

Contaminants of Emerging Concern-A Review

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Abstract: Emerging contaminants are being released into the environment at an accelerative rate, raising concerns for environmental quality and human health. The term “emerging contaminants” relates to the substances that are released in the environment for which currently no regulations are established for their environmental monitoring. Emerging contaminants of major concern include endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs), but are not restricted to these two. The transport, distribution and fate of emerging contaminants in the environment may be affected by many processes including sorption, bioaccumulation, degradation, retention which can further be influenced by factors like physicochemical properties of the contaminants, environmental conditions as well as the chemical discharge patterns. Although the number of these contaminants might be minute compared with the macrocosm of both regulated and yet-to-be identified contaminants, an inherent assumption is that these selective lists of contaminants are responsible for the most significant share of risk with respect to environmental or economic impairment or to human health. These compounds, belonging to several categories, have not been regulated yet. The reason can be either the lack of information regarding their occurrence and environmental effects, or the lack of appropriate analytical methods for their determination in complex environmental samples, or both. Taking into account adequate regulatory and policy frameworks, as well as precautionary measures will help in removal of these contaminants. These contaminants may be candidates for future regulation, depending on research on their potential health effects. Contaminants of emerging concern will remain as a stimulating target as new chemical compounds are continuously being produced.

Keywords: *Emerging contaminants, EDC, PPCP.*

1. INTRODUCTION

The revolutionized development of resources and technologies has produced more chemicals and compounds which has consequently increased the number of compounds that are identified as possessing potential environmental threats to the livings. This ever-increasing number of unregulated compounds possess potential environmental threat to the living organism [1]. The US Geological Survey define an emerging contaminant (EC) as "any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and (or)

human health effects. In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognised until new detection methods were developed. In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of emerging contaminants” [2]. The acronym ECs encompasses a wide variety of substances other than recognized pollutants. ECs range from inorganic (e.g., perchlorates, antimony, and cobalt) to organic chemicals (e.g., alkylphenols, benzotriazoles, dioxane, siloxanes, naphthenic acids, musks, organophosphates, methyl tert-butyl ether (MTBE), polyfluorinated alkyl substances, dioxin-like compounds, and pesticide by-products), not speciated matrices as well as nanoparticles, and even microbial contaminants (e.g., adenoviruses and caliciviruses). These contaminants are not currently included in routine monitoring programs; nevertheless, they may be candidate for future regulation, on the basis of outcomes of researches on toxicity, occurrence in various environmental compartments, and public perception [3]. Risks induced by ECs are frequently associated to high direct toxicity or biochemical reactivity causing adverse effects in animals and humans, like immune toxicity, neurotoxicity, endocrine disruption, and carcinogenicity. Besides that, ECs can bioaccumulate and/or persist in the environment. The long-term exposure to ECs or intake of trace levels of them through contact, inhalation, or ingestion is suspected to cause adverse health effects in most organisms at concentrations as low as a few nanograms per liter; moreover, additive or synergistic effects are possible [4]. The EC persistence allows them to diffuse into the environment reaching all compartments; in particular, they can move from the production/release areas up to rural and remote regions, giving raise to regional- and global-scale pollution. The identification, analysis and characterization of the risks posed by these substances, classified as the so-called emerging contaminants, has focused attention and awakened concern among the scientific community during the last few years [5]. Due to their continuous introduction into the environment, emerging contaminants can be considered as “pseudo-persistent” pollutants, which may be able to cause the same exposure potential as regulated persistent pollutants, since their high transformation and removal rates can be compensated by their continuous input into the environment [6].

2. SOURCES

Sources of emerging pollutants in the environment that may eventually impact groundwater can be divided into point-sources and diffuse sources of pollution. Point-source pollution originates from discrete locations whose inputs into aquatic systems can often be defined in a spatially discrete manner. The spatial extent or plume of pollution is therefore generally more constrained. Important examples include industrial effluents, municipal sewage treatment plants and combined sewage storm- water overflows, resource extraction, waste disposal sites and buried septic tanks. Diffuse pollution, in contrast, originates from poorly defined, diffuse sources that typically occur over broad geographical scales. Examples of diffuse source pollution include agricultural runoff from

bio-solids and manure sources, storm-water and urban runoff, leakage from reticulated urban sewerage systems and diffuse aerial deposition [7].

