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Emerging Contaminants – The Problem, Examples and Bioremediation Alternatives
Part I

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Abstract

Over the last decades, a large variety of persistent organic contaminants have accumulated in the environment (soil, water, sediments-sludges). Such contaminants have not been detected until recently because of the technological incapacity of detecting them.

The term "emerging contaminants" is complex and refers to both the classic contaminants that were produced and accumulated in the environment for a long time (such as perchlorates and a series of detergents), as well as to the most recently synthesized contaminants accidentally released in the environment (such as NDMA or TCP). A boost in the general interest research of emerging contaminants is happening while funding opportunities abound for the development of innovative methods of assessment and remediation of such emerging contaminants.

In this review, we discuss the main emerging criteria along with four emerging contaminants. The emerging contaminants briefly reviewed here are: 1,4 dioxane, NDMA (N-Nitrosodimethylamine), TCP (1,2,3-Tricloropropane) and perchlorates (perchloric acid and its salts). A brief review of their properties, uses, production, as well as the criteria qualifying them as emerging is provided for each contaminant. Also, a brief discussion of the biotechnological methods available for remediation of these contaminants will follow in Part II of this review.

Keywords: 1,4 dioxane, NDMA (N-Nitrosodimethylamine), TCP (1,2,3-Tricloropropane), perchlorates, bioremediation, biotechnology, sources, environmental behavior

Introduction

Many contaminants have found their way and largely spread into the environment including into groundwater streams on a worldwide basis and are considered emergent. Some are new, but most could have been in the environment for ages, and have remained undetected until recently. A simple question arises: What is emergent? In a very general way, emerging contaminants are potentially toxic substances whose effects or presence is poorly known, either because these are new contaminants that are starting to spread out or simply because of our past limitations of understanding the environmental fate and impact of old well-established contaminants. Currently, there is a big gap in both our knowledge related to long-term impact of such emerging contaminants, as well as in their regulation. Basically, chemical pollutants that are regulated under various international, federal, and state programs represent but a small fraction of the universe chemicals that occur in the environment as a result of both natural processes and human influence [1]. In the U.S., only very few pollutants are regulated. These are known as "priority pollutants". Yet, the potential risk from the unregulated chemicals exists and recent advances in science and technology have resulted in our awareness and understanding of such risks. It is of major importance to establish the basis (criteria) of understanding how a chemical could become harmful, how we can determine this and classify a contaminant as emergent.

This review will start by pointing out some criteria that may classify a contaminant or contamination event as emergent, with the understanding that there may be many other aspects to be identified and discussed in future work. The main purpose of this review is to share information on four out of eight emerging contaminants of environmental concern. Three of these compounds (1,4 dioxane, N-nitrosodimethylamine and 1,2,3-tricholoro propane) are identified as emerging contaminants by the United States Department of Defense.

Emerging Contaminant Criteria

Emerging Pollutants vs. Emerging Concerns

There are two main types of emergent contaminants: the new "truly emerging" pollutants that have just gained entry into the environment (for example because they are new to commerce) and the old pollutants that have been produced for a long time and for which new concerns (new aspects of their occurrence, fate, or effects etc.) are currently raised according to a large variety of criteria discussed in this section. These criteria are all based on recent data that trigger our awareness and will be discussed further. The term "emergent" is often intended not to refer to the pollutant itself, but rather to a newly hypothesized concern regarding an old pollutant.

New insights into Persistence, Bioaccumulation and Toxicity

The three traits listed here are usually commonalities that dictated the highest propensity for adverse effects from chemical stressors [1]. Persistence relates to long environmental half-lives, thus resisting biodegradation and degradation in general and it is a measure of the structural stability of a chemical. Bioaccumulation represents bioconcentration of a certain chemical in a living organism via the food chain and relates to the chemical propensity for accumulating lipids and fat. Toxicity refers to the capacity of a chemical to possess acute or chronic toxicity in its own right. These are the main factors to be considered when establishing the risk that a chemical may pose to humans and the environment. We know the definition of each of these traits and based on such criteria priority pollutants have been established and are already regulated.

