PERSISTENT ORGANIC POLLUTANTS (POPS): ENVIRONMENT PERSISTENCE AND **BIOACCUMULATION POTENTIAL**

Ana-Maria ENE

Scientific Research, MAGISTRA S.A, Constanta, Romania

Abstract: Persistent organic pollutants (POPs) are widely environmental contaminants and represent a global problem. The environmental chemistry and ecotoxicology of persistent organic pollutants (POPs) represent every interesting domain of scientific research. Persistent organic pollutants toxicity in humans and wildlife is caused by their environment persistence and by their bioaccumulation potential in the tissues of animals and humans through the food chain.

This paper objective is to provide an overview aboutpersistent organic pollutants, about their harmful effects on biota, and make some comments about: sample collection, extraction methods, analytical methods, POPs biomonitoring, POPs in atmospheric environment, POPs in the terrestrial environment and POPs in marine and freshwater environments. Keywords: POPs · bioaccumulation · biota · biomonitoring · environment

1. INTRODUCTION

Environmental forensics appeared in the 1980s as a consequenceof legislative frameworksfor seek compensation with regard to contamination or injury due todamage to the environment. [1]

There are more than 100,000 existing chemicals on the market as an integral part of our modern life.

A number of these chemicals are substances of very high concern and they are persistent, bioaccumulativeand toxic (PBT).

Chemicals categorized as PBT have the following properties:

- PBT are not break downeasily in the environment;
- PBT accumulate in the tissues of organisms
- PBT aretoxic.

Persistent organic pollutants (POPs) are a subcategory of the PBT category. POPs are compounds which are organic (natural or anthropogenic) innature and resist to biological, chemical and photolytic degradation.[2] POPs have been used for more than one century.

A substance can be classified as persistent if it has a half-life exceeding one of the following levels:

- soil or sediment: 180 days;
- surface water: 60 days;
- air: 2 days.

Single media calculations of half-life (Table 1) were undertaken in controlled laboratory environmentsand have been criticized by Gramatica and Papa. [3]

Table 1. Estimated half-lives of several POPs in different media

| Compounds | Estimated half-life in air (days) | Estimated half-life in water (days) | Estimated half-life in soil (days) | Estimated half-life in sediment (days) |
|-----------------------------------------------|-----------------------------------|-------------------------------------|------------------------------------|----------------------------------------|
| Aldrin | 0.21 | 710 | 710 | 2300 |
| Chlordane | 2.3 | 710 | 710 | 2300 |
| p,p'-DDT | 7.1 | 230 | 710 | 2300 |
| Dieldrin | 2.3 | 710 | 710 | 2300 |
| HCB | 710 | 2300 | 2300 | 2300 |
| PCB 3 | 7.1 | 230 | 710 | 710 |
| PCB 209 | 2300 | 2300 | 2300 | 2300 |
| 2,3,7,8-Tetrachlorodibenzo- pdioxin (TCDD) | 7.1 | 23 | 710 | 2300 |
| OCDF | 23 | 230 | 2300 | 2300 |
| Toxaphene | 7.1 | 2300 | 2300 | 2300 |

POPs, once released to the environment, have long half-lives persisting in the environment (soils, sediments,air, or biota) for extended periods.

Combining POPs stability and inclination to exist in the gaseous phase means that they are subject for longrangetransportation and that they accumulate in food chains.

The physiochemical properties described in the previous section begin to explain why POPs behavethe way they do.

The main environmental processes that control the persistenceof a compound are:

- Transport: volatilization, dilution and advection;
- Partitioning: sorption, uptake by organisms;
- Degradation: biodegradation (aerobic, anaerobic, and degradation metabolism) andabiotic (hvdrolvsis. photolysis, oxidation and reduction).

POPs in the environment are not present in just one phase, there is aconstant dynamic equilibrium whereby POPs are shifting through the differentphases.

POP proportion in each phase is dependent upon thechemicals physiochemical parameters. The main processes are presented in Figure 1.

In soils, POPs tend to bind to organic matter and to be fairly localized contaminants as transportation in ground water is minimal.

In aquatic medium, POPs tend to bind strongly to solid particles and therefore can be only detected in low concentrations in dissolved phase.

These compounds with semi-volatile character can be found in the gaseous phase in association with atmospheric particles or distributed between these two phases.

The air is the main transport media for the global distribution of POPs.

Once released into the environment, they travel in by evaporation, condensation and air transportation.