3. PHYSICAL AND CHEMICAL PROPERTIES

It is important to consider the physical and chemical properties of each compound while examining the transport and fate of a compound. After a chemical compound is formed, the route that it takes between its introductory observation and concluding observations is quoted as a pathway. Common pathways include manufacture to foremost use, foremost use to its disposal and foremost use to release to the environment. The result of inter relationship between a chemical compound and its environment over a series of events is known as its fate. Thus the study of a chemical compound's fate and pathway allows us to understand where a particular compound goes and how it is affected by different parameters. One commonly used physical property is partitioning coefficient. Partitioning refers to the tendency of a chemical to concentrate in one phase of a two-phase mixture at equilibrium. The octanol-water partitioning coefficient is a measure of the partitioning between octanol and water, which describes the hydrophobicity of a compound and is inversely related to the solubility of a compound in water. Compounds with a high K_{ow} have been shown to preferentially adsorb to soil and sediment particles in water [7]. Similarly, a sludge adsorption coefficient or k_a , is a ratio of the amount of compound adsorbed to sludge compared to the amount present in aqueous solution under the specific conditions the measurement was taken. The sludge adsorption coefficient is commonly used to predict the extent to which a compound can be removed by physical adsorption to sludge particles in a primary or secondary clarification unit. A commonly used chemical property is the acid dissociation constant of K_a . It is a measure of the strength of an acid in solution and is the concentration ratio of ionized to un-ionized species of a compound at equilibrium. The K_a of a compound enables the concentration of ionized or un-ionized versions of a chemical to be calculated for a given pH. Due to the large range in magnitudes of K_a , the logarithmic constant (pK_a) is commonly used [8].

4. TRANSPORT AND FATE

The transport, distribution and fate of emerging contaminants in the environment may be affected by many processes including sorption, bioaccumulation, degradation, retention which can further be influenced by factors like physicochemical properties of the contaminants, environmental conditions as well as the chemical discharge patterns. The major exposure route both for humans and animals is by ingestion of ECs via food/drink intake which leads to bioaccumulation and biomagnification, especially towards species at top level of food chain.

Sorption: Stronger sorption is often observed for compounds with lower aqueous solubilities and for sediments with higher organic carbon content [9]. Unlike the persistent hydrophobic

contaminants, which can bioaccumulate in the environment, most pharmaceutical compounds are generally hydrophilic with low values of $\log K_{ow}$. Pharmaceuticals would be expected to associate with the aqueous phases in the environment with relatively low sorption affinities for particulate matter including organic fractions of sludges and suspended sediments [10]. Antimicrobial compounds such as TCS and triclocarban (TCC) generally exhibit moderate to high absorption rates onto the solid phase and have a tendency to accumulate in sludge where they can persist [11].

Degradation and transformation: Some of the commonly reported pathways for degradation of organic compounds in the environment include: (i) hydrolysis, (ii) photolysis, (iii) surface catalyzed degradation, (iv) biotic and abiotic degradation and (v) degradation under aerobic or anaerobic conditions [12]. Researchers have found that ibuprofen achieved total removal under most conditions, but several ibuprofen metabolites, including ibuprofen carboxylic acid, 2-hydroxylated ibuprofen, and 1-hydroxylated ibuprofen were formed [13].

Dilution: It is better in wet climates or during rainy seasons. It does not change the chemical composition of an emerging contaminant. Most relevant to wet regions where rivers or lakes have volumes considerably higher than the volumes of discharged wastewater. Probably dilution is considered as an attenuation process but not “enough” to have complete degradation.

Retention in soils and sediments: Researchers found that carbamazepine has low leaching potential and is highly adsorbed onto soils, particularly within the first 30 cm surface, and in soils of greater organic carbon content [14]. High retention of synthetic musks, was detected particularly with polycyclic structure (e.g., methylated pyran, tetraline, etc), in sediments collected from the Liangtan River (China), with decreasing concentration gradients between upstream and downstream of urban sources [15].

5. EFFECTS

Hormone-like effects of chemicals have been observed for decades in fish, wildlife and humans, at levels of exposure that in many cases exceed the normal environmental concentrations [16]. In recent years, considerably greater evidence has been accumulated showing that some chemicals (e.g. estradiols, nonylphenol, bisphenol A, PCBs and some pesticides) at certain concentrations can cause disruption to endocrine systems that control development in aquatic organisms and wildlife [17]. These include imposex of molluscs by organotin compounds [18]; developmental abnormalities, demasculinisation and feminisation of alligators in Florida by organochlorines [19]; feminisation of fish by waste water effluent from sewage treatment plants and paper mills [20]. There are reports that human testicular and breast cancer rates have increased during the last four decades, especially in developed countries [21]. PPCPs include many classes of drugs such as

hormone steroids, antibiotics, blood lipid regulators, antidepressants, antiepileptics, antineoplastics, retinoids, and many personal care products such as fragrances, preservatives and disinfectants [22]. There are some reports on the effects of PPCPs on non target organisms. They include hormonal disruption by steroid drugs [23], bacterial resistance to antibiotics and antimicrobials [24], physiological responses from antidepressants such as inducing spawning of bivalves by serotonin [25], and toxicity of amino nitro musk transformation products to aquatic organisms [26].

