Chapter 11 Sampling and Analysis of Emerging Pollutants

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1.1 Introduction

Historically, environmental monitoring programs have tended to focus on organic chemicals, particularly those that are known to resist degradation, bioaccumulate in the fatty tissues of organisms, and have a known adverse toxicological effect. The Stockholm Convention on Persistent Organic Pollutants (http://chm.pops.int) identified several classes of chemicals of environmental concern--chlorinated pesticides, polychlorinated biphenyls, polychlorinated dioxins, and furans--and later developed policy criteria leading to the worldwide limitation or ban on the use of a dozen chemicals in these classes (UNEP, 2005). These chemicals and others which fit the described criteria are typically referred to as persistent organic pollutants (POPs).

Recently, it has been recognized that risks to aquatic and terrestrial organisms, including humans, are not limited to chemicals fitting the classical POP definition. An examination of the complex mixtures of chemicals present in natural water reveals the presence of organic chemicals covering a wide range of water solubilities and environmental half-lives. Many of these chemicals have been termed "emerging contaminants" by the scientific community.

"Emerging contaminants" (ECs) is a phrase commonly used to broadly classify chemicals which do not fall under standard monitoring and regulatory programs but may be candidates for future regulation once more is known about their toxicity and health effects (Glassmeyer, 2007). The term "emerging" can be misinterpreted as an indication that the chemical's presence in the

environment is new, when in fact it means the chemical has recently gained the interest of scientific and regulatory communities. Chemicals such as polybrominated diphenyl ether (PBDE) flame retardants, musk fragrances, and pharmaceuticals have been present in the environment since their first use decades ago (Garrison et al., 1976; Hignite and Azarnoff, 1977; Yamagishi et al., 1981; de Wit, 2002), but only recently have they emerged into the spotlight due to advances in monitoring techniques and the increased understanding of their toxicological impact. Other chemicals, like nanomaterials, can truly be defined as emerging, i.e., "new". Although, nanomaterials have been present in research laboratories since the early 1980s, it has only been since the early 2000s that nanomaterials have been produced in sufficient quantities for consumer use (Englert, 2007). Some of these new nanomaterials may become a concern as the probability is high for their continual release into the aquatic environment via multiple consumer applications such as nanosilver disinfectants released into washing machines, water purifiers, and athletic socks and nano-titanium dioxide in cosmetics and sunblocks (Woodrow Wilson International Center for Scholars Nanotechnology Project Inventories, 2009).

Effluents, treated and non-treated, from wastewater treatment plants (WWTPs) and industrial complexes, leaking septic tanks, rural and urban surface runoff, and improper disposal of wastes are all common sources of ECs. ECs commonly include complex mixtures of new generation pesticides, antibiotics, prescription and nonprescription drugs (human and veterinary), personal-care products, household and industrial compounds such as antimicrobials, fragrances,

surfactants, and fire retardants (Alvarez et al., 2005). The fate of such contaminants in WWTPs is largely unknown; however, the limited data that does exist suggests that many of these chemicals survive treatment and some others are transformed back into their biologically active form via deconjugation of metabolites (Desbrow et al., 1998; Halling-Sørensen et al., 1998; Daughton and Ternes, 1999).

The plethora of the ECs in the environment is highlighted by Kolpin et al. (2002), who found at least one EC in 80% of the 139 streams sampled across the United States. Rowe et al. (2004) reported that at least one EC was present in 76% of shallow urban wells sampled in the Great and Little Miami River Basins in Ohio and found that the number of ECs detected increased with increasing urban land use. Urban streams are impacted by EC contamination due to the concentration of people and potential point sources; however, surface and groundwater systems in rural areas can also be at risk due to less efficient waste treatment systems and non-point source contamination from agricultural practices (Barnes et al., 2008; Focazio et al., 2008). Widespread use of pesticides and land application of manure from large animal feeding operations are common contributors of anthropogenic contaminants to rural water systems (Boxall et al., 2003; Sarmah et al., 2006; Burkholder et al., 2007).

Diminishing fresh water supplies has prompted a “use and reuse” practice where water is often used, treated, and released back into a reservoir or river, before being reused again as drinking

water by the same or downstream communities (Drewes et al., 2002 ; US Environmental Protection Agency, 2004; Radjenović et al., 2008). The pathways for removal of ECs from wastewater streams are poorly understood and as a result, many ECs survive conventional water treatment processes and persist in drinking water supplies (Stackelberg et al., 2007; Benotti et al., 2009). Gibbs et al. (2007) found that 52 of 98 ECs remained unaltered in chlorinated drinking water 10 days after treatment.