Figure 1. The influence of dynamic equilibriums scheme of the POPs proportion ineach phase

POPs are typically hydrophobic and lipophilic, so once they enter into a biological system, they are not easily excreted. In biological systems, POPs tend to partition into lipids which causes POPs accumulation into organs and fat tissue.

Over time POPs accumulate in the living tissue of organism, proces called bioaccumulation.

POPs biomagnification is the increase in POPs concentration when the contaminated materials (like plant and animals) pass up the trophic levels of the food chain.

POPs bioaccumulation and magnify in the food chain affects us at the end, so is very important that POPs presence and levels are highly analysed for the researchers.

2. SAMPLE COLLECTION

Sample collection information data must provide a commentary of all activities that take place, potentially including the following:

- Date and times on location
- Weather conditions
- Personnel present
- Site conditions
- Site activities
- Simplified site schematics
- Relevant conversations
- Sample identification numbers
- Sample locations and collection methods
- Times of sample collection
- Notes regarding the description of samples taken.

The containers normally used for standard environmental sampling routines samples are coolers.

However, most coolers used for transport have a large, loose opening that cannot be locked, thus potentially tampered with.

For an additional degree of security, coolers can be sourced with lockable clasps.

Security seal or "legal tape" is standard tape used to provide a seal on individual sample vessels and carriage equipment.

There are numerous technologies that can provide additional security to standard security seals, strongly advised for legal sampling events:

- Frangible tape
- Leaves indicative residue
- Printed serial number
- Barcode
- Shrink band

Temperature control is a very important factor for numerous environmental samples.

If the samples are not maintained at a specified temperature this can invalidate samples, due to potential loss of contaminants by enhanced degradation and volatilization.

The maintaining on a specified temperature is often managed with ice, ice packs, or ice-blocks.

Samples should be cooled, but they should not be frozen so the target maintaining temperature for numerous samples is4°C.

Achieving and maintaining a good temperature control is only worthwhile if it can be effectively demonstrated.

Effective demonstration removes doubt and provides a very strong line of evidence for sample (temperature) integrity.

Modern temperature data loggers are miniatural sealed devices that can be transported amongstsamples.

Receiving the samples from the investigator normally occurs in the analytical laboratory.

At this moment, the sample overpack containment must be inspected for integrity both by the investigator and the laboratory receiver.

Often is used a photographic evidence at this point to proving the sample integrity. Photographic documentation at this point provides certain evidence that sample integrity was maintained. After photographic evidence, the containment seals must then be broken and the sample list must be checked off against the physical sample inventory.

Seals on samples must be inspected for evidence of tampering, but these seals must remain intact at this point.

Sample collection and management for environmental forensic investigations begins a long time before field activities.

In fact, most of the actual field activities are the same as nonforensic investigations.

The quality systems around which the investigation

is built actually makes a field event robust and defensible.

3. EXTRACTION METHODS

Over 100,000 chemicals are currently in use or present in consumer productswith over 30,000 considered to be in wide commercial use.[4]

Most of these compounds are persistent, toxic and bioaccumulative and they are detected in all types of environmental matrices. The Stockholm Convention on persistent organic pollutants (POPs) targetsonly 21 compounds or compound groups including the original 12 as listedin Table 2: 9 organochlorine (OC) pesticides, polychlorinated biphenyls(PCBs), polychlorinated dibenzo-pdioxins (PCDDs), and polychlorinateddibenzofurans (PCDFs) [5].

A very important step in the field of analytical chemistry is to use the properextraction, preparation and instrumental techniques. The purpose that the accuracyand uncertainty of the technique is acceptable to meet the required data quality between the final idea is that the analytical method used is fit for the purpose for which it was intended.

Table 2. List of compounds under the Stockholm Convention

| Catanami | Commonweald |
|---------------------------------------------------------------|------------------------------------------------------|
| Category | Compounds |
| Pesticides | Aldrin |
| | Chlordane |
| | Dieldrin |
| | DDT |
| | Endrin |
| | Heptachlor |
| | Hexachlorobenzene (HCB) |
| | Mirex |
| | Toxaphene |
| Industrial chemicals | PCBs |
| Unintentional production | PCDDs and PCDFs |
| | PCBs |
| | HCB |
| Added – May 2009 | Chlordecone |
| | α-hexachlorocyclohexane |
| | β-hexachlorocyclohexane |
| | Hexabromobiphenyl |
| | Hexabromodiphenyl ether and heptabromodiphenylether |
| | Lindane (v-hexachlorocyclohexane) |
| | Pentachlorobenzene |
| | PFOS, its salts and perfluorooctanesulfonyl fluoride |
| | Tetrabromodiphenyl ether and pentabromodiphenylether |
| Compounds under review, nominated for addition – October 2009 | SCCPs |
| | Endosulfan |
| | HBCD |
| Compounds under review, nominated for addition – October 2009 | Endosulfan HBCD |

