Constituents of Emerging Concern: An Overview

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ABSTRACT

Emerging constituents of concern have been with us from the beginning of the environmental era 45 years ago. They were behind the 1974 Safe Drinking Water Act. They are behind our struggle with disinfection byproducts. They were behind the development of the 129 (126) priority pollutants. They were behind RCRA and the Superfund. Now they are "emerging" as endocrine disruptors, pharmaceuticals, personal care products, persistent organic pollutants, etc. The issue will never be settled science, because it is emerging science. As a result it is important that we find a way to organize our regulatory policies and priorities so that they are more suitable for implementation in the context of immature science. Closer examination of the precautionary approach seems a good way to start.

KEYWORDS

Pharmaceuticals, personal care products, endocrine disruptors, persistent organic pollutants, emerging contaminants

INTRODUCTION

Four and a half decades ago, when Rachel Carlson published *Silent Spring* and described the dangers of DDT and other chemicals in the environment (Carson, 1962), she not only got the attention of President Kennedy who, upon reading her book, directed his Science Advisory Committee to investigate, but she sent a message that resonated throughout the scientific community, worldwide. Manmade chemicals, particularly organic chemicals may have consequences beyond those for which they were originally intended and those consequences may not all be good for us. Gordon Robeck, head of drinking water research for the Public Health Service at the time, began encouraging efforts to understand the degree to which man-made organic chemicals might be present in the nation's drinking water supplies. In the 1960s analytical methods were a serious limitation so the research began by running a specified amount of water through a small GAC column, extracting the column with chloroform, evaporating the extract and determining its mass. The method, called the carbon chloroform extract (CCE) did not give very satisfactory results (Buelow, et al., 1973). Over the following decade, analytical techniques improved and it was, in part, the preliminary results of the National Organics Reconnaissance Survey (NORS) led by Drs. Robeck and Symons (Symons, et al., 1975) which stimulated the 1974 Safe Drinking Water Act.

DISINFECTANT BYPRODUCTS

In that same year, two members of that EPA team, Bellar and Lichtenberg, using a new purge and trap technique and a gas chromatograph with a Hall detector identified four trihalmethanes (THMs) that were observed to increase following chlorination (Bellar and Lichtenberg, 1974). Meanwhile in that same year a chemist working in Rotterdam, J. J. Rook, using a headspace technique and gas chromatography, made the same finding (Rook, 1974). These were truly revolutionary findings and they began a struggle that is still under way three decades later, namely a struggle to find ways to protect and even extend the benefits of drinking water disinfection, one of the cornerstones of modern civilization, without forming undesirable chemical byproducts that could jeopardize those benefits.

For approximately a decade the focus in drinking water remained on the THMs, particularly chloroform, but from the beginning it was clear that the reaction between chlorine and the natural organic matter in drinking water formed a large number of organic compounds, the THMs being only a small fraction of the whole. Today that work continues and we are experiencing the third round of drinking water regulations on disinfection by-products (USEPA, 2006) and the discovery of yet, new disinfectant byproducts (Najm & Trussell, 2001). It seems unlikely that the water industry has seen the end of this struggle. The struggle is an important one because it has placed an important constraint on the development of alternatives for disinfecting water, gradually driving the industry away from simple chlorination.

VOC'S IN GROUNDWATER

In the meantime the same improvements in analytical technique that enabled the identification of the THMs also revealed other organic contaminants in drinking water. Early on, it was not so much that synthetic organic compounds were found in the nation's surface waters. In fact neither the NORS, mentioned earlier, nor the National Organics Monitoring Survey (NOMS), also lead by Dr. James Symons, and which followed shortly behind the NORS, found contamination at levels that would ultimately drive new regulations (USEPA, 1978). Some significant industrial spills were later identified, and Cincinnati Ohio installed granular activated carbon treatment. But it was discovery of volatile organic solvents (VOC) in the deep protected groundwater supplies in California, which occurred near the end of the 1970s, and similar findings throughout the nation that stimulated action. First EPA's Office of Water promulgated a regulation on VOCs in 1986 (USEPA, 1986). Compounds addressed in this first regulation were trichloroethylene, carbon tetrachloride, 1,2-dichloroethane, vinyl chloride, benzene, 1,1-dichloroethylene, and, ultimately tetrachloroethylene. The VOC findings also gave new momentum to existing efforts under the Resource Conservation and Recover Act (RCRA) and resulted in 1986 Superfund Revenue Act (CERCLA) and the 1986 RCRA amendments and, over then next decade, these became the foundation for the Nation's largest environmental program, much of which is focused on protecting ground water supplies. New synthetic compounds continued to be found in ground water. Some examples are dichlorobromopropane (DCBP), *N*-nitrosodimethylamine (NDMA), methyl tertiary butyl Ether (MtBE), perchlorate and many others. All except perchlorate are organic.

