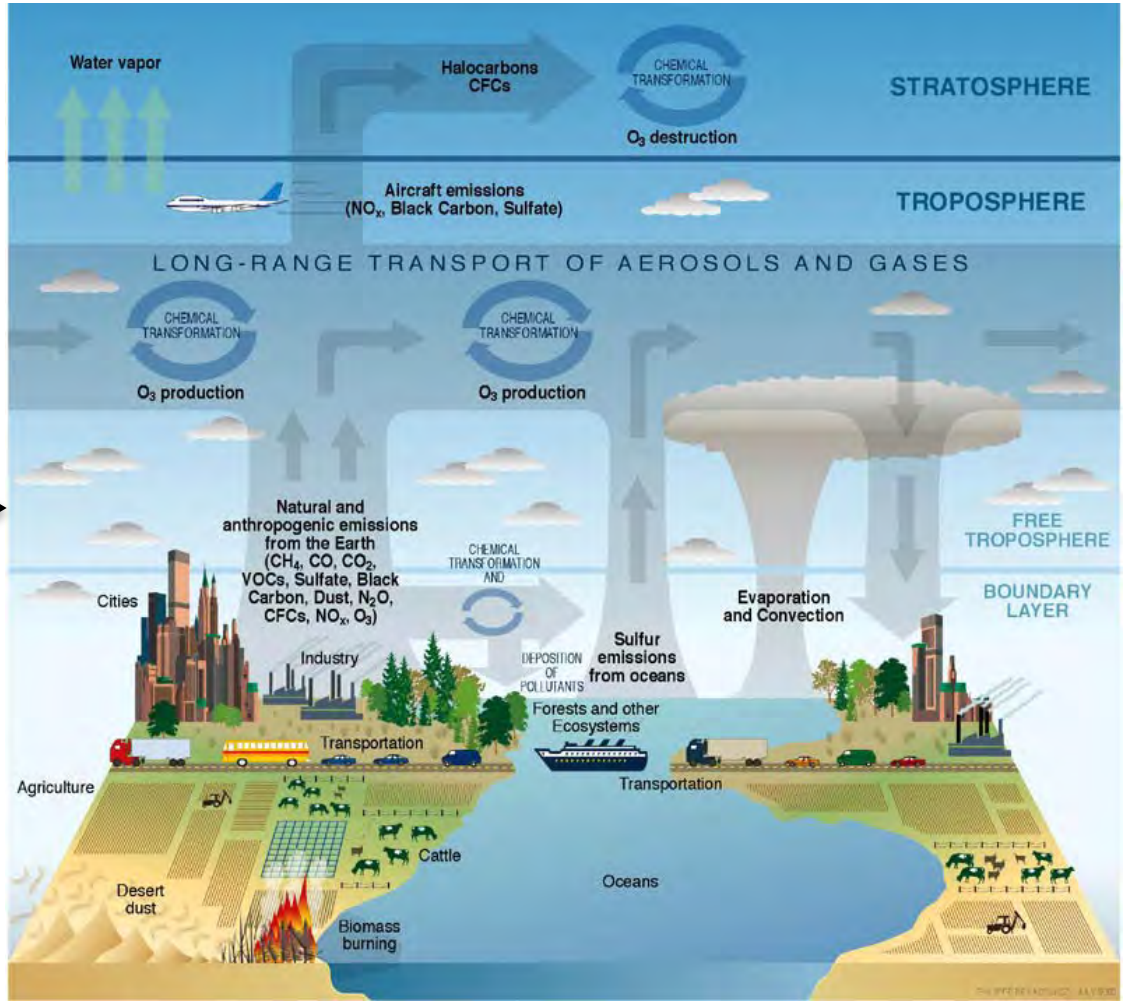
(C-C 346, C-N 305, C-O 358, C-Cl 327 kJ/mol

Properties

- Thermally stable (in excess of 150° C)
- Resists degradation (acid, alkali, oxidizing agents, bio…)
- Hydrophobic and oleo phobic (3 phases in Kow)
- Good surfactants, lubricants
- Non-flammable
- Chemically inert

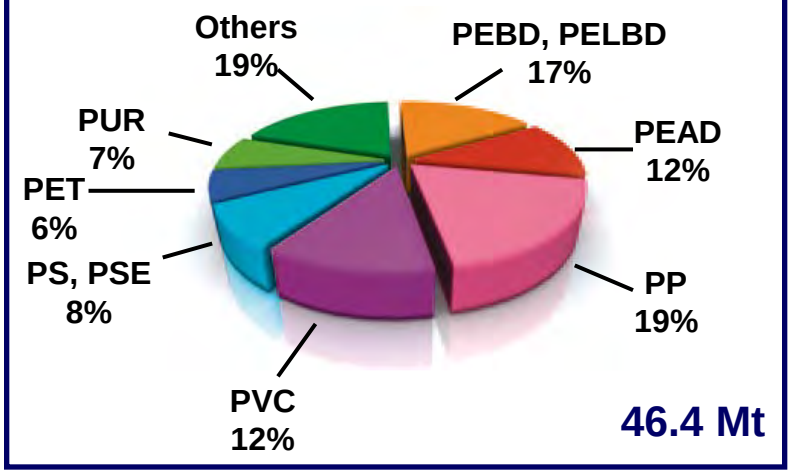
Perfluorinated compounds in sea plastic pellets