6. LEGISLATION AND REGULATIONS

There are currently no laws delimiting the maximal concentration of emerging contaminants in wastewater effluent, drinking water or the environment. In the United States, the Environmental Protection Agency (EPA) maintains a list of compounds called the Contaminant Candidate List (CCL), which is a list of contaminants that are not subject to any drinking water regulations but are being monitored and may be included in future regulations. The most recent version, CCL3 was published in 2008 and includes several endocrine-disrupting compounds such as estrone, perfluorinated compounds such as PFOS, and some flame-retardants but no pharmaceuticals or personal care products (EPA CCL3, 2008). In the aquatic environment, the Food and Drug Administration currently does not require ecological testing of pharmaceuticals unless the environmental concentration exceeds $1\mu\text{g/L}$ [27]. This is a much greater than the ng/L level at which pharmaceuticals have been shown to interact with the aquatic environment [28]. In Europe, the European Commission of the Environment called for the development of a comprehensive list of emerging contaminants in 2006 to comprehend the scope of contamination and develop steps to reduce contaminant levels [29]. In 2011, the World Health Organization published a report entitled *Pharmaceuticals in Drinking-water* which reviews the risks to human health associated with exposure to trace concentrations of pharmaceuticals in drinking-water.

7. SUMMARY

Emerging contaminants are comprised of a wide spectrum of compounds- extensive and expanding characterization lists and acceptable ranges of newly identified compounds are being developed (WHO, US EPA). New compounds are being diagnosed and many of these contaminants are likely to be interminable in the environment. Complication of emerging contaminants in their form and mechanisms of actions are not yet clearly understood. There is no customary method for monitoring, detection and measurement of these compounds. Depressed level of occurrence of these compounds is difficult to detect by most analytical instruments. Limited proficiency base regards the fate and transport of emerging contaminants in the environment and waste resources. Putting in place adequate administrative and policy frameworks, as well as discreet measures will help in removal of these compounds. The burden of proof is on the scientific community to show

emerging contaminants affect the environment in a contradictory manner without which there is no motivation for governments to limit their use and exposure.

REFERENCES

- [1] Bolong N, Ismail A F, Salim M R, Matsuura T. *A review of the effects of emerging contaminants in wastewater and options for their removal*. *Desalination* 2009; 239:229–246.
- [2] U.S. geological survey 2011.
- [3] Richardson S D, Ternes T A. *Water analysis: emerging contaminants and current issues*. *Anal Chem* 2011; 83:4614–4648.
- [4] Blasco J, DelValls A. *Impact of emergent contaminants in the environment: environmental risk*. *Hdb. Env. Chem.* 2008; 5:169-188.
- [5] Petrovic M, Barceló D. *Analysis of Emerging Contaminants of Municipal and Industrial waste*. *Hdb Env. Chem.* 2008; 5(S/1).
- [6] Gros M, Petrovic M, Barceló D. *Development of a multi-residue analytical methodology based on liquid chromatography-tandem mass spectrometry (LC-MS/MS) for screening and trace level determination of pharmaceuticals in surface and wastewaters*. *Talanta* 2006; 70:678-690.
- [7] Thomaidis N S, Asimakopoulos A G, Bletsou A A. *Emerging contaminants: a tutorial mini-review*. *Global NEST Journal* 2012; 14(1):72-79.
- [8] Shaver, D. *Sources and Fate of Emerging Contaminants in Municipal Wastewater Treatment*. M.Tech Thesis 2011; The University of Guelph, Guelph, Ontario, Canada.
- [9] Lee L S, Strock T J, Sarmah A K, Rao P S C. *Sorption and Dissipation of Testosterone, Estrogens, and Their Primary Transformation Products in Soils and Sediment*. *Environmental Science and Technology* 2003; 37(18):4098-105.
- [10] Mills G A, Vrana B, Allan I, Alvarez D A, Huckins J N, Greenwood R. *Trends in monitoring pharmaceuticals and personal-care products in the aquatic environment by use of passive sampling devices*. *Analytical and Bioanalytical Chemistry* 2007; 387(4):1153-1157.
- [11] Heidler J, Sapkota A, Halden R U. *Partitioning, Persistence, and Accumulation in Digested Sludge of the Topical Antiseptic Triclocarban during Wastewater Treatment*. *Environmental Science and Technology* 2006; 40(11):3634-39.
- [12] Colucci M S, Bork H, Topp E. *Persistence of estrogenic hormones in agricultural soils: I. 17-Estradiol and estrone*. *J. Environ. Qual.* 2001; 30(6):2070-2076.
- [13] Climent L F, Collado N, Buttiglieri G, Gros M, Roda I R, Mozaz S R, Barceló D. *Comprehensive study of ibuprofen and its metabolites in activated sludge batch experiments and aquatic environment*. *Science of the Total Environment* 2012; 438:404–413.
- [14] Walker C W, Watson J E, Williams C. *Occurrence of Carbamazepine in Soils under Different Land Uses Receiving Wastewater*. *J. Environ. Qual.* 2012; 41(4):1263–1267.
- [15] Sang W, Zhang Y, Zhou X, Ma L, Sun X. *Occurrence and Distribution of Synthetic Musks in Surface Sediments of Liangtan River, West China*. *Environ. Eng. Sci.* 2012; 29(1):19–25.
- [16] Colborn T, Saal F S, Soto A. *Developmental effects of endocrine-disrupting chemicals in wild-life and humans*. *Environmental Health Perspectives* 1993; 101:378-384.
- [17] Hayes T B, Collins A, Lee M, Mendoza M, Noriega N, Stuart A A, Vonk A. *Hermaphroditic, demasculinised frogs after exposure to the herbicide atrazine at low ecologically relevant doses*. *PANS* 2002; 99:5476-5480.
- [18] Alzieu C. *Impact of tributyltin on marine invertebrates*. *Ecotoxicology* 2000; 9:71-76.

