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Emerging Chemicals and Analytical Methods

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Emerging contaminants in the water environment continues to be a strong research focus, as evidenced by the abundance of material published during 2004. This review summarizes peer-reviewed literature pertinent to the field of environmental engineering and science and related to analysis, occurrence, and fate of emerging chemical contaminants in the water environment, focusing on the following broad categories of emerging organic contaminants: antibiotics and pharmaceuticals; personal care products ingredients (PCPIs), endocrine disrupting compounds (EDCs), halogenated compounds (particularly brominated and fluorinated compounds), and disinfection byproducts (DBPs). To maintain this focus, articles pertaining specifically to human and ecological toxicity, bioconcentration or bioaccumulation, risk assessments, and innovative treatment and destruction methods are not included in this review. Additionally, summaries of literature covering organometallic compounds are not included in this review as in past years. Because of the sheer volume of literature covered by this topic, this review should not be considered to be comprehensive.

Acronyms that are used in this review for chemical species and analytical methods are summarized in Tables 1 and 2, respectively.

Table 1. Contaminant-Related Abbreviations.

AHTN	7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene	NDMA	N-nitrosodimethylamine
APEO	alkylphenol ethoxylate	NOR	norfloxacin
BFR	brominated flame retardant	NP	nonylphenol, or 4- <i>tert</i> -nonylphenol
BPA	bisphenol A, or 4,4'-isopropylidenediphenol	NP1EO	4-nonylphenol monoethoxylate
CIP	ciprofloxacin	NP2EO	4-nonylphenol diethoxylate
CTC	chlortetracycline	NPEO or NPnEO	nonylphenol polyethoxylate (n=1 to 17)
DBP	disinfection by-product	NSAID	non-steroidal anti-inflammatory drug
DEET	N,N-diethyl-3-toluamide	OP	4- <i>tert</i> -octylphenol
DEHP	bis-(2-ethylhexyl) phthalate, or di(2-ethylhexyl) phthalate	OPEO	octylphenol polyethoxylates
DES	diethylstilbestrol	OTC	oxytetracycline
DPMI	6,7-dihydro-1,1,2,3,3-pentamethyl-4(5 <i>H</i>)-indanone	OTNE	7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene
E1	estrone	PBDE	polybrominated diphenyl

			ether
E2	17 β -estradiol	PFA	perfluorinated acids
E3	estriol	PFCA	perfluoroalkyl carboxylate
EDC	endocrine disrupting compound	PFOS	perfluorooctane sulfonate
EE2	17 α -ethinylestradiol	PPCP	pharmaceuticals and personal care products
FQ	fluoroquinolone antibacterial agents	PCPI	Personal care product ingredients
HAA	haloacetic acids	TBBPA	tetrabromobisphenol A
HBCD	hexabromocyclododecane	TC	tetracycline
HHCB	1,-3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- γ -2-benzopyran	TYL	tylosin

Table 2. Abbreviations of Analytical Terms.

BSTFA	N,O-bis(trimethyl-silyl)-trifluoroacetamide
DAD	diode array detection
ELISA	enzyme-linked immunosorbent assay
ESI	electrospray ionization
GC	gas chromatography
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
IC	ion chromatography
ICP	Inductively coupled plasma
LC-MS	liquid chromatography – mass spectrometry
LLE	liquid-liquid extraction
MS	mass spectrometry
MS-MS	tandem mass spectrometry
MT-BSTFA	<i>N</i> -methyl- <i>N</i> -(<i>tert</i> -butyldimethylsilyl)trifluoroacetamide
MSTFA	<i>N</i> -methyl- <i>N</i> -(trimethylsilyl)trifluoroacetamide
PA	polyacrylate
PDMS	poly(dimethylsiloxane)
SIM	selected ion monitoring
SPE	solid phase extraction
SPME	solid phase microextraction
TOF	time of flight

General Reviews and Multiple Contaminant Types

Emerging contaminants are now well established as a major research area with the environmental science and engineering community. Richardson (2004) reviewed significant new developments in environmental applications of mass spectrometry published between 2002 and early 2004. In addition to an overview of general review articles and monographs related to emerging contaminants in general, new analytical methods were reviewed for several specific types of contaminants, including EDCs, pharmaceuticals, PBDEs, and fluorinated compounds. The review covered significant advances in extraction, separation (LC and GC), and MS detection methods.

Analysis of polar organic chemicals in water treatment systems using liquid chromatography-mass spectrometry (LC/MS) was reviewed by Zweiner and Frimmel (2004a). The reviewers provide a brief description of commonly-used ionization techniques and non-magnetic mass analyzers such as quadrupoles, ion traps, time-of-flight instruments. Widely-used and innovative extraction separation techniques are also discussed with an emphasis on chemistries required for polar contaminants. Finally, options for dealing with effects of sample matrices, and integrative (toxicity-directed) chemical analysis are discussed with particular applications in endocrine disrupting compounds. In a companion article, Zweiner and Frimmel (2004b) review published methods utilizing LC/MS for the analysis of emerging contaminants including pharmaceuticals, estrogens, surfactants, cyanotoxins, and pesticides. They also summarize papers describing the use of LC/MS for the analysis of humic substances, DBPs, microorganisms, speciation of inorganics, organometallics, and perchlorate.

The occurrence, fate, and transport of pharmaceuticals and EDCs during recharge of groundwater with treated wastewater is an emerging issue of importance, particularly in arid regions such as the southwest United States. The associated health and regulatory issues were reviewed by Asano and Cotruvo (2004) and Daughton (2004). Currently, there are uncertainties related to health concerns, which has limited the use of this water reclamation method.

Analysis. Raynie (2004) reviewed modern extraction techniques, including recent (2002-2003) developments in SPE, SPME, pressurized liquid extraction, and other methods. New developments in extraction techniques are often driven by analytical requirements related to emerging contaminants in environmental samples.

Because of the high chemical variability in sewage treatment plant effluents, a series of bioassays may provide very useful information for detecting potential toxicity risks (Aguayo et al., 2004). Commonly detected compounds in wastewater effluent included BPA, OP, and DEHP. Through the use of a SPE procedure along with the GC/MS identification and the information from bioassays, it is possible to select the compounds requiring further research.

Petrovic et al (2004) provide a review on toxicity identification evaluation (TIE) analysis for endocrine disrupting compounds in environmental samples. TIE methods utilize a bioassay screening method for measuring endocrine effects of samples and extracts prior to analysis by instrumental methods. The advantage to this integrated approach is that a sample or extract is first identified as having an estrogenic or androgenic activity prior to instrumental analysis to determine the cause for the activity. Several studies using TIE are described in the review with the details of the

extraction/fractionation screening and analysis, with most using solid phase extraction and GC/MS for the detection of hormones and other steroids, alkylphenols, surfactants and pesticides.

To characterize the compounds that contribute to the estrogenicity of wastewater effluents, Heisterkamp et al. (2004) developed a method that combines a bioassay with LC-MS analysis. Samples underwent liquid-liquid extraction (LLE) and fraction using size exclusion chromatography, prior to analysis by LC-ESI-MS-MS and a recombinant yeast screen to measure estrogenicity. The combined method is promising, although the levels of quantitation need to be improved.

Benijts et al (2004a) evaluate methods for minimizing matrix effects which result in ion suppression in analysis of endocrine disrupters using electrospray ionization liquid chromatography mass spectrometry. The use of ammonium formate in the mobile phase, efficient sample clean-up, and the use of labeled internal standards all proved beneficial in the analysis of hormones, plasticizers, and pesticides. They recommend procedures to assess matrix effects in quantitative method development and validation using LC/MS/MS. A related article by Benijts et al (2004b) describes a method for measurement of 35 endocrine disrupting chemicals using polymeric solid-phase extraction combined with both negative and positive ion LC-ESI-MS/MS. They report detection limits between 0.1 and 20.0 ng/L, and apply the method to samples of municipal waste water, river water and industrial wastewater.

Nineteen analytes, including pharmaceuticals, hormones, antioxidants, and a plasticizer, were extracted from water samples using continuous liquid-liquid extraction of 40 liter samples with dichloromethane (Soliman et al., 2004). Methylene chloride

extracts required no cleanup or derivatization prior to GC-MS analysis. Quantitation limits were 8-250 ng/L, and the method was used to detect many of the compounds in treated wastewater from water reuse plants in southern California.

Simultaneous extraction and determination of 8 estrogens, 5 pesticides, and BPA was accomplished by concentrating a 500-mL sample onto an RP-18 SPE cartridge, followed by HPLC-MS using atmospheric pressure chemical ionization (Rodriguez-Mozaz et al., 2004c). Positive ion mode was used for pesticides, while negative ion mode was used for BPA and the estrogens. This method achieved detection limits of 2-15 ng/L, and was used to verify that these contaminants were removed to below detection limits during drinking water treatment.

Occurrence and Fate – Wastewater Treatment Systems. Based on observations at wastewater treatment plants in Austria, removals of many EDCs and pharmaceuticals in wastewater treatment plants are correlated to the sludge retention time (SRT) (Kreuzinger et al., 2004). Higher SRT, as found in plants including nitrification, were found to have better removals of many compounds, including total natural steroids, BPA, and NP and its metabolites. However, carbamazepin and diazepam were not effectively removed under any of the conditions studied.

Concentrations of selected pharmaceuticals (analgesics, β -blockers and anti-depressants) as well as caffeine, the anti-bacterial triclosan, and the insect repellent DEET were determined in different sewage samples from Tromsø/Norway and in seawater from Tromsø-Sound (Weigel et al., 2004a). Caffeine, triclosan, ibuprofen and its major metabolites hydroxy- and carboxy-ibuprofen were present in all sewage samples, and additional pharmaceuticals were observed in sewage containing hospital

effluents. Concentrations were in the range of 20-293 µg/L for caffeine, 0-2-2.4 µg/L for triclosan and 0.1-20 µg/L total for ibuprofen and its metabolites. In seawater samples, only caffeine (7-87 ng/L), DEET (0.4-13 ng/L) and ibuprofen and its metabolites (sum concentration up to 7.7 ng/L) were detected.

Occurrence and Fate – Surface Water and Sediment. Integrated bioassay screening and instrumental analysis for detection of potential endocrine disrupting compounds in surface water and sediment samples was described by Céspedes et al. (2004). Twenty seven compounds (non-ionic surfactants, alkylphenols, steroid sex hormones, and phthalates) were screened for estrogenic activity, and analyzed in river water samples and sediment extracts using reverse-phase solid phase extraction (SPE) coupled with liquid chromatography electrospray ionization mass spectrometry. Sediments were extracted using pressurized liquid extraction followed by SPE clean-up. Detection limits using selection ion monitoring averaged near 0.1 µg/L for water and near 1 µg/kg for sediments for most compounds. Estrogenic activity in river water was correlated to the presence of nonylphenolic compounds at concentrations up to 44 µg/L and 1172 µg/kg in sediments, and to the intermittently detected estrogens detected low ng/L concentrations in river water.

Occurrence and Fate – Sludges, Soil, and Groundwater. Snyder et al. (2004) studied biological attenuation of PPCPs and EDCs in water reuse applications using lab and field studies. Some compounds were found to biodegrade rapidly (>90% removal), whereas others were recalcitrant. Results of laboratory batch biodegradation experiments were confirmed in field observations, suggesting that some of these compounds will be attenuated in unsaturated and saturated zones of the subsurface.

Barnes et al. (2004) analyzed groundwater impacted by leachate from a closed landfill in Oklahoma and found DEET and tri(2-chloroethyl) phosphate (a fire retardant) in samples from 4 wells screened in the leachate plume. Results indicate that landfills can be a source of PPCPs, EDCs, surfactants, hormones, and other “emerging” contaminants that are persistent in groundwater.

Antibiotics and Other Pharmaceuticals

This category of emerging contaminants includes both human and veterinary antimicrobial drugs, analgesics, antidepressants, and a host of other pharmaceutically-active compounds (PhACs). Dębska et al. (2004) presented a brief review of pharmaceutical compounds in the aquatic environment, focusing on inputs, fate and transformations, and analytical methods.