Releases of ECs into the environment, albeit at trace (parts per billion and parts per trillion) concentrations, have the potential to cause adverse biological effects across a range of species (Daughton and Ternes, 1999; Sumpter and Johnson, 2005). Several common ECs are known or suspected to alter the endocrine function in fish, resulting in impaired reproductive function, feminization or masculinization of the opposite sex, and other anomalies (Sumpter and Johnson, 2005). Pharmaceuticals designed for human or veterinary use have a specific biological mode of action; however, the impact on non-target species is rarely known. Since ECs are released into the environment as complex mixtures, and not single compounds, the possibility exists for synergistic or antagonistic interactions resulting in unexpected biological effects. The concentrations of ECs in water supplies are likely to be below any level of direct risk to humans; however, the presence of antibiotics in the environment may result in the development of antibiotic-resistant strains of bacteria which could become a serious threat to human health (Schwartz, 2003; Kümmerer, 2004; Josephson et al., 2006; Schwartz, 2006).

The first step in understanding the potential biological impact of ECs in the environment is to identify and quantify the types of ECs that are present. To do so, innovative sampling methodologies need to be coupled with analytical techniques which can confirm the identity of targeted and unknown chemicals at trace concentrations in complex environmental samples. This chapter will discuss common techniques which can be used to address the issues of sampling and analysis of ECs, such as pharmaceuticals, hormones, personal care products, perfluorinated chemicals, and nanomaterials in water.

11.2 Sampling Methods

11.2.1 Development of a Sampling Plan

Obtaining a sample of the matrix of interest is an often-overlooked but vital component of any environmental monitoring program. Failure to properly collect a sample can invalidate any results subsequently obtained. The sample should be representative of the original environmental matrix (air, water, sediment, biota, etc.) and be free of any contamination arising during sample collection and transport to the analytical facility. The collection of a representative sample starts in the office or laboratory with the training of personnel and formulation of a sampling plan, moves to the field for the actual sampling, and ends with the shipment of the sample to the laboratory.

A successful sampling strategy must begin with a thorough plan and established protocols. Areas of questions which need to be addressed while planning the sampling trip include: 1) selection of the sampling method to obtain a representative sample, 2) determination of the sample quantity needed to meet the minimum quantitation limits of the analytical method, 3) identification of quality control (QC) measures to be taken to address any bias introduced by the sample collection, 4) identification of safety measures that need to be taken, and 5) determination of sampling objectives. The study plan must define the chemicals to be assayed in the sample and sample size requirements of the analytical methods. Different extraction and processing procedures may be needed to isolate targeted chemical classes from each other and potential interferences, resulting in larger sample size requirements. If sample size is limited, then alterations to the processing methods or changes to the overall study design may need to be made. If possible, reconnaissance trips to sampling sites will greatly aid in the determination of the logistical needs of the sampling plan.

Documentation of the sampling trip is critical as observations and measurements made in the field are often necessary for the integrity of the sample and can be instrumental in the final interpretation of the chemical analyses. Depending on the study design and properties of the targeted chemicals, water quality parameters such as temperature, flow, pH, turbidity, etc., may need to be taken. The field log should include sample collection procedures, location of the

sampling sites on maps, global positioning system (GPS) coordinates or other data to identify the site(s), date and time samples were collected, types of QC that were used, and names of the personnel involved in the sample collection. Additional information on weather conditions during sampling, visible point sources of contamination and surrounding land use can be useful during the final interpretation of the data. Photographs of the sampling sites are often helpful, especially if the project officer or the scientists interpreting the data and writing the report are not familiar with the location.

