PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN SAN FRANCISCO BAY

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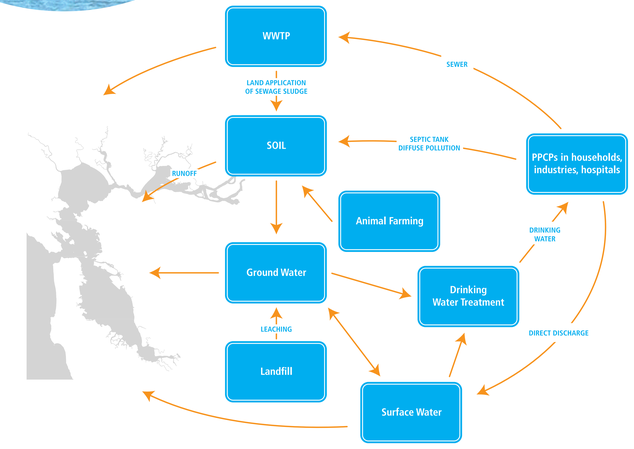
Abstract

Pharmaceuticals and personal care product ingredients (PPCPs) are detected frequently in US waterways, creating concern for their potential to impact wildlife as well as humans. PPCPs can enter waterways through wastewater treatment plant (WWTP) effluent, stormwater, and groundwater. Forty-six Bay Area WWTPs likely provide the primary pathway for these contaminants to enter the Bay. The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has monitored select PPCPs in Bay surface water, sediment, and biota since 2002. In 2006, the RMP analyzed South Bay surface water for 39 pharmaceuticals, 18 of which were detected at levels comparable to those observed in similar studies of receiving waters. A 2010 follow-up study of five sites located throughout the Bay found that out of the 104 PPCPs analyzed, 31, 10, and 17 were detected in water, sediment, and mussels, respectively. Concentrations of PPCPs in Bay samples were generally an order of magnitude or more below concentrations expected to elicit toxic effects in aquatic organisms. However, a few exceptions deserve special attention, including plasticizers bis(2-ethylhexyl) phthalate and butylbenzyl phthalate, and the antibiotic sulfamethoxazole. In general, the majority of toxicity data currently available for PPCPs are based on acute effects studies, and the potential for sub-lethal effects, as well as those triggered by chronic exposures or exposures to mixtures of contaminants, remains a concern. The RMP is considering future studies that will expand the number of PPCPs analyzed in Bay samples following an evaluation of recent data on aquatic toxicity and detections in similar ecosystems.

Introduction

The continuous introduction of PPCPs to surface waters worldwide via the discharge of treated wastewater and other pathways (Figure 1) has led to a number of efforts to assess their occurrence and potential impacts on aquatic organisms.

The RMP has evaluated the presence of over 100 PPCPs in San Francisco Bay water, sediment, and mussels. Most studies examine the occurrence and potential effects of PPCPs in freshwater systems, making these estuarine studies particularly valuable [1,2].

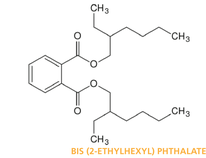


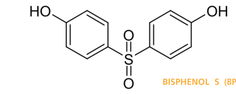
How are PPCPs introduced into the environment?

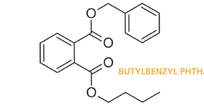
- PPCPs are widely manufactured and used.
- Pharmaceuticals:
  - High rates of antibiotic prescriptions in the US: 75% of office and 74% of outpatient visits result in antibiotic prescriptions[3].
  - The most common drug classes prescribed in 2010 were: analgesics, antidiabetics, and antihyperlipidemics[3].
  - The most common drugs (active ingredient) prescribed in 2010 were: aspirin (acetylsalicylic acid), Lisinopril, and Albuterol (albuterol sulfate)[3].
  - Agricultural activities such as animal husbandry involve use of pharmaceuticals[4].
- Personal care product ingredients:
  - Sunscreen active ingredients as well as other UV filters and antimicrobials added to personal care products for protection against degradation and microbial growth may persist in the environment [2,4].
  - Plasticizers like phthalates and bisphenol A, which have endocrine disrupting properties, are often monitored in conjunction with typical PPCPs; some phthalates are present in PPCPs as pill coatings or fragrance ingredients[5].
- A major pathway for PPCPs to enter the environment is via treated wastewater (Figure 1).
  - PPCPs enter wastewater via human waste, flushing of unwanted medications, and cleaning and bathing activities.
  - Wastewater treatment plants were designed to treat human and food waste, and thus do not necessarily have effective mechanisms for complete PPCP removal, resulting in chemical discharge into the environment.
- Other pathways include landfill and septic tank leachates, direct release to surface waters (urban runoff etc.), and land application of sewage sludge (Figure 1)[4,6].