Analytical Methods. *Multiple analytes.* Cahill et al. (2004) describe a method for 17 commonly-used pharmaceuticals likely to occur in surface and ground water using solid phase extraction LC-ESI-MS. Detection limits ranged from 0.003 to 0.15 µg/L. The method was used in a national reconnaissance study pharmaceuticals of United State streams with nonprescription compounds, such as acetaminophen, caffeine, and cotinine (a nicotine metabolite) detected most frequently.

Stolker et al. (2004) use liquid chromatography tandem mass spectrometry (LC/MS/MS) for the detection and quantification of 13 commonly-used pharmaceuticals in surface, drinking, and groundwater. Samples are extracted using the cation exchange form of the Waters OasisTM HLB solid phase extraction cartridges. Detection limits for four analgesics (acetylsalicylic acid, diclofenac, ibuprofen, and paracetamol), three

antibiotics (sulfamethoxazole, erythromycin, and chloramphenicol), five blood-lipid regulators and beta-blockers (fenofibrate, bezafibrate, clofibric acid, bisoprolol, and metoprolol), and the anti-epileptic carbamazepine ranged from 5-25 ng/L. Trace levels of acetylsalicylic acid, carbamazepine, clofibric acid, and sulfamethoxazole were detected in nearly all sample types. The identity and concentration of these pharmaceuticals were confirmed in several samples using liquid chromatography-quadrupole time-of-flight (Q-TOF) MS.

Two different drug types, lipid regulators (clofibric acid, bezafibrate, gemfibrozil, fenofibrate) and β -blockers (atenolol, sotalol, metoprolol, betaxolol), were extracted from water samples by SPE and determined LC-ESI-MS-MS (Hernando et al., 2004b). Negative ion mode was used for acidic compounds and positive ion mode was used for basic compounds. Detection limits in effluent samples ranged from 0.017 – 1.25 $\mu\text{g/L}$.

A automated capillary LC-MS-MS method was developed for analyzing pharmaceuticals (sulphamethoxazole, bezafibrate, metoprolol, carbamazepine and bisoprolol) in surface waters (Pitarch et al., 2004). Detection limits were around 50 ng/L (somewhat higher than typical SPE-LC-MS-MS methods) using a 25 μL sample, and the method was proposed for screening these compounds in water samples.

Zuehlke et al. (2004) describe a method for measuring trace levels of several analgesic and antipyretic pharmaceuticals (dimethylaminophenazone, phenazone, propyphenazone, metamizole, and carbamazepine) and their metabolites using in situ derivatization reverse-phase solid phase extraction with atmospheric pressure chemical ionization LC-MS-MS. APCI was found to be less prone to matrix interferences than ESI and thus more suitable for analysis of wastewater extracts. In situ derivatization was

necessary to improve recovery of some of the metabolites, and detection limits were estimated near 0.01 to 0.02 µg/L. The method was applied to samples of treated and untreated wastewater, as well as treated and untreated river and lake water.

Antibiotics. A multi-residue method for analysis of 4 sulfonamide and 5 fluoroquinolone antibiotics, and the dehydrate reductase inhibitor trimethoprim, is proposed by Renew and Huang (2004). The method utilizes an anion-exchange cartridge in tandem with a hydrophilic–lipophilic balance (HLB) to help minimize interferences prior to analysis by liquid chromatography electrospray mass spectrometry with a single quadrupole. Among the seven antibiotics monitored, ciprofloxacin, ofloxacin, sulfamethoxazole, and trimethoprim were frequently detected in the secondary effluents of two wastewater treatment plants from the southwestern United States.

Lindberg et al. (2004) developed a method for determination of several classes of antibiotics (FQs, sulfonamides, trimethoprim, β-lactams, nitroimidazoles, and TCs) in hospital wastewater using reverse phase SPE with liquid chromatography-ion trap tandem mass spectrometry. Chemically and structurally similar compounds were used as internal standards to help correct for variation in recovery using the C₂/ENV+ SPE cartridges and suppression due to sample matrix. Six antibiotics were detected in raw hospital sewage; the ranges detected for CIP and metronidazole were 3.6–101.0 µg/L and 0.1–90.2 µg/L, respectively.

Capillary electrophoresis with fluorescence detection with broad wavelength excitation (200–400 nm) was used for analysis of nine (fluoro)quinolones, including CIP and NOR (Ferdig et al., 2004). Without pre-concentration, detection limits were 3–45

ng/L for eight of the analytes and 145 ng/L for flumequine. SPE improved detection limits to the low ng/L and eliminated matrix interferences. SPE (Oasis HLB) and analysis by reversed phase HPLC with fluorimetric detection was found to be applicable for quantifying ten veterinary quinolones in water samples (Prat et al., 2004). Detection levels were in the low ng/L range for pre-concentration of a 250-mL sample.

Fluoroquinolones (norfloxacin and ciprofloxacin) in soils can be screened using a microwave assisted extraction method coupled with derivatization and fluorometric detection (Morales-Muñoz et al., 2004). The derivatization step produced highly fluorescent FQ complexes by reaction in a terbium (Tb^{3+})/tri-*n*-octylphosphine oxide (TOPO)/cetylpyridinium chloride (CPCI)/acetate buffer solution. The method provides qualitative information on levels of FQ contamination and does not differentiate between specific FQs.

The veterinary antibiotics OTC, TYL, and sulfachloropyridazine (SCP) were simultaneously extracted from groundwater and surface water samples using two SPE cartridges in series: a strong anion exchange cartridge followed by an Oasis HLB cartridge (Blackwell et al., 2004a). Analytes were determined using a gradient elution HPLC method with UV detection, resulting in detection limits of 0.35 µg/L for OTC and TYL and 0.25 µg/L for SCP for concentration of a 0.4-L sample. The method was also used for recovering the same three antibiotics from soils and pig slurry after extraction by ultrasonication (Blackwell et al., 2004b). Additional fluorescence detection was used for detection of SCP. Detection limits for OTC were 18 µg/kg and 70 µg/L in soil and pig slurry, respectively; 40 µg/kg for TYL in soils; and 18 µg/kg and 140 µg/L for SCP in soil and pig slurry, respectively.

Another method utilizing ion trap LC/MS/MS with SPE for macrolide antibiotics (erythromycin, tylosin, and roxithromycin) was described by Yang and Carlson (2004a) with detection limits below 0.10 µg/L. Samples of river water and sewage treatment plant influent and effluent were analyzed by the method with trace levels of an erythromycin degradate and tylosin occurring only in the sewage-impacted water.

A combined SPE/radioimmunoassay method was found to be an effective tool for monitoring TCs and sulfonamides in surface waters and wastewaters (Yang and Carlson, 2004b). The method provides a composite result for compounds within each antibiotic family and was found to have detection limits of about 0.05 µg/L. SPE (Oasis HLB) followed by LC-MS-MS effectively quantifies seven TC and six sulfonamide antibiotics (Yang et al., 2004). The method could be used for a ranged of water matrices, with method detection limits of about 0.05 µg/L for extraction of 120-mL samples. TYL and TC concentrations in surface water and groundwater samples were measured using ELISA techniques commonly used for measuring antibiotic residues in foods (Kumar et al., 2004). TYL and TC detection limits were 0.1 and 0.05 µg/L, respectively.

Enrofloxacin, a FQ antibiotic used for swine production, was extracted from swine wastewater samples by liquid-liquid extraction with dichloromethane and analyzed by reversed phase HPLC-DAD (Pierini et al., 2004). The method had detection limits of 0.6 µg/L in lagoon sewage. Enrofloxacin was detected in pigsty holding tanks at 0.27-0.51 mg/L, but was not detected in lagoon wastewater due to a combination of solids deposition, dilution with rainwater, or degradation processes.

Pressurized liquid extraction was used to extract tetracycline, macrolide and sulfonamide antibiotics from agricultural soils (Jacobsen et al., 2004). Extracts were cleaned up with tandem SPE and analyzed by two slightly different LC-MS-MS methods. Detection limits were <5.6 µg/kg for CTC and OTC, <5.5 µg/kg for tylosin A.

Gobel et al. (2004) used reverse-phase LC-MS-MS for detection of four macrolides, six sulfonamides, a human sulfonamide metabolite, and trimethoprim in wastewater samples. Oasis HLB SPE cartridges were used for extraction. The method was applicable to raw and treated wastewaters, with detection limits for most analytes <100 ng/L in raw wastewater and <25 ng/L in secondary effluent.

Analgesics/NSAIDs. Quintana and Reemtsma (2004) describe a multi-residue method for analysis of 12 acidic pharmaceuticals (non-steroidal anti-inflammatory drugs and bezafibrate), two metabolites and triclosan in surface and wastewater by liquid chromatography tandem mass spectrometry. An ion pairing agent was added to improve chromatography and increase signal intensity. Polymeric (Oasis HLBTM) solid phase extraction was used to concentrate analytes and provided detection limits from 5-200 ng/L. Traces of salicylic acid, clofibric acid, ketoprofen, bezafibrate, diclofenac, and indomethac were detected in untreated and treated wastewater, as well a lake in Spain receiving treated wastewater.

NSAIDs (ibuprofen, naproxen, ketoprofen, tolfenamic acid and diclofenac) in water samples can be extracted using a polyacrylate SPME fiber and derivatized on-fiber prior to GC-MS analysis (Rodriguez et al., 2004). After extraction of a 22-mL sample, the SPME fiber was placed in the headspace of a vial with MTBSTFA. The method

provided results comparable to a more complicated SPE procedure, and achieved quantification limits of 12-40 ng/L.

Four anti-inflammatory drugs (ibuprofen, naproxen, tolfenamic acid, and diclofenac) were analyzed in water samples using an automated SPME method (PA fiber), with on-fiber silylation with MT-BSTFA, and analysis using GC-MS (Carpinteiro et al., 2004). To screen a large number of samples, an algorithm was developed for strategic compositing of samples in order to reduce the number of extractions and analyses. After analysis of composited samples, concentrations of each drug in the original samples could be accurately estimated.

A hollow-fiber liquid phase microextraction procedure effectively extracts acidic drugs (including clofibric acid, naproxen, ibuprofen, and diclofenac) from 22-mL water samples for analysis by LC-ESI-MS-MS (Quintana et al., 2004b). The hollow fiber was a tubular polypropylene membrane impregnated with 1-octanol, filled with 10 mM ammonium carbonate, and placed in the sample, which was adjusted to pH 2. Although the method eliminates matrix effects and has detection levels of 0.5-42 ng/L, method precision was low because of the manual operation of the procedure. A similar method was reported by Wen et al. (2004) for analysis of NSAIDs in wastewater samples. The major difference was an additional liquid-liquid extraction step, wherein the first extract was acidified and used as the donor solution for another hollow-fiber extraction into 0.01 M NaOH. With the high enrichment factor, analytes can be detected by HPLC with UV detection at 280 nm. The detection limit for ibuprofen in wastewater was 100 ng/L.

Oasis HLB SPE cartridges were also used for extraction of acidic and neutral drugs from surface water (Weigel et al., 2004b). GC-MS was used for analysis after

derivatization with methyl chloromethanoate. For 1-L samples, the quantitation limit for ibuprofen was 0.05 ng/L and <0.4 ng/L for seven other analytes.

Other. Lamas et al. (2004) utilize aqueous derivatization with solid phase micro-extraction (SPME) and gas chromatography mass spectrometry to measure selective serotonin uptake inhibitors – venlafaxine, fluvoxamine, fluoxetine, citalopram and sertraline – in water samples. Detection limits were estimated to be less than 0.1 µg/L, and untreated wastewater was found to contain traces of venlafaxine and citalopram.

Occurrence and Fate – Wastewater Treatment Systems. Removals of triclosan and several acidic, neutral, and basic pharmaceuticals in 10 European wastewater treatment plants were studied by Paxéus (2004). Ibuprofen and triclosan were removed to the greatest extent (90%) followed by naproxen (80%), gemfibrozil (55%) and diclofenac (39%). Effluent concentrations ranged from 0.05 µg/L for trimethoprim to 0.56 µg/L for gemfibrozil. Activated sludge treatment usually removed <10% of the neutral compound carbamazepine and the basic compounds atenolol, metoprolol and trimethoprim.

