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Approaches for Quantifying the Attenuation of Wastewater-Derived Contaminants in the Aquatic Environment

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Abstract: The effluent from municipal wastewater treatment plants contains trace concentrations of a variety of organic compounds. To assess the removal of these compounds in full-scale treatment systems and effluent-receiving waters, approaches are needed for quantifying removal rates and mechanisms. For processes that result in near complete removal of wastewater-derived contaminants, it is reasonable to measure concentrations entering and leaving the treatment system. However, for those compounds that are not completely removed, alternative methods are needed. This paper describes several examples of approaches that combine laboratory and field studies to assess the attenuation of wastewater-derived contaminants.

Keywords: Chlorine · Estradiol · Nitrosodimethylamine (NDMA) · Pharmaceuticals · Sewage

Introduction

As population density increases throughout the world, especially in arid regions with limited water supplies, the reuse of effluent from municipal wastewater treatment plants has become more important [1]. During dry periods, municipal wastewater effluent accounts for the majority of water flow in rivers in many populated regions. Furthermore, municipal wastewater effluent sometimes is used to augment potable water supplies. In such potable water reuse systems, wastewater effluent may be percolated into aquifers after secondary or tertiary biological treatment or injected into aquifers or discharged into reservoirs after advanced treatment processes.

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The practice of water reuse has been applied in some form by most modern civilizations with little concern for potential adverse effects on human health or aquatic organisms. However, recent studies suggest that trace amounts of chemical contaminants present in wastewater effluent can have measurable effects on aquatic organisms. In particular, the part-per-trillion levels of steroid hormones in wastewater effluent has been shown to cause male fish to undergo a process referred to as feminization, in which they exhibit characteristics normally associated with female fish [2]. The observation of such effects in fish has raised questions about the possible occurrence of adverse effects of wastewater-derived contaminants in humans.

Early research in this area documented the occurrence of a variety of wastewater-derived contaminants including human pharmaceuticals [3–7], steroid hormones [2][8] and consumer products. To develop a better understanding of the distance from their sources at which the wastewater-derived contaminants can cause adverse effects and to develop approaches for minimizing these effects, research is needed on the fate, transport, and transformation of the wastewater-derived contaminants. This paper reviews current research on this topic being conducted in our research group.

Attenuation of Wastewater-Derived Contaminants During Wastewater Treatment

In many cases, it may be appropriate to study the attenuation of wastewater-derived contaminants in wastewater treatment plants by measuring concentrations before and after a treatment process. For example, we have used this approach to quantify the ability of an advanced treatment system (*i.e.* the West Central Basin Groundwater Replenishment Project) to remove pharmaceuticals by application of microfiltration and thin-film composite reverse osmosis (Fig. 1). Concentrations of pharmaceuticals measured before and after microfiltration are nearly identical whereas concentrations decrease to levels below detection limits after reverse osmosis treatment [9]. These results suggest that full-scale reverse osmosis systems effectively remove most pharmaceuticals.

The attenuation of wastewater-derived contaminants is relatively easy to study by collecting grab samples before and after different treatment processes when complete removal occurs, as is the case with the pharmaceuticals treated by reverse osmosis. Such simplistic approaches are much more difficult to apply when incomplete removal occurs during treatment. For exam-