Due to PFASs properties are used in a plethora of industrial applications



Perfluorinated compounds in sea plastic pellets

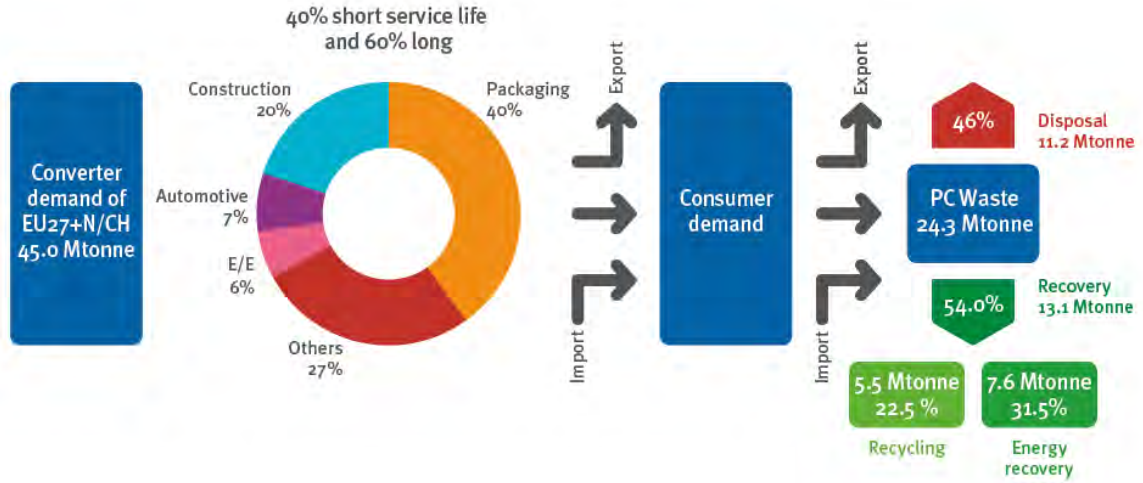
Plastic European demand (2010)



European plastics production in 2010

~ 57 Mt

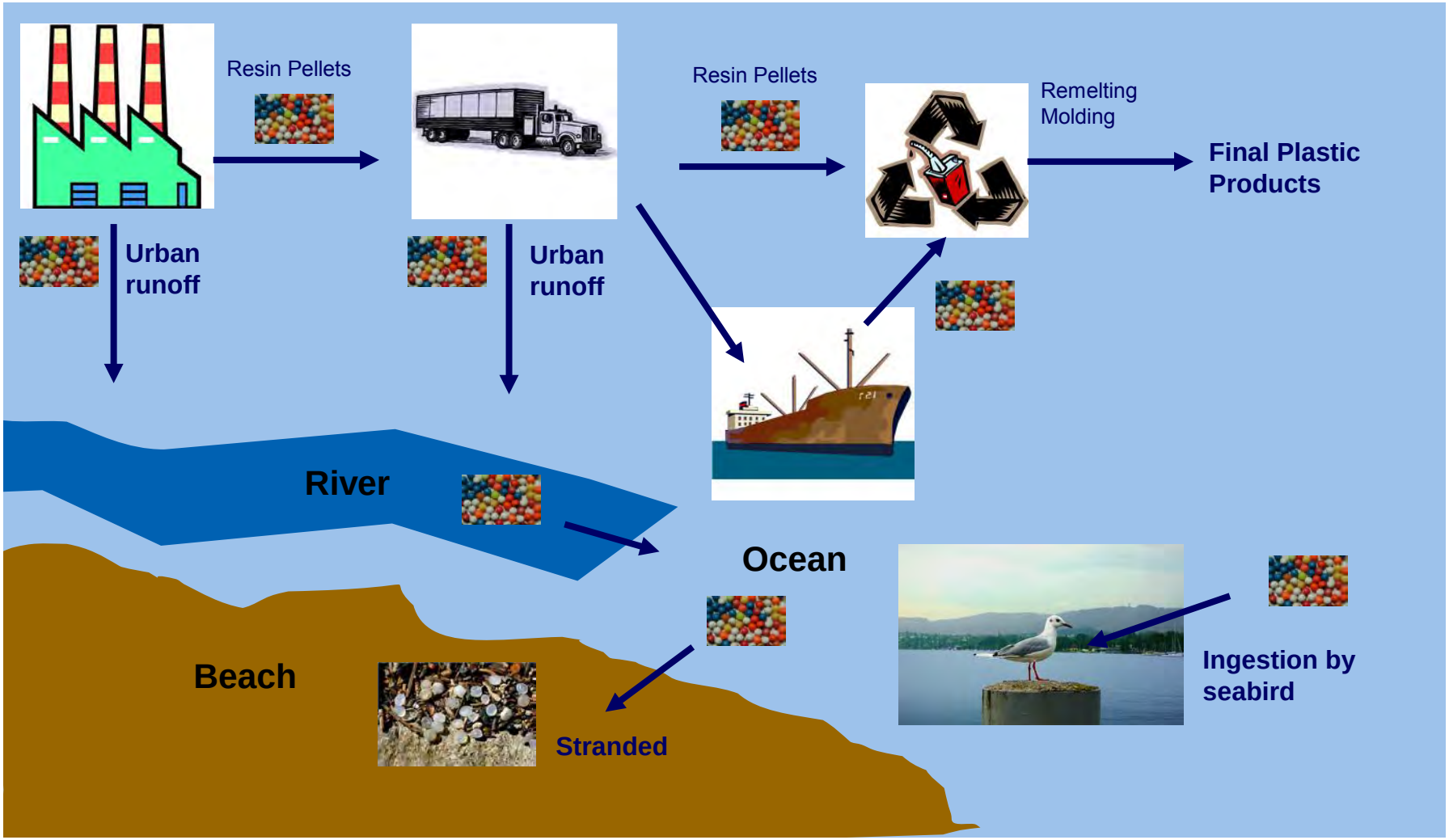
Plastics, value chain during its lifecycle



