PSEUDO-PERSISTENT POLLUTANT IN THE ENVIRONMENT: EMERGING SUBSTANCES

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ABSTRACT

In the recent time, considerable interest has grown concerning the presence of the emerging substances, EmS. These are contaminants that have been recently detected in the environment due to their long-term, pseudo-persistent and increased use. Most of EmS are wide spread and applied in different fields using as pharmaceuticals, for both human and animal uses, household chemicals, personal care products, nanomaterial, anticorrosive and agriculture chemicals and others. European legislation did not regulate the status and the maximum allowed concentration of most EmS. EmS might jeopardize surface water and ground water resources, particularly, drinking water production. The preliminary results of Danube surface water in vicinity of Novi Sad show presence of benzotriasole and caffeine. These newly recognized contaminants represent a shift in traditional thinking of protection scenario and eco status of environment and water bodies.

Keywords: emerging substances, pseudo-persistent, surface and ground water

INTRODUCTION

Chemicals are a part of modern life and are present in all spheres of human life. They are used as pharmaceuticals, pesticides, detergents, fertilizers, dyes, paints, finish, preservatives, food additives, anticorrosive materials among others. The biggest number of organic and inorganic chemicals belongs to so called emerging chemicals. They contribute to our well being, high life expectancy and economic prosperity. As new chemicals are introduced or others find new applications, and analytical methods improve, the occurrence of previously undetected chemicals, termed "emerging substances", EmS in surface ground water, drinking water is frequently noticed.

EmS include global organic and some inorganic substances, such as flame retardants, pharmaceuticals, personal care products, endocrine-modulating chemicals, nanoparticles and biological metabolites. It is almost inevitable that very small amounts of these substances, which are manufactured to protect human health, improve consumer goods, or optimize agricultural production, are unintentionally released into the environment. Recent improvements in sophisticated analytical methods have enabled the identification and quantification of these substances, in very low concentrations (ppb, ppt), which likely have been present in waters for decades.

In Europe, millions of people depend on river surface waters (Danube, Meuse, Rhine) as the sources of drinking water. Surface waters are contaminated with thousands of chemical compounds originating from industry, agriculture, household use which number is still increasing. Therefore the presence of EmS residues in the environmental mediums has become a subject of growing concern in the past decade.
Project NORMAN identified a list of the currently most frequently discussed EmS today [2]. According to NORMAN EmS can be defined as substances that have been detected in the environment, but which are currently not included in routine monitoring programs in EU and whose fate, behavior and (eco) toxicological effects are not well understood. Within NORMAN EmS are divided into 23 categories (classes) with 79 subcategories/subclasses with examples of individual emerging substances more than 700, whose list is still open.
Some portion of EmS will enter wastewater as part of the influent. Unless specifically removed by wastewater treatment processes, they may persist and be released into receiving waters as trace pollutants. Some fraction of the organic compounds used for agricultural purposes will runoff into a surface water body, while another fraction of the compounds will infiltrate and reach the groundwater system.
The term trace pollutant indicates very low concentrations of an environmental contaminant in the $\mu g\ L^{-1}$ range or lower which is one of the basic properties of EmS. It is believed that long-term consumption of EmS can cause adverse health effects in most organisms at concentrations as low as a few $ng\ L^{-1}$. Predicting the human health effects caused by exposure to EmS is a difficult task [3].
The objectives of this paper are to provide an overview on the residues of EmS in freshwater, in order to prioritize further EmS research needs.

CLASSIFICATION OF EMERGING SUBSTANCES

Most of EmS have been present in the environment for a long time, but their significance and finding are only now being elucidated and, therefore, they are generally not included in the legislation. EmS can be classified under this category according to their chemical class (chemicals of totally new structure), type of use (new uses in industry or in consumer realms), type of effect (new discovered effects), source (new or previously unknown origins for existing chemicals), and exposure (pathways that had not been anticipated or had been previously discounted as not possible). Taking into account these criteria, compounds that can be considered as EmS are the pharmaceuticals and personal care products (PPCPs), steroids, xenoestrogens and other endocrine disrupting compounds (EDCs), methyl *tert*-butyl ether (MTBE) and related compounds, surfactants and their metabolites (alkylphenolic compounds, linear alkylbenzenesulfonate (LAS) and sulfophenyl carboxylates (SPC)), drinking water disinfection by-products (DBPs) including *N*-nitroso-dimethylamine (NDMA) and nitrosamines, gasoline additives, brominated flame retardants (polybrominated diphenyl ethers), industrial additives and agents, algal toxins, and other pathogens, organotins, perfluorooctanoic acid (PFOA) and perflluorooctanesulfonate (PFOS), pesticide degradation products, chiral contaminants, chemical warfare agents, and a variety of miscellaneous chemicals such as caffeine, cholesterol, etc.
Exposure to EmS in the aquatic ecosystem is of particular concern, since aquatic organisms are subjected to continual impact of EmS. This fact makes EmS, even those that some of them have relatively short environmental half-lives, to be assumed as pseudo-persistent. Moreover, the polar and non-volatile nature of some EmS prevents their escape from the aquatic realm.
Pharmaceuticals. The possibility of emission of pharmaceuticals in the environment has been recognized in environmental science since several decades. Conventional municipal sewage