Different degrees of sensitivityor selectivity may be required and as a result different methods couldbe used in order to answer each one of these questions. Cost and speed

can also be important considerations.

Table 3presentsthe LD50 concentrations for the rat by increasing toxicity from top tobottom.

Table 3. Relative Toxicity of Various POPs

| Compounds | LD50 Oral – Rat (mg/kg) |
|---------------------|-------------------------|
| HCB | 10,000 |
| α-BHC | >2000 |
| Total PCB (Aroclor) | 1000 |
| DDE | 880 |
| 2,4-D | 370 |
| 3,4,5-T | 300 |
| PFOS | 250 |
| Mirex | 235 |
| Chlordane | 200 |
| DDT | 87 |
| Lindane (γ-BHC) | 76 |
| Toxaphene (total) | 50 |
| Aldrin | 39 |
| Dieldrin | 38 |
| Pentachlorophenol | 27 |
| Endosufan | 18 |
| Endrin | 3 |
| PCN 67 | 1 |
| PCB-126 | 0.2 |
| 2,3,7,8-TCDD | 0.02 |

Table 4 summarizes possible methods that can be used to analyzesome of the compounds presented in Table 2 and Table 3.

Table 4. Analytical Schemes for some POPs examples

| Compounds | AnalyticalMethod |
|--------------------|------------------|
| Chlorobenzene | GC-ECD |
| PCBs (total) | GC-ECD |
| OC pesticides | GC-ECD |
| PCBs – Congener | GC-ECD |
| | GC/MS |
| PAHs | GC/MS |
| BDEs | GC/MS |
| | GC/HRMS |
| PCNs | GC-ECD |
| | GC/NCI MS |
| PCBs (dioxin-like) | GC/MS |
| | GC/HRMS |
| Dioxins/furans | GC/HRMS |
| | GC/MS/MS |

Generally, when the toxicityof the compound increase, the required method become more complex, requiring larger sample sizes, more comprehensive cleanup schemes, smallerfinal extract volumes, more sensitive and selective instruments, longer analysistimes and greater costs.

Analytical methods used for POPs follow the same basicanalytical scheme:

- extraction of analytes from matrix;

- separation of analytesfrom interfering matrix coextractables;

- analysis of cleaned extract usingchromatographic separation followed by instrumental detection.

Selecting the correct analytical approach is critical in order to obtain the best quality datapossible.

Sample extraction is a critical step that is required to separate the analytesof interest from the bulk matrix so that they can be cleaned by chromatographicseparation, concentration and instrumental analysis.

Internal standards are prior to extraction and are typically added to the sample for qualitycontrol.

Accuracy and precision are strongly dependenton the number of internal standards and type of calibration used.

Aqueous samples and other liquid samples like biological fluids have classicallybeen extracted using liquid/liquid extraction.

If samples for persistent organic pollutants analysiscontain particles, they can be filtered to isolate the particles.

If the analytesof interest are present at significant levels on the particles (e.g., dioxins,PCBs, BDEs (brominated diphenylethers)), they can be extracted using solidextraction procedures.

Aqueous samples can also be extractedusing solidphase extraction (SPE), a technique that uses a stationary phase, in an extraction cartridge or discto extract nonpolar analytes like dioxins, PCBs from polar liquids or divinylbenzene(DVB) for more polar compounds.

Extraction of samples by SPE also allows for the particles to be trapped on top of the extraction disc or bed.

Other procedures can also be used to extract aqueous samples, includingsorptive stir-bar extraction (SBSE) with thermal desorption directly into thegas chromatograph (GC) [6] or hollow fiber liquid-phase microextraction(HF-LPME) [7] where small amounts of solvent are trapped in the pores ofthe hollow fiber extract concentrating the analytes of interest. Solid-phasemicroextraction is a technique where a

fiber is coated with a specific stationaryphase.