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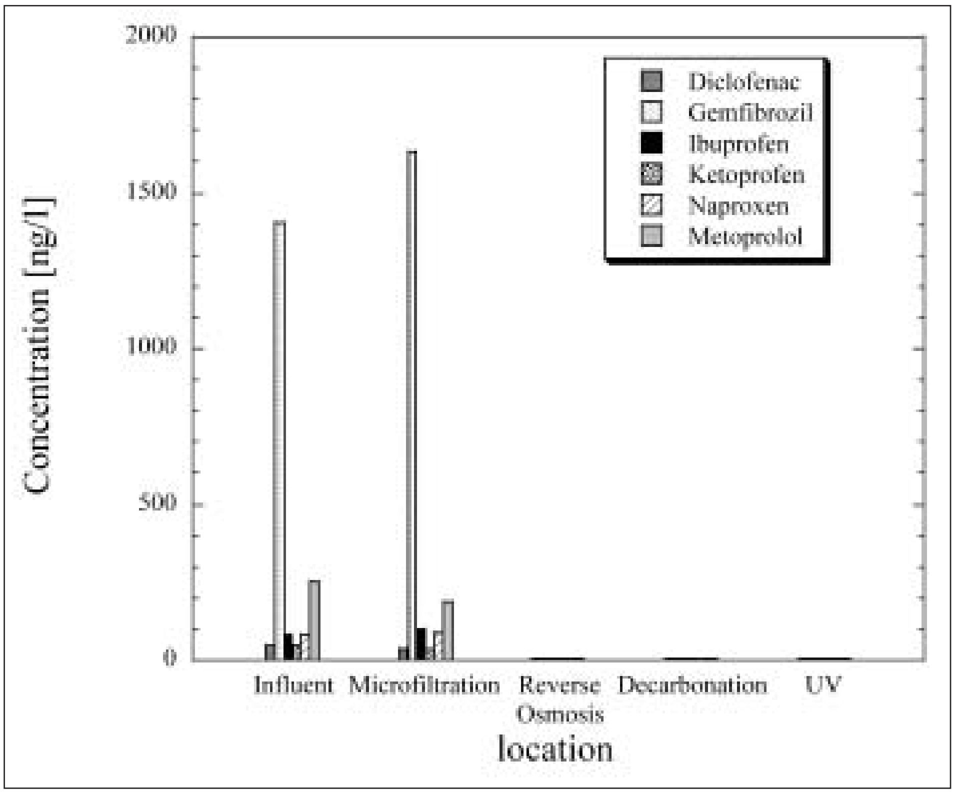

Fig. 1. Concentrations of pharmaceutical measured after different unit processes at the West Central Basin Groundwater Replenishment Project. After reverse osmosis treatment concentrations of all pharmaceuticals are below 10 ng/l.