The sample collection plan becomes a balancing game between the numbers of samples which can be taken, defined by sample availability and funding, and the amount of uncertainty that can be tolerated by the study objectives. When collecting samples, regardless of the matrix, the amount of uncertainty associated with the sampling decreases with increasing number of samples. Sample collection can follow a judgmental, systematic, or random pattern approach (Keith, 1991; Radtke, 2005). A judgmental approach focuses the sampling points around a predetermined spot such as a known point source. A systematic approach involves taking samples from locations identified by a consistent grid pattern. The random approach has no defined locations for sample collection and requires a high number of samples to be taken, but generally results in the lowest uncertainty

Regardless of the type of sample matrix method used, issues of sample preservation, storage

conditions and time, and shipping methods must be resolved. Samples should be collected with equipment made of stainless steel, aluminum, glass, or fluorocarbon polymers. Materials made of polyethylene, rubber, Tygon®, or other plastics should be avoided due to the potential for these materials to absorb or desorb targeted chemicals from/into the collected sample. Since plasticizers and flame retardants are commonly targeted ECs, plastics should not be used as they may contain high levels of these chemicals from the manufacturing process. The need for sample preservation, which can vary among chemical classes, often requires the addition of chemicals to water samples, but this is generally not recommended for most ECs. If elevated levels of residual chlorine are present in a water sample, sodium thiosulfate is often added to prevent the formation of chlorinated by-products (Keith, 1991; US Environmental Protection Agency, 2007a, 2007b). To prevent alteration, samples are shipped chilled (<4-6 °C) via overnight carrier to the laboratory and if ECs are potentially sensitive to UV radiation, amber bottles are used to prevent photodegradation.

11.2.2 Traditional Sampling Techniques

Water is an extremely heterogeneous matrix both spatially and temporally (Keith, 1990). The mixing and distribution of waterborne chemicals in a water body are controlled by the hydrodynamics of the water, the sorption partition coefficients of the chemicals, and the amount of organic matter (suspended sediment, colloids, and dissolved organic carbon) present. Stratification due to changes in temperature, water movement, and water composition can occur

in lakes and oceans resulting in dramatic changes in chemical concentrations with depth (Keith, 1990). Because episodic events from surface runoff, spills, and other point source contamination can result in isolated and/or short-lived chemical pulses in the water, sampling sites and methods must be carefully selected.

11.2.2.1 Surface Water

The most common method for collecting surface water samples is taking grab or spot samples. This may involve taking a single sample or a composite sample representative of a width- and depth-integrated profile. Collecting a sample by hand directly into the shipping sample container is the easiest method, especially in small, wadeable streams. In deeper water such as lakes and reservoirs, samples are often taken using bailers or thief samplers (Lane et al., 2003). Common samplers include the Kemmerer, Van Dorn, and double check-valve bailer designs (Figure 11.1), all of which consist of a tube or bottle that collects the water sample. The sample is constrained by caps or check valves which close upon being released by a messenger (a weight or other object which is released along a tether line from the surface). These types of samplers are useful for collecting discrete samples from specific depths.

Depth-integrated samplers generally fall into two categories: hand-held samplers used in wadeable streams, and cable-and-reel samplers for non-wadeable bodies of water (Lane et al., 2003). These samplers are designed to accumulate a representative water sample as the sampler

is moved across a vertical cross-section of the water body. Depth-integrated samplers often are a torpedo-shaped device which maintains a horizontal orientation as it is raised and lowered in the water column (Figure 11.1). Water enters through a small port in the nose and is collected in a container inside the sampler.

Automated sampling systems are often used in remote locations (ephemeral, small streams, storm drains, effluent discharges) where the presence of water may be intermittent, and to collect composite samples over time. They can be programmed to take samples at predetermined intervals or be started by an external sensor such as a flow meter or depth gauge. A basic system consists of a pump to draw water into a collection vessel, while more sophisticated systems can collect multiple samples, have refrigerated storage chambers, and can transmit and receive programming and data via land-line or cellular phone connections.

11.2.2.2 Groundwater

Groundwater samples are generally collected from existing supply wells or monitoring wells. The sampling methods vary depending on water depth and well size. Because monitoring wells are generally small, sampling is less frequent. Samplers as discussed above are often used due to their ease of use at multiple sites. Portable peristaltic pumps can also be used to obtain groundwater from monitoring wells. Because supply wells for domestic, industrial, and agricultural use often require routine monitoring, large-capacity pumps and autosampling

systems are often permanently installed.