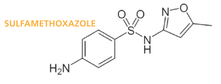
COMPOUND	SURFACE WATERS (NG/L)		SEDIMENTS (NG/G DW)		MUSSELS (NG/G DW)	
	CONCENTRATION	SAMPLES WITH CHEMICAL DETECTED / TOTAL SAMPLES	CONCENTRATION	SAMPLES WITH CHEMICAL DETECTED / TOTAL SAMPLES	CONCENTRATION	SAMPLES WITH CHEMICAL DETECTED / TOTAL SAMPLES
Albuterol	1	1/15	<0.3		<4.9	
Amitriptyline	0.6	2/5	<1.4		6.2	8/14
10-hydroxy-amitriptyline	0.3	2/5	<0.2		<0.6	
Amphetamine	9.7	2/5	3.3	2/5	31	5/14
Atenolol	37	5/5	<0.9		13	3/14
Benzoylecgonine	7.2	5/5	<0.3		<1.3	
Bis(2-ethylhexyl) phthalate	459	5/15	605, (32,000*)	10/10	968	11/22
Butylbenzyl phthalate	14	7/11	323	22/22	<10	
Caffeine	132	12/15	34	3/5	<59	
Carbamazepine	44	5/5	NQ		35	5/14
Celestolide	NA		NA		93	5/39
Ciprofloxacin	<6.0-1300*		678	2/2	<24	
Clarithromycin	18	2/5	<1.5		<5.9	
Cocaine	2.4	4/5	0.2	1/4	1.6	4/14
Cotinine	25	4/15	<1.5		<14	
Dehydronifedipine	1.3	4/5	NQ		4.8	5/14
Desmethyldiltiazem	1.7	2/5	NQ		<1.0	
Diazepam	0.5	1/5	<0.3		<3.0	
Di-n-butyl phthalate	35	6/13	94	10/11	2620	21/22
Digoxigenin	<568		NQ		73	3/14
Diltiazem	13.7	12/15	NQ		1.5	4/14
Diphenhydramine	1.9	4/5	NQ		42	11/14
Enalapril	<1.5		<0.3		1	2/14
Enrofluxacin	<6.6-1400*		NQ		11	1/9
Erythromycin-H20	41.6	14/15	3.4	1/5	2.1	5/14
Fluoxetine	<34.4		<7.1		7.2	4/14
Galaxolide	NA		NA		855	19/39
Gemfibrozil	38	15/15	<1.6		<12	
Hydrocodone	7.2	1/5	<1.5		<46	
Ibuprofen	38	1/15	<16		<58	
Lomefloxacin	<3.8		NQ		90	6/9
Meprobamate	36	5/5	<4.0		<16	
Methylprednisolone	<4.0		<4.0		46	1/14
Metoprolol	26	3/5	<1.5		<7.9	
N, N-diethyl-m-toluamide (DEET)	21	5/5	3.4	2/5	92	10/10
Naproxen	8.2	1/5	<3.1		<12	
Ofloxacin	<15		NQ		12.6	1/9
Propoxyphene	0.7	2/5	<4.5		<3.2	
Propranolol	<2.0		<2.0		8.2	1/14
Ranitidine	<3.0		<0.6		24	6/14
Sertraline	<0.4		<0.4		19	10/14
Sulfamethazine	<0.6-351*		<1.5		89	1/14
Sulfamethizole	16	1/15	<0.8		1.5	1/14
Sulfamethoxazole	1060	12/15	0.7	1/5	<4.7	
Thiabendazole	2.5	1/5	9.1	2/5	<5.9	
Tonalide	NA		NA		516	24/39
Triamterene	9.6	5/5	11	5/5	9.1	4/14
Triclocarban	<3.0		33	3/5	11	2/10
Triclosan	<60		41	9/17	<238	
Trimethoprim	8.54	3/15	18	1/5	<5.9	
Valsartan	92	5/5	NQ		<16	
Verapamil	<0.2		NQ		1	1/14
Versalide	NA		NA		56	3/39
Virginiamycin	<34.4		NQ		14	2/10

