Stormwater Runoff Water Quality Science/Engineering Newsletter Devoted to Urban/Rural Stormwater Runoff Water Quality Management Issues

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Editor: Anne Jones-Lee, PhD
Contributor to this Issue:
G. Fred Lee, PhD, PE, DEE

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This issue of the Stormwater Runoff Water Quality Science/Engineering Newsletter is devoted to **Unrecognized Environmental Pollutants.** The "Clean Water Act" of 1972 required that the US EPA develop a list of the Priority Pollutants and develop water quality criteria for them. The Agency was not given sufficient funding by Congress to accomplish this requirement, and therefore did not meet the congressionally established deadline. Litigation by an environmental group led to an agreement which established 129 Priority Pollutants. The list was developed by attorneys with limited technical input. It was not peer-reviewed by the US EPA staff who were experts in this area or by professionals outside the Agency. It is recognized that the Priority Pollutant list did not and does not represent an appropriate listing of the wide variety of chemicals that are a threat to cause water pollution.

It is recognized that the currently regulated pollutants, such as the Priority Pollutants, represent a very small part of the chemicals that are present in municipal, industrial and agricultural wastewaters and stormwater runoff that are a potential threat to water quality-beneficial uses of waterbodies. Unfortunately, however, the focus of water pollution control programs has been largely devoted to the Priority Pollutants, while ignoring many of the other chemicals that are used by urban populations, industry and agriculture that are a threat to cause water pollution. As an example, there are over 150 pesticides used in the Central Valley of California, yet less than half a dozen receive any regulatory attention by the Central Valley Regional Water Quality Control Board (CVRWQCB). Further, new registered pesticides are introduced into urban and agricultural areas which are in stormwater runoff from the areas where the pesticides are applied. As discussed by Lee (2001), current federal and state pesticide registration does not restrict the use of pesticides that can be present in stormwater runoff from the area where the pesticide is applied that causes toxicity in the receiving waters for the runoff. The inadequacy of the current pesticide registration process necessitates that local water quality regulatory agencies take a proactive approach for evaluating the potential water quality impacts of currently used and new pesticides. Lee (2001) has described a proactive approach to screen the use of pesticides for water quality problems associated with stormwater runoff.

Periodically, previously unrecognized significant environmental pollutants are being found in aquatic systems. Two recent examples of this type of situation are perchlorate and the polybrominated diphenyl ethers (PBDEs). With respect to perchlorate as a widespread water pollutant, Silva (2003) of the Santa Clara Valley Water District, has discussed the potential for highway safety flares to be a significant source of perchlorate

(ClO_4^-) contamination to water, even when the flares are 100-percent burned. According to Silva,

> *"A single unburned 20-minute flare can potentially contaminate up to 2.2 acre-feet* [726,000 gallons] *of drinking water to just above the California Department of Health Services' current Action Level of 4 µg/L* [for perchlorate]*."*

Silva points out that, *"More than 40 metric tons of flares were used/burned in 2002 alone in Santa Clara County."* Silva also indicates that fully burned flares can leach up to almost 2,000 µg of perchlorate per flare. California's Office of Environmental Health Hazard Assessment (OEHHA, 2004) has recently proposed a public health goal for perchlorate of 6 µg/L. As of December 2003, there were 354 public wells in California with perchlorate above the proposed limit of 6 µg/L.

Another widespread "new" pollutant has been recently discussed by Dr. K. Hooper (2003) of the Hazardous Materials Laboratory, Department of Toxic Substances Control, California EPA. In his abstract, he states,

> *"Over the past 25 years, tens of thousands of new chemicals (7 chemicals per day) are introduced into commerce after evaluation by USEPA. Few (100-200) of the 85,000 chemicals presently in commerce are regulated. We have reasons to believe that a much larger number than 200 adversely affect human health and the environment."*

As an example of unidentified hazardous chemicals in the environment, Hooper discussed finding PBDE (polybrominated diphenyl ether) in human breast milk and in San Francisco Bay seals. Archived human breast milk shows that this is a problem that has been occurring for over 20 years. According to McDonald (2003) of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment,