PRIORITY POLLUTANTS

Meanwhile in the arena of the Clean Water Act, organic chemicals were also becoming an issue. Prior to 1972 the CWA efforts focused on regulating the discharge of conventional pollutants. Limits were set on a case-by-case basis, determined by the assimilative capacity of the receiving waters. “Toxic chemicals” were given no special attention.

The Natural Resources Defense Council (NRDC) and other environmental groups were dissatisfied with EPA’s approach and sued the Agency. In June 1976 a consent decree between the parties was reached (NRDC vs. Train, 1976). This consent decree reorganized EPA’s view of toxic chemicals. Congress incorporated most of the details of the consent decree in 1977 amendments to the Clean Water Act (P.L.95-217).

The consent decree became known as the Toxics Consent Decree or the Flannery Decision (named after the presiding Judge, Thomas Flannery). The Decree required EPA to regulate a specific list of 65 chemicals and “classes of chemicals”. The 65 were subsequently divided into 129 distinct compounds, which are now commonly referred to as "the priority pollutants".

A major change also took place in the administration of Clean Water Act as of 1977, namely the specification of different standards for toxic pollutants than for conventional pollutants. EPA to developed effluent limits based on "best available technology economically achievable" (BAT) for control of the 65 classes of toxic priority pollutants referred to in the act. For conventional pollutants, BAT was replaced by "best conventional pollution control Technology" (BCT), and the deadline was extended to 1984. BCT was to be as strict as the "best practicable control technology" (BPT), but no more strict than BAT. Finally, to enforce all these standards, a system of permits, the National Pollution Discharge Elimination System (NPDES), was established for all dischargers.

LEACHING OF CONTAMINANTS INTO DRINKING WATER

Again in the late 1970s concerns also began to develop about contaminants leaching into drinking water either through or from the facilities used to deliver the water, both in the utility’s system and in the consumer plumbing. These concerns can be divided into four groups: (a) contaminants in water treatment chemicals, (b) contaminants leaching from the environment, through plastic pipe, and into the drinking water, (c) contaminants leaching from coatings used to protect the surface of water facilities and (d) metals leaching from the water conduits themselves. All of these ultimately impacted either water treatment strategies or the materials used in water systems.

Potential contaminants in water treatment chemicals became a concern when carbon tetrachloride was found as a contaminant in chlorine. EPA funded an NRC panel led by Bill Glaze to look at the matter and the interim outcome was a *Drinking Water Chemicals Codex* (NRC, 1982), modeled after the *Food Chemicals Codex*, published by the NRC and funded by the FDA. About the same time a number of contaminants, particularly VOCs were found to leach from linings and coatings used by the industry. EPA asked the NRC to reconvene the Glaze Committee to provide guidance on a third party process for certification of drinking water chemicals and for drinking water system components as well. The net result was process that established NSF Standards 60 (water treatment chemicals) and 61 (Drinking water system components).

ENDOCRINE DISRUPTERS

In 1996, Colburn et al. published a powerful articulation of the endocrine disruptor hypothesis (Colburn et al., 1996). In simple form, the endocrine disrupter hypothesis is the suggestion that certain synthetic chemicals may mimic natural hormones -- binding with endocrine receptors, but producing "unnatural" outcomes. This hypothesis has its roots in certain chemicals that are known to mimics the behavior of natural hormones. Perhaps the most easily understood examples occur in the reproductive system. For example the synthetic compound, ethinyl estradiol is used in birth control pills to mimic the behavior of estrogen. One of the most widely recognized endocrine disrupters also affects the reproductive system. That chemical is Diethylstibestrol, or DES. DES was widely used as a hormone therapy for pregnant women in the 50's and 60's. It is now known to result in some serious abnormalities in children of these mothers. The use of DES has been banned since 1971.

