

**National Capital Area Chapter of Society of Toxicology
Emerging Issues in Water Contamination**

Chemical Pollutants in Water: The Emerging Challenges Stakeholders Face

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**Washington, D.C.
April 15, 2010**

Water is no stranger to controversy. It has been a bitterly contentious topic in California and elsewhere well before Mark Twain famously remarked that “water’s for fighting over.” As important as the subject of water availability is today, 21st century water wars are as likely to be about what is in water as its availability and allocation. This document provides background on the complex science, legal, and communication challenges water stakeholders face in managing chemical contaminants in water.

Old Problem: New Twists

Water contamination is certainly not new. Congress passed the Clean Water Act in 1972 with a broad mandate to “restore and maintain the chemical, physical, and biological integrity of the Nation’s waters” and eventually to eliminate water pollution.

While water treatment technologies are much advanced, new challenges await resolution. Recent advances in contaminant identification methodologies, sampling instrumentation, and analytical chemistry have resulted in an explosion of knowledge regarding the presence of previously undetected “organic micropollutants” as they are referred to in water and wastewater circles. While it does not follow that the presence alone of chemical contaminants results in human health and/or environmental harm, particularly when the occurrence is at very small levels (measured in microgram to subnanogram levels), public health experts, epidemiologists, regulators, and other stakeholders are not sitting idly by.

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Given the fundamental necessity of water to all life forms, emerging data about the potential presence of substances heretofore undetected has garnered the attention of consumers, regulators, elected officials, and the media.

A key aspect of the debate surrounding organic micropollutants involves the concept of micro “dose,” or, to use the vernacular of the scientific community, “low dose.” Some argue that high doses of certain classes of chemical substances may not be appropriate to predict the safety of low doses of substances, particularly hormonally active or modulating compounds. For these compounds, some believe that health effects may present at very low doses, and that the timing of the exposure may be as relevant as the dose itself. As National Institute of Environmental Health Sciences (NIEHS)/National Toxicology Program Director Dr. Linda Birnbaum stated recently, care needs to be taken to focus more precisely on “critical windows of vulnerability” to such substances to prevent disease.²

Low dose data exist for a growing number of substances, including bisphenol A (BPA), dioxins, and phthalates, among others. Debate over the capacity to these substances to cause harm, particularly to vulnerable subpopulations, including infants and children, at very low levels of exposure is contentious and inspiring a precautionary approach by many. Lest there be any doubt, reflect upon the precipitous removal of virtually all polycarbonate baby bottles from store shelves in Canada in 2008 after Health Canada released its findings regarding the safety of BPA. This retail mega-disaster is proof that products resulting in absurdly low levels of exposure to BPA -- levels well below health-based levels set by international authoritative bodies -- may be sacrificed at the altar of precaution.³

Discussed below are several examples of water and wastewater organic micropollutants that have emerged as high profile contaminants and are certain to be carefully identified, monitored, and controlled due solely to their presumptive potential to cause adverse human and environmental health impacts. Also discussed are a few technical challenges regulators and others face in defining, managing, and communicating the potential risk posed by these substances. How these substances are managed, and how well and accurately they are profiled by regulators, the media, and other stakeholders may influence how other micropollutants are managed for years to come.

² See Birnbaum, L. (2009). Applying Research to Public Health Question: Timing and the Environmentally Relevant Dose. *Environ. Health Perspect.* 117(11):478.

³ Health Canada, “Government of Canada Takes Action on Another Chemical of Concern: Bisphenol A” (Apr. 18, 2008), available at http://www.hc-sc.gc.ca/ahc-asc/media/nr-cp/2008/2008_59-eng.php; Layton, L., and Lee, C., “Canada Bans BPA From Baby Bottles,” *Washington Post* (Apr. 19, 2008), available at <http://www.washingtonpost.com/wp-dyn/content/article/2008/04/18/AR2008041803036.html>; Austen, I., “Canada Takes Steps to Ban Most Plastic Baby Bottles,” *NY Times* (Apr. 19, 2008), available at <http://www.nytimes.com/2008/04/19/business/worldbusiness/19plastic.html>.