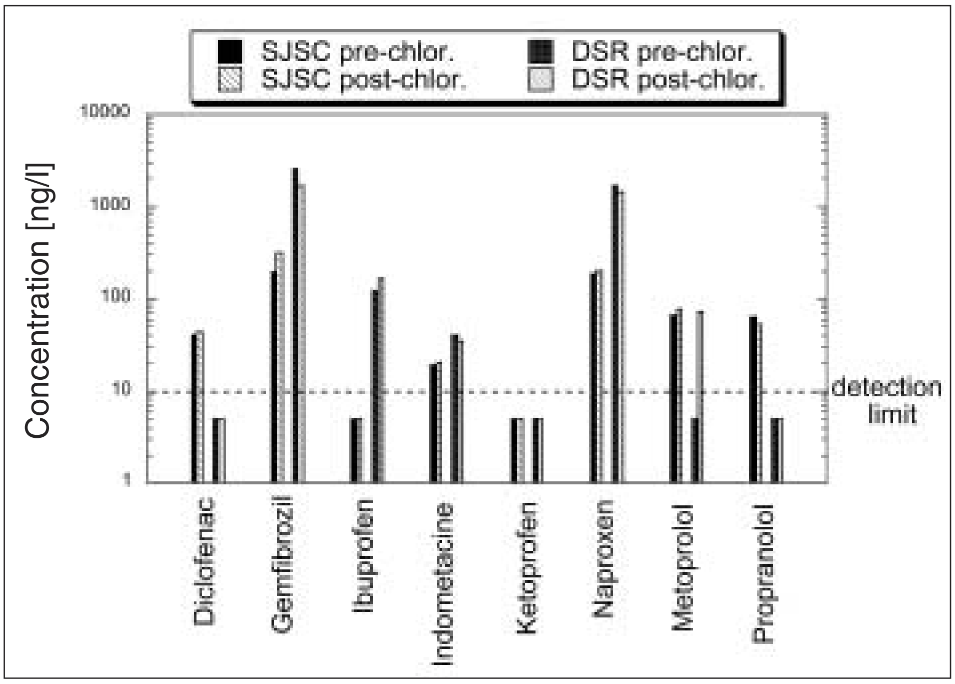

Fig. 2. Concentrations of drugs detected at the San Jose/Santa Clara (SJSC) and Dublin/San Ramon (DSR) Wastewater Treatment Plants. The detection limit for all compounds was 10 ng/l. Concentrations below the detection limit are plotted at half the detection limit.

ple, many pharmaceuticals are transformed by reactions with hypochlorous acid and/or monochloramine [10], which are the forms of chlorine present during chlorine disinfection of wastewater. However, the reactions are relatively slow and complete transformation of the compounds is not expected during full-scale treatment. As a result of the variations in concentration of pharmaceuticals in the wastewater, it is extremely difficult to detect the transformation of pharmaceuticals during disinfection at full-scale treatment plants simply by analyzing grab samples (Fig. 2). Due to variations in concentrations in wastewater effluent, in some cases, it may even appear that concentrations increase during treatment. These problems can be minimized to some degree through the collection of composite samples, provided that the reaction is quenched by adding an appropriate reagent to the sample collection bottle.

To study attenuation processes that result in partial removal of wastewater-derived contaminants, we have complemented field studies with laboratory studies that address the mechanisms and kinetics of these processes. For example, nitrosodimethylamine (NDMA) is a highly carcinogenic compound that is formed when municipal wastewater effluent is subjected to chlorine disinfection. To gain insight into approaches for minimizing the formation of this compound, we have focused our attention on laboratory studies of the formation mechanism of NDMA [11]. This approach has led to the development of a standard method for quantifying the NDMA precursors [12] that could be used for studies of full-scale treatment plants as well as surface waters [13][14]. The collection of grab and composite samples from full-scale treatment plants indicates that a significant fraction of the NDMA precursors originate in polymers used to assist in processes including sludge thickening and control of foam-producing organisms.

Attenuation of Wastewater-Derived Contaminants in Engineered Treatment Wetlands

Engineered treatment wetlands offer a potentially attractive means of removing contaminants from wastewater effluent. However, much like the case observed for wastewater treatment, variation in concentrations of wastewater-derived contaminants in wastewater effluent can greatly complicate analysis of these systems. Most studies of the performance of engineered treatment wetlands rely upon samples collected at the wetland inlet (*i.e.* the wastewater effluent) and the wetland outlet. In our preliminary studies [8] of the fate of hormones in engineered treatment wetlands we used such an approach (Fig. 3). The results of this analysis suggested that more than 75% of the hormones were removed well during the 6-day hydraulic retention time of the wetland. However, more concentrated sampling in the wetland has indicated much less efficient removal of hormones [15][16]. The discrepancies between the inlet and outlet samples collected on different dates are attributable to variations in hormone concentrations in the wastewater effluent: 24-hour composite samples of wastewater effluent show variations in concentrations of 17β-estradiol of as much as an order of magnitude between samples collected at 2-day intervals [15].

Our research on engineered wetlands also indicates that concentrations of different hormones are not always correlated. For example, the highest concentrations of the hormones testosterone, 17β-estradiol and medroxyprogesterone in the engineered treatment wetland occurred on different dates [16]. The presence of these other hormones is significant because they can serve as pheromones that alter the behavior of fish.