treatment plants appeared to play an important role in the introduction of pharmaceuticals in the environment purifying household waste water mainly by subsequent application of bacterial degradation of organic matter, and coagulation/flocculation for the removal of suspended solids and phosphates. In these processes, which are predominantly optimized for the degradation of waste of natural origin, organic contaminants are primarily removed by bacterial degradation and sorption to solids. The past decades have shown that this treatment is rather inadequate in removing pharmaceuticals in effluents and receiving waters in their original form, or as degradation products. Besides household sewage, other emission sources of human pharmaceuticals are waste waters from manufacturers, hospitals, and disposal of unconsumed drugs via solid waste. It is estimated that up to 65% of sold pharmaceuticals are never consumed.

Furthermore, large quantities of pharmaceuticals, e.g. antibiotics and inflammatory drugs do not pass sewage treatment. Several studies have reported that some pharmaceuticals are not completely removed by drinking water treatment and are found at trace levels in drinking water [3]. It was demonstrated that the environment is also contaminated with drugs with predominantly non-medical applications. It is estimated that up to 5% of the world population uses illicit drugs, like cocaine, heroin, cannabinoids (hashish, marijuana), and amphetamine-like stimulants (such as ecstasy). In 2005, Zuccato et al. published a first systematic study on the presence of cocaine and its degradation product benzoylecgonine in surface and waste water samples from the Italian river Po. The results were interesting not only from an environmental but also from a societal-forensic point of view. Based on the measured concentrations, the authors calculated that cocaine consumption was considerably higher than estimated. Also non-controlled stimulatory compounds, such as caffeine from coffee, tea, and soft drinks and nicotine from tobacco were often included in these investigations. Illicit and non-controlled drugs were structurally found at ng/L or lower concentrations in waste and surface waters. Degradation in sewage treatment plants varied considerably between different drugs.

Personal care products, PCPs comprise active ingredients of cosmetics, toiletries, and fragrances. They are applied as preservative or to alter odor, appearance, touch, or taste. One group of PCPs consists of compounds used as fragrance, such as polycylic musks. A second group comprises preservatives like parabenes applied in shampoos, creams, and toiletries to prevent bacterial decay. Disinfectants like triclosan and clorophene are used on a large scale. Triclosan for example has been used for decades in a wide variety of consumer products, ranging from toothpaste and hand soap to toys and socks. Compounds such as benzophenone in sun screen lotions that block UV light have gained interest of environmental chemists and biologists. Alkylated siloxanes are compounds used in soaps, hair-care products, etc. PCPs enter the environment *via* sewage treatment effluent as a result of showering, washing off, washing clothes, etc., but are also directly released in surface waters by recreational activities as swimming and sunbathing [5]. PCPs are observed regularly in effluents and surface waters worldwide. Some of them can accumulate in exposed organisms. Some personal care products are suspected to have potentially adverse potencies, such as estrogenic hormone-like activity (UV blockers, parabens), developmental toxicity (UV blockers), and extreme bioaccumulation (musks).

Nanoparticles - constitute a rapidly growing research area. They are extremely small in size with diameters between 1 and 100 nm and have properties that differ from smaller (molecules) or larger (bulk materials) particles of the same composition. Besides inorganic compounds, such as TiO_2 and nanosilver, and also organic compounds, such as carbon nanotubes and "nano-C60", fullerene, are examples of nanoparticles. They can be of natural origin as well as manufactured and a wide variety of applications is foreseen or already implemented (in medicine and food industries). Meanwhile, questions about their environmental fate and possible human-health risks arise. Due to their small size, their surface is relatively large and their chemical reactivity and biological activity remain relatively high. Nanoparticles can enter the body and cells more easily than larger particles. It is suggested that they might evoke inflammatory responses and DNA damage. However, very little is as yet known about possible toxic properties of nanoparticles. Although currently environmental data are scarce, techniques for the analysis of nanoparticles in environmental samples are developing fast, and it is expected that monitoring data will become available soon.