Out of 31 antimicrobial drugs analyzed, ciprofloxacin, clarithromycin, erythromycin-H₂O, ofloxacin, sulfamethoxazole, sulfapyridine and tetracycline were frequently detected in the effluents of 8 wastewater treatment plants in 5 Canadian cities (Miao, et al., 2004). However, the concentrations did not exceed 1µg/L, meaning the levels are unlikely to adversely affect aquatic organisms. The antimicrobials frequently detected in effluents appeared to be those heavily prescribed in Canada for medical applications; no antimicrobials used exclusively for veterinary applications were detected. The

detection of sulfapyridine in effluents was the first report of the compound in environmental studies.

Carbamazepine is a very persistent substance and may be a useful parameter for detecting wastewater in the aquatic environment (Clara et al., 2004b). Wastewater treatment plant influent concentrations were as high as 2,500 ng/L, and carbamazepine was found not to degrade or be retained on solids in wastewater treatment plants over a range of solids retention times. During soil infiltration and subsurface flow, only insignificant concentration variations were detectable, apparently because dilution was the dominant process affecting the measured concentrations.

Removals of carbamazepine, diclofenac, ibuprofen and bezafibrate as a function of solids retention time (SRT) in lab-scale and full-scale WWTPs were investigated by Strenn et al. (2004). In lab-scale experiments, ibuprofen and bezafibrate were completely removed at $SRT > 1-2$ d, whereas carbamazepine and diclofenac were not significantly removed at any SRT. In a related study, Clara et al. (2004a) removal rates of these compounds, as well as EE2 and two polycyclic musks, were similar in membrane bioreactors and conventional activated sludge systems.

Amoxicillin is easily removed in by biological treatment, ion exchange, reverse osmosis, and UV oxidation (Morse and Jackson, 2004). Eighteen antibiotics were not readily biodegraded in standardized biodegradation tests, although some compounds were degraded abiotically (Alexy et al., 2004). When sodium acetate was included in the tests, some of the compounds were partially biodegraded, but toxicity was not completely eliminated.

The effects of six common pharmaceuticals (carbamazepine, sulfamethoxazole, propranolol hydrochloride, diclofenac sodium, ofloxacin and clofibric acid) on the anaerobic digestion process were assessed (Fountoulakis et al., 2004). Clofibric acid and sulfamethoxazole had little effect at concentrations up to 400 mg/L, whereas diclofenac sodium and propranolol at >100 mg/L completely inhibited methane production. Inhibition of methanogenesis was correlated with the compounds' tendency to sorb to anaerobic biomass.

Occurrence and Fate – Surface Water and Sediment. Environmental fate of antibiotics is closely related to pH because it governs the form of these compounds: anionic, neutral, or cationic (Qiang and Adams, 2004). Potentiometric methods were used to measure pK_a values of 26 common human and veterinary antibiotics. Results will facilitate further research and predictions of the environmental fate of these contaminants.

The Pharmaceutical Assessment and Transport Evaluation (PhATE) model was developed to estimate environmental concentrations of pharmaceutical compounds in watersheds, and is based on a mass balance which includes inputs from upstream reaches, discharges from POTWs, transformation and loss mechanisms with a river, and man-made withdrawals of water (Anderson et al., 2004). Mass loading includes per capita usage and excretion, as well as removal in POTWs depending on treatment methods, prior to discharge to receiving waters. Losses in surface waters were modeled as composite first-order degradation reaction which accounts for biodegradation, photolysis, sorption, and any other loss mechanisms. Estimated concentrations were highly dependent on inputs such as removals in POTWs and loss

coefficients in streams. The model was intended to be a screening tool for estimating environmental or human health risks due to these compounds in surface waters.

Twelve PhACs representing different therapeutic types, selected on the basis of potential risk, were monitored in surface waters and WWTP effluents of the United Kingdom (Ashton et al., 2004). Of the 10 compounds detected in effluent samples, propranolol and ibuprofen were detected in 100% and 84% of the samples, respectively, at median concentrations of 76 ng/L and 3086 ng/L, respectively. Concentrations and frequency of detection were lower in surface waters, although potential long-term environmental risks are unknown.

Pharmaceuticals and metabolites were found to be ubiquitous in the River Elbe and its tributaries in Germany and the Czech Republic (Wiegel et al., 2004). The main substances found in the Elbe in 1998 were diclofenac, ibuprofen and carbamazepine as well as various antibiotics and lipid regulators in the concentration range of <20-140 ng/L. Additional sampling and analyses in 1999 and 2000 showed that metabolites of several drugs (phenazone, isopropyl-phenazone and paracetamol) contributed significantly to the total concentration of pharmaceuticals. The metamizole metabolites N-aceyl-4-aminoantipyrine (AAA) and N-formyl-4-aminoantipyrine (FAA) were found in concentrations from <20-939 ng/L.

The presence of seven PPCPs and EDCs (clofibric acid, naproxen, ibuprofen, fluoxetine, chlorophene, triclosan, bisphenol A) in surface waters near New Orleans, Louisiana was attributed to non-point source pollution with sewage from the aging wastewater collection system (Boyd et al., 2004). Analytes were extracted using SPE disks, derivatized with BSTFA, and quantified by GC-MS. BPA was detected up to 158

ng/L, ibuprofen up to 674 ng/L, triclosan up to 29 ng/L, naproxen up to 145 ng/L, and the other analytes were not detected over a 6-month sampling period.

Under abiotic conditions both hydrolysis and direct photolysis could be responsible for the transformation and removal of amoxicillin in aquatic environment, especially in slightly basic media (Andreozzi et al., 2004). Based on indirect photolysis experiments in the presence of natural photosensitizers, nitrate ions have no influence on the photodegradation rate of amoxicillin, while humic acids are enable to enhance the photodegradation rate. The results of batch experiments performed under biotic conditions show that biodegradation by activated sludge is an effective pathway through which amoxicillin can be removed from the aquatic environment. Five sulfa drugs with five-membered heterocyclic substituents (sulfamethoxazole, sulfisoxazole, sulfamethizole, sulfathiazole, and sulfamoxole) undergo photolytic degradation, with rates dependent on pH and the specific substituent (Boreen et al., 2004). Direct photolysis of these compounds produces sulfanilic acid as a common photodegradation product.

Occurrence and Fate – Sludges, Soil, and Groundwater. Pharmaceutical residues have been detected in soils, sediments and sludges and tend to be persistent (Beausse, 2004). Some compounds are completely biodegraded, while others tend to strongly sorb and remain persistent and biologically active. Drug types of most concern in solid environmental matrices appear to be FQs, TCs, steroid hormones, analgesics and anti-inflammatories, and avermectin. The practice of land-applying solid residuals from municipal and agricultural wastewater results in diffuse antimicrobial contamination

which may have serious impacts (Rooklidge, 2004). Presently, mobility and fate of most of these compounds in soils as well as their potential risks are poorly understood.

The main risk of using animal wastes containing antibiotics as fertilizers is the potential for development of antibiotic-resistant soil bacteria, which has been demonstrated in soil column studies (Rysz and Alvarez, 2004). Leaching potential from soil was measured for several pharmaceuticals to assess risk to groundwater (Oppel et al., 2004). In the soils tested, leaching potential was low for diazepam, ibuprofen, ivermectin and carbamazepine, whereas clofibric acid and iopromide were very mobile.

Kinetic and equilibrium expressions that can be incorporated into hydrogeologic models to predict performance of bank filtration systems and groundwater recharge for removal of PhACs were presented by Heberer et al. (2004). Bank filtration decreased contaminant concentrations by dilution (carbamazepine and primidone) or partial removal (diclofenac), or completely removed PhACs (antibiotics and estrogens). Several polar PhACs, particularly primidone, were found to be readily transported during bank filtration and was proposed as an indicator of whether wastewater effluent is being transported to groundwater at bank filtration sites.

Adsorption of five sulfonamide antibiotics (sulfanilamide, sulfadimidine, sulfadiazine, sulfadimethoxine, and sulfapyridine) was nonlinear and increased with aromaticity and electronegativity of functional groups (Thiele-Bruhn et al., 2004). Freundlich adsorption coefficients (K_f) ranged from 0.5 – 6.5 and $1/n \leq 0.76$, and the antibiotics strongly interacted with soil organic matter. Adsorption of these antibiotics to pig slurries was much stronger (Thiele-Bruhn and Aust, 2004). Addition of pig slurry to soils resulted in a pH decrease, which reduced the sorption and increased the mobility of the

sulfonamides. Because possible pH changes due to manure addition can affect sorption and mobility, these effects should be included when assessing retention of pharmaceutical residues in agricultural soils.

Sorption of three tetracyclines (OTC, chlortetracycline [CTC], and TC) to kaolinite and montmorillonite clays is due to cation exchange and surface complexation (Figuerola et al., 2004). Sorption of these compounds is affected by solution pH competing ions. Kulshrestha et al. (2004) also explored sorption of OTC to clays and determined Freundlich parameters. Sorption was found to decrease with increasing pH. At lower pH, OTC has a net positive charge and more effectively interacts with negative surface charges of clay particles. Dissolved organic matter impeded sorption of OTC, which may have implications for mobility in soil systems. In autoclaved soil pore water, the chemical stability of CTC and four of its degradation products was dependent on photolysis, temperature, and components of the soil matrix (Soeberg et al., 2004). Half-lives also increased as pH decreased.

Respirometer testing can be used to assess the effects of veterinary antibiotics in soils (Vaclavik et al., 2004). Although some transformation of the antibiotics (including TC, OTC, TYL, and SCP) occurred, they were not used as substrates and significantly reduced respiration by soil microorganisms.

Drinking Water Treatment. The analgesic drugs phenazone, propyphenazone, and dimethylaminophenazone and two phenazone metabolites were detected in Berlin drinking water (Zühlke et al., 2004a). These compounds were analyzed by first derivatizing the analytes by addition of acetic anhydride to the samples to improve SPE

recoveries, followed by automated SPE and further derivatization with MTBSFA.

Analysis by GC-MS resulted in quantitation limits of 3-6 ng/L.

Under conditions similar to those found in disinfection systems, many pharmaceuticals are rapidly oxidized by chlorine, but react very slowly with monochloramine (Pinkston and Sedlak, 2004). The possible impacts of chlorination products are currently unknown. During chlorination of drinking waters and wastewaters, sulfamethoxazole (SMX) should be rapidly transformed (Dodd and Huang, 2004). At pH 7 and 25°C, SMX reacts rapidly with 1.4 mg/L free chlorine (half-life of 23 seconds), but reacts very slowly (half-life of 38 hours) with combined chlorine under similar conditions. Reaction mechanisms and products were also identified.

Endocrine Disrupting Compounds – Hormones

Analytical Methods. Six natural and synthetic estrogens (diethylstilbestrol (DES), E1, E2, mestranol (MES), EE2, and estriol) were simultaneously quantified in wastewater at detection levels between 1 and 6 ng/L by Quintana et al. (2004). The method included concentration using off-line SPE (Oasis HLB cartridges); silylation of –OH groups with MSTFA; and analysis by GC-MS or GC-MS-MS. Using this method, it was determined that estriol was completely removed, estradiol was partially removed, and estrone was not removed during wastewater treatment. The same research group developed a SPME method for determination of the same hormones at low ng/L levels (Carpinteiro et al., 2004). After extraction onto a polar polyacrylate SPME fiber, analytes were derivatized on-fiber with MSTFA and analyzed by GC-MS-MS. Detection

limits for the five analytes were similar to SPE methods and ranged from 0.2 – 3 ng/L; however, the method was not effective for detection of DES and MES in raw sewage.