Compounds in bold were detected in at least one matrix; a For '<XX', XX=maximum MDL for all samples in most cases; where the maximum MDL from the earlier, Hamold et al. (2009) study is over 50x greater than that of the Klosterhaus et al. (2013) study, both are listed to reflect significant improvements to the analytical method; dw=dry weight; ww=wet weight; NA=not analyzed NQ=not quantifiable; The following compounds were not detected above the detection limit in any analyzed matrix: Acetotominophen, Alprosolam, Amlodopine, Atorvastatin, Azithromycin, Benztropine, Betamethasone, Bisphenol A, Carbadox, Cefotaxime, Cimetidine, Clinafloxacin, Clonidine, Cloxacillin, Codeine, Digoxin, 1,7-Dimethylxanthine, Flumequine, Fluocinonide, Fluticasone propionate, Furosemide- Glipizide, Hydrocortisoltisuide, Hydrocortisone, Ibuprofen 2-hydroxy-, Lincomycin, Metformin, Miconazole, Musk ambrette, Musk ketone, Musk moskene, Musk xylene, Norfloxacin, Norfluoxetine, Norgestimate, Norverapamil, Ormetoprim, Oxacillin, Oxolinic acid, Oxycodone, Paroxetine, Penicillin G, Penicillin V, Prednisolone, Prednisone, Promethazine, Roxithromycin, Sarafloxcin, Simvastatin, Sulfachloropyridazine, Sulfadiazine, Sulfadimethoxine, Sulfamerazine, Sulfanilamide, Sulfathiazole, Theophylline, Trenbolone, Trenbolone acetate Tylosin, Warfarin









Chemicals of particular concern

- **Butylbenzyl phthalate** (BBP), **bis (2-ethylhexyl) phthalate** (DEHP), and **bisphenol S** (BPS), plasticizer s commonly used in PVC, wires, containers etc. Studies indicate these compounds may be endocrine disruptors[8,9].
  - Concentrations of BBP in Bay sediment (maximum of 323 ng/g) exceed the "low apparent effects threshold" (LAET) of 63 ng/g.
  - The LAET is based on a correlation between chemical concentrations in field sediment (containing multiple chemicals) and toxicity to aquatic organisms or benthic communities[10].
  - For DEHP, the LAET, 1300 ng/g was not exceeded but concentrations are high enough (maximum of 605 ng/g) to signal concern.
  - BPS is infrequently analyzed in the environment and does not have a LAET, but its increasing use as a BPA substitute and its high stability, particularly in marine settings, suggest it could become a concern for environmental health.
  - Maximum concentrations of plasticizers in the Bay:
    - ***DEHP*** 459 ng/L water, 605 ng/g sediment, 968 ng/g mussel
    - ***BBP*** 14 ng/L water, 323 ng/g sediment, <10 ng/g mussel
    - ***BPS*** has yet to be examined.
- **Sulfamethoxazole**, an antibiotic commonly found in studies of surface water around the world at concentrations above the PNEC (predicted no effect concentration), 118 ng/L[11].
  - Three South or Lower South Bay water samples had levels close to or exceeding the PNEC (1,060, 736 and 113 ng/L)[7].
  - 12 additional samples were below the PNEC[1,7].
  - Maximum concentration in the Bay:
    - 1,060 ng/L water, 0.7 ng/g sediment, <4.7 ng/g mussel.

Results

- South Bay surface waters were sampled in 2006 as a "worst case scenario", these waters being the least diluted in the Bay.
  - 18 of the 39 PPCPs analyzed were measured at levels comparable to those reported in similar studies[7].
- A follow up study in 2010, which analyzed five sites throughout the Bay, detected 31, 10, and 17 chemicals (out of the 104 analyzed) in water, sediment and mussel tissue, respectively[1].
- Maximum concentrations from both studies (pharmaceuticals) (all sediment and mussel concentrations presented in dry weight):
  - 1,060 ng/L in water (sulfamethoxazole)
  - 678 ng/g in sediments (ciprofloxacin)
  - 90 ng/g in mussels (lomefloxacin)
  - All of these compounds are antibiotics.
- Maximum concentrations from both studies (personal care products):
  - 459 ng/L in water (bis(2-ethylhexyl) phthalate)
  - 605 ng/g in sediments (bis(2-ethylhexyl) phthalate)
  - 2,620 ng/g in mussels (di-n-butyl phthalate)
- In both studies, concentrations were generally at least 10-fold lower than concentrations expected to elicit toxic effects in organisms.

Conclusions / Future directions

- The concentration of PPCPs analyzed are generally below levels expected to produce adverse impacts.
- Dilution and biodegradation are most likely keeping PPCPs at acceptable levels.
- As the Bay Area population grows, PPCP levels in the Bay may increase unless better protocols are followed during prescription writing and drug disposal.
- The RMP is currently developing a new list of PPCPs to target in monitoring.
- Toxicity thresholds of PPCPs already evaluated in the Bay are also being scrutinized to determine if newly available toxicity data will affect the estimated risk associated with any chemicals.

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