Plastics Europe Market Research Group (PEMRG)

Perfluorinated compounds in sea plastic pellets

Plastic Resin Pellets in the ocean



Perfluorinated compounds in sea plastic pellets

- Plastic pellets (small granules 1-5 mm diameter) are therefore widely distributed in the ocean all over the world.
- The environmental concerns related to these wastes are:
  - as source of contamination
  - the accumulation and transport of persistent organic pollutants that is done while they float on the sea surface.
- They are hydrophobic organic material thus they are favourable medium for persistent organic contaminants.
- Pellets demonstrating a certain degree of erosion are expected to have enough contact area with water contaminants and thus, reach the equilibrium with the pollutants in the water phase.
- Nowadays, monitoring media which can easily collected and shipped with low cost is important for monitoring diffuse pollution.
- In this context a new analytical approach has been developed **to assess 18 PFASs in plastic pellets in the Mediterranean Sea**, and these data was compared with contamination in sediments from the same sampling areas.

Perfluorinated compounds in sea plastic pellets

Sampling - Mediterranean Sea (Greece)

Sampling Poing	Sample type	Sampling site	Possible contamination source
Corfu Island	Plastic Pellet	Beach surface	International Airport and harbour
	Sediment	Beach face	
Lavrio beach	Plastic Pellet	Beach surface	Mazut and natural gas power plant; DOW chemicals plant; near to Athens city
	Sediment	Beach face	
Kato Achaia beach	Plastic Pellet	Beach surface	Harbour
	Sediment	Beach face	
Leros Island	Plastic Pellet	Beach surface	Airport and harbour
	Sediment	Beach face	
Loutropyrgos	Plastic Pellet	Beach surface	Oil refineries (Aspropyrgos and Elefsina); Near to Athens city
	Sediment	Near shore zone	
Pagasitikos Gulf	Sediment	Beach face	Central Greece International Airport Cement Industry (Aget Heracles Industry)
Amvrakikos Gulf	Sediment	Bottom of the sea	National Airport of Preveza-Lefkada Air force base (Mazona lagoon)
Aliveri	Sediment	Bottom of the sea	Cement plant (Heracles); Near to Athens city

Perfluorinated compounds in sea plastic pellets

Analytical method

Sample pre-treatment and SPE

- 1 g sea sand (or Plastic Pellet) + I.S. + 10 mL MeOH
- 1h Ultrasonic bath
- Centrifugation 20' 4000 rpm, 25ºC
- Supernatant dried under N_2
- Reconstitution in 50 mL Water and SPE (Oasis WAX)
- 150 µL (MeOH/Water)+ I.S