Endocrine Disrupting Compounds

Concern with endocrine disrupting compounds (EDCs) is not new, and the question of whether EDCs can cause toxicity at low doses has been debated for over a decade.⁴ A heightened concern with the potential effects of exposure to EDCs was reflected in Congress' enactment in 1996 of the Food Quality Protection Act and the Safe Drinking Water Act Amendments. Both laws include provisions requiring the U.S. Environmental Protection Agency (EPA) to identify, characterize, and regulate EDCs, as appropriate.⁵

EPA believed that it lacked sufficient scientific data and information on most of the estimated 83,000 chemicals listed on the Toxic Substances Control Act Inventory (and far fewer of which are actually transacted in commerce) to facilitate a defensible evaluation of endocrine-associated risks. EPA developed a two-tier screening and testing program. Under Tier I, EPA identified chemicals that it determined have the potential to interact with the endocrine system.⁶ Under Tier II, EPA developed longer-term assays to identify the specific impact caused by each endocrine disruptor and established methodologies to determine a dose at which the effect is believed to occur.

Because there were a large number of chemicals on one or more of the candidate lists of substances, EPA established priorities for selecting chemicals for initial screening. EPA gave priority in the selection process to chemicals that appeared most often in the exposure pathway databases. In April 2009, EPA published the final list of the first group of chemicals that will be screened under the EDSP and subject to endocrine screening testing

⁴ Melnik, R., Lucier, G., Wolfe, M., *et al.* (2002). Summary of the National Toxicology Program's Report on the Endocrine Disruptors Low-Dose Peer Review. *Environ. Health Perspect.* 110(4):427-431.

⁵ To achieve this Congressional goal, EPA developed a conceptual approach for identifying and validating EDCs. EPA established the Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) in 1996. The EDSTAC, which consisted of representatives from diverse stakeholder groups, was charged with providing advice and recommendations to EPA regarding a strategy to determine whether chemical substances may have an effect on humans similar to effects produced by naturally occurring hormones. In response to the EDSTAC's recommendations, EPA initiated in 1998 the Endocrine Disruptor Screening Program (EDSP). EPA stated its intent to screen pesticide chemicals and environmental contaminants for their potential to affect the endocrine systems of humans and wildlife.

⁶ The Tier I screening tests consist of a variety of endocrine test methods. These include an estrogen receptor binding assay, androgen receptor binding assay, steroidogenesis assay, aromatase assay, uterotrophic assay, Hershberger assay, pubertal assay, and fish reproductive screening.

orders.⁷ These orders compel the testing of some 67 chemical substances to assess their endocrine disruption potential. EPA began issuing testing orders in October 2009 to obtain data on whether endocrine effects exist, and will continue issuing orders for these chemicals through the early part of 2010. EPA announced on March 5, 2010, that 756 test orders were issued for the 67 chemicals, and were sent to more than 440 companies. EPA is required to publish a list of no fewer than 100 chemicals for Tier I screening by October of this year.

Congressional, federal and state regulatory, and public health and consumer interest in EDCs continues to increase. News reports on the potential effects of “gender-bending” chemicals in tap water increasingly are common in mainstream media. As an example, not long ago it was reported that male small mouth bass found in the Potomac watershed near Washington, D.C. have rapidly transformed into intersex fish that display female characteristics. A more recent survey reportedly found that 100 percent of the male small mouth bass in the Potomac watershed now are producing eggs.⁸ Similar news articles on related anomalies suspected to be related to endocrine disrupting effects are often reported, and not only in obscure scientific journals, but in mainstream media. This coverage has succeeded in greatly enhancing consumer interest in and concern over these substances and the effects they are claimed to cause.

Pharmaceuticals/Personal Care Products

The presence of pharmaceuticals and chemicals commonly found in personal care products (PCPs) in wastewater and drinking water is also an issue of growing concern. Pharmaceuticals are prescribed to address and/or prevent illness or infection and are intentionally designed to interfere with a biological system. Veterinary medicine is also included within this grouping. PCPs are typically synthetic, organic compounds derived for use by individuals in soaps, lotions, beauty aids, sunscreens, fragrances, and related PCPs and are not typically designed to interact with biological systems.