Flame retardants, FR are a class of chemicals that are widely used in plastics, textiles, furnishing foams, sofas, computers, televisions and other contemporary products, to slow down inflammation in the event of a fire and reduction of fire risks. In the past, mainly polybrominated biphenyl and polybrominated diphenyl ethers were used for this purpose. These compounds are structurally similar to ''conventional'' contaminants as polychlorinated biphenyls, and likewise is their behavior in the environment. Brominated FRs are structurally detected in tissues, blood and breast milk of wildlife and humans. This is worrying, that these compounds and their degradation products have several potentially toxic properties, such as the ability to disrupt the thyroid, androgenic and estrogenic hormone systems (Legler 2008), toxicity for the nervous system and they might also be carcinogenic. Because of their low solubility in water, they tend to sorb to sediments in rivers (Rahman et al. 2001) instead of reaching high concentrations in water. Another class of FRs are organophosphate FR with tributylphosphate and tris(2-chloroethyl)phosphate as important representatives. Their widespread use may even increase since many brominated FR have been banned. Organophosphate FR, for which toxicity data still are scarce, are persistent, although better soluble in water than brominated ones, and several studies have reported their presence in surface and waste waters.

ANALYTICAL DETERMINATION OF EMS

For most of the EmS there are lack of environmental data, basically because they are not, or have not been, determined and regulated in the environment. Another reason for this is the shortage of sophisticated analytical methods and equipment for proper monitoring of waste and for a risk assessment of surface and groundwater quality. At the beginning the analysis of organic EmS has been performed by high performance liquid chromatography coupled to ultraviolet detection (HPLC–UV) and gas chromatography (GC) coupled to flame ionization detection (GC–FID), electron capture detection (GC–ECD) and mass spectrometry (GC–MS). However, after the introduction of atmospheric pressure ionization, liquid-chromatography coupled to mass spectrometry (LC–MS) has largely replaced GC methods. In the particular case of emerging pollutants, for most compound classes, LC–MS and especially UPLC (TOF) MS^2 which provides additional selectivity and sensitivity, has become the technique of choice. Although the use of MS, and especially MS–MS, allows increasing sensitivity, an analyte preconcentration procedure is almost always necessary to reach limits of detection low enough to determine the ultra trace levels, within the ng/L or lower range at which EmS, are present in the environment. For this purpose, solid phase extraction (SPE) is the most widely used preconcentration procedure as well as to remove interfering components from the matrix [1].

Improved analytical methods have resulted in the identification of many more chemicals in ambient waters or the tissues of organisms than were previously believed to occur. Considering the current information on EmS, those with the highest propensity for adverse biological effects include those that are persistent and pseudo-persistent, bioaccumulative, carcinogenic, lipophilic, toxic, endocrine disruptors, and/or sized in the nanoscale range. Persistence may be caused by the structural stability of the chemical (*e.g.*, a long half-life) or it may be a result of constant loading to the environment - pseudo-persistent. Even if there is some degree of degradation, the parent compounds will nevertheless be present at constant levels in the environment if the input rate is higher than their rate of degradation or mineralization. This can be called second order persistency or pseudo persistency, $V_{input} > V_{degradation}$. Persistency is one of the most important criteria in the environmental assessment of chemicals. Pseudopersistent, lipophilic, bioaccumulative, endocrine-disrupting compounds that may also be carcinogenic should therefore be the highest priority for regulatory control and risk assessment. Recent research suggests that some nanomaterial also possess many of these high-risk properties [3].

INSTEAD OF CONCLUSION

Rapid improvements in chemical analysis techniques (HPLC-TOF-MS^2) during the last decades have led to the discovery of myriads of EmS in surface waters at very low concentrations (ppb and ppt), that could not be observed earlier. EmS can pass intact through conventional sewage treatment facilities, into waterways and even aquifers posing a threat to underlying. The presence of EmS in very low doses, their pseudopersistancy, no regulations for their maximal allowed concentration, unknown negative effect on environment, biota and human beings, generated the new shift in traditional approach and thinking within the environmental protection's scenario. This new approach focused on EmS requires holistic joint efforts of the scientific community and water sector. Our preliminary results of Danube surface water show presence of benzotriasole and caffeine. This is the first research of this kind done in Danube surface water near Novi Sad and is part of the national and ino projects.

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