Chromatography

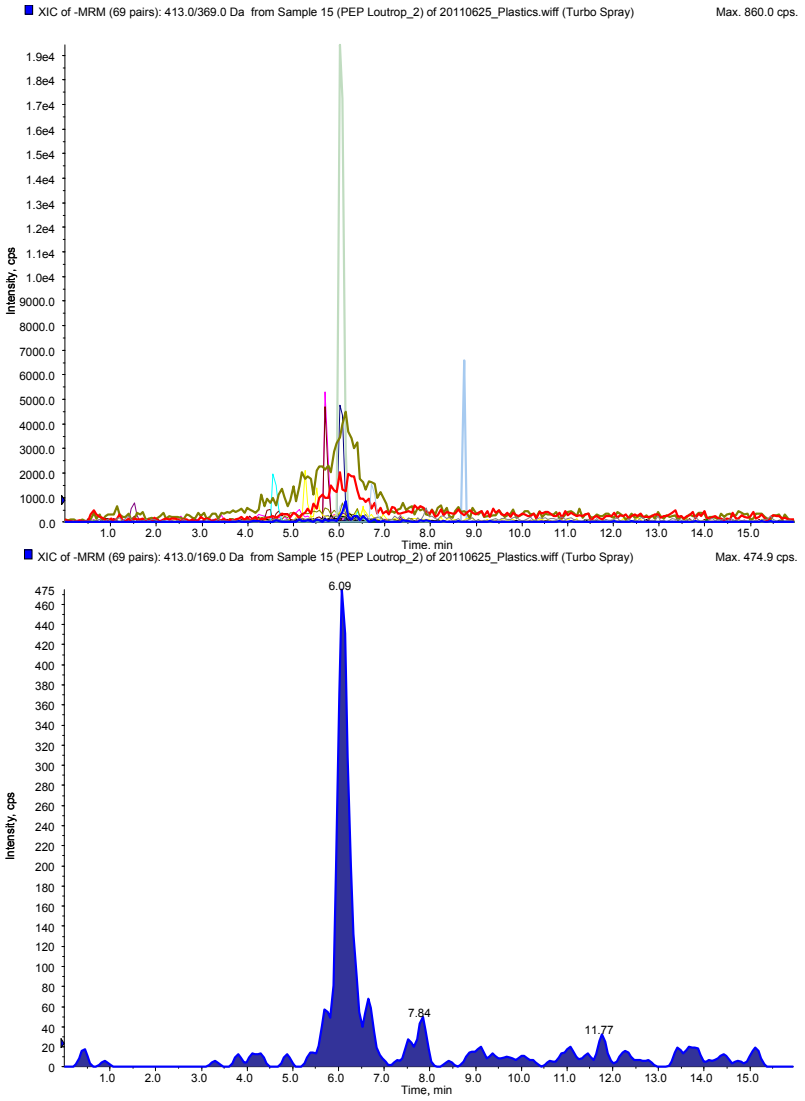
Mobile phase (A) aqueous ammonium acetate 20mM

(B) MeOH.

Flow rate: 0.5 mL/min and 10 µL injection volume.