> *"Approximately 75 million pounds of PBDEs are used each year in the U.S. as flame retardant additives for plastics in computers, televisions, appliances, building materials and vehicle parts; and foams for furniture. PBDEs migrate out of these products and into the environment, where they bioaccumulate. PBDEs are now ubiquitous in the environment and have been measured in indoor and outdoor air, house dust, food, streams and lakes, terrestrial and aquatic biota, and human tissues. Concentrations of PBDE measured in fish, marine mammals and people from the San Francisco Bay region are among the highest in the world, and these levels appear to be increasing with each passing year."*

PBDEs are similar to PCBs and are considered carcinogens. Some of the PBDEs are being banned in the US and in other countries.

The perchlorate and PBDE situations are not atypical of what could be expected based on the approach that is normally used to define constituents of concern in water pollution control programs. Based on the vast arena of chemicals that are used in commerce, many of which could be present in aquatic systems through wastewater and stormwater runoff, it is likely that many other chemicals will be discovered in the future that are a threat to public health and aquatic ecosystems. There is obvious need to significantly expand water quality monitoring programs to specifically search for new, unrecognized water pollutants. As demonstrated by the perchlorate and PBDE examples, current monitoring programs, focusing on conventional and Priority Pollutants, are significantly deficient in properly defining constituents of concern with respect to impairing beneficial uses of waterbodies.

PPCPs as Environmental Pollutants

At the February 2004 California Bay-Delta Authority (CBDA) Contaminant Stressors Workshop, Dr. Christian Daughton, Chief, Environmental Chemistry Branch, US EPA National Exposure Research Laboratory, made a presentation, "Ubiquitous Pollution from Health and Cosmetic Care: Significance, Concern, Solutions, Stewardship – Pollution from Personal Actions" This presentation covered information on pharmaceuticals and personal care products (PPCPs) as environmental pollutants. He also discussed the relationship between endocrine disruptors and PPCPs. (A copy of Daughton's presentation at the CBDA workshop, which consisted of 64 PowerPoint Slides, is available upon request from gfredlee@aol.com.)

Daughton pointed out that there are a wide variety of chemicals that are introduced into domestic wastewaters that are being found in the environment. These include various chemicals (pharmaceuticals) that are derived from usage by individuals and pets, disposal of outdated medications in sewerage systems, release of treated and untreated hospital wastes to domestic sewerage systems, transfer of sewage solids ("biosolids") to land, industrial waste streams, releases from aquaculture of medicated feeds, etc. Many of these chemicals are not new chemicals. They have been in wastewaters for some time, but are only now beginning to be recognized as potentially significant water pollutants. They are largely unregulated as water pollutants.

According to Daughton (2004),

> *"PPCPs are a diverse group of chemicals comprising all human and veterinary drugs (available by prescription or over-the-counter; including the new genre of "biologics"), diagnostic agents (e.g., X-ray contrast media), "nutraceuticals" (bioactive food supplements such as huperzine A), and other consumer chemicals, such as fragrances (e.g., musks) and sun-screen agents (e.g., mehylbenzylidene camphor); also included are "excipients" (so-called "inert" ingredients used in PPCP manufacturing and formulation)."*
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> *"Since the 1970s, the impact of chemical pollution has focused almost exclusively on conventional "priority pollutants," especially on those collectively referred to as "persistent, bioaccumulative, toxic" (PBT) pollutants, "persistent organic pollutants" (POPs), or "bioaccumulative chemicals of concern (BCCs).*
> *The "dirty dozen" is a ubiquitous, notorious subset of these, comprising highly halogenated organics (e.g., DDT, PCBs).*

The conventional priority pollutants, however, are only one piece of the larger risk puzzle."

Daughton has indicated that there are over 22 million organic and inorganic substances, with nearly 6 million commercially available. The current water quality regulatory approach addresses less than 200 of these chemicals, where in general PPCPs are not regulated. According to Daughton, "*Regulated pollutants compose but a very small piece of the universe of chemical stressors to which organisms can be exposed on a continual basis."* Additional information on PPCPs is available at www.epa.gov/nerlesd1/chemistry/pharma/index.htm. With increasing urban population and industrial activities, the significance of PPCPs and other pollutants derived from urban and industrial activities, as a cause of water quality problems, will increase.