Komori et al. (2004) developed an analytical method for simultaneous determination of a wide range of free and conjugated estrogens. The method included SPE with Oasis HLB, two cleanup steps, and analysis by LC-MS-MS, resulting in detection limits <1.4 ng/L. The method was used to determine that about 50% of the influent estrogens are removed during wastewater treatment. A method for simultaneous quantification of a range of EDCs, including E1, E2, EE2, BPA, NP, and OP, was developed by Liu et al. (2004). After extraction with Oasis HLB cartridges and derivatization with BSTFA, SIM-GC-MS was used for analysis with limits of quantitation between 1 and 17.4 ng/L. The method was used to analyze river water and wastewater effluent samples.

Rodriguez-Moza et al. (2004a) describe a highly specific and sensitive method for analysis of natural and synthetic estrogens in water samples using automated on-line solid phase extraction coupled with electrospray ionization tandem mass spectrometry. Estradiol, estrone, estriol, estradiol-17-glucuronide, estradiol-17-acetate, estrone-3-sulfate, ethynyl estradiol, and DES were determined in surface and treated water with detection limits between 0.02 and 1.02 ng/L. The method was applied raw and finished samples from a drinking water treatment plant to evaluate removal efficiency. Only estrone and estrone-3-sulfate were detected in the river water used as source. After progressive removal through the various treatment steps, no estrogens were detected in the finished drinking water.

A method for simultaneous determination of 35 EDCs in environmental water samples was developed and validated (Benijts et al., 2004a). The method utilized wide

spectrum SPE (Oasis HLB) cartridges for pre-concentration, followed by positive and negative electrospray ionization with LC/MS/MS. Detection levels were generally lower for positive ionization, with quantitation limits ranging from 0.1-2.0 ng/L. The method also utilized stable isotope-labeled standards to account for matrix effects and analyte losses during extraction. In a related paper, extended sample cleanup, particularly the SPE wash step, was suggested as a means of eliminating many matrix effects for analysis of these compounds (Benijts et al., 2004b).

Gomes et al (2004) discuss sample preparation and LC/MS considerations in the steroid estrogens in sediment and sewage sludge using a case study approach to illustrate the development of an analytical method. Variations in recovery of added estrogens could be attributed to biotransformation, matrix suppression, and co-eluting interferences when using a single mass analyzer.

Biosensors have many applications for monitoring EDCs in environmental samples, as covered in a review by Rodriguez-Moza et al. (2004c). Biosensors that detect specific compounds, a group of related compounds, or endocrine disrupting effects are currently available. Seifert (2004) developed a sensitive enzyme-linked receptor assay with a luminescent substrate for analysis of E2 in water samples. The method had detection limit of 20 ng/L. Tschmelak et al. (2004) developed an automated immunoassay method for estrone with a quantitation level of 1.4 ng/L, comparable to many chromatographic-MS methods. The method utilized an optical biosensor, and required no sample pretreatment or pre-concentration of the 1-mL sample. A prototype optical immunosensor was developed to rapidly and simultaneously analyze atrazine, isoproturon, and estrone in river waters at detection limits of 0.155, 0.046, and 0.084

µg/L, respectively (Rodriguez-Moza et al., 2004b). The device is based on a rapid fluoroimmunoassay using an optical transducer chip with derivatives of the three contaminants in discrete locations. Total run time per sample is about 15 minutes, which includes sample preparation and analysis and a regeneration step.

Schneider et al. (2004) developed an alternative immunoassay method for detection of EE2 in water and wastewater samples. The method is based on a novel long chain biotinylated EE2 derivative for use in an optimized direct competitive ELISA. The method had a detection limit of 14 ng/L, but showed cross-reactivity with some EE2 metabolites. Hanselman et al (2004) compared three commercially available enzyme immunoassays for measuring estrogens in dairy wastewater. Estrogens were extracted with ethyl ether prior to measurement. Because of coeluting matrix interferences, the three methods did not give similar results, and GC-MS analyses were unable to determine which assay was most accurate.

BSTFA and MTBSTFA, commonly used for derivatization of E1 and EE2, produces silylated derivatives (Shareef et al., 2004). For EE2, these derivatives can be partially converted to their E1 derivatives during the derivatization procedure or during chromatographic analysis. These results suggest that some previous studies using these derivatization agents may have overestimated E1 concentrations while underestimating EE2.

Occurrence and Fate – Wastewater Treatment Systems. A model for predicting concentrations of E1, E2, and EE2 in raw and treated wastewater was presented by Johnson and Williams (2004). The model was based on a mass balance that included inputs from different groups of the human population with different amounts excreted,

partial transformation in sewer systems, and removals in activated sludge wastewater treatment plants. The model provided fairly good predictions, and could be useful to predict potential impacts on receiving waters. Joss et al. (2004) presented a model for predicting removals of E1, E2, and EE2 in wastewater treatment plants, based on observed removals in laboratory testing and in full-scale treatment systems. The model includes sorption to sludge solids and biodegradation. More than 90% of these compounds can be typically removed in plants that include nitrogen removal by nitrification/denitrification.

Estrogenic activities of the influent and effluent of 8 wastewater treatment plants was assessed by Coors et al. (2004) using a reporter gene-based bioassay. Influent estradiol equivalents (EEQ) ranged from 5.7 to 65.8 ng/L, with higher levels associated with higher inputs from industrial sources. After secondary or tertiary treatment, EEQs were as high as 5.4 and 1.4 ng/L, respectively. Decant waters from dewatering of anaerobically digested sludge had EEQs as high as 74.3 ng/L, but levels from dewatering undigested sludge were lower. Aerni et al. (2004) analyzed 90 effluent samples from five wastewater treatment plants for chemical analysis and bioassays. E1, E2, and EE2 concentrations were as high as 51, 6, and 2 ng/L, respectively. Surfactants and their metabolites were often detected, but these compounds contributed little to the overall estrogenicity of the samples.

A group of seven sex hormones, nonylphenol polyethoxylates, and their metabolites were measured in samples from pilot-scale treatment plants treating spiked, synthetic wastewater (Esperanza et al., 2004). Steroids and surfactants were extracted by SPE using C18 and graphitized carbon black phases, respectively, with subsequent analysis

by HPLC-diode array detection or GC-MS. Total NPnEO removal was greater than 96%, although some metabolites were apparently formed during treatment.

Testosterone, androstenedione, and progesterone were completely removed from the aqueous phase and more than 94% of the estradiol was removed, but removals were poor for estrone and estriol.

E1, E2, E3, and EE2 can be biodegraded in nitrifying activated sludge and by nitrifiers such as *Nitrosomonas europaea* (Shi et al., 2004). Of these compounds, E2 was the most rapidly degraded by NAS, producing E1 and other metabolites in succession; however, E2 was not biodegraded by pure cultures of *N. europaea*. The importance of an activated sludge consortium in degrading these compounds was demonstrated.

During wastewater treatment, 17 β -estradiol and 17 α -ethinylestradiol sorb to colloidal organic carbon (COC) with partitioning coefficients ranging up to 179 $\times 10^3$ and 430 $\times 10^3$ L/kg_{COC}, respectively (Holbrook et al., 2004). Sorption to COC is not completely explained by sorption to colloidal proteins or polysaccharides. Results suggested that sorption can influence the fate of these compounds during activated sludge treatment.

Estrone was used as a model EDC to assess removal from secondary effluent by coagulation with FeCl₃, adsorption to powdered activated carbon (PAC), and a PAC-microfiltration process (Chang et al., 2004). E1 was not removed by coagulation, but was effectively removed using the processes with PAC. PAC dosage and contact time were apparently the most important process parameters.

E1, E2, E3, and EE2 were detected by GC-MS in wastewater and surface water samples from Paris, France (Cargouët et al., 2004). Concentrations ranged from 2.7 to 17.6 ng/L in wastewater and 1.0 to 3.2 ng/L in river water. Most of the estrogenicity of

river water samples, measured with the MCF-7 human breast carcinoma cell line, was due to the synthetic EE2, apparently because it was more resistant to biodegradation as compared to the other estrogens.

Occurrence and Fate – Surface Water and Sediment. Feedlot effluent from a site in Nebraska significantly altered reproductive biology of fathead minnows (Orlando et al., 2004). Masculinization of female fish was observed downstream of the feedlot. This was the first study demonstrating endocrine effects of feedlot effluent on wild fish. In a related study, androgenic and estrogenic effects were observed in samples tested using the E-SCREEN and A-SCREEN bioassays (Soto et al., 2004). Samples from a feedlot retention pond contained androgenic and estrogenic activity equivalent to 9.6 pM methyltrienolone and 1.7 pM E2, respectively; androgenic activity was attributed to natural androgens. Samples from the same location had E1 concentrations as high as 8,300 pg/L as measured by GC-HRMS.

Confined animal feeding operations (CAFOs) were found to be significant potential sources of hormones. Kolodziej et al. (2004) detected E1, E2, testosterone, and androstenedione in CAFO wastewater lagoon samples at concentrations of up to 650, 10, 0.5, and 7 ng/L, but no impact was found in nearby groundwater samples. Water samples from fish hatcheries and rivers with spawning salmon had hormones at concentrations up to 1 ng/L. Raman et al. (2004) characterized E1, E2, and 17 α -estradiol concentrations in swine and dairy wastewaters and storage lagoons of the southeastern United States and correlated their results to macronutrient (N, P, and K) concentrations. 17 α -estradiol was found at the highest concentrations in dairy wastewaters (up to 80 μ g/L), whereas the highest E1 and E2 liquid phase

concentrations were found in swine operations (about 55 and 40 µg/L, respectively). Emissions factors [$\text{mg}\cdot\text{d}^{-1}\cdot(1000 \text{ kg live animal weight})^{-1}$] for all three compounds were proposed.

Fate of estrogenic activity from WWTP effluent was monitored along a 25-mile reach of the Santa Cruz River, Arizona composed completely of wastewater effluent (Quanrud et al., 2004). Estrogenic activity was determined by concentrating samples on C18 SPE disks, then testing extracts with an in vitro bioassay. Estrogenic activity was attenuated along the river, with a 60% reduction over a travel time of “a few days”.

E1, E2, and EE2 were studied in the water cycle of Berlin, Germany using a new analytical method using automated SPE with LC-MS/MS (Zühlke et al., 2004b). Detection limits in raw sewage ranged from 1-2 ng/L, and in drinking water, surface water, and wastewater effluent, 0.1-0.4 ng/L. All 3 compounds were present in influent wastewater at concentrations of 8.6-160 ng/L, but all three were removed to a large extent in activated sludge WWTPs. Only E1 was detected in surface waters and in groundwater, at levels around 1 ng/L and 0.1 ng/L, respectively.

The steroidal compounds progesterone, 17 α -hydroxyprogesterone, androstenedione, and other androgens can be produced by microbial conversion of plant sterols found in paper mill effluent, suggesting an indirect source of EDCs in surface waters (Jenkins et al., 2004). Analysis of river water samples in Japan showed that some estrogenicity could be attributed to E1 and E2, but that some estrogenicity was due to the plant isoflavone genistein (Kawanishi et al., 2004). The phytoestrogens genistein and daizein were measured at concentrations of 143 and 43 µg/L,

respectively, which may be high enough to have biological impacts. The origin of these compounds was not identified.

A group of Austrian scientists conducted a year long survey of EDCs (including E1, E2, EE2, BPA, NP and NPEO, and OP and OPEOs) in Austrian surface and groundwaters (Bursch et al., 2004). The study included selected steroidal hormones as well as industrial chemicals, primarily NP, OP, their metabolites, and BPA. In general, concentrations were similar to or lower than previously-published concentrations; nonylphenol and ethinyl estradiol levels were the most significant compounds detected. In the 261 surface water samples from 27 locations, some effects in fish were observed, and EE2 was detected only four times, whereas E2 was detected in about half the samples at concentrations up to 1.2 ng/L. In 112 groundwater samples from 59 locations, NP was detected in 77 samples (up to 1500 ng/L) and E2 was detected in 58 samples (up to 0.79 ng/L). Hohenblum et al. (2004) described in detail the analytical methodology used for the monitoring program.