Solid matrices (e.g., soil/sediment, biota, or vegetation) have classicallybeen extracted using Soxhlet extraction.

Pressurized liquid extraction (PLE – also known as acceleratedsolvent extraction (ASE)) [8], microwave-assisted extraction (MAE)[9] and sonication can also be used.

Wet samples(sediments, biota, and vegetation) can be Soxhlet extracted with a device which separates water from

less dense nonpolar solvent.

Supercritical fluid extraction [10, 11] is a procedure that uses supercriticalcarbon dioxide and requires no solvent for extraction and only a very smallamount of solvent to trap the analytes or elute them from the carbon or trapping material.

Usually, sample extracts must be concentrated prior to cleanup.

Thereare a variety of sample concentration procedures that can be used, includingnitrogen or gas blow down, rotary evaporation, KudernaDanish concentration,or automated evaporative concentration.

4. ANALYTICAL METHODS

Most extraction procedures for persistent organic pollutants are quantitative and able to extracta variety of organic compounds as well as other organic matrixcoextractables.

The detection of analytes can be accomplished using a number of different instruments.

When selectingthe instrument and instrumental analytical procedures, sensitivity and selectivity are the main considerations.

Nonselective detectors, such as flame ionization detection (FID) and electron capture detector (ECD), were used extensivelyprior to 1990, but are now used mainly for screening.

Spectacular advances in mass spectrometry have given rise during the past two decades to commercially availableinstruments, that are highly automated, simple to operate and lessexpensive to acquire.

Mass spectrometry is at this moment the most selective and sensitive detector formost of environmental forensics applications and also offers thekey advantage of using mass-labeled internal standards, which can significantlyincrease accuracy and precision.

Mass spectrometry gives accurate and precise results and it is critical in regulatory, forensicand litigation applications.

A laboratory must have a comprehensive quality assurance/qualitycontrol program that includes accreditation for asmany analytes as practicable in order to ensure the best possible results are produced.

Accreditation ensures that laboratories are followingproper procedures and participating in performance evaluation studiesto assess data quality.

The first step in the accreditation process is full method validation and initial performance evaluation.

Critical steps in the production of a ruggedanalytical method that produces reproducible results with the required accuracyand uncertainty are method development and validation.

Key method attributes are: sensitivity (detection limits), selectivity, accuracy, anduncertainty (precision) and are important considerationswhen selecting an analytical method. There are threetypes of analytical methods:

- Reference method
- Modified method
- In-house method

Calibration is one of the most important steps that determines the data qualityof a method.

It defines the accuracy and precision of the method. Thevarious types of calibration are detailed below. The instrument must be standardized to ensure it is analyzing the requiredanalyte.

For mass spectrometers, this involves calibration of the mass scaleusing calibration compounds. Mass calibration is critical for high-resolution mass spectrometerswhich must be continuously calibrated to ensure mass accuracy.

5. POPS BIOMONITORING

Biomonitoring has become an indispensable tool for studying occupational and environmental exposure to chemicals, including persistent organic pollutants (POPs) [12].

Using of biomonitoring data in a forensic context is the reason to understand the potential exposures to specific sources or to identify historical elevations in exposure.

Biomonitoring requires consideration of many factors like:

- differential toxicokinetic properties of POPs;

- issues in analytical determination and measurement of POPs concentrations in human biological matrices;
- typical patterns of biomonitoring results in populations without unusual exposure;
- efficacy of potential and demonstrated routes of exposure.

Persistent organic pollutants have been the object of biomonitoring studies for more than 60 years.

Biomonitoring has become the primary tool for human exposure characterization for persistent organic pollutants.

POPs have some physical and chemical characteristics that lead their persistence in the environment and into biological systems, with limited metabolism, slow elimination, and resulting bioaccumulation.

The measured levels and patterns results obtained of POPs in human tissues requires consideration of the details of the toxicokinetics of the compounds as well as consideration of exposure patterns several decades.

The utility of biomonitoring for exposure assessment for POPs are related with their fundamental physical and chemical characteristics, their extreme hydrophobicity (and resulting lipophilicity) and resistance to biological or chemical degradation.

These fundamental characteristics influence the resulting biomarker concentrations reflecting these processes and the absorption, distribution, metabolism and elimination of POPs.