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New Contaminants Found in Drinking Waters

Recently the US EPA has posted the following discussion of new contaminants that are being found in drinking waters.

U.S. Environmental Protection Agency

Ecosystems Research Division

What is in Our Drinking Water?

Identification of New Chemical Disinfection By-products (DBPs)

What is a DBP? A drinking water disinfection by-product (DBP) is formed when the chemical used for disinfecting the drinking water reacts with natural organic matter and/or bromide/iodide in the source water. Popular disinfectants include chlorine, ozone, chlorine dioxide, and chloramine. Source waters include rivers, lakes, streams, groundwater, and sometimes seawater. We have only known about DBPs since 1974, when chloroform was identified by Rook as a DBP resulting from the chlorination of tap water. Since then, hundreds of DBPs have been identified in drinking water.

So what? Millions of people in the U.S. are exposed to these drinking water DBPs every day. While it is vitally important to disinfect drinking water, as thousands of people died from waterborne illnesses before we started disinfection practices in the early 1900s, it is also important to minimize the chemical DBPs formed. Several DBPs have been linked to cancer in laboratory animals, and as a result, the U.S. EPA has some of these DBPs regulated. However, there are many more DBPs that have still not been identified and tested for toxicity or cancer effects. Currently, we have only identified <50% of the total organic halide (TOX) that is measured in chlorinated drinking water. There is much less known about DBPs from the newer alternative disinfectants, such as ozone, chlorine dioxide, and chloramine, which are gaining in popularity in the U.S. Are these alternative disinfectants safer than chlorine? Or do they produce more harmful by-products? And, what about the unidentified chlorine DBPs that people are exposed to through their drinking water-both from drinking and showering/bathing? The objective of our research is to find out what these DBPs are--to thoroughly characterize the chemicals formed in drinking water treatment--and to ultimately minimize any harmful ones that are formed.

Our research approach

- Gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS), and gas chromatography/infrared spectroscopy (GC/IR) techniques are used to identify the unknown by-products

- NIST and Wiley mass spectral databases are used first to identify any DBPs that happen to be present in these databases

- Because many DBPs are not in these databases, most of our work involves unconventional MS and IR techniques, as well as a great deal of scientific interpretation of the spectra

    - High resolution MS provides empirical formula information for the unknown chemical (e.g., how many carbons, hydrogens, oxygens, nitrogens, etc. are in the chemical's structure)

- Chemical ionization MS provides molecular weight information when this is not provided in conventional electron ionization mass spectra
- IR spectroscopy provides functional group information (e.g., whether the oxygens are due to a carboxylic acid group, a ketone, an alcohol, or an aldehyde)
- LC/MS is used to identify compounds that cannot be extracted from water (the highly polar, hydrophilic ones). This is a major missing gap in our knowledge about DBPs--so far, most DBPs identified have been those that are easily extracted from water
- Novel derivatization techniques are also applied to aid in the identification of highly polar DBPs

- Once DBPs are identified, ones that are predicted to have adverse health effects are studied in order to determine how they are formed (so that the treatment can be modified to ultimately minimize their presence in drinking water)

Currently

We recently completed a major nationwide DBP occurrence study EPA/600/R-02/068, where we sampled drinking water across the U.S. (disinfected with the different disinfectants and with different water quality, including elevated levels of bromide in the source water). A group of >50 high priority DBPs that resulted from a prioritization of >500 DBPs in the literature for predicted adverse health effects was quantified in these drinking waters. In addition to obtaining important quantitative information on these new DBPs (to help in prioritizing health effects testing), important new discoveries were made regarding the use of alternative disinfectants. While the use of alternative disinfectants lowered the levels of the four regulated trihalomethanes and five haloacetic acids (as compared to chlorine), many of the high priority DBPs were formed at higher levels with these alternative disinfectants. For example, the highest levels of iodinated DBPs were found in chloraminated drinking water, the highest levels of trihalonitromethanes were found in pre-ozonated drinking water, MX and brominated MX analogs (BMXs) were highest at a plant using chlorine dioxide (followed by chlorine-chloramines), and dihaloaldehydes were highest at a plant using chloramines and ozone.