In an effort to determine sources of EDCs (primarily nonionic surfactants) in Spanish harbors and coastal waters, Pere-Trepat et al. (2004) utilized various chemometric methods, including principle component analysis and multivariate curve resolution-alternating least-squares analysis. The main sources were found to be point sources from municipalities and industries, although the compounds were widely distributed in the surface waters studied.

Spatial distributions of EDCs were measured in sediments of a shallow, eutrophic lake in Japan (Mibu et al., 2004). EE2 and estriol were not detected in any sediment

samples, whereas E1 concentrations were as high as 3.5 µg/kg dry weight. NP concentrations ranged from 11.8 µg/kg to 21 mg/kg dry weight.

Occurrence and Fate – Sludges, Soils, and Groundwater. Although sorption is hypothesized to be a significant mechanism for elimination of estrogens and progestogens from the aquatic environment, literature on the presence of these compounds in sewage sludges, sediments, and soils is limited (Kuster et al., 2004). The primary limitation appears to be lack of suitable analytical methods for analyzing low levels of these compounds in complex environmental matrices. The few data that are available suggest that these compounds can be found in sludges and soils.

Mansell and Drewes (2004) studied the fates of E2, E3, and testosterone during soil-aquifer treatment using laboratory column studies and field studies. The mobility of these hormones was generally found to be low, and estriol and testosterone not detected (<0.6 ng/L) in groundwater. E2 was consistently detected after 1.5 m travel through porous media, at concentrations of about 1.8 ng/L. Oxidation-reduction conditions (aerobic vs. anoxic) did not appear to influence mobility of these hormones. Removal mechanisms of E2, E3, and testosterone during soil aquifer treatment of recycled wastewater were determined (Mansell et al., 2004). The primary removal mechanism was sorption to aquifer solids, with some biotransformation contributing to removals.

Fate of E2 and EE2 was studied in slurry reactors with aquifer sediment and groundwater and with sediment and effluent by Ying et al. (2004). EE2 had slightly higher K_d (10.6 L/kg) than E2 (7.7 L/kg) for sorption to an aquifer sediment with 0.5% organic carbon and 3.1% clay. E2 was rapidly biodegraded under aerobic conditions

with >90% biodegraded within 1 week, but degradation was much slower under anaerobic conditions. EE2 was much more persistent, with little loss under aerobic or anaerobic conditions over 10 weeks.

Testosterone and E2 sorbed strongly to soils in column transport experiments but were still transformed (Das et al., 2004). Log K_{oc} ranging from 2.8 – 3.7 for transport through a silty clay loam and a sand. A first-order modeling approach worked well, but was unable to completely describe transport and degradation of the parent compounds and metabolites. Casey et al. (2004) conducted batch and column studies with radiolabeled testosterone in agricultural soils. Testosterone was found to weakly sorb to a range of soils (K_d ranged from 0.01 to 1.0 L/g), although correlations with surface area and organic matter were weak. Testosterone was also degraded to some extent, but may be more mobile in soils than E2 because of its weak sorption.

Testosterone, E1, and E2 were found in surface water runoff after rain events after 3 years of drought at concentrations of up to 6 ng/L (Shore et al., 2004). In a subsequent year with record rainfall, none of these compounds were observed. The study suggested that testosterone accumulates in pastures and fish ponds, and can be washed out of watersheds with surface runoff and by leaching from soil.

The animal growth promoters trenbolone (TbOH) and melengestrol acetate (MGA) tend to sorb strongly to soil organic matter (Schiffer et al., 2004). Batch sorption tests were used to determine Freundlich isotherm parameters for both compounds in two soils, and in column studies, rapid breakthrough occurred for both compounds, particularly MGA. Analytes were detected by an immunoassay system and HPLC with UV detection, and confirmed using LC-MS.

Drinking Water Treatment. Reverse osmosis was found to be a more effective than ozonation, nanofiltration, and microfiltration for removing a range of common hormones and pharmaceuticals from recycled wastewater (Khan et al., 2004).

Many estrogenic compounds should be effectively eliminated during disinfection of drinking water by chlorination or ozonation. Ozonation reduces but does not completely eliminate the estrogenicity of EE2 (Huber et al., 2004). Oxidation products of EE2 as well as E1 and E2 were identified. Results indicated that the phenolic functional groups of these compounds are rapidly oxidized by ozone. Ozone (1.5 mg/L) and chlorine (1.0 mg/L) effectively oxidize BPA, E2 and EE2 (Alum et al., 2004). Oxidation byproducts were found to have weak estrogenicity compared to the parent compounds.

Deborde et al. (2004) studied the chlorination of six endocrine disruptors (4-*n*-nonylphenol, E1, E2, EE2, estriol, and, progesterone). Progesterone did not react, whereas all compounds with a phenolic functional group were rapidly oxidized in the presence of high total HOCl concentrations, with maximum reaction rates at pH 9. Separately, chloroethynylestradiol (4-CIEE2) and 2,4-dichloroethynylestradiol (2,4-diCIEE2) were identified as major chlorination products of EE2 (Moriyama et al., 2004). EE2 was almost completely oxidized within 5 minutes; however, the two byproducts were persistent for >60 minutes in highly chlorinated solutions. 4-CIEE2 was shown to have similar estrogenicity as EE2, but estrogenicity of 2,4-diCIEE2 was about 10 times lower.

Endocrine Disrupting Compounds – Surfactants, Plasticizers, and Other

Many nonionic surfactants, plasticizers, and their metabolites can have endocrine-disrupting effects and are classified as EDCs. This section focuses on analysis and occurrence of these compounds and other synthetic EDCs.

Filali-Meknassi et al. (2004) presented an overview of potential EDCs, their modes of action, detection methods, and removal of these compounds during wastewater treatment. They also stated that research should focus on better quantifying the fate of EDCs in current and future wastewater treatment systems and receiving waters; optimization of wastewater treatment plants to remove EDCs; and improving EDC identification methods. Impurities in technical grade BPA may account for some of its estrogenic activity (Terasaki et al., 2004). Fifteen impurities were identified and structurally characterized; many of these components have the phenolic groups which is thought to account for estrogenicity of BPA.

Analytical Methods. GC-MS with BSTFA derivatization was compared to GC-MS-MS without derivatization for the analysis of several EDCs (E1, E2, EE2, OP, and BPA) in water (Hernando et al., 2004a). Results were generally similar, although derivatization provided lower detection limits for all compounds except BPA. For routine analysis, the authors suggested that GC-MS-MS may be easier and faster because the derivatization process can be avoided.

LC-MS with electrospray ionization was used for detection of seven EDCs, including NP, BPA, and 4-*tert*-butylphenol (*t*-BP), which were extracted from water samples by SPE using Oasis HLB cartridges (Carabias-Martinez et al., 2004). Post-column addition of a volatile base (1,8-diazabicyclo-(5,4,0)undec-7-en, or DBU) enhanced the sensitivity

of the method and provided detection limits of 25 ng/L for BPA, 9 ng/L for NP, and 11 ng/L for *t*-BP. An unspiked drinking water sample was found to have 64 ng/L *t*-BP.

Six EDCs in wastewater were extracted by SPE followed by cleanup and derivitization with heptafluorobutyric acid anhydride (HFBA) prior to analysis by GC-MS (Stehmann et al., 2004). Two different ionization techniques (positive electron impact ionisation (EI) or negative chemical ionisation (NCI)) were tested, with NCI producing lower detection limits. The method was used to measure 4-NP in raw wastewater at 10.305 ng/L and BPA in treated effluent at 723 ng/L.

BPA and alkylphenols were extracted from 10-mL river water samples by sorption to a PDMS-coated stir bar (Nakamura and Daishima, 2004; Kawaguchi et al., 2004a). Acetic acid anhydride was added to the sample for derivatization during sorption, and sorbed analytes were thermally desorbed and analyzed by GC-MS. Quantitation limits were 10 and 20 ng/L for BPA and 4-nonylphenol, respectively, and generally <20 ng/L for other alkylphenols. A similar method was used for analysis of estrogens (E1, E2, and EE2) in river water samples (Kawaguchi et al., 2004b). The major difference was that multiple stir bars were used for extraction and were thermally desorbed for each sample in a “multi-shot” mode. Quantitation limits were ≤5 ng/L for all three analytes.

A novel surfactant-modified γ -alumina was prepared for the concentration of hydrophobic compounds from water samples (Saitoh et al., 2004). The material had a high adsorption capacity and exhibited recoveries of >90% for 4-*tert*-octylphenol, 4-*n*-nonylphenol, and dibutyl phthalate. This sample extraction compared favorably to typical SPE materials, and may even be loaded with a water sample at a faster rate, reducing sample analysis time. Alkylphenols and BPA were extracted from aqueous

samples using a liquid phase micro-extraction procedure, followed by derivatization with BSTFA in the GC injection port (Basheer and Lee, 2004). Analysis by GC-MS resulted in quantitation limits of 0.012 – 0.026 µg/L. The method agreed well with results of liquid-liquid extraction.

In-field SPE followed by further enrichment by automated SPE and LC-MS was used for simultaneous analysis of 21 EDCs (pesticides, phenols, and phthalates) (Lopez-Roldan et al., 2004). System automation resulted in high precision and high sample throughput. A carbowax/templated resin SPME fiber was used to extract BPA, NP, and OP from water samples (Cai et al., 2004). Analytes were analyzed by HPLC with fluorescence detection. The method achieved detection limits of <0.5 µg/L for all three analytes.

Microwave assisted extraction with methanol as the solvent effectively recovered >74% of a range of EDCs (BPA, OP, NP, E1, E2, EE2, and 16α-hydroxyestrone) from sediments (Liu et al., 2004). Extract cleanup with silica gel was required prior to GC-MS analysis. Quantitation levels were ranged from 0.5-3.4 ng/g dry weight.

Several reviews of current and potential methods for detecting endocrine disruptors were presented. Scrimshaw and Lester (2004) reviewed in-vitro assays that can be used to measure estrogenic activity. Mueller (2004) described the mechanism of action of EDCs, and reviewed in vitro screening tests for estrogenic and antiestrogenic activity. Estévez-Alberola and Marco (2004) reviewed many different immunochemical methods for detecting specific EDCs, including BPA, phthalates, alkylphenols, and alkylphenol polyethoxylates. These methods are generally very sensitive, highly selective, and amenable to rapid sample processing, and in many cases, reagents and methods are

commercially available. These methods are likely to become more common for monitoring discharges to the environment.

Alkylphenol polyethoxylates and alcohol ethoxylates were extracted from sewage sludge using sodium dodecane sulphonate under acidic conditions and quantified by HPLC with atmospheric pressure chemical ionization/ion trap MS (Cantero et al., 2004). The extraction procedure resulted in phase separation of undissolved solids, an aqueous phase, and a surfactant phase containing the analytes. The method yielded polyethoxylated surfactant detection limits in sludge of 0.09–0.38 mg/kg. Hata et al. (2004) describe a similar method for concentrating DEHP from river water for determination by HPLC with UV detection at 222 nm. By adding 4-tifluoromethylanilinium and dodecylbenzenesulfonate ions to the sample, DEHP is quantitatively extracted to an organic phase that is separated by centrifugation. The DEHP detection limit for this method was estimated as 0.07 µg/L.

Plasticizers. HPLC with electrochemical detection was used to measure BPA in environmental samples at <1 ng/L (Watabe et al., 2004a,b). To achieve such low detection limits, interferences from laboratory glassware and sample preparation equipment must be eliminated. The method included automated SPE pretreatment using a molecularly-imprinted polymer (MIP) specifically prepared for extraction and concentration of BPA from water samples. A similar method using an MIP was developed for extraction of chlorinated BPAs with chlorine substitutions at the 3,5-positions (Kubo et al., 2004).