Many of these pharmaceuticals and PCPs contain a broad spectrum of substances that represent a range of physico-chemical properties that alone or in combination with other substances and at certain concentrations potentially could result in ecological or human

⁷ 74 Fed. Reg. 17579 (Apr. 15, 2009). In separate *Federal Register* notices, EPA described other aspects of the EDSP, such as the “policies and procedures” for initial screening (74 Fed. Reg. 17560 (Apr. 15, 2009)), and the final test guidelines (74 Fed. Reg. 17479 (Apr. 15, 2009)).

⁸ On December 3, 2009, Senator John Kerry (D-MA) and Representative Jim Moran (D-VA) introduced legislation to facilitate the research necessary to assess endocrine disruption effects. H.R. 4190 would authorize a research program at NIEHS to identify EDCs, among other provisions. The legislation was in large part in response to the EDCs found in the Potomac River and their potential effect on the small mouth bass.

health effects. These substances in wastewater also may influence more mundane operations like sample preparation and analytical methods.

A recent article published by The Royal Society categorized common pharmaceuticals and PCPs by chemical compound classes as follows:⁹ acidic pharmaceuticals, including ibuprofen, naproxen, diclofenac, and benazafibrate; neutral pharmaceuticals, including antiepileptics, psychiatrics, and lipid regulators; betablockers such as metoprolol, atenolol, sotalol, and salbutamol; iodinated X-ray contrast media, including diatrizoate, iopamidol, and iopromide; and antibiotics such as triclosan, tetracyclines, and penicillins.

Issues concerning the presence of these organic micropollutants in tap water have gained significant momentum over the years. The U.S. House of Representatives recently weighed in and passed in 2009 the National Water Research and Development Initiative Act of 2009.¹⁰ The bill is designed to coordinate federal research and development efforts regarding water use, supply, and demand, and specifically calls for federal research on the impact of trace amounts of pharmaceuticals and other contaminants in drinking water. Other legislative and regulatory initiatives are pending in Congress, state legislatures, and governmental bodies around the country and elsewhere.

Engineered Nanomaterials

Consumer applications of nanoscale materials have received much media scrutiny in the recent past. The rapid commercialization of products containing nanoscale materials is difficult to measure with precision, but most would agree it is sizable. Estimates range from \$1 trillion to \$3.1 trillion by 2015.¹¹ An inventory of consumer products maintained by the Project on Emerging Nanotechnologies (PEN) at the Woodrow Wilson International Center for Scholars identifies over 1,000 nano-enabled products in commerce today, marketed in over 21 countries.¹² While the PEN inventory is only one and an admittedly imprecise measure of the rapid deployment of nanotechnology in consumer products, it is cited frequently as a fairly reliable gauge of nano commercialization. The vast majority of the products on the inventory are cosmetics, clothing, personal care items, sporting goods, and sunscreens.

⁹ Comerton, A., *et al.* (2009). Practical Overview of Analytical Methods for Endocrine-Disrupting Compounds, Pharmaceutical and Personal Care Products in Water and Wastewater. *Phil. Trans. R. Soc. A.* 367:3923-3939.

¹⁰ H.R. 1145, sponsored by Rep. Bart Gordon (D-TN).

¹¹ Breggin, L., *et al.* "Securing the Promise of Nanotechnologies: Toward Transatlantic Regulatory Cooperation" (Sept. 2009) at 10, available at http://www.chathamhouse.org.uk/files/14692_r0909_nanotechnologies.pdf.

¹² The PEN consumer products inventory is available at <http://www.nanotechproject.org/inventories/consumer/>.

Given the nature of these products, nanoparticles may enter wastewater streams in several ways. Releases to the environment may occur during product manufacture. Nanoparticles may be embedded in products that are later released when the products are used as intended. The intended use of certain products may result in nanoparticles either becoming a contaminant in a water body or part of the influent being treated at a publicly owned treatment works. For example, sunscreen lotions may be rinsed off in ponds, lakes, rivers, swimming pools, and showers. Nanoparticles also may be released into the environment when fabrics that contain embedded nanoparticles as a fiber finish are laundered or as certain antifouling paint and coatings for use on vessels and/or off-shore structures weather and degrade over time. Nanoparticles may also be released into the environment when products containing them are discarded and degrade, and contribute to groundwater or surface water pollution.