11.2.2.3 Soil and Sediment Pore Water

Pore water samples are an important component in assessing toxicity to benthic invertebrates and understanding the potential trophic transfer of contaminants (Winger and Lasier, 1991; Ankley and Schubauer-Berigan, 1994). Pore water can also be a marker of chemicals which may be released into the overlying water column. Pore water samples can be collected *in situ* using passive sampling devices (section 11.2.3.3) or in the laboratory. Collection of pore water from sediment samples in the laboratory can be achieved by centrifugation, squeezing, and vacuum filtration (Bufflap and Allen, 1995; Angelidis, 1997). Centrifugation involves placing a soil/sediment sample in a centrifuge tube and then centrifuging until the soil/sediment forms a pellet in the bottom of the tube. The supernatant is then decanted and filtered prior to further processing or analysis. The squeezing method uses pressurized systems with either a diaphragm or piston to compress the sediment and release the interstitial water. Vacuum filtration can be performed in the laboratory or as an *in situ* active sampling method that involves a sediment probe made of porous plastic, ceramic, or other material which is placed in the sediment. The probe is attached via a length of tubing to a syringe, hand-operated or automatic vacuum pump which withdraws the pore water from the sediment. Since pore water samples collected by vacuum filtration are not exposed to air, pore water characteristics are retained and loss of volatile chemicals is minimized (Winger and Lasier, 1991).

11.2.3 Time-Integrated (Passive) Sampling Techniques

Because time-weighted average (TWA) concentrations of chemicals are commonly used to determine exposure, they are a fundamental part of an ecological risk assessment process for chemical stressors (Huckins et al., 2006). Since grab samples only represent the concentration of chemicals at the instant of sampling, TWA exposure is difficult to accurately estimate even with repetitive sampling. Episodic events are often missed with routine grab sampling schedules. In addition, the detection of trace concentrations of ECs can be problematic as standard methods are designed to handle small (<5 L) volumes of water. Passive sampling devices provide an alternative to grab sampling, overcoming many of the inherent limitations of those traditional techniques.

Successful use of personal passive monitors or dosimeters in determining TWA concentrations of chemicals to measure exposure in the workplace (Fowler, 1982), has contributed to the application of the same principle to dissolved organic contaminants in water (Huckins et al., 2006). Integrative or equilibrium passive samplers can be used depending on their design, the exposure time in the field, and the properties of the targeted chemicals. Integrative samplers are characterized by having an infinite sink for the retention of sampled chemicals, providing a higher degree of assurance that episodic changes of chemical concentrations in the water will not be missed. The use of an integrative sampler is essential for the determination of TWA

concentrations. Equilibrium samplers are characterized by having low capacity for retaining chemicals and high chemical loss rates. Although simplicity in the uptake models makes equilibrium samplers an attractive option, one of the difficulties encountered is assessing whether equilibrium—which can be affected by temperature, water flow, and biofouling—has been reached or not (Huckins et al., 2006).

11.2.3.1 Surface Water

The major use of passive sampling devices outside of occupational-exposure monitoring for human health and safety in the workplace is in surface water applications. A growing number of passive samplers have been developed for sampling organic chemicals in water. These samplers include, but are not limited to, semipermeable membrane devices (SPMD), polar organic chemical integrative samplers (POCIS), Chemcatchers, polyethylene strips, polymers on glass, and solid-phase microextraction (SPME) devices (Namieśnik et al., 2005). The SPMD and POCIS are two of the most widely used passive samplers for measuring ECs in surface water (Figure 11.2). SPMDs consist of a layflat low density polyethylene membrane tube containing a neutral lipid such as triolein (Huckins et al., 2006). The POCIS consists of a solid phase sorbent or mixture of sorbents contained between two sheets of a microporous polyethersulfone membrane (Alvarez et al., 2004; 2007). SPMDs sample chemicals with moderate to high (>3) octanol-to-water partition coefficients (K_{ow}s) due to the affinity of these hydrophobic chemicals to partition into the lipid and hydrophobic membrane of the sampler. Chemicals with log K_{ow}s

<3 are sampled using the POCIS, which has a hydrophilic membrane and modified adsorbents to remove polar organics from the water. By using the two samplers in concert, a wide range of organic chemicals can be measured.

A generic processing scheme for SPMDs and POCIS (Figure 11.3) begins with collecting the passive sampler used in the field or laboratory and storing it at <0 °C in a solvent-rinsed airtight container, such as a metal can, for transport to the laboratory and storage until processing. At the onset of processing, the exterior of the sampler is gently cleaned with a soft toothbrush and running water to remove any particulate matter on the surface which may fall into the sample on opening. Chemical residues are recovered from the sampler by extraction using a suitable method such as dialysis for the SPMD or solvent extraction of the sorbent for the POCIS. Depending on the requirements of the analytical method, the extract can undergo further enrichment and fractionation to isolate the targeted chemicals from potential interferences. The extracts are then available for analysis using common analytical instrumentation, for bioassay or toxicity testing, or for dosing experiments to determine effects on organisms.