Surfactants. Jahnke et al. (2004) used LC-MS-MS to simultaneously measure alkylphenol ethoxylates and their degradation products in raw wastewater. The 8

analytes were extracted by SPE using Oasis HLB cartridges. Limits of detection ranged from 0.04 – 12 ng/L. A single extraction and preparation procedure was described for analysis of NPEOs and their estrogenic metabolites (Martinez et al., 2004). Several different cleanup and LC-ESI-MS methods were used to analyze different ranges of these compounds. Detection limits were in the low ng/L range. Four dicarboxylic degradation products of NPEOs were synthesized and characterized GC-MS, which will allow more accurate analysis of these compounds in surface waters and sediments (Hoai et al., 2004).

Pentafluoropyridine was used for solid-phase derivatization of phenolic compounds (including alkylphenols) after SPE using Oasis MAX cartridges (Kojima et al., 2004). This method allowed potential interferences to be eluted from the SPE cartridge prior to derivatization. After derivatization, analysis was accomplished with GC-MS, resulting in detection limits of 8.5 ng/L for nonylphenol and 0.45-2.3 ng/L for other alkylphenols.

Levy et al. (2004) proposed use of the retinol-binding protein (RBP) mRNA expression as a molecular biomarker for assessing all modes of action for EDCs. RBP levels were found to represent all possible effects caused by EDCs in environmental samples. Three recombinant human steroid receptors (hPR, hER α , and hAR) were proposed for use in radioreceptor assays as a novel screening method for EDCs (Scippo et al., 2004). Some common EDCs were found to bind strongly to the hPR, allowing this method to be used as a first assessment of a chemical's endocrine disrupting potential.

An ELISA was developed for detection of alkylphenol polyethoxylates and their metabolites in river water (Goda et al., 2004). The method has a NP10EO detection

limit of 16 µg/L with 10% methanol as the assay diluent. Although the method cannot determine isomer distributions, it has many advantages over HPLC methods.

Development of a direct competitive ELISA based on polyclonal and monoclonal antibodies raised against NP was described by Zeravik et al. (2004). The monoclonal antibody that the authors produced allowed sensitive detection of linear long-chain alkylphenols.

Andreescu and Sadik (2004) described development of a tyrosinase-based biosensor that may be useful for detecting EDCs. Tyrosinase catalyzes the oxidation of phenolic groups, present in many estrogenic compounds, to *o*-diphenols in the presence of oxygen and further oxidation to *o*-quinones. An electrode incorporating tyrosinase had a detection limit of about 0.15 µM for BPA.

Occurrence and Fate – Wastewater Treatment Systems. Influent to 6 WWTPs in Northeast Spain had NPEO concentrations ranging from 60 -190 µg/L, while influent NP concentrations ranged from 0.2 -18 µg/L (Gonzalez et al., 2004). Although 93-96% of NPEOs were removed, effluent concentrations of estrogenic nonylphenols exceeded 20 µg/L in many cases. These compounds were also detected in sediments near WWTP outfalls. BPA, OP, and DEHP were frequently detected in effluent samples from 7 Spanish WWTPs (Aguayo et al., 2004). OP and BPA were detected at concentrations up to 24 and 5.7 µg/L, respectively.

The presence of nonylphenol polyethoxylates had little effect on removal of biochemical oxygen demand in bench-scale activated sludge systems (Lozada et al., 2004). NP10EO was degraded, and NP3EO, NP1EO, and NP accumulated. The

continuous addition of NP10EO resulted in a shift in the bacterial community composition and slightly lower chemical oxygen demand removals.

BPA, E2, and EE2 all strongly adsorb to WWTP sludge, with distribution coefficients on the order of 1000 L/kg (Clara et al., 2004c). Because sludge has a high adsorption potential for these compounds, elimination with waste activated sludge is an important removal mechanism in WWTPs. BPA readily adsorbs to anaerobic sludge solids ($\log K_d = 2.09-2.30$ and $\log K_{oc} = 2.72-3.11$), but can desorb during high pH sludge conditioning with lime (Ivashechkin et al., 2004). FeCl_3 conditioning had little effect on BPA sorption. Other EDCs with similar acid dissociation constants are expected to behave similarly.

Occurrence and Fate – Surface Water and Sediment. BPA, OP, and NP were detected in the Haihe River, China at concentrations generally ranging from 19.1-106 ng/L, 18-20.2 ng/L, and 106-296 ng/L, respectively (Jin et al., 2004). One sampling site had 8.3 μg BPA/L and 0.55 μg NP/L. Eleven phenolic compounds, including nonylphenol (NP), t-octylphenol and BPA were measured in samples from Shihwa Lake, Korea in February, June and October 2002 (Li et al., 2004b). NP was the most abundant of these, with concentrations in dissolved water, particulates and surface sediments from Shihwa Lake of 17.4-1533.1 ng/L, 4.3-831.2 ng/L and 10.4-5054.1 ng/g dry weight, respectively. The dissolved NP concentration varied with seasons, with highest concentrations in June and lowest concentrations in February. NP concentrations decreased gradually with distance from industrial sites, and dissolved NP concentrations correlated with particulate concentrations.

Plasticizers. Two strains of aerobic bacteria that can degrade phthalic acid esters (PAE) were isolated from river sediment and petrochemical sludge (Chang et al., 2004a). PAE degradation rates decreased with increasing alkyl chain length.

BPA and four of its biodegradation products were monitored in river water (Suzuki et al., 2004). Using SPE with GC-MS, BPA was detected at concentrations up to 230 ng/L; the metabolites were present at lower levels, generally <75 ng/L. BPA was not persistent while incubated in river water under aerobic conditions; however, three metabolites persisted for >14 days. Two persistent metabolites of the plasticizers DEHP and di-(2-ethylhexyl) adipate (DEHA) were detected in water and sediment samples near Montreal, Canada (Horn et al., 2004). 2-ethylhexanol and 2-ethylhexanoic acid were detected at concentrations up to 0.85 and 6.7 µg/L, respectively in water samples, and at concentrations of about 105 ppb in a sediment sample.

Adsorption of dimethyl phthalate to untreated marine sediments follows a linear isotherm and is primarily due to partitioning to organic carbon in sediments (Zhao et al., 2004). The partitioning coefficient for adsorption from natural seawater to sediment with 2.7% organic carbon and 23% clay was $K_d = 0.587$ L/g. As salinity increases, the aqueous solubility of dimethyl phthalate decreases, resulting in increased adsorption to sediment and increased partitioning coefficients.

The photodegradation of BPA is enhanced by the presence of dissolved organic matter (Chin et al., 2004). BPA photodegradation was found to be faster than biodegradation; thus, decomposition reactions due to UV light may be a significant fate mechanism in natural waters.

Surfactants. Anaerobic microorganisms from river sediments in Taiwan biodegraded NP and nonylphenol monoethoxylate (Chang et al., 2004b). Half-lives for NP and NP1EO ranged from 46-69 days and 50 – 77 days, respectively. Degradation rates were affected incubation conditions.

NP isomers in freshwaters and sediments were monitored in the Rieti district in Italy by Vitali et al. (2004) during 2002 and 2003. The sampling showed that NP was present in surface waters at relatively low concentrations (<0.1-1.4 µg/L) and in sediments at concentrations up to 567 µg/kg dry weight. NP concentrations were closely correlated to the presence of urban or industrial activities near the sampling point and were generally present over short distances from contamination sources. The authors also summarized literature on occurrence of NP in aquatic environments.

Water, suspended particle, and sediment samples were analyzed in a Korean river by Li et al. (2004a) during summer, winter and autumn, showing NP concentrations ranges of 23.3-187.6 ng/L in water, 6.8-190.8 ng/L in suspended particle and 25.4-932.0 ng/g dry weight in sediment. Water and suspended particle concentrations were higher in warmer seasons than in colder seasons. A reasonable correlation was obtained for concentrations in water and adsorbed to suspended particles; however, no seasonal variation of the concentration in sediment was noticed.

APEOs were found in coastal waters and rivers of Israel at concentrations up to 25 and 75 µg/L, respectively (Zoller et al., 2004). These levels could have potentially negative impacts on some aquatic species. Trace concentrations were also found in groundwaters adjacent to highly impacted rivers.

Occurrence and Fate – Sludges, Soil, and Groundwater. Petrovic and Barcelo (2004) presented an overview of analytical methods that are currently available for analyzing surfactants and their metabolites in sludges and sludge-amended soils. One of the major challenges is the extraction of analytes; any extraction method must overcome the strong sorption of these analytes to soil and sludge particles. Current analytical methods are focused on various LC-MS and GC-MS techniques.

Phthalates and nonylphenol were found in leachate from Danish landfills at concentrations up to 340 and 7 µg/L, respectively (Baun et al., 2004).

Drinking Water Treatment. Concentrations of 17 nonylphenol ethoxylates (NP1–17EO) and two nonylphenoxycarboxylic acids (NP1–2EC) were monitored over 1 year at 11 Canadian drinking water plants downstream of pulp and paper mills (Berryman, et al., 2004). In drinking water produced by 10 of these plants, the total concentration of these compounds was generally low, with a yearly average ranging from 0.02 to 2.8 µg/L. However, finished drinking water at one plant (which did not include ozonation) had a yearly average of 10.4 µg/L and a maximum monthly concentration of 43.3 µg/L.

Membrane processes such as membrane bioreactors, reverse osmosis, and nanofiltration systems can effectively remove EDCs from wastewater and landfill leachates (Wintgens et al., 2004). These treatment methods removed 70-99% of target EDCs, which included BPA and NP. In membrane bioreactors, compounds were removed by a combination of size exclusion and biodegradation.

Upon chlorination at neutral pH, the half-life of BPA is <1.5 hours with a chlorine residual >0.2 mg/L (Gallard et al., 2004). To eliminate chlorinated BPA congeners, the authors suggested providing a high residual chlorinate concentration in drinking water

distribution systems. BPA and 4-NP can be effectively removed by oxidation with sodium hypochlorite, ClO_2 or O_3 ; however, oxidation with sodium hypochlorite increased estrogenic activity (Lenz et al., 2004). 4-nonylphenol ethoxylates (NP1EO and NP2EO) were oxidized effectively (>92% removed) by ClO_2 , but less effectively by O_3 (<30%) and NaClO (<20%).

Chlorinated derivatives of BPA and 4-nonylphenol were synthesized by Stehmann and Schröder (2004). Both compounds reacted with halogenated acetic acid anhydrides to produce halogenated acetyl derivatives. The compounds produced will be useful in positively quantifying compounds produced upon chlorination of BPA and 4-nonylphenol.

Personal Care Product Ingredients

PCPIs include disinfectants, pesticides and fungicides, preservatives, antioxidants, and synthetic musk compounds, which are used as fragrances in many consumer products. Although these compounds are typically not major product ingredients, they are commonly used and therefore widely detected in the water environment. The broad range of PCPIs in use today poses a many potentially complex and not very well understood environmental issues (Ternes et al., 2004). Some of these chemicals are removed in during wastewater treatment, but the fate of many PPCPs is unclear. Reducing the inputs of these contaminants to wastewater treatment plants, either by separate treatment of liquid wastes or alternate disposal methods for PPCPs, is a logical first step in reducing inputs to the environment through wastewater treatment plants.

Analytical Methods. *Disinfectants.* Benzothiazoles in wastewater were measured using a LC-ESI-MS method (Kloepfer et al., 2004b). Oasis HLB cartridges were used for SPE. Two LC-MS runs were required; positive ion mode was used to detect 2-aminobenzothiazole, benzothiazole and 2-methylthiobenzothiazole, and negative ion mode was used for detection of benzothiazole-2-sulfonic acid (BTSA), 2-mercaptobenzothiazole and 2-hydroxybenzothiazole. Quantification limits in raw wastewater were 65-620 ng/L and 25-200 ng/L in secondary effluent.

Triclocarban (TCC) is a polychlorinated phenyl urea pesticide that has been used for several decades as an antibacterial additive in personal care products (Halden and Paull, 2004). A LC-ESI-MS method was developed for analyzing triclocarban following concentration by SPE, with detection limits ranging from 3-50 ng/L. River water and wastewater samples taken near Baltimore, Maryland had TCC concentrations >5000 ng/L, whereas TCC was undetectable in drinking water.

