ENVIRONMENTAL ASPECTS OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS

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WATER QUALITY MONITORING OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS USING PASSIVE SAMPLERS

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Introduction

The demand on freshwater to sustain the needs of the growing population is of worldwide concern. Often this water is used, treated and released for reuse by other communities. The anthropogenic contaminants present in this water may include complex mixtures of pesticides, prescription and nonprescription drugs, personal care and common consumer products, industrial and domestic-use materials and degradation products of these compounds. Although the fate of these pharmaceuticals and personal care products (PPCPs) in wastewater treatment facilities is largely unknown, the limited data that does exist suggests that many of these chemicals survive treatment and some others are returned to their biologically active form *via* deconjugation of metabolites[1-3].

Traditional water sampling methods (*i.e.*, grab or composite samples) often require the concentration of large amounts of water to detect trace levels of PPCPs. A passive sampler, the polar organic chemical integrative sampler (POCIS), has been developed to integratively concentrate the trace levels of these chemicals, determine the time-

weighted average water concentrations and provide a method of estimating the potential exposure of aquatic organisms to these complex mixtures of waterborne contaminants[4-5]. The POCIS (U.S. Patent number 6,478,961) consists of a hydrophilic microporous membrane, acting as a semipermeable barrier, enveloping various solid-phase sorbents that retain the sampled chemicals. Sampling rates for individual chemicals determined in the laboratory are used in conjunction with theoretical uptake models to provide estimates of the ambient water concentrations of those chemicals.

Materials and Methods

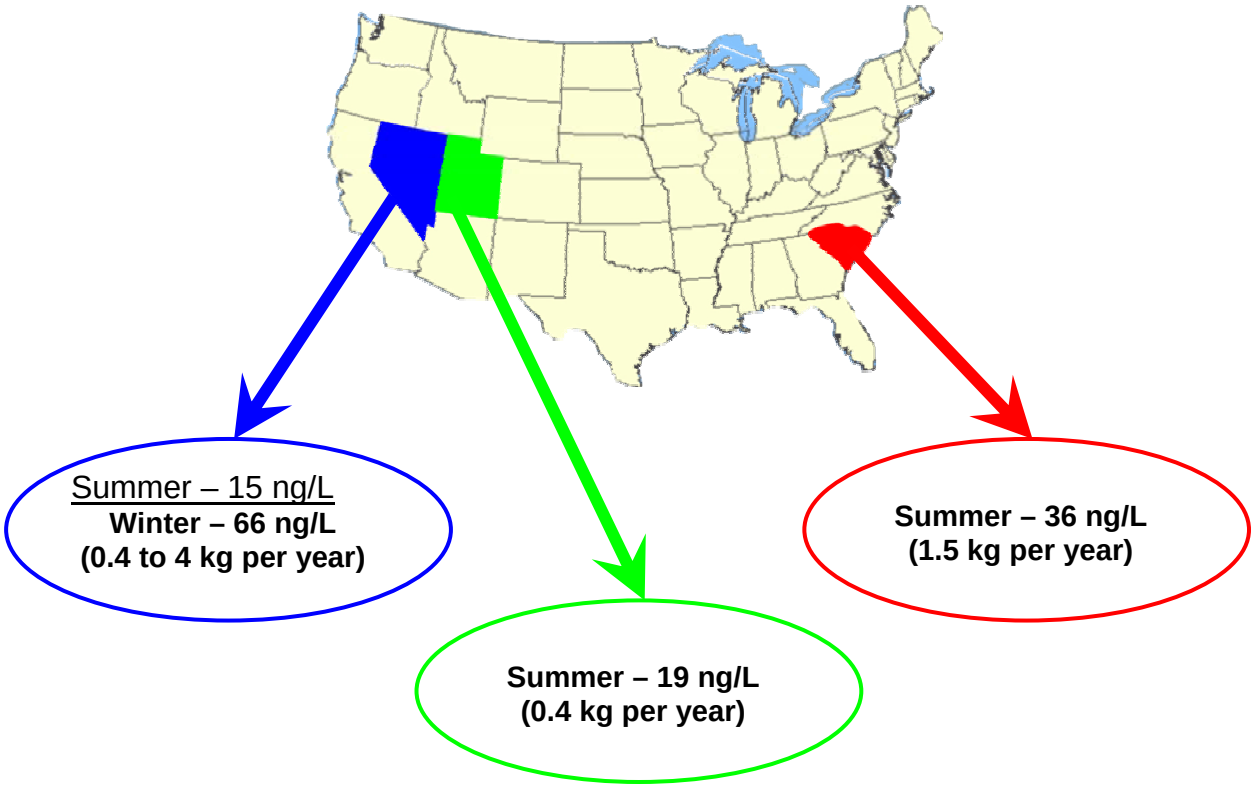
The POCIS is prepared according to previously described methods[4]. Briefly, each POCIS contained 200 mg of a sequestration sorbent and consisted of $\cong$ 41 cm^2 of effective sampling surface area. For the various field deployments, two variations of the POCIS were used. A configuration optimized for the sampling of pharmaceuticals was prepared using Oasis HLB as the sorbent. The other configuration targeting pesticides and other hydrophilic organic chemicals contained a triphasic admixture of Isolute ENV+ and Ambersorb 1500 dispersed on S-X3 BioBeads.