New Criteria for Assessing Persistence. Yet, it is our assessment of such criteria that may leave gaps in identifying all the contaminants that may pose a risk. Any of these criteria could be reassess and generate a new list of possible emergent contaminants [1]. For instance, what is it that makes a contaminant persistent? Apart from its chemical structural stability, there are others factors that can make contaminants persistent, such as: a continual release, as in the case of sewage sludge wastes released continuously into receiving water stream. Thus, regardless of structural stability, a compound will persist in the environment if it is continuously released. Therefore, each contaminant should be judged and integrated into the specific environmental conditions.

New Criteria for Assessing Bioaccumulation. The bioaccumulation tendency relates to how easy a chemical can penetrate through living organisms. If we take a look at the broad picture, the ability to bind to lipids and fats is only one factor that may facilitate the chemical accumulation in organisms. Another factor may be the dimension of the particle. This is the case of nanoparticles. Their small, sub-cellular scale facilitates their entrance and transport within living cells.

New Criteria for Assessing Toxicity. Here again we can enlarge our understanding of what makes a compound toxic. If we think in terms of effect (toxicity to humans), several potential causes may be found, only one of which relates to the toxicity of the compound itself. The environmental set of conditions related to a certain contaminant release may determine toxic effects of otherwise not harmful compounds. These compounds may be viewed as indirect toxicants. For example, there are antibiotics that may elicit adverse outcomes by way of selecting for pathogen resistance. Nanoparticles represent another example of indirect toxicants. While not toxic by themselves, when entering the human body, they could impair cellular function and defense. Another reason for our lack of current identification of all the toxic compounds may be our methodology of assessing toxicity. Thus, toxicological studies have usually limited time-frames and the conclusions are related to the harmful effects that a chemical may induce after a limited period of observation. Well, what about effects that may appear much later in time, a long time after the exposure has ceased? These will always escape the classic toxicological studies. An example here of a chemical with potent delayed onset toxicity is the pyrrolizidine alkaloids [1].

However, there are many other factors that could make a chemical to be of environmental significance. These factors are related to toxicological data (potential for cancer, or potential effects by exposure at low levels on a life time basis, or potential interference and disruption of physiological functions in humans), detection (widespread detection in environment or human body, or uncontrollable sources), and also to environmental conditions (including unpredictable mixing effects, interfaces phenomena – accumulation of contaminants at interfaces, and hidden reservoirs of contaminants).

Some general information on several selected emerging contaminants will follow.

1,4-dioxane

1, 4 –dioxane is an emergent compound due to its persistence and mobility in the environment, its increased detection in domestic and municipal water-supply wells, as well as its reasonably anticipated human carcinogenic effect [2, 3, 4]. This carcinogenic effect is based on animal evidence studies indicating its ability to produce skin cancer, hepatocellular carcinomas, hepatomas and carcinomas of the gallbladder, as well as lung tumors. To date, there is inadequate evidence for its carcinogenicity in humans [3].

1,4 dioxane is a volatile, colorless liquid with a mild ethereal odor, miscible with water, alcohol, ether, most organic solvents, aromatic hydrocarbons and oils. It is flammable and may form explosive peroxides, a process accelerated by sunlight. The compound is sensitive to heat, hygroscopic and can react vigorously with oxidizers. Hydrogen and hot Raney nickel, silver perchlorate, sulphur trioxide, nitromethane, boron trifluoride and decaborane can form explosive mixtures with 1, 4-dioxane.

Production and Uses

The commercial production of 1, 4-dioxane in the U.S. was first in 1951, but commercial quantities were produced prior to 1951 [5, 6, 7, 8]. The three major producers in the United States are Ferro Corporation (Baton Rouge, LA), CPS Chemical Company (Old Bridge, NJ), and Dow Chemical Company (Freeport, Texas). The 1979 Toxic Substances Control Act (TSCA) Inventory identified seven U.S. Companies producing approximately 25 million pounds of 1,4-dioxane. Sales of 1,4-dioxane in the United States were reported to be 7.4 million pounds in 1981 [9].