It is important to continue to test and develop more sensitive analytical methods for environmental chemicals:

- to determine the normal human chemicals levels shown to be toxic to certain animals;
- to continue monitoring chemical levelsthat are decreasing in populations around the world;
- to provide better analytical coefficient of variations of chemicals;
- to provide a lower analytical coefficient of variations translates directly into higher statistical power in epidemiological studies.

A widely exposure characterization tool in studies of populations with potentially elevated exposures to POPs (both inan environmental and an occupational context) has been biomonitoringas well as in studies of general population groups without known elevated exposures in order to explore possible exposure-response relationships.

Exposure events occurring many years in the past may be detectable through the use of biomonitoring because of the extreme persistence of these compounds.

It is a known fact that biomonitoring data can be used to evaluate exposure assessments based on measurements in environmental media or on judgments regarding exposure potential.

These data can also provide insight into the relative importance of various exposure pathways.

Biomonitoring may also provide insight into the effectiveness of exposure interdiction strategies.

6. POPS IN THE ATMOSPHERIC ENVIRONMENT

The atmospheric transport and fate of persistent organic pollutants (POPs) have been the subject of intensive research and regulatory actions for many years. a) Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are

compartments, including atmosphere, water, sediments, and soils.

- In nature, PAHs are produced:
- by diagenesis of organic matter at low temperatures;
- during formation of petroleum and coal;

- by incomplete orinsufficient combustion at moderate to high temperatures (pyrolysis);

by biosynthesis.

PAHs are produced by a variety of sources, which can be divided intoseveral major categories: natural, domestic, mobile, industrial, and agriculturalsources [13].

Globally, the major sources of PAH emissions are biofuel (includingstraw, firewood and animal dung), wildfires, and consumer product usage,which includes PAHs emitted during the use of personal care products,household products, automotive after-market products, adhesives and sealants,coatings, and other regulated products [14].

PAHs are subject to several atmospheric processes that contribute to theirresidence times in the air: partitioning between gas and particlephases, wet and dry particle deposition, diffusive exchange betweenwater bodies, photolysis and chemical reactions with atmospheric oxidants. b) Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are persistent semivolatile organic compoundsthat have been extensively used since 1930 for a variety ofindustrial uses. During the period of their production and use, direct emission to the atmospherewas the major air pollution source and pathway and soil was a primarydepository of PCBs. PCBs in the atmosphere exist in two compartments: gas phase and particlephase; this partitioning affects their transport and reactivity in the atmosphere.

c) Polybrominated compounds

There is a wide variety of brominated compounds that are commerciallymanufactured, the majority of which are used as flame retardants, fumigants, and antifungals [15].

d) They are added to a wide variety of plastics, foams, polymers, and textilesin furnishings, electronics, building materials, and vehicles. Some of them are used as additives and many brominated compounds are added to plastics and foams at concentrations of up to 30%by weight and are not chemically bound to the plastic matrix, but someof them are instead "reactive" and can be covalently bound to theplastic matrix [16]. *Perfluorinated compounds*

Polyfluorinated compounds and perfluorinated alkyl compounds (PFCs) are a highly valued groupof anthropogenic chemicals that represent a large global commercial market.

PFCs are characterized by a saturated fluorinated alkyl chain on one end andare generally capped on the other by a polar nonfluorinated moiety. The identification of PFCs in remote Arctic and southern hemisphere environmentshighlights the significance of atmospheric transport of these anthropogenicinputs [17]. The high stability of PFCs is allowed by the strong carbon-fluorine bonds and determine the persistence of compounds.

e) Polychlorinated dibenzo-p-dioxins and dibenzofurans

Polychlorinated dibenzo-p-dioxins (PCDDs or "dioxins") and polychlorinateddibenzofurans (PCDFs or "furans") are not created intentionally, but are producedby a number of human activities like chemicalmanufacturing and incomplete combustion or by natural processes like volcanoes, forest fires and geologic processes. Dioxins and furans are the most

studied chemicals in terms of their formation processes, environmental occurrence and toxicity.

7. POPS IN THE TERRESTRIAL ENVIRONMENT

Terrestrial enviroment means land-based areas and the biota that live there and includesman-made and natural surfaces, subsurface features and the interfaces with the atmosphere and the oceans.

Persistent organic pollutants (POPs) income into the terrestrial environment by use and disposal; this includesintentional discharges and unintentional spillages and leaks.

POPs are relatively immobile and do not readily degrade. This is the reason that after releases to the environment, they can remain in soils and sediments in localized areas at high concentrations.