Fragrance Compounds. Seven synthetic musks and two fragrances were analyzed by a combination of closed-loop stripping analysis (CLSA) and GC/MS detection (Mitjans and Ventura, 2004). Levels of detection were 5-10 ng/L for all nine compounds. The method was used to detect significant concentrations of AHTN, HHCB, acetyl cedrene, and amberonone in wastewater influent and effluent samples from five European countries.

Other. Four UV filter compounds that are used in sunscreen formulations were extracted from water samples using C18 SPE disks, followed by HPLC-DAD or GC-MS analysis (Giokas et al., 2004). Analysis by HPLC-DAD required modification of the acetonitrile:water (80:20) mobile phase with 3.5 mM sodium dodecyl sulfate for

separation of all analytes, and resulted in quantitation levels from 8-24 ng/L. GC-MS could only detect three of the four compounds, with quantitation levels from 0.7-1.4 ng/L.

Occurrence and Fate – Wastewater Treatment Systems. Knepper et al. (2004) described European efforts to understand the fate of persistent polar pollutants in wastewater treatment systems and to improve removals. Many of the polar compounds are not readily biodegraded or removed by sorption. For some contaminants, membrane bioreactors may provide better removals.

A group of 13 PPCPs corresponding to different types of substances (two musk fragrances/cosmetics, eight pharmaceuticals and three hormones) were studied for their overall removal efficiency in a sewage treatment plant receiving the wastes of 100,000 people (Carballa et al., 2004). In the primary treatment, only the fragrances (30-50%) and the 17 β -estradiol (20%) were partially removed. The aerobic treatment (activated sludge) caused an important reduction in all compounds detected (35-75%) except for the iopromide, which remained in the aqueous phase. The overall removal efficiency ranged between 70-90% for the fragrances, 40-65% for the anti-inflammatories, 60% for the antibiotic sulfamethoxazole and 65% for 17 β -estradiol.

Two polycyclic musk fragrances HHCB/galaxolide (1900 ng/l for influent concentration and 3000 ng/g for the sludge) and AHTN/tonalide (580 ng/l and 1500 ng/g) were measured in wastewater and sludge of a German sewage treatment plant by Bester et al. (2004). About 35% of both substances passed through the plant unaltered. For the sludge, about 50% of the HHCB was sorbed to the sludge and disposed of accordingly while about 80% of the AHTN was sorbed to the sludge. Biotransformation

does not seem to play dominant role in the sewage treatment plant. Because some plants are able to biodegrade polycyclic musk compounds, that shows that optimization of the sewage treatment processes may be feasible to minimize the discharge of these two compounds as well as organic micro-contaminants in general.

The fate of benzothiazoles during biological treatment was investigated by Kloepper et al. (2004a). BTSA, which is strongly acidic and the most polar of these analytes, was typically the most prominent compound in raw wastewater (1.7 µg/L). During biological treatment, <10% of the total benzothiazoles were removed by conventional activated sludge, whereas a membrane bioreactor system provide somewhat higher removals (~43%).

Bayrepel and DEET have been monitored in German wastewaters by Knepper (2004a). Bayrepel (1-piperidine carboxylic acid, 2-(2-hydroxyethyl) -, 1-methylpropylester) was substituted for DEET in 1999, and since then, DEET levels have steadily decreased in wastewater influent and effluent and in surface waters. Whereas DEET was only partially removed in WWTPs, Bayrepel is almost completely eliminated during wastewater treatment by aerobic biodegradation (Knepper, 2004b). Bayrepel metabolites were determined by several different MS methods. One of the metabolites, Bayrepel-acid, was found to be very stable.

Occurrence and Fate – Surface Water. Multiple organic wastewater contaminants (OWC) were detected in surface waters of Iowa impacted by urban areas, particularly during low stream flows (Kolpin et al., 2004). At low flows, the most frequently detected antibiotic (in 20% of samples) was sulfamethoxazole at a maximum concentration of

0.07 µg/L. Carbamazepine was detected in 70% of low-flow samples at a maximum of 0.263 µg/L.

Several compounds that were previously unreported in surface waters were detected in the Lippe River, Germany and attributed to anthropogenic inputs (Dsikowitzky et al., 2004a,b). These compounds include a plasticizer (2,2,4-trimethyl-1,3-pentandiol diisobutyrate) at up to 100 ng/L and a surfactant (2,4,7,9-tetramethyl-5-decyne-4,7-diol) at up to 660 ng/L. Numerous other PhACs and household products were also detected. In a related study of the Lippe River sediments (Kronimus et al., 2004), common PPCP-related compounds such as polycyclic musks and methyltriclosan, as well as previously unknown contaminants including 3,6-dichlorocarbazole and bis(4-octylphenyl) amine, were detected. Accumulation of contaminants in sediments can be used as an indicator of overall health of a water body.

Ambient water and air concentrations of six polycyclic musks (including AHTN, HHCB, and DPMP) and two nitro musks (musk xylene and musk ketone) were measured at Lake Michigan and the air of urban Milwaukee (Peck and Hornbuckle, 2004). DPMP was the only compound not detected, while HHCB and AHTN were found in the highest concentrations at averages of 4.7 ng/L and 1.0 ng/L in lake water. A mass balance analysis showed that discharges from wastewater treatment plants are the major source (3480 kg/yr) of the synthetic musks, whereas atmospheric deposition contributes less than 1%.

Low concentrations of UV filter compounds from sunscreens were found in two Swiss lakes (Poiger et al., 2004). Five of these compounds were analyzed by GC-MS,

and the highest individual concentration detected was benzophenone-3 at 125 ng/L. Mass balance calculations overestimated the expected concentrations, possibly because not all fate mechanisms are known for these compounds.

Triclosan photodegradation products in wastewater were monitored with a LC-time-of-flight MS method (Ferrer et al., 2004). Four different byproducts were found, and a tentative degradation pathway for triclosan photolysis was proposed.

Occurrence and Fate – Soils. Partitioning coefficients (K_d) for a range of pharmaceuticals (antiphlogistics, estrogens, lipid regulators, anti-epileptic and cytostatic agents) and polycyclic musk fragrances (HHCB, AHTN) were determined in primary and secondary sludges from German WWTPs (Ternes et al., 2004a). For most pharmaceuticals, removal by sorption during wastewater treatment will probably be minimal. K_d ranged from <1 – 500 L/kg for pharmaceuticals, but were much higher for the musk compounds (5300 and 4900 L/kg for AHTN and HHCB, respectively).

Absorption to sludge is a possible removal mechanism for fragrance materials (FMs) in wastewater, but the sludge application to land may be a route through which fragrance materials are released to the soil environment (DiFrancesco et al., 2004). Nine FMs were detected in digested sludges from two wastewater treatment plants. After amending soils with digested sludge, seven FMs (AHTN, HHCB, musk ketone, musk xylene, acetyl cedrene, OTNE and DPME) remained at concentrations greater than the quantitation limits after three months, while the only FMs remaining after one year were musk ketone and AHTN. DPME was the only FM that leached significantly from the amended soils.

Brominated Compounds

A range of brominated compounds, and specifically brominated flame retardants (BFRs), have recently emerged as a class of persistent organic pollutants. Due to their widespread usage in many commercial products, PBDEs are apparently ubiquitous in the environment, with concentrations in most environmental compartments doubling every 4-6 years (Hites, 2004). Hites reviewed PBDE concentrations that have been measured in human and environmental samples and also presented ideas for future research, including identification of release and exposure mechanisms. D'Silva et al. (2004) presented a review of the types of flame retardants that have been and are currently in use, and the potential environmental impacts of PBDEs and other brominated organic contaminants in the environment. These compounds have been found in many environmental samples due to their persistence, but their toxicity, transformation, and potential ecological impacts are as yet unclear.

Analysis. The influence of GC analytical conditions on analysis of PBDEs was explored by Björklund et al. (2004). Different chromatographic columns and injection methods resulted in a wide variation in results, and poor chromatographic conditions may lead to complete loss of some higher molecular weight congeners. Eljarrat and Barcelo (2004) reviewed published methods for extraction and instrumental analysis of brominated flame retardants such as PBDEs, HBCD, and TBBPA, focusing on sewage sludge and soil samples. Typical analytical methods have included various types of GC-MS analysis, but various difficulties in analyzing these components have also encouraged development of LC-MS methods. The review also included a summary of BFR concentrations that have been detected to date in these environmental matrices.

A headspace SPME method using was developed for analysis of PBDEs in water samples, avoiding a lengthy extraction and cleanup procedure (Polo et al., 2004). The most effective extraction conditions were found with a PDMS fiber and stirring of the 10-mL sample during extraction. GC-MS-MS analysis resulted in limits of detection ranging from 20 – 190 pg/L for the six PBDE congeners tested.

Eljarrat et al. (2004a) developed a selective pressurized liquid extraction (SPLE) method followed by GC-MS with negative chemical ionization for determining PBDE-209 in sediment samples. The SPLE method was operated at 100°C and 1500 psi, and required no further sample cleanup. The procedure provided a detection limit of within the range of 30 - 110 pg/g dry weight.

An alternative BFR to PBDEs, decabromodiphenyl ethane (DeBDethane), has also been recently detected in environmental samples (Kierkegaard et al., 2004). After solvent extraction and cleanup of sewage sludge and sediment samples, DeBDethane was identified and quantified using a GC-HRMS system. DeBDethane was detected in 25 of 50 sewage sludge samples from various locations around Sweden, at concentrations up to about 100 ng/g, and in a single sediment sample from the Netherlands at about 24 ng/g.

Occurrence. *Water.* Levels of HBCD isomers and TBBPA were measured by an LC-MS method in effluents from sewage treatment plants and in landfill leachates in areas surrounding the North Sea (Morris et al., 2004). Partitioning and removal in sewage treatment plants was associated appeared to be correlated to hydrophobicity. The total HBCD and TBBPA concentrations in sewage sludges were as high as 9.1 mg/kg and 100 µg/kg (both measured as dry weight), respectively. PBDE

concentrations were measured in a wastewater treatment plant treating about 25 million gallons per day in Palo Alto, California (North, 2004). In wastewater effluent, concentrations ranged from 4 – 29,000 pg/L, while concentrations in sludge ranged from 61 – 1440 µg/kg dry weight. Although influent concentrations were not measured, the author stated that the overwhelming majority of PBDEs sorbed to sludge solids and were incinerated during sludge disposal.

In numerous samples taken from various environmental media in Sweden, HBCD was found to be ubiquitous (Remberger et al., 2004). In water samples, HBCD ranged from 3 ng/L in landfill leachate to 31 ng/L at a laundry facility. HBCD was detected in primary sewage sludge, but was below the detection limit of 1 µg/kg in digested sewage sludge, suggesting the possibility of an anaerobic degradation mechanism. Three PBDE isomers and TBBPA were found at levels up to 4,000 pg/L and 620,000 pg/L, respectively in landfill leachate samples taken in Japan (Osako, et al., 2004). Contaminant levels appeared to correlate with the landfill history, particularly the types of wastes deposited in each landfill. Leachate treatment which included multiple biological treatment steps and adsorption to activated carbon generally provided excellent removal of these contaminants.

Sediment. Hexabromocyclodecane (HBCD) and 40 PBDE congeners (up to PBDE-209) in river sediments both upstream and downstream of an industrialized town of Spain were measured by Eljarrat et al. (2004b) using a pressurized liquid extraction method, followed by GC-MS analysis. HBCD and PBDEs were detected at concentrations up to 514 ng/g and 42 ng/g dry weight, respectively. The highest contaminant concentrations were found in samples impacted directly by industrial

activity. PBDEs were measured in sediments from Lake Superior and annual PBDE inputs from atmospheric fluxes were estimated (Song et al., 2004). The sum of PBDE congener concentrations was 0.49 – 3.1 ng/g dry weight, with an average of 1.4 ng/g dry weight. Surficial sediment samples generally had the highest PBDE concentrations.