The above description represents a simplified way of describing the endocrine disrupter hypothesis. As pointed out by the NAS (NRC, 1999), the issue has grown to include the larger question of the possible influence of any hormonally active agent. Such agents might mimic hormones, they might interfere with the ability of hormones to carry out their normal function, they might degrade hormones, they might interfere with the body's ability to synthesize hormones, they might influence the ability to hormones to enter the target cell, etc. etc. All these activities would fall under the purview of current concerns of those who discuss endocrine disrupters.

During the past decade several studies have reported hormonally active agents in the environment. For example tributyl-tin has been shown to result in masculization of female mollusks (Rejinders, et al, 1992). Pesticides have been associated with the decline of American Alligators in Florida (EPA, 1994), and feminization of fish has been observed downstream of sewage discharges in several instances (Purdom, et al, 1994, Jobling, et al, 1995, 1998).

Several classes of chemicals have now been implicated. These include synthetic steroids, pesticides and herbicides, phthalates, Alkylphenol ethoxylate surfactants (Soto, et al, 1991), the dioxins (Bishop et al, 1991), the PCBs (Bitman & Cecil, 1970), as well as natural chemicals like natural estrogen and the phytoestrogens found in many plants, including the soy bean (NRC, 1999.). A more detailed discussion can be found in Trussell (2001).

PHARMACEUTICALS AND PERSONAL CARE PRODUCTS, OTHERS

Analytical techniques continue to improve and surveys, first those in Europe (Stan and Heberer, 1997; Ternes, 1998) and more recently those in the U.S. (Kolpin et al., 2002) have demonstrated that a variety of compounds can be found in surface waters and a few ground waters at very low levels. These include some of the pharmaceuticals, antibiotics, and personal care products we use on ourselves as well as household compounds, solvent stabilizers, flame retardants, pesticides/herbicides and so on. A few of the most persistent of these compounds have also been found in drinking water as well. In particular some of these are associated with wastewater. Some are known to be hormonally active.

Table 1 was prepared by the author to summarize some 62 compounds that the author has found in the literature a being found or implicated in municipal effluent. Very broad comments are also made regarding the degree to which these compounds degrade during biological treatment or oxidize during exposure to free chlorine. It should be noted that most evidence is that almost none of the compounds listed in Table 1 are biodegraded by conventional activated sludge (CAS) at the low SRTs that are commonly used for the removal of carbonaceous BOD alone. Compounds marked as biodegradable in Table 1 can be substantially biodegraded in CAS operating at an SRT of 10 or more, as in plants designed for nitrification. The results in the Table have been collected by the author over several years as information appeared in the literature and the results regarding the biodegradability of some compounds is inconsistent. Some of these compounds are shown in the Table with a grey bar, signifying the indecisive nature of the information available. The Table also displays the sensitivity of some compounds to chlorination. Generally free chlorine was applied.

DISCUSSIONS OF RISK

As the human population on the earth increases and as these humans use their intelligence to develop technologies that allow for a longer, more comfortable life, one of the consequences is an inevitable conflict between the stability of the earth's ecosystem and human development. One of the biggest challenges during the past thirty years has been figuring out how to properly allocate scarce resources among various potential environmental hazards. The management of emerging contaminants is at the center of this challenge.

The present decision-making structure in the U.S. is based on understanding the risks associated with different environmental threats. It has its roots in a 1983 report by the National Academies that developed a four-part framework consisting of: a) hazard identification, b) dose-response assessment, c) exposure assessment, and d) risk characterization (NRC, 1983) and it has been continually developed with contributions from the NRC the EPA SAB and other. Notable among those efforts was the 1987 EP report on the relative risks associated with different environmental problems (USEPA,

1987) and the 1990 report by EPA's SAB recommending that relative risk be used as a tool for allocating resources among environmental problems (USEPA, 1990). These and related works have been important developments which have vastly improved our understanding of environmental challenges and have helped to move at least some of the job of allocating resources out of the political arena.