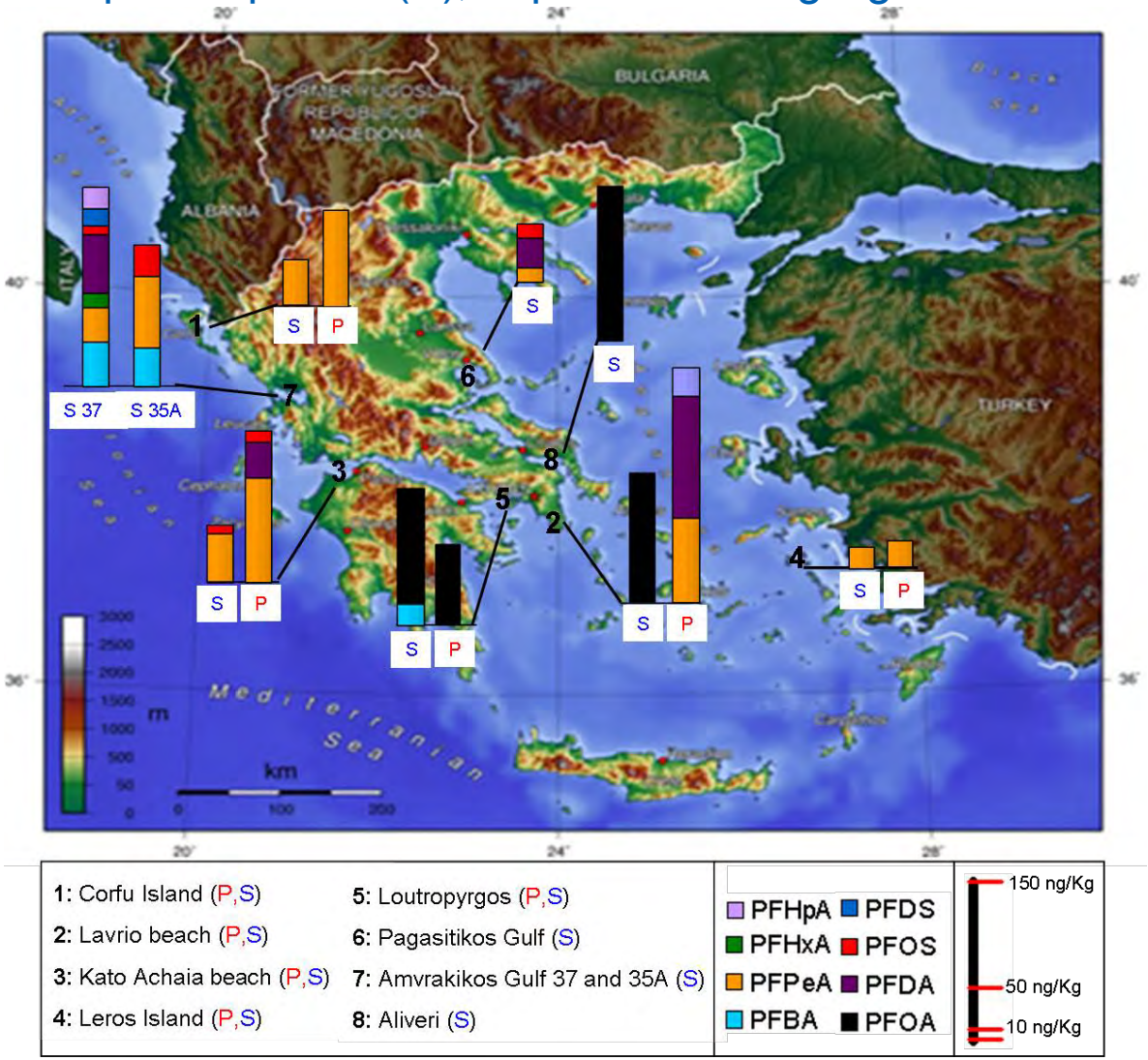
Mass spectrometry

Mass spectrometer (QLIT-MS/MS) 4000 QTRAP (Applied Biosystems), equipped with a Turbo Ion Spray source employed in the negative electrospray ionization mode (ESI(-)).



Perfluorinated compounds in sea plastic pellets

Results: Sampling sites (Greece) and accumulated concentration of PFASs in sediments (S) and plastic pellets (P), expressed as ng/Kg



Perfluorinated compounds in sea plastic pellets

Results

PLASTIC PELLET SAMPLES

Concentration range: 11 to 116 ng/Kg
(most of the compounds detected at quantificable concentrations)

PFPeA = 24 - 98 ng/Kg (four samples)
PFHpA = 28 ng/Kg (one sample)
PFOA = 76 ng/Kg (one sample)
PFDA = 35 and 116 ng/Kg (two samples)
PFOS = 11 ng/Kg (one sample)

The highest concentration were found at Lavrio beach and Kato Achaia beach

SEDIMENT SAMPLES

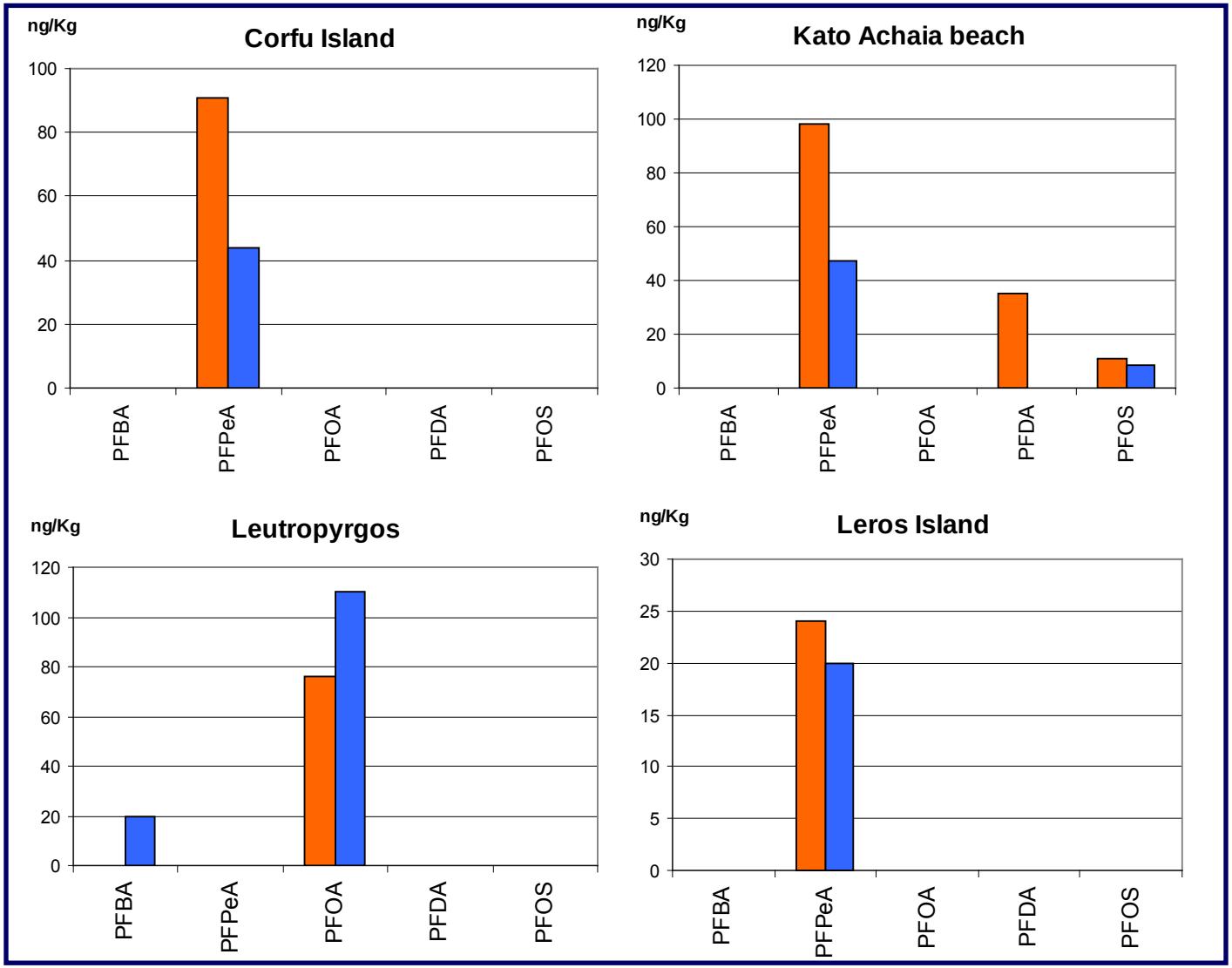
Concentration range: 8.2 to 146 ng/Kg
(most of the compounds detected at quantificable concentrations)