Nanoparticle-containing products that may result in releases of nanoparticles to receiving waters or treatment facilities are also being marketed. For example, several manufacturers are marketing socks that the manufacturer claims contain nanosilver particles as an antibacterial agent. A recent study asserts that when the socks are washed, some of the silver nanoparticles may be released into the water.¹³

The marketing opportunities offered by nanosilver impregnated articles have caused an increase in the number of silver pesticide registration applications under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). EPA is at the early stages of assessing the utility and adequacy of existing FIFRA registration guidelines and protocols with respect to nanoscale pesticides. Because of this early stage, EPA's Office of Pesticide Programs recently requested guidance from the Scientific Advisory Panel (SAP) and convened a meeting "to consider and review a set of scientific issues related to the assessment of hazard and exposure associated with nanosilver and other nanometal pesticide products."¹⁴ The SAP released its meeting minutes on January 28, 2010. The Panel recommended that nanosilver be subjected to enhanced review and testing. It recommended that FIFRA registration applications for nanosilver be addressed by EPA on a case-by-case basis given the unique attributes of nanosilver applications and uses.

An example of the types of products EPA's pesticide office has considered in the recent past include Samsung's SilverCare™, an option on several models of washing machines. Samsung advertised the generation of silver nanoparticles in the rinse cycle as a benefit derivative of silver's well-established antibacterial properties and because the option

¹³ Benn, T.M. and Westerhoff, P. (2008). Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. *Environ. Sci. Technol.* 42(11):4133-4139, available at <http://pubs.acs.org/cgi-bin/abstract.cgi/esthag/2008/42/i11/abs/es7032718.html>.

¹⁴ Bergeson, L., "FIFRA Scientific Advisory Panel Considers Nanosilver," *ELR News & Analysis*, 39 ELR 11143 (Dec. 2009), available at http://www.lawbc.com/other_pdfs/00053867.PDF.

allowed clothes to be washed in cooler water, resulting in energy and cost savings.¹⁵ Consumers and some wastewater treatment facility owners and operators expressed concern, however, about the potential consequences of using SilverCare™ products. These products were taken off the market briefly in Sweden due to concerns over the potential toxic effects of discharging silver nanoparticles from these machines to wastewater treatment plants.¹⁶ In the United States, EPA ultimately determined that the washing machines required registration as pesticides under FIFRA, perhaps in part due to concerns expressed by the National Association of Clean Water Agencies and an organization representing treatment facilities in California.¹⁷

The growing commercialization of nano-enabled products has added renewed urgency in the debate over the sufficiency of data and health effects information on nanoparticles and human health and the environment. The Environmental Working Group (EWG) asserts in its 2009 Sunscreen Investigation that many sunscreens contain nano-scale ingredients, including zinc oxide and titanium dioxide, and that due to a lack of data, it remains unclear whether the nano-ingredients found in these and other consumer products can impact human health and the environment.

Somewhat ironically, certain applications of nanotechnology are also used for water treatment and embedded in filtration systems to improve water purification. According to many nanotechnology enthusiasts, nanotechnology holds particular promise in at least four key water industry segments: monitoring, desalination, purification, and wastewater treatment. With regard to monitoring, there are promising nanotechnology applications where sensitive machinery uses ultrapure water and detection of impurities is critical to efficient operations.¹⁸ Wastewater treatment applications are also well known. Zero-valent nanoscale iron is known to be particularly effective as an in-situ groundwater treatment of dense non-aqueous phase liquids (DNAPLS), reported by EPA to be at

¹⁵ Nanowerk News, *Concerns About Nanotechnology Washing Machine* (Nov. 16, 2006), available at <http://www.nanowerk.com/news/newsid=1037.php>.

¹⁶ Senjen, R., *Nanosilver -- A Threat to Soil, Water and Human Health?* Friends of the Earth Australia (Mar. 2007), available at http://www.foe.org/pdf/FoE_Australia_Nanosilver_report.pdf.