- [19] Guillette, L. J., Jr., T. S. Gross, G. R. Masson, J. M. Matter, H. F. Percival, and A. R. Woodward. (1994) Developmental abnormalities of the gonad and abnormal sex hormone concentrations in juvenile American alligators from contaminated and control lakes in Florida. *Environmental Health Perspectives* 102, 680–688.
- [20] Jobling, S., Nolan, M., Tyler, C.R., Brighty, G. and Sumpter, J.P. (1998) Widespread sexual disruption in wild fish. *Environmental Science and Technology* 32, 2498-2506.
- [21] Brown L M, Pottern L M, Hoover R N, Devesa S S, Aselton P, Flannery T. *Testicular cancer in the U.S. trends in incidence and mortality*. *International Journal of Epidemiology* 1986; 15:164-170.
- [22] Daughton C G, Ternes T A. *Pharmaceuticals and personal care products in the environment: agents of subtle change?* *Environmental Health Perspectives* 1999; 107(6):907-942.
- [23] Purdom C E, Hardiman P A, Bye V J, Eno N C, Tyler C R, Sumpter J P. *Estrogenic effects of effluents from sewage treatment works*. *Journal of Chemical Ecology* 1994; 8:275-285.
- [24] Reinthaler F F, Posch J, Feierl G, Wust G, Haas D, Ruckebauer G, Mascher F, Marth E. *Antibiotic resistance of E. coli in sewage and sludge*. *Water Research* 2003;37:1685-169.
- [25] Fong P P. *Zebra mussel spawning is induced in low concentrations of putative serotonin reuptake inhibitors*. *The Biological Bulletin* 1998; 194:143-149.
- [26] Behechti A, Schramm K W, Attar A, Niederfellner J, Kettrup A. *Acute aquatic toxicities of four musk xylene derivatives on Daphnia magna*. *Water Research* 1998; 32(5):1704-1707.
- [27] Synder S, Westerhoff P, Yoon Y, Sedlak D. *Pharmaceuticals, Personal Care Products, and Endocrine Disruptors in Water: Implications for the Water Industry*. *Environmental Engineering Science*, (2003) 20:5:449-469.
- [28] Hirsch R, Ternes TA, Haberer K, Mehlich A, Ballwanz F, Kratz KL. (1998) *Determination of antibiotics in different water compartments via liquid chromatography-electrospray tandem mass spectrometry*. *J Chromatogr A*. 31;815(2):213-23.
- [29] Brown, Gregory K.; Zaugg, Steven D.; Barber, Larry B. (1999) *Wastewater analysis by gas chromatography/mass spectrometry*. *Water Resour. Invest. Rep. U.S. Geol Surv.No. 99 4018B*, 431 435.