PFBA = 20 – 42 ng/Kg (three samples)
PFPeA = 14 – 68 ng/Kg (seven samples)
PFHxA = 13 ng/Kg (one sample)
PFHpA = 20 ng/Kg (one sample)
PFOA = 110 - 146 ng/Kg (three samples)
PFDA = 28 – 56 ng/Kg (two sample)
PFOS = 8.2 – 14 ng/Kg (three samples)
PFDS = 15 ng/Kg (one sample)

The highest concentration were found at Amvrakikos Gulf and Aliveri beach (this samples from the bottom of the sea)

Perfluorinated compounds in sea plastic pellets

Results: Relationship between plastic pellets and sediment samples



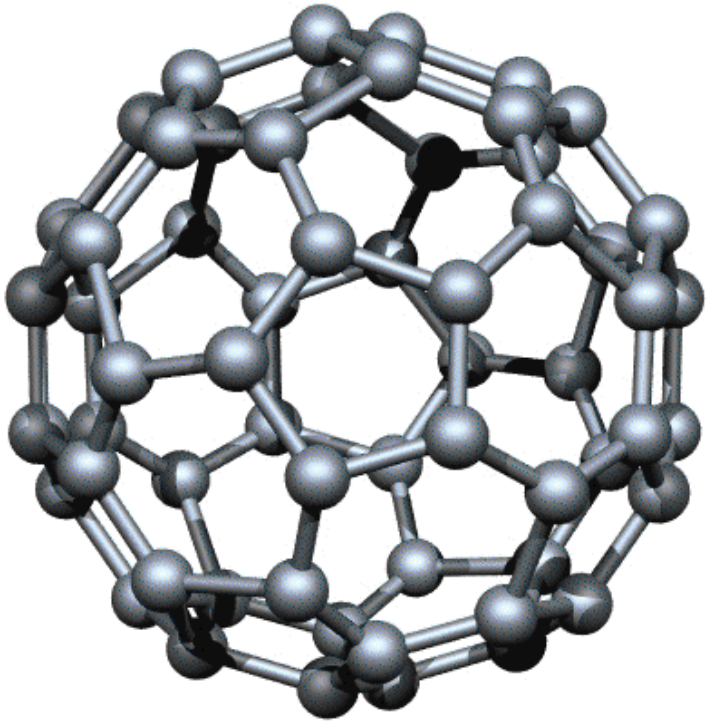
Perfluorinated compounds in sea plastic pellets

Conclusions

- **Main results from beach sediments** (Corfu Island, Kato Achaia beach, Loutropyrgos and Leros Island) indicates that more contaminated areas were Corfu, Leros , Loutropyrgos and areas near harbours
    - **Airports** (Cordu and Leros Islands) due to the combustible
    - **Harbors** due to the combustible and the use of paints and surface treatments for water repellence for ship and doc protection
    - **Oil refinery** (near to Loutropyrgos)
- The prevalent compound in sediment samples was PFPeA
- **Plastic pellet concentrations > Sediment concentrations from beach**, indicating the higher accumulation capacity of plastic pellets
- The similar pattern of PFASs in plastic pellets and sediment beach samples indicates that the residence time of plastic pellets in water is high enough to accumulate these compounds from the water and did not come from longer distances.

Case study II

Nanomaterials in contaminated soils



Fullerenes in contaminated soil

Nanomaterials (NMs)

On 18 October 2011, the European Commission adopted the following definition of a nanomaterial

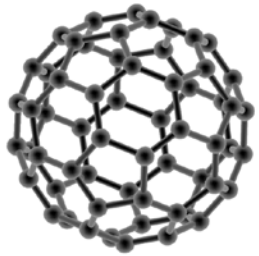
A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the **size range 1 nm – 100 nm**.

In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%.