1, 4-dioxane is primarily used as a stabilizer in chlorinated solvents, which accounts for about 90% of the 1, 4-dioxane produced in the United States [10]. Dioxane is also found in food additives, with detection around 10 parts per million, and in shrimp, chicken, tomatoes, coffee and some condiments [11]. It is also used as an additive in aircraft deicing fluid formulations. Other uses of 1,4-dioxane include: as solvent in many industrial activities and/or as an ingredient in many products including dyes, resins, oils, fats, waxes, greases, cellulose acetate, ethyl cellulose, benzyl cellulose, lacquers, plastics, varnishes and paints. 1,4-dioxane serves as a reaction medium solvent in organic chemical manufacturing, as a wetting agent and dispersing agent in textile processing, as a solvent for specific biological applications, as a liquid scintillation counting medium, in the preparation of histological sections for microscopic exams, in paint and varnish strippers, as a laboratory reagent, and in stained print compositions. Additionally, 1,4-dioxane may be used as a solvent in coatings, sealants, adhesives, cosmetics, and pharmaceuticals [12].

N-Nitrosodimethylamine (NDMA)

Contamination of surface and groundwater supplies from NDMA has resulted in significant concerns, while the formation of NDMA during chlorination of drinking water (the widely used disinfectant monochloramine was described as a precursor to NDMA formation during chlorination) or the treatment of sewage for wastewater recycling raises even greater concerns. These occurrences, associated with NDMA water solubility and its anticipated human carcinogenic effect [13, 14] define NDMA as an emerging contaminant. The anticipated carcinogenic effects are based on animal studies; no adequate human studies related to human cancer risks have been reported [13].

Properties

NDMA is a volatile, yellow, oily liquid of low viscosity. It is soluble in water, alcohol, ether, other organic solvents, and lipids. It is sensitive to light, undergoing rapid photolytic degradation and is combustive. When heated to decomposition, NDMA emits toxic fumes of nitrogen oxides.

Production and Uses

Commercial production of NDMA began in mid 1950s in the manufacture of 1,1-dimethylhydrazine [13]. The last commercial producer of NDMA ceased operation in 1976.

Chem Sources [6] reported that there were nine United States suppliers of NDMA in 2000. Current production data were not available [13, 15], while the 1979 TSCA Inventory reported four United States Companies producing 1,000 pounds in 1977. No import or export data were reported [16].

The primary use of NDMA is as research chemical. Prior to April 1, 1976, it was also used as intermediate in the electrolytic production of 1, 1-dimethylhydrazine, a storable liquid rocket fuel containing approx. 0.1% NDMA (as impurity). Other uses include: the control of nematodes and inhibition of nitrification in soil; plasticizer for rubber and acrylonitrile polymers; use in active metal anode-electrolyte systems (high energy batteries); in the preparation of thiocarbonyl fluoride polymers; as solvent in the fiber and plastic industry; as well as antioxidant, softener of copolymers, and additive to lubricants [17, 18].

1,2,3-Trichloropropane (TCP)

TCP is considered emergent due to its environmental mobility and persistence, especially in groundwater, as well as its reasonably anticipated human carcinogenic effect [13, 14]. This carcinogenic effect is based on animal studies indicating its ability to produce multiple tumors in mice and rats, increased incidences of tumors of the fore-stomach, oral mucosa, Zymbal gland, liver, harderian gland, uterus, kidney, and pancreas [19, 20, 21]. No adequate data is available regarding the carcinogenicity of TCP in humans [22, 23, 24, 25, 26].