Soils and sediments a)

Persistent organic pollutants can enter the soil through intentional discharges, unintentional spillagesand leaks and aerial deposition.

Once they have been released to theenvironment. POPs can be carried out all overthe globe by atmospheric transport that can occur through the vapor pathway, windblown dust and particulate matter which has beencontaminated with POPs.

Global distillation and cold condensation describehow POPs volatilize fromwarm source areas, undergo long-range atmospheric transport and subsequently condense onto surfaces, such as soil, vegetation, or snow, atlow temperatures, effectively accumulating in the polar regions.

Herbage b)

In theory, POPs can enter vegetation through two main media, air andsoil; however, the exact pathways are not fully understood or quantified.

There are many variations, such as wind speed, temperature, the reactivesurface of the leaf, and the permeability of cuticle wax, which can all affect he intake of POPs through air. For most vegetation, the uptake from the soil is considered negligible.

A summary of potential pathways forPOPs to enter vegetation includes: contamination of shoots and cuticles from aerial deposition of wet anddry particulates, uptake through roots and xylem transport to other parts of the plant, uptake of airborne vapors through stomata and adsorption and absorption onto roots and tubers in the ground and partsof the plant in close proximity to the ground.[18]

The main properties of persistent organic pollutants are: generally highly lipophilic, low volatility and low solubility, therefore, the transfer of POPs from the soil to vegetation would be expected to be relatively low but real.

Wildlife C)

The main ways that persistent organic pollutants enter animals is ingestion of contaminated food.

Polychlorinated biphenyls (PCBs) and other persistent organic pollutants present in fish strongly influence the profile in fish eatingbirds present in the food chain. The studies result showsdifferent concentrations and profiles found in terrestrialpredatory birds feeding on small mammals in comparison to predatory birdsfeeding on small passerine birds. d) Humans

POPs can enter humans through three main pathways: ingestion, inhalation, and dermal contact (through the skin).

The vast majority of people will onlybe exposed to background concentrations of POPs, which will occur throughout their lifetime. The majority of this exposure will occur through ingestionof contaminated foods [19].

8. POPS IN MARINE AND FRESHWATER ENVIRONMENTS

Persistent organic pollutants (POPs) are organic compounds of natural oranthropogenic origin that resist photolytic, chemical, and biological degradation.

Examples include polychlorinated biphenyls (PCBs), dioxins and furans, many pesticides and certain metals, particularly mercury. Although manycountries have banned or severely restricted the production and use of POPs inrecent decades, these substances are pervasive and can be found in remoteenvironments around the world [20, 21].

It is a fact well known that POPs have theability to migrate long distances from their original source.

Inputs of POPsfrom the atmosphere and surface waters, and rereleases from sediments and removal pathways such as volatilization and sedimentation may explain, inpart, why countries that banned the use of certain POPs are experiencing lessdramatic declines in environmental concentrations nearly a decade later [22].

POPs are hydrophobic and lipophilic chemicals. In aquatic environments and soils they partition strongly toorganic matter and avoid the aqueous phase. Persistent organic pollutantsdistributebetween particles, colloids and the water phase.

When POPs sorb to particles and colloids, the freely dissolved concentrationsdecrease and, thus, also the bioavailability to aquatic organisms.

On the other hand, the sorption of POPs to colloids can enhance environmentaltransport due to the higher mobility of small colloids compared to larger particles. Colloids can alsofacilitate the transport of POPs over the thin stagnant aqueous films (i.e., diffusiveboundary layers) that are present at the interface between water and sediment or on passive samplers.

The extent of sorption to particlesand colloids and the distribution between different phases in the aquaticenvironment has a large impact on POP migration in the environment andfate processes, such as sedimentation, bioavailability, and degradation.[23]

Polyfluoroalkyl compounds a)

The occurrence and fate of fluorinated compounds in the aquatic environmentis recognized as an important . 1990s, emerging contaminant issue. Since the knowledgeabout variety, worldwide distribution, environmental fate and transport pathways of polyfluoroalkyl compounds has advanced substantiallyconcurrent with improving analytical methods.

PFASs are persistent and bioaccumulative and have been detected in variousenvironmental matrices, including freshwater [24] and marine waters [25, 26].

Pharmaceuticals and personal care products b)

Pharmaceuticals and personal care products (PPCPs) are a largeclassof thousands of chemical substances, including prescription and no prescription over-the-counterdrugs, veterinary drugs, fragrances, sunscreens, detergentsand cosmetics. Among this category of compounds, some are capableof disrupting the endocrine system of animals, including fish, wildlife, andhumans; these substances are termed endocrine disrupting chemicals (EDCs) and are the most dangerous ones.