One approach for addressing variations in the concentrations of wastewater-derived contaminants from wastewater effluents involves the development of a hydraulic model of flow and attenuation in the wetland. The hydraulic model was calibrated using results from a lithium tracer test. Inlet and outlet samples then were collected at 2-day intervals over a 14-day period. Results were analyzed with a statistical model to estimate attenuation rates. This approach resulted in a conclusion that hormones are slowly attenuated in the wetland with half-lives of approximately two weeks. The most likely mechanism of hormone attenuation is indirect photolysis, with a species such as singlet oxygen or triplet dissolved organic matter serving as the photoreactive transient [15].

A second approach for assessing hormone attenuation in engineered wetlands involves the addition of a pulse of hormones to a wetland along with a conservative tracer. By quantifying both the hormone and the conservative tracer in the effluent from the wetland, it is possible to estimate hormone attenuation rates. Results from such a study, conducted at a series of test cells within a larger engineered treatment wetland indicated that approximately 30–40% of the steroid hormones were removed during a 5-day hydraulic residence time [15].

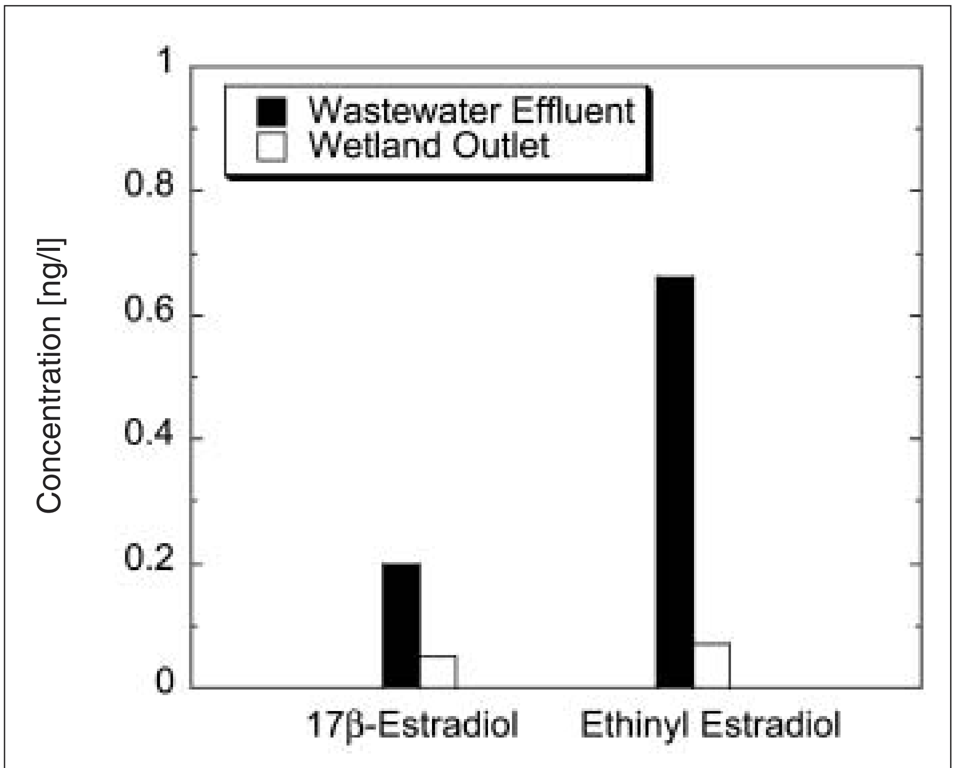

Fig. 3. Concentrations of steroid hormones measured in initial studies at an engineered treatment wetland. Fig. redrawn from data in [8].

Future Research Needs

As described in this brief review of current research, studying the attenuation of wastewater-derived contaminants presents a number of challenges to environmental chemists. In particular, it is difficult to study full-scale treatment processes or processes that occur in the aquatic environment because the effects of dilution and variations in concentrations in wastewater are difficult to quantify. Laboratory studies of processes that are responsible for attenuation as well as a better overall understanding of treatment processes are crucial to further development in this area. Furthermore, the development of conservative and reactive tracers for wastewater-derived contaminants may provide valuable insight into these processes.

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