Results and Discussion

Accumulation of chemicals by passive samplers typically follows first-order kinetics, which is characterized by an initial integrative phase, followed by curvilinear and equilibrium partitioning phases. In the integrative sampling phase, the sampling device acts as an infinite sink for contaminants of interest and analyte uptake is linear. This approach provides an estimate of the time-weighted average (TWA) concentration of contaminants during a specified exposure period. Unlike samplers that rapidly achieve equilibrium (characterized by high loss rates and low capacity), chemical residues from episodic events during the integrative part of an exposure are retained in the POCIS. Sampling rates for individual chemicals determined in the laboratory allow for estimates of water concentrations to be made. Rates for chemical uptake of hydrophilic organic chemicals (log K_{ow} < 3) are generally controlled by diffusion across an aqueous boundary layer at the membrane surface. Increased turbulence at the membrane surface reduces the aqueous boundary layer thickness and, thereby, increases the rate of chemical uptake.

Four widely prescribed pharmaceuticals, azithromycin, fluoxetine, levothyroxine and omeprazole, were selected as model pharmaceuticals in the development of the POCIS. Sites receiving treated effluent from urban wastewater treatment plants in Nevada, Utah and South Carolina were monitored for these chemicals by deploying the POCIS for 30 days during the summer. A winter sampling at the Nevada site was also performed. Azithromycin was found in all of the treated wastewater streams at levels ranging from 15 to 66 ng/L (Figure 1). Comparison between the summer and winter deployments at the Nevada site indicated increased levels of azithromycin in the winter as might be expected due to increased antibiotic usage during the cold and flu season.

Figure 1. Estimated water concentrations of azithromycin measured from POCIS deployments in the treated effluents of wastewater treatment plants and their yearly environmental loadings.



A comparison of the POCIS to standard water-column sampling methodologies was performed at two sites in a New Jersey creek that received effluent from a wastewater treatment facility. Composite water samples were taken at each site four times during the 54-day POCIS deployment. Analysis of the POCIS extracts and the water samples revealed 33 chemicals in the POCIS extracts compared with 29 in the water samples (Table 1). Ten chemicals were identified exclusively in the POCIS, including nonionic detergent metabolites, insecticides, fragrances and pharmaceuticals. The data demonstrates the utility of the POCIS for detecting chemicals that dissipate quickly or enter the watershed *via* an episodic event, as less than half of the chemicals detected in the water samples were present in all four samples.

Table 1. Pharmaceuticals and other organic wastewater contaminants detected in POCIS extracts from a New Jersey stream receiving effluent from a wastewater treatment plant.

3-methyl-1H-indole	Fryol FR2
4-cumylphenol	Hexahydrohexamethylcyclopentabenzopyran
4-*tert*-octylphenol	(HHCB)
5-methyl-1H-benzotriazole	Indole
Acetaminophen	Methyl salicylate
Anthraquinone	Metolachlor
Atrazine	Pentachlorophenol
Benzophenone	Prometon
Caffeine	Nonylphenol, diethoxy
Carbamazepine	Sulfamethoxazole
Cotinine	Thiabendazole
DEET	Tonalide (AHTN)
Dehydronifedipine	Tributyl phosphate
Diazinon	Triclosan
Diethylhexylphthalate	Triethyl citrate
Diphenhydramine	Triphenyl phosphate
Fryol CEF	Tri(2-butoxyethyl)phosphate

References

1. Desbrow, C., Routledge, E., Brighty, G., Sumpter, J. and Waldock, M. (1998). *Environ Sci Technol* **32**,1549-1558.
2. Halling-Sørensen, B., Nors Nielsen, S., Lanzley, P., Ingerslev, F., Holten Lützhøft, H. and Jørgensen, S. (1998). *Chemosphere* **36**, 357-393.
3. Daughton, C. and Ternes, T. (1999). *Environ Health Perspect* **107** (suppl. 6), 907-938.
4. Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P. and Manahan, S.E., (2004). *Environ. Toxicol. Chem.* in press.
5. Petty, J.D., Huckins, J.N., Alvarez, D.A., Brumbaugh, W.G., Cranor, W.L., Gale, R.W., Rastall, A.C., Jones-Lepp, T.L., Leiker, T.J., Rostad, C.E. and Furlong, E.T., (2004). *Chemosphere*, **54**, 695-705.

NOTICE

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