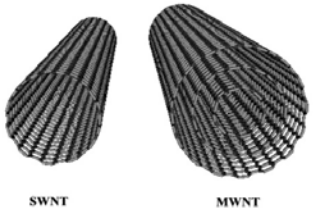
Fullerenes in contaminated soil

CARBON BASED NMs

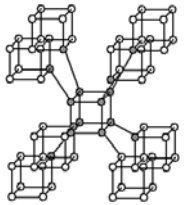
- Fullerenes



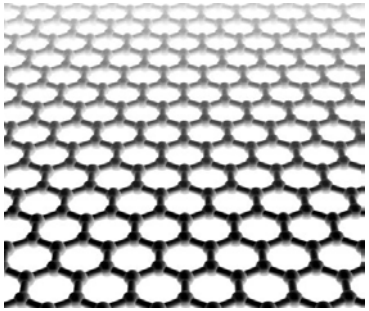
- Carbon nanotubes (CNT)
  - Single wall CNTs (SWCNT)
  - Multi wall CNTs (MWCNT)



- Nanodiamonds



- Graphone



Fullerenes in contaminated soil

Sources of FULLERENES

- **Natural fullerenes**
  - Volcanic eruptions
  - Forest fires
  - Minerals

Shungite

Chondrite

Cretaceous–Tertiary boundary sediments

- **Incidental Emission**
  - Car and plane brakes
  - Car emmisions
  - Industrial processes

CURRENTLY MAIN SOURCE

- **Nanotechnology**
  - Microelectronics
  - Consumers products
  - Nanomedicine

FUTURE MAIN SOURCE????

Fullerenes in contaminated soil

Analysis traditionally make use of laser-desorption mass spectrometry	There is a need for developing new chromatographic methods
(+) Simple sample preparation (+) Good ionization of fullerenes (-) Poor quantification (-) Fullerene self-generation issue	(+) Further matrix separation (+) Better limits of detection (+) Solid quantification (-) Need for extraction → poor recovery yields

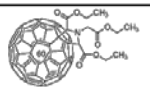
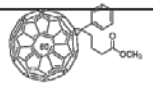
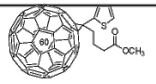
The extraction of fullerenes from high complex matrices (as those with a high content of ash) is a challenge issue, because then recovery yields are too low and matrix too strong.

In this context, the main objectives of the present work were:

- Develop a quantitative method
- Assess the contents of fullerenes in different areas of Saudi Arabia

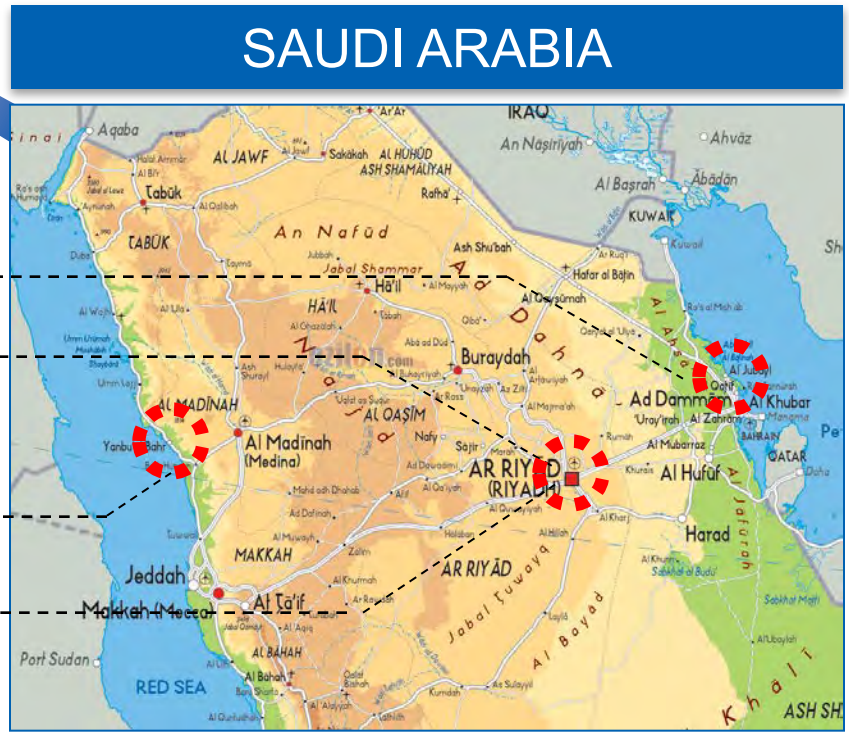
Fullerenes in contaminated soil

Selected analytes

	Compounds	Empirical formula	Structure	Transition	D.P. (V)	C.E. (V)	CXP (V)	EP (V)
Unfunctionalized fullerenes	Fullerene C_{60}	C_{60}		720>720	55	14	9	12
				721>721	55	14	9	12
	Fullerene C_{70}	C_{70}		840>840	80	8	11	15
				841>841	80	8	11	15
	Fullerene C_{76}	C_{76}		912>912	80	8	11	15
				913>913	80	8	11	15
	Fullerene C_{78}	C_{78}		936>936	80	8	11	15
				937>937	80	8	11	15
	Fullerene C_{84}	C_{84}		1008>1008	80	8	11	15
				1009>1009	80	8	11	15
Funcionalized fullerenes	C_{60} Pyrrolidine tris-acid ethyl este	$C_{72}H_{19}O_6N$		993.5>720	50	100	47	12
				994.5>721	50	100	47	12
	[6.6]-Phenyl C_{61} butyric acid methyl ester (PCBM)	$C_{72}H_{14}O_2$		910>720	45	110	55	10
				911>721	45	110	55	10
	[6.6]-Thienyl C_{61} butyric acid methyl ester	$C_{70}H_{12}O_2S$		916>720	50	100	27	15
				917>721	50	100	27	15
Isotope-labelled fullerenes	^{13}C-labelled fullerene C_{60}	$^{13}C_{60}$		736>736	55	14	9	12
				737>737	55	14	9	12
	^{13}C-labelled fullerene C_{70}	$^{13}C_{70}$		756>756	80	8	11	15
				757>757	80	8	11	15