SPMDs and POCIS are commonly used for measuring levels of ECs in surface water. Leiker et al. (2009) determined levels of methyl triclosan in Las Vegas Wash, a channel receiving treated WWTP effluents from the city of Las Vegas, Nevada, using SPMDs. Trace water concentrations of PBDEs have been measured using SPMDs in the Columbia River (WA, USA) and off the

Dutch coast (Booij et al., 2002; Morace, 2006). POCIS have been used in numerous surface water monitoring studies to assess pharmaceuticals and other ECs in WWTP effluents (Jones-Lepp et al., 2004; Alvarez et al., 2005, 2009; MacLeod et al., 2007; Mills et al., 2007). Chemicals such as antibiotics, fragrances, plasticizers, and surfactants were commonly found in these studies. Comparisons between POCIS and traditional grab sampling techniques have shown that the latter can miss the sporadic or low level occurrence of ECs and that TWA data are less variable and easier to interpret than data obtained using repetitive grab samples (Alvarez et al., 2005; Vermeirssen et al., 2006).

11.2.3.2 Groundwater

Passive samplers which have a minimal effect on water circulation and preserve stratification of water within a well have an advantage over active sampling techniques (Vrana et al., 2005). Samplers based on diffusion have been used for the monitoring volatile organic compounds (VOCs) since the early 1990s (Vroblesky et al., 1991). While most groundwater passive samplers have focused on VOCs, semivolatile organic compounds have been sampled using SPMDs (Vrana et al., 2005; Huckins et al., 2006). The use of any passive sampler such as the SPMD which has a large capacity and high sampling or clearance rates can be limited in systems with low groundwater flow. If the exchange volume of the well is less than the clearance volume of the SPMD, chemicals can potentially be depleted changing the equilibrium between the sediment and water (Vrana et al., 2005). This can be avoided by using smaller SPMDs or

choosing a different passive sampler which has a clearance volume less than the groundwater recharge rate.

11.2.3.3 Soil and Pore Water

Collection of pore water samples *in situ* avoids possible alteration during collection, shipment, storage, and processing of whole sediment samples. A dialysis sampler gives more accurate estimates of the pore water concentrations than centrifugation because sediment-water interactions can result in altered chemical measurements (Angelidis, 1997). The most common passive sampler for pore water is a dialysis system occasionally referred to as Peepers or the Hesslein In-situ Pore Water Sampler (Hesslein, 1976). Peepers that are based on the diffusion of chemicals across a membrane are equilibrium samplers, whose efficiency is determined by the equilibration time and the diffusion coefficient for a chemical, temperature, and sediment porosity.

The development of the solid-phase microextraction device (SPME) which is an equilibrium sampler consisting of a coated fiber housed in a syringe body provides a new means of collecting an *in situ* sample of organic chemicals in pore water. The fiber is plunged into the sediment where it reaches equilibrium with the pore water and then is retracted into the syringe body (Ouyang and Pawliszyn, 2007; Maruya et al., 2009). Specially outfitted gas chromatographs can allow the SPME fiber to be inserted into an injector where the sampled chemicals are recovered

via thermal desorption and directly analyzed.

11.2.4 Quality Control (QC)

Bias in the form of variability and sample contamination which is present in every sample can be identified by the use of appropriate QC measures. Common types of QC samples include replicates, blanks, and fortified samples (spikes). Identical conditions (i.e., sampling devices, containers, and protocols) must be used for both the field and QC samples. The selection of the matrix for blank and spiked QC samples must be nearly identical to the field sample matrix but free of the chemicals of interest in the study.

Three types of blanks are commonly used: field, trip, and equipment blanks. Field blanks are exposed to the ambient air during the sampling process to measure any potential contamination. Generally, these blanks consist of analyte-free water, freshly prepared passive samplers, or some other surrogate matrix. In contrast, trip blanks which are not exposed to the air accompany the field samples from the sampling site to the laboratory to assess contamination during shipping, handling, and storage. Equipment blanks are rinses of the sampling equipment (e.g., buckets, bailers, autosamplers, etc.) which are collected to determine how adequately the equipment was decontaminated between uses. Steps to minimize sample contamination include thoroughly cleaning the sampling equipment, reducing exposure time to ambient air, and avoiding contact with or consumption of personal-use products and medications which may contain the chemicals

of interest.