Soils. Hassanin et al. (2004) analyzed surface soils (0-5 cm) from remote/rural woodland and grassland locations in the United Kingdom and Norway for PBDEs to assess background concentrations in soil. The concentrations ranged from 65-12,000 ng/kg dry weight for total PBDEs, due to atmospheric deposition. The major constituents of the penta-BDE technical product (PBDE-47, -99, -100, -153 and -154) dominated the average congener pattern of the soils. There was evidence of latitudinal fractionation, with the relative contribution of PBDE-47 and other lighter congeners increasing northwards.

Fate. Results of several experiments suggest that photodecomposition may be a relevant fate mechanism for BPDEs in some surface waters. Decabromodiphenyl ether (PBDE-209) dissolved in hexane can be transformed by ultraviolet irradiation to other PBDEs (Bezares-Cruz, et al., 2004). Photolytic debromination of PBDE-209 was also studied in toluene and adsorbed to solid surfaces including sediments and soils (Söderström et al., 2004). Different matrices affected the half-lives, with slower reactions reported for PBDE-209 adsorbed to sand or soil, but did not affect the types of byproducts formed. Some PBDEs detected in environmental samples may be byproducts of PBDE-209 degradation or from mixtures of PBDEs used in commercial products. Photodecomposition of 15 different PBDE congeners with different levels of bromination and their reaction byproducts were studied in methanol/water mixtures

(Eriksson et al., 2004). PBDE-209 was found to be rapidly debrominated to congeners with 6 bromine atoms, and further decomposition products were tentatively identified.

Fluorinated Compounds

Fluorinated surfactants and related compounds are another class that has recently been found to be nearly ubiquitous in the environment. Research has focused on improved analytical methods, as well as determining the distribution and fate of these compounds throughout the environment.

Analysis. Martin et al. (2004a) described analytical challenges which have impeded research on perfluoroalkyl compounds in the environment. These challenges include impurities in analytical standards; the lack of available analytical standards for different isomers; and interferences from complex environmental samples. These and other difficulties currently limit environmental research on perfluoroalkyl compounds.

Low-level (parts-per-trillion or parts-per-quadrillion) analysis of perfluorinated acids was accomplished by Yamashita et al. (2004) by eliminating contamination sources in procedural and instrumentation blanks. By eliminating contamination, six different PFAs were measured at ppq levels in seawater using a method that included SPE and HPLC-MS/MS; limits of detection were ≤ 5 pg/L for all six compounds. In water samples from Tokyo Bay, PFOS and PFOA were detected at concentrations up to 25,400 and 192,000 pg/L, respectively.

HPLC with suppressed conductivity detection was used for detection of various perfluorocarboxylic acids and perfluorosulfonates with C_3 – C_8 perfluoroalkyl groups, with detection limits of 0.12 – 0.66 mg/L (Hori et al., 2004). Analytes were separated using a

Tosoh TSKgel Super-ODS column and an eluent of methanol and 20 mM NaH₂PO₄ (pH 3.0). Sample pre-concentration by SPE improved detection limits to about 50 µg/L for compounds with C₄–C₈ perfluoroalkyl groups. Alzaga and Bayona (2004) developed a rapid, sensitive, and solvent-free method for analyzing PFCAs in aqueous samples. After extraction by SPME, analytes were derivatized to their respective butyl esters, and analyzed by GC-MS with negative ion chemical ionization. This method achieved quantification limits of about 50 ng/L and reduced sample analysis time compared to conventional analytical methods.

Fluorotelemer sulfonate surfactants are components of firefighting foams. A LC-MS-MS method was developed to quantify these compounds in groundwater (Schultz et al., 2004). The method was also useful for analyzing perfluoroalkyl sulfonates and perfluoroalkyl carboxylates, and quantitation limits for all analytes were <0.62 µg/L. Total fluorotelemer sulfonate concentrations were as high as 14,600 µg/L in a groundwater sample from an air force base in Florida.

Occurrence. Several papers reported on concentrations fluorinated organics (including of PFOS, PFOA, and long-chain PFCAs) in aquatic biota from the Canadian Arctic (Martin et al., 2004b), Lake Ontario (Martin et al., 2004c), and the Eastern Arctic (Tomy et al., 2004). Fluorinated compounds were ubiquitously detected in the tested organisms at various levels of the food chain. Perfluorooctane surfactant concentrations in water samples from 4 locations in Lake Erie and 4 locations in Lake Ontario were measured by Boulanger et al. (2004). Samples were extracted using C18 SPE cartridges, and analyzed by LC-MS and LC-MS/MS. Somewhat higher

concentrations were detected in samples from Lake Ontario, with PFOA and PFOS levels as high as 70 and 121 ng/L, respectively.

Perfluorinated compounds in Southeast Asia seawater were measured using SPE and HPLC-HRMS (So et al., 2004). PFOS and PFOA concentrations as high as 730 ng/L and 320 ng/L, respectively, were detected off the coast of Korea. High concentrations were associated with industrial activity and discharges from rivers.

Fate. Meesters and Schroder (2004) investigated the biodegradation of anionic fluorinated surfactants (PFOA and PFOS) in wastewater under aerobic and anaerobic conditions. Both compounds were degraded under anaerobic conditions, but were recalcitrant under aerobic conditions. An increase in fluoride ions was not observed, indicating that the compounds were not completely mineralized.

Disinfection By-Products – Drinking Water and Wastewater

New disinfection byproducts (DBPs) and drinking water contaminants continue to be discovered, and the conditions and mechanisms under which they are formed are being studied to understand how DBP formation can be minimized.

Analysis. Paull and Barron (2004) reviewed the current understanding of HAA formation mechanisms, as well as pre-concentration and analytical methods. Most IC methods require some sort of preconcentration, which in most cases has poor reproducibility. Automated preconcentration and the use of suppressed IC coupled with electrospray ionization-MS or ICP-MS are promising methods, but require further development.

Low concentrations of nine chlorinated and brominated haloacetic acids (HAAs) were detected using ion chromatography coupled (IC) with ICP/MS (Liu et al., 2004). The eluent was sodium hydroxide, and eluent conductivity was suppressed after the IC. The detection limits ranged from 15.6 to 23.6 µg/L for the mono-, di-, and trichloroacetic acids, and were significantly lower for the six brominated HAAs (0.34-0.99 µg/L). Sample pretreatment for chloride removal was required for analysis of these compounds in many matrices.

Domino et al. (2004) optimized the derivatization procedures for haloacetic acids to improve sensitivity, precision, and accuracy. The standard procedure utilizes acidic methanol to esterify HAAs, with limited efficiency for brominated trihaloacetic acids (HAA3). Using an alternate solvent (tertiary-amyl methyl ether) increased the methylation efficiency for tribromoacetic acid to 82%, and several other modifications greatly improved the method. All nine HAAs were analyzed without derivatization using a supported liquid membrane microextraction procedure followed by HPLC-UV detection (Kou et al., 2004). Extraction time was 60 minutes and HPLC run time was 15 minutes. Method detection limits were <0.25 µg/L for all compounds except monochloroacetic acid, which had a detection limit of 2.69 µg/L.

Barron and Paull (2004) developed an ion chromatography method for improving the detection of haloacetate DBPs by reducing baseline noise. Detection limits of 0.09-21.5 µg/L were achieved using SPE for sample pre-concentration, without interference from chloride or sulfate. The method utilizes a high capacity microbore column, a hydroxide eluent gradient, and a Dionex Atlas electrolytic suppressor. A patented ion chromatography suppressor system not only suppresses eluent conductivity, but also

removes carbonic acid from the eluent (Bose et al., 2004). The system improves sensitivity and detection limits for common anions as well as inorganic DBPs. Detection limits for bromate, bromide, chlorate, and chlorate ranged from 0.22 – 1.36 µg/L for a 200 µL injection volume with no sample pre-concentration.

Chloride ion fragments can be used as a fingerprint for identification of chlorinated DBPs in water samples when analyzed by electrospray ionization MS/MS (Zhang et al., 2004). Using this method required relatively high collision energy and collision gas pressure, as well as a narrow scan range (m/z 30-40) to detect chloride, but lower collision energy was required to obtain structural information. Highly polar or high molecular weight chlorinated DBPs were effectively isolated by ultrafiltration and size exclusion chromatography.

Rantakokko et al. (2004) described methods for improving the detection of MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5*H*)-furanone) and its brominated analogues in drinking water. Their method utilized calibration standards prepared in real sample matrices, as well as SPE, derivitization with 2-propanol, and GC/MS. One of the major difficulties was degradation of brominated MX compounds with the GC/MS system.

A method for low-level quantification of eight nitrosamines in groundwater was developed by Charrois et al. (2004). The method utilizes SPE for extraction, followed by GC/MS with ammonia positive chemical ionization to achieve detection limits ranging from 0.4 to 1.6 ng/L. The method was used to measure NDMA in drinking water at 2-180 ng/L, as well as N-nitrosopyrrolidine and N-nitrosomorpholine at concentrations between 1 and 4 ng/L. The latter two compounds have not been previously reported in drinking water.

Identificatin, Occurrence, and Formation. Siddiqui and Atasi (2004) reviewed information on the occurrence, toxicology, applicable regulations, and possible methods for minimizing formation of NDMA in wastewater treatment. NDMA can be formed in wastewater treatment plants from a range of precursors, particularly from a range of tertiary and quaternary amines as well as dimethylamine itself. NDMA is a disinfection byproduct and a potential carcinogen that poses a threat to groundwaters from reclaimed wastewaters.

NDMA formation was measured after extended chlorination of both model precursors and samples from wastewater treatment plants (Mitch and Sedlak, 2004). Of the model precursors that were chlorinated, only dimethylamine, tertiary amines with dimethylamine functional groups, and dimethylamides formed significant NDMA concentrations. Biological treatment effectively removed the known NDMA precursor dimethylamine; however, biological treatment was less effective at removing other NDMA precursors. NDMA formation could be prevented by eliminating dimethylamine-based polymers used for sludge treatment, removing ammonia via nitrification, and using filtration to remove particle-associated precursors.

Rodriguez et al. (2004) studied the temporal and spatial distribution of THMs and HAAs in a Canadian drinking water distribution system with significant annual temperature variations. Concentrations of both types of DBPs varied widely throughout the distribution system and throughout the year, although patterns for the two types of DBPs varied, with HAAs decreasing and total THMs increasing near the extremities of the distribution system. There was evidence that HAAs were biodegraded within the distribution system.

The factors influencing the formation of HAAs in humic acid solutions and treated wastewater, prior to disinfection, were studied by Qi et al. (2004). The method of monochloramine application significantly affected the distribution and quantity of HAAs produced. Higher initial ratios of Cl:N always resulted in higher HAA production, and presence of bromide tended to result in production of brominated HAAs, as well as increase the production of total HAAs.

Chloraminated drinking waters produced from high bromide and iodide source waters may contain iodacids and likely other iodo-DBPs (Plewa et al., 2004b). These iodo DBPs were studied and detected in finished drinking waters using GC/MS after derivatization with BF_3 -methanol; tentative chemical structures were proposed. One of these compounds, iodoacetic acid (IA), is the most toxic and genotoxic disinfection byproduct (DBP) in mammalian cells reported in the literature.

Total organic bromine correlated closely to mutagenicity of chlorinated drinking waters, and in many cases, brominated DBPs account for a significant portion of the toxicity due to DBP formation (Echigo et al., 2004). The reaction between hypobromous acid and humic acids resulted in 2-6 times the mutagenic activity of the reaction produced by the reaction between hypochlorous acid and humic acids. Using a chromosomal aberration test, bromate produced by ozonation was found not to produce significant mutagenicity.

Halonitromethanes, a poorly understood class of drinking water DBPs, were identified and synthesized (Plewa et al., 2004a). Nine of these compounds were synthesized, and several were identified at concentrations $<1 \mu\text{g/L}$ in finished drinking waters disinfected with pre-ozonation followed by chlorination or chloramination.

Because many of these compounds are thermally unstable, detection of these compounds was accomplished using GC-MS with lower injection port and transfer line temperatures than typical methods.

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