Fullerenes in contaminated soil

Soils from Saudi Arabia: Sampling locations



Samples were taken from **4 sample locations.**

Fullerenes in contaminated soil

Soils from Saudi Arabia: Sampling locations

Riyadh	TOWN (outside)	5 samples
	DOWNTOWN (inside)	5 samples
	INDUSTRIAL AREA	5 samples
Al-Diriyah	NEIGHBORHOOD 1	7 samples
	NEIGHBORHOOD 2	4 samples
	NEIGHBORHOOD 3	1sample
Yanbu' Al Bahr	OLD CITY (inside)	5 samples
	OLD CITY (outside)	5 samples
	INDUSTRIAL CITY (inside)	5 samples
	INDUSTRIAL CITY (outside)	4 samples
Al Jubail	INDUSTRIAL AREA (inside)	4 samples
	INDUSTRIAL AREA (outside)	4 samples
	OLD CITY	4 samples

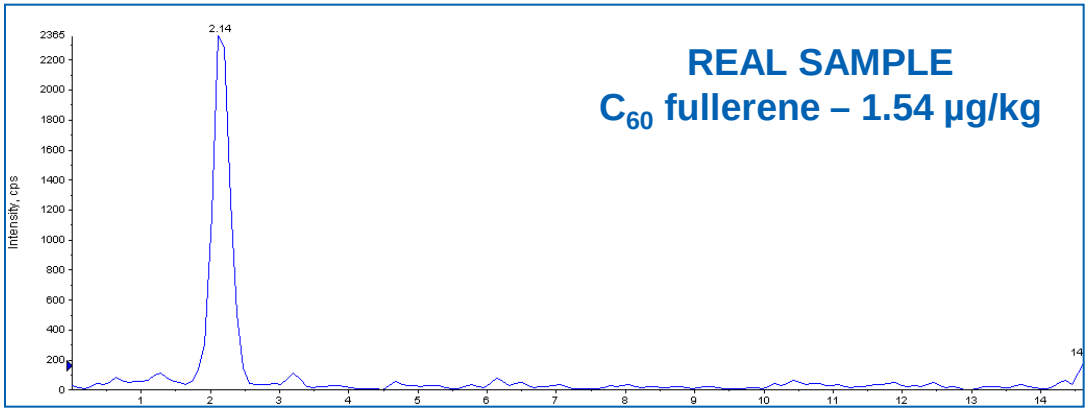
58 SAMPLES

Fullerenes in contaminated soil

Ultrasound assisted extraction with toluene during **8 hours** show good performance in most of the samples, **however for some of them with high contents of ash C_{60} was detected but the quantification was not possible**

Four samples present quantifiable concentrations of C_{60} fullerene:

- Riyadh (outside)
- Riyadh (outside)
- Al-Jubail (industrial area)
- Yanbu' Al Bahr (old city)



Fullerenes in contaminated soil

Some of the samples presented C_{60} but other fullerenes were not detected, indicating that the origin is combustion processes from cars or from industrial areas.

Positive samples from cities can be directly related to traffic engines. The range of concentrations was 0.15 and 2.15 ng/g

Industrial areas were suspected to be contaminated with both C_{60} and C_{70}, but quantification was not achieved because a strong ion suppression and low recovery rates

Positive samples from industrial areas presented also C_{60} and the concentrations found were higher that in city areas presenting values between 4.35-6.83 ng/g

Conclusion

- Two analytical method have been developed and applied to the analysis of emerging contaminants in the environment.
- In case of plastic pellets, perfluoroalkyl substances were analysed in comparison to sediments from same sampling areas. Good correlation was found between both matrices, but plastic pellets presented higher concentrations.
- Plastic are relevant sources of contamination because during the first periods these materials acts as a source of contaminants. In addition are highly persisten materials that can act stabilizing other contaminants, such as POPs.
- On the other hand, sea plastic pellets are possible passive samplers of the diffuse pollution in an area, as in the examples presented here for PFASs
- Carbon based materials are an emerging class of contamination because the increasing amount of combustion processes and is expected by the nanotechnology.
- In this case the presence of fullerenes was studied in different areas of Saudi Arabia and the results showed that this type of contamination can be associated to some industrial processes and traffic engines but not to the nanotechnology. However the method presented here should be refined to overcome some limitations associated to highly contaminated samples with ash.