Properties

TCP is a clear colorless to straw-colored liquid with a strong acrid odor similar to chloroform or TCE odor. At normal temperatures it evaporates at rates similar to water. It is soluble in ethanol, ether and chloroform, and only slightly soluble in water. TCP dissolves oils, waxes, fats, and numerous resins, and reacts with active metals, strong caustics and oxidizers. TCP is sensitive to prolonged exposure to light and heat. It is flammable and when heated to decomposition, yields hydrogen chloride gas [15].

Production and Uses

Little information is available on the amounts of TCP manufactured and the specific uses. The estimated production in 1977 ranged from 21 to 110 million pounds [27], while in 1985, two manufacturing facilities had a combined annual production greater than 10,000 pounds [19]. According to Chem Sources [6] there are currently two U.S. facilities that produce TCP and nine suppliers (TSCA, 1979). A significant quantity of TCP may result as a byproduct of the production of other chlorinated compounds [27] and of epichlorohydrin production.

The primary historical use of TCP was as a solvent and extractive agent (as a solvent it was used as paint and varnish remover, cleaning and degreasing agent, and cleaning and maintenance solvent). TCP is currently used as a chemical intermediate in the production of polysulfone liquid polymers and dichloropropene, in synthesis of hexafluoropropylene, and as a cross-linking agent in the synthesis of polysulfides [27]. It is important to also mention that TCP has been formulated with dichloropropenes in the manufacture of a soil fumigant D-D [21].

Perchlorate

Perchlorate has gained dominance as a global contaminant of the 2000's. A variety of factors (criteria) combine to elevate the importance of perchlorate as a global contaminant, and classify it as emergent. Such factors include the increasing number of detections of perchlorate in water wells, crops and cow's milk nationwide due to the improved ability to analytically detect perchlorate, its alleged health impacts at low concentrations, its high solubility and resistance to degradation in groundwater, and its potential presence in soil and groundwater at military installations throughout the world [28]. Little research has been performed regarding the health impacts from perchlorate exposure. Perchlorate can affect the thyroid glad, obstructing the uptake of iodine and in turn disrupting production of thyroid hormones (29). In the United States, one of the most publicized perchlorate impacted sites is the Kerr McGee facility at Henderson, Nevada which has impacted water in the Colorado River (30). The Colorado River is the main drinking water source for about 15 million homes in the Southwest and contains perchlorate at concentrations in the single digit parts per billion (31).

Properties

The term *perchlorate* generically refers to solid salts usually of ammonium, potassium and sodium perchlorate. Of the perchlorate salts, ammonium perchlorate accounts for over 90% of the total production of perchlorate in the United States [32]. The perchlorate anion is an inert, non-volatile and highly soluble compound in water and a number of solvents. While this characteristic makes the perchlorate anion an excellent oxidizing agent, it is slow to react (perchlorate adsorbs weakly to most soil minerals) and is resistant to degradation as it travels through the subsurface [28].

Production and Uses

The production of perchlorate began in the 1940's with the first continuous process of perchlorate manufacturing commencing in 1944. During World War II, the military used perchlorate in jet-assisted take-off units that were manufactured by Aero-General Corporation located in eastern Sacramento County, California [33].

The primary use of perchlorate is by military operations as a primary solid rocket fuel ingredient. Other uses of perchlorate are: in fireworks, highway safety flares and match manufacturing; in automobile airbags; as additive in lubricating oils; as a fixer in fabrics and dyes; as well as in applications in chemical analysis and organic synthesis (perchloric acid is used as catalyst), in industry and commerce [34]. Perchlorate was also used in medical treatments for patients with severe hyperthyroid problems before serious side effects discontinued its use in the 1960s [35].

Conclusions

This article briefly pointed out some dimensions of emerging contamination, such as different circumstances that could classify a contaminant as emergent. Few selected emergent contaminants were also presented. It is our hope that the current article will help to identify and track new environmental problems and improve our knowledge and understanding of the possible causes. While it is hard to define what is really emerging, it is easier to identify what may cause a contaminant or contamination event to be classified as emergent. To do this, we need to understand the many dimensions of the problem and relates to some practical examples of emerging contamination events.

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