Engineered nanomaterials c)

Engineered nanomaterials (ENMs) enter the aquatic environment through controlled and uncontrolledatmospheric emissions and solid or liquid waste streams from severalindustrial sectors:

semiconductors;

- memory and storage technologies;
- display, optical, and photonic technologies;
- energy;
- biotechnology;
- paints and pigments; pharmaceuticals; _
- - textiles;
- health care and personalcare product manufacturers.
- Flame retardant compounds d)

Flame retardants are chemicals used in thermoplastics, thermosets, textiles, and coatings to inhibit flammability or resist the spread of fire. There aremore than 175 different types of flame retardants, which are generallydivided into four classes that include the halogenated organic (usually brominatedor chlorinated), phosphorus-

containing, nitrogen-containing, and inorganicflame retardants. This is the most significant class of substances andinclude five major types-brominated bisphenols, diphenyl ethers, cyclododecanes,phenols, and phthalic acid derivatives. [27]. Polycyclic aromatic hydrocarbons PAHs are weakly volatile, have a low solubilityand

are chemicallyinactive but bond to particulate matter. In surfacewater, PAHs volatilize, photolyze, oxidize, biodegrade, bind to suspendedparticles or sediments or accumulate in aquatic organisms (lowest trophic level). Polycyclic aromatic

hydrocarbons are widely environmental contaminants. Although they can beformed naturally, their main anthropogenicemissions source is and the highest concentrations of PAH are generally found aroundurban centers. Concentrations of PAHs in the aquatic environment aregenerally highest in sediment, intermediate in biota and lowest in the watercolumn.

CONCLUSION

The environmental chemistry and ecotoxicology of persistent organic pollutants is very important area of scientific enquiry. This pollution impact of POPs is a fascinating, active, multidisciplinary and energetic domain of science at this moment.

Proper removal techniques of persistent organic pollutantsfrom the environment are still unclear, due to fear that more toxic byproducts may result from uninvestigated degradation techniques. Current efforts are more focused on banning the use and production of POPs worldwide rather than removal of POPs. Active areas of current and future research for the next few years may be:

- improvements in the source inventories and refinements in pathways and exposure analyses;
- more detailed, sophisticated and refined studies on the air surface exchange of POPs;
- global scale analysis and a more comprehensive geographical coverage of chemical concentration and flux data;
- increasing the sophistication of the development of physicochemical property-based models;
- studies on the form, bioavailability, fixing and remediation of POPs in soils, sediments and groundwater;
- studies of POPs effects on humans and wildlife, including biodegradation, transformation and toxicity mechanisms;
- studies of `newer' and perhaps more polar persistent compounds classes of POPs;

analytical methods improvement to identify and quantify new POPs, notably metabolites, stereoisomer's and more polar POPs.