Our new work includes obtaining quantitative occurrence information on the iodo-acids that were identified for the first time in the Nationwide DBP Occurrence Study. Chloraminated waters (where levels are expected to be highest) will be targeted for this work. In addition, a toxicity-based identification approach (using mammalian cell and medaka fish assays) will be used to ensure toxicologically important DBPs are not being missed. The full study of the Four Lab Study is also expected to begin in 2004 (where drinking water is treated and concentrated, comprehensive DBP identifications are carried out, and drinking water concentrates are tested in a battery of in vivo and in vitro toxicity assays, with an emphasis on newer reproductive and developmental health effects. Finally, work continues in determining how the toxicologically significant bromonitromethane DBPs are formed. These bromonitromethanes are more genotoxic and cytotoxic to mammalian cells than most of the DBPs currently regulated and are also currently the focus of in vivo testing at NHEERL (RTP, NC).

Some results

- More than 200 previously unidentified DBPs have been identified for the first time
- A recent Nationwide DBP Occurrence Study has provided important new quantitative information on unregulated DBPs that have been predicted to cause adverse health effects; several of these DBPs have concentrations similar to some that are regulated

- The use of alternative disinfectants can produce higher levels of 'high priority' DBPs, as compared to chlorine

- The presence of natural bromide in the source water results in a tremendous shift from chlorine-containing DBPs to bromine-containing DBPs when chlorine or chloramine is used as a disinfectant (even in combination with ozone)

- New analytical methods have been developed (and are continuing to be developed) for the analysis of highly polar DBPs

- Collaborations have been forged with health effects researchers to study selected DBPs for potential adverse health effects

Useful publications

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***For more information, contact Susan Richardson at richardson.susan@epa.gov**

Why should Urban Stormwater Water Quality Managers be Concerned About Drinking Water and Wastewater Potential Pollutants?

Chemicals in domestic water supplies become chemicals in urban stormwater runoff through leaking sanitary sewers and fugitive irrigation waters such as used on lawns. Further, in some arid areas, with increased emphasis on use of reclaimed domestic wastewaters, there is increasing use of treated domestic wastewaters for park, roadside vegetation and golf course irrigation. While these waters can be treated with high levels of disinfection and filtration so that they represent low levels of public health threats due to enteric pathogens, the treatment does not necessarily remove the wide variety of PPCPs and other potential pollutants.

There is a tendency for regulatory agencies to make provisions which encourage the use of recycled domestic wastewaters in order to promote water recycling, where there is inadequate regulation of potential health and environmental problems due to non-Priority Pollutants in reclaimed wastewaters. As an example, the California State Water Resources Control Board (SWRCB, 2004) staff recently issued the following guidance to the Regional Boards:

> *"Consequently, regional boards should include the following language in water recycling requirements.*
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>> *'The incidental discharge of recycled water to waters of the State is not a violation of these requirements if the incidental discharge does not unreasonably affect the beneficial uses of the water, and does not result in exceeding an applicable water quality objective in the receiving water.'"*

Since many of the chemicals that are now becoming recognized as drinking water disinfection byproducts and PPCPs that are present in domestic wastewaters, which are a potential threat to water quality, do not have water quality standards by which to judge excessive concentrations, the use of recycled wastewaters for irrigation, which in turn leads to stormwater runoff from the irrigated areas containing these chemicals, could lead to significant water quality problems in the receiving waters for the runoff. As discussed by Lee and Jones-Lee (1995) the widespread use of reclaimed domestic wastewaters will lead to pollutants in urban stormwater runoff from the irrigated areas that are not normally present in urban stormwater runoff.

Overall, it is important to understand that the current regulatory approach for identifying potential pollutants in urban and agricultural stormwater runoff addresses only a small number of the vast arena of chemicals present in this runoff that can be adverse to the water quality of the receiving waters for the runoff. There is need to significantly expand the characterization of urban stormwater runoff associated chemicals to determine what is present and what the impact is of the runoff on the beneficial uses of the receiving waters. This will require a significantly expanded stormwater runoff water quality monitoring/evaluation program from that currently practiced, which focuses on conventional and Priority Pollutants.

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