¹⁷ Sellers, K. and Bergeson, L., *Nanomaterials Down the Drain: Perception and Reality*, poster presented at the Nano Science and Technology Institute (NSTI) Nanotech 2008 conference held June 1-5, 2008.

¹⁸ Loncto, J., Walker, M., and Foster, L., *Nanotechnology in the Water Industry, Nanotechnology Law & Business* (June 2007), available at http://cleantechlawandbusiness.com/shared/files/Nanotech_in_Water_Industry.pdf.

approximately 60-70% of all Superfund sites listed on the National Priority List.¹⁹ The literature is full of citations to studies of promising desalination and purification nanotechnology applications.²⁰

The foregoing examples present just a few illustrations of the types of issues organic micropollutants present and the challenges they pose. Similar concerns have been raised with antibacterial agents such as triclosan, detergents that contain alkylphenol ethoxylates, and pesticides.

Technical Challenges

While debate continues over whether there is evidence of a link between exposure to these organic micropollutants and adverse health effects, there is consensus that much more can be learned about the presence of these compounds in water, and the effectiveness of conventional drinking water and wastewater processes to remove them. Relatively few studies appear to exist that measure both wastewater treatment plant influent and effluent concentrations. A complicating related fact is that the absence of a pollutant may not necessarily mean treatment has occurred. It could also mean that chemical transformation of one sort or another has occurred and the parent compound has transformed into another or other unknown and/or unmeasured degradates, or the contaminant is below detection capability.

Other issues arise from the application of conventional pollutant treatment methodologies and tools to address newer, more exotic pollutants found in very low concentrations. The removal of EDCs, for example, by conventional drinking water processes is difficult to study at full scale.²¹ It is also not clear sampling methodologies and tools exist to identify and/or characterize in all cases the presence of organic micropollutants in complex water matrices.

Another challenge is the sheer number of contaminants. There are several thousand compounds that can be classified as EDCs, PCPs, nanoscale materials in wastewater, or other organic micropollutants. These compounds, and their metabolites, represent a wide range of physico-chemical properties. It is difficult to develop analytical methods for all of these compounds. Given cash-strapped municipalities and wastewater treatment operators, the resources to develop new and cutting-edge detection methods are simply not there.

¹⁹ Dunn, C. (2006). Environmental Cleanup Technology Earns Top Honors. *Technology Innovation* 13(1):13-16, available at http://ipp.nasa.gov/innovation/innovation131/innovation_v13_n1.pdf.

²⁰ For more information, see Karn, B. and Bergeson, L., Green Nanotechnology: Straddling Promise and Uncertainty, *Natural Resources & Environment*, Vol. 24, No. 2, Fall 2009, available at http://www.lawbc.com/other_pdfs/00051031.PDF.

²¹ *Supra*, note 9, at 3927.

It is also important to recognize these new challenges are in addition to existing, more “routine” challenges facing wastewater treatment operators. As the population grows, municipalities must process more water with fewer resources and with an aging infrastructure.

Managing sewage overruns is also increasingly a problem. As noted recently by the *New York Times*, “as cities have grown rapidly across the nation, many have neglected infrastructure projects and paved over green spaces that once absorbed rainwater. That has contributed to sewage backups into more than 400,000 basements and spills into thousands of streets, according to data collected by state and federal officials. Sometimes, waste has overflowed just upstream from drinking water intake points or near public beaches. There is no national record-keeping of how many illnesses are caused by sewage spills. But academic research suggests that as many as 20 million people each year become ill from drinking water containing bacteria and other pathogens that are often spread by untreated waste.”²²

Lawyers, regulators, scientists, and interested others with a stake in these issues are challenged to understand the complex science underlying the debate, and the application of somewhat dated laws and governance systems to address potential risk scenarios posed by these emerging issues. All stakeholders must be scrupulously mindful of what is known, and what remains to be clarified based on sound scientific rigor, and seek to contribute meaningfully to helping resolve the complex science and legal challenges that deserve open and transparent deliberation.

²² Duhigg, C., “As Sewers Fill, Waste Poisons Waterways,” *NY Times* (Nov. 22, 2009), available at <http://www.nytimes.com/2009/11/23/us/23sewer.html>.