Nevertheless, as the discovery process moves forward, the list of potential problems to be assessed is vastly outstripping the resources we have available for using formal risk analysis to allocate remedial resources. As a result, we find ourselves with an increasingly long list of unregulated compounds of unknown significance.

In Europe the Precautionary Principle has been advanced as an alternative means for dealing with these problems. In concept, the precautionary principle is, "…a general rule of public policy action to be used in situations of potentially serious or irreversible threats to health or the environment, where there is a need to act to reduce potential hazards before there is strong proof of harm." (Harremoës, et al., 2001). The principle was first advanced in connection with the Montreal Protocol on Substances that deplete the ozone layer in 1987 and was captured in the Rio Declaration on Environment and development in 1992. It's obvious on the face of it that the precautionary principle, implemented in a simple way could quickly deplete resources to solve problem that may not ultimately prove important. As a result the U.S. has, so far, refused to engage in a dialogue about it and our risk-based strategy remains in tact.

It's time the U.S. engaged this dialogue. Crudely implemented the precautionary approach wastes resources. Presently implemented our risk-based approach has us frozen in time.

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Table 1 Several Emerging Chemicals and their Approximate Behavior

Compound	Use	Biodegradable		Oxidized by Cl2	
		yes	no	yes	no
17 α-ethynylestradiol	contraceptive	■			
17 ß-estradiol	femaie hormone	■		■	
Acetaminophen	Antipyretic	■			
Androstenedione	Testosterone precursor				
Atrazine	Herbicide				
Bezafibrate	Lipid regulator	■			
Bisphenol-A	Anti-oxidant	■			
Bromoform	DBP				■
Caffiene	Stimulant	■			
Carbamazdepine	Antiepileptic		■	■	
chloroform	DBP				■
Clofibric acid	lipid regulator				
Cholesterol	fat				
Coprostanol	fecal seroid				
Cotinine	nocotine metabolite				
DEET	Insect repellant	▒	▒		■
Diazepam	Tranqulizer			■	
Dichlorprop	Herbicide				
Diclofenac	Lipid regulator		■	■	
Dilantin	Antiepileptic		■	■	
EDTA	Chelating agent		■		
Erythromycin-H2O	Antibiotic		■	■	
Estriol	femaie hormone				
Estrone	femaie hormone	■			
Fenofibrate	Triglyceride regulator				
Fluoxetine	Antidepressant	■			■
Galaxolide	Fragrance	■		■	
Gemfribrozil (TCIPP)	Lipid regulator				
Hydrocodone	Cough suppressant		■	■	
Ibuprofen	Analgesic	▒	▒		
Iopromide	Contrast media		■		
Ketoprofen	Anti-inflammatory				
Lincomycim	Antibiotic				
Mecoprop	Herbicide		■		
Meprobamate	Anti-anexiety agent		■		■
metaprolol	Beta blocker	■			
Metolachlor	Herbicide				■
Naproxen	Analgesic		■		
NDMA	Rx byproduct				■
Nonlylphenoxyacetic acid	detergent metabolite	■			
Nonylphenol	detergent metabolite	■			
Nonylphenol diethoxylate	detergent metabolite	■			
Nonylphenol monoethoxylate	detergent metabolite	■			
Nonylphenoxyacetic acid	detergent metabolite	■			
Octylphenol	detergent metabolite	■			
Octylphenol diethoxylate	detergent metabolite	■			
Octylphenol monoethoxylate	detergent metabolite	■			
Oxybenzone	sunblock				
Pentoxifylline	blood thiner				
Phenacetine	Analgesic		■		
Primidone	Anti-epileptic		■		
Progesterone	hormone				■
Propranolol	betablocker				
Roxithromycin	Antibiotic		■		
Salicyclic acid	Analgesic	■			
sulfathometaoxazole	Antibiotic		■		
TCEP	Flame retardant				■
TDCPP	Flame retardant				
Testosterone	hormone				
Tonalide	Fragrance	■			
Triclosan	antibacterial	■			
Trimethoprim	Antibiotic	■			