REFERENCES

- B. Jones, N. Parpworth, Environmental Liabilities, Shaw, Crayford, 2004
- 2. D.C. Muir, P.H. Howard, Are there other persistent organic pollutants? A challenge forenvironmental chemists, Environ. Sci. Technol. 40 (2006) 7157-7166
- P. Gramatica, E. Papa, Screening and ranking of POPs for global half-life: QSARapproaches for prioritization based on molecular 3. structure, Environ. Sci. Technol. 41(2007) 2833-2839
- 4. P.H. Howard, D.C.G. Muir, Identifying new persistent and bioaccumulative organicsamong chemicals in commerce, Environ. Sci. Technol. 44 (7) (2010) 2277-2285
- 5.
- Stockholm Convention Secretariat, UNEP,<u>http://chm.pops.int</u> (2001) A. Prieto, O. Zuloaga, A. Usobiaga, N. Etxebarria, L.A. Fernandez, Development of a stirbar sorptive extraction and thermal 6. desorption-gas-chromatography mass spectrometrymethod for the simultaneous determination of several persistent organic pollutants inwater samples, J. Chromatogr. A 1174 (2007) 49
- G. Li, L. Zhang, Z. Zhang, Determination of polychlorinated biphenyls in water usingdynamic hollow fiber liquid-phase 7. microextraction and gas chromatography mass spectrometry, J. Chromatogr. A 1204 (2008) 119-122
- 8. P. Antunes, P. Viana, T. Vinhas, J.L. Capelo, J. Rivera, E.M.S.M. Gaspar, Optimizationof pressurized liquid extraction (PLE) of dioxins-furans and dioxin-like PCBs from environmentalsamples, Talanta 75 (2008) 916-925
- K. Srogi, A review: application of microwave techniques for environmental analyticalchemistry, Anal. Lett. 39 (2007) 1261-1288 9
- 10. T. Miyawaki, A. Kawashima, K. Honda, Development of supercritical carbon dioxideextraction with a solid phase trap for dioxins in soils and sediments, Chemosphere 70(2008) 648-655
- D. Garcia-Rodriguez, A.M. Carro-Diaz, R.A. Lorenzo-Ferreira, Supercritical fluid extractionof polyhalogenated pollutants from 11 aquaculture and marine environmental samples: areview, J. Sep. Sci. 31 (2008) 1333-1345
- K. Sexton, L.L. Needham, J.L. Pirkle, Human biomonitoring of environmental chemicals, Am. Sci. 92 (2004) 38-45 12.
- K. Ravindra, R. Sokhi, R. van Grieken, Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and 13. regulation, Atmos. Environ. 42 (2008) 2895-2921
- 14 Y. Zhang, S. Tao, Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004, Atmos. Environ. 43 (2009) 812-819
- 15. M. Duo, M. Zhang, Y-Y. Luk, D. Ren, Inhibition of Candida albicans growth by brominated furanones, Appl. Microbiol. Biotechnol. 85 (5) (2010) 1551-1563
- A. Covaci, S. Harrad, M.A.-E. Abdallah, N. Ali, R.J. Law, D. Herzke, et al., Novel brominated flame retardants: a review of their 16. analysis, environmental fate and behavior, Environ. Int. 37 (2011) 532-556
- I. Stemmler, G. Lammel, Pathways of PFOA to the Arctic: variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources, Atmos. Chem. Phys. 10 (2010) 9965-9980 17
- C.S. Creaser, M.D. Wood, R. Alcock, D. Copplestone, P.J. Crook, UK Soil and Herbage Pollutant Survey Report No. 8, 18. Environmental Concentrations of Polychlorinated Biphenyls (PCBs) in UK Soil and Herbage. Environment Agency, UK, 2007
- D.G. Patterson, G. O'Sullivan, C.D. Sandau, The use and misuse of the National Health and Nutrition Examination Survey 19. (NHANES) data for assessing human exposure to environmental chemicals, in: R.D. Morrison, G. O'Sullivan (Eds.), Environmental Forensics, RSC Publishing, Cambridge, 2009, 188-201 L. Ritter, K.R. Solomon, J. Forget, M. Stemeroff, C. O'Leary, Persistent Organic Pollutants, United Nations Environment
- 20. Programme, 2007
- 21. C.A. De Wit, D.C.G. Muir, An overview of temporal trends of legacy and emerging contaminants in the Arctic and possible implications for top predators and humans, Organohalogen Compd. 72 (2010) 1392-1395
- D. Muir, R. Lohmann, Water as a new matrix for global assessment of hydrophilic POPs, Trends Anal. Chem. 46 (2013) 162-172 22.
- P. Mayer, M.M. Fernqvist, P.S. Christensen, U. Karlson, S. Trapp, Enhanced diffusion of polycyclic aromatic hydrocarbons in 23.
- artificial and natural aqueous solutions, Environ. Sci. Technol. 41 (2007) 6148-6155
- M.S. McLachlan, K.E. Holmstrom, M. Reth, U. Berger, Riverine discharge of perfluorinated carboxylates from the European continent, Environ. Sci. Technol. 41 (21) (2007) 7260-7265 24
- 25. L. Ahrens, S. Felizeter, R. Ebinghaus, Spatial distribution of polyfluoroalkyl compounds in seawater of the German Bight, Chemosphere 76 (2009) 179-184

 L. Ahrens, S. Felizeter, R. Sturm, Z. Xie, R. Ebinghaus, Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the River Elbe, Germany, Mar. Pollut. Bull. 58 (2009) 1326-1333

27. G. O'Sullivan, C. Sandau, Environmental Forensics for Persistent Organic Pollutants, Elsevier (2014)

28. K.C. Jones, P. de Voogt, Persistent organic pollutants (POPs): state of the science, Environmental Pollution 100 (1999) 209-221