Quality control spikes can include field-spiked samples where known quantities of targeted chemicals are added to collected samples to identify field, transportation, and matrix effects (Keith, 1991). If there is not sufficient sample available in the field, a surrogate matrix can be used for these spike samples. Budgetary constraints can limit the amount of QC that is used; however, it should not limit the types of samples which are collected. As an alternative, the field blanks can be analyzed and the remaining QC samples archived unless problems are identified in the field blanks (Keith, 1991).

11.3 Sample Preparation, Extraction, Cleanup and Analysis

One of the challenges facing the analytical chemistry community is the development of robust and standardized analytical methods and technologies that can easily be transferred to laboratories worldwide. While today's analysts can detect pg L^{-1} and ng L^{-1} concentrations of numerous ECs (e.g., PFOS, PFOAs, pharmaceuticals, nonyl- and alkyl-phenolethoxylates, steroids, hormones, and their metabolites) in various water matrices (e.g., surface waters, wastewaters, groundwater), proper analytical methods must still be followed. Table 1 provides a summary of the methods discussed in this section.

11.3.1 Preparation, Extraction, and Cleanup

Concentrations of ECs found in the water samples are typically below the μg L^{-1} range, making extraction, pre-concentration, and cleanup prior to detection an important step. Solid phase extraction (SPE) is one of the most widely reported methods for isolating ECs from environmental aqueous samples. SPE was developed as an alternative to liquid-liquid extraction (LLE) which is labor intensive, difficult to automate, and requires large portions of high-purity solvents, such as methylene chloride. Nevertheless, LLE has been used to extract ECs containing hydroxyl groups (e.g., bisphenol A, nonylphenol ethoxylates, alkylphenol ethoxylates, and most steroids and hormones) from water. This process often requires derivatization of the hydroxyl groups prior to extraction using agents such as *N*-methyl-*N*-(tert-butyldimethylsilyl) trifluoroacetamide (MTBSTFA), bis(trimethylsilyl) trifluoroacetamide (BSTFA), and *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA), and less frequently diazomethane (Kelly, 2000; Moeder et al., 2000; Mol, et al. 2000; Öllers et al. 2001; Ternes, et al., 2002; Liu et al., 2004). Most of the LLE methods described below use derivatization before gas chromatography-mass spectrometry (GC-MS) analysis.

11.3.1.1 Liquid-Liquid Extraction

Mol et al. (2000) proposed a specific LLE procedure for several nonyl- and octyl-phenols, 4-*tert*-butylbenzoic acid, bisphenol A, 17β-estradiol, and 17β-ethynylestradiol where water samples are acidified and extracted with two portions of ethyl acetate. The extracts are then reduced in

volume and derivatized prior to analysis by gas chromatography-mass spectrometry (GC-MS). Zaugg et al. (2007) described a continuous LLE (CLLE) procedure for extracting several classes of ECs (e.g., alkylphenol ethoxylate nonionic surfactants, flame retardants, plasticizers, fecal sterols, and disinfectants) from surface and storm-sewer overflow water samples that are not pH-adjusted or filtered. This method is different from traditional LLE methods in that it uses smaller amounts of methylene chloride, and shorter extraction times (6 vs. 24 hrs). The extracts are then concentrated and analyzed by GC-MS.

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The American Society for Testing and Materials (ASTM) (2007) published a standard test method for the determination of nonylphenols, bisphenol A, p-tert-octylphenol, nonylphenol monoethoxylate, and nonylphenol diethoxylate in environmental waters using LLE as an extraction method with subsequent detection by GC-MS. This method calls for acidified water samples, placed into a LLE along with methylene chloride, and extracting the water sample for 18 to 24 hours. After the extraction is complete the extracts are concentrated, dried over anhydrous sodium sulfate, and subsequently analyzed by GC-MS.

Richardson et al. (2008) reported a LLE-gas chromatography-negative chemical ionization mass spectrometry (GC/NCI-MS) method for a newly recognized class of ECs, namely, iodo-disinfection byproducts. The iodo-acids that are produced during disinfection of drinking water using chloramines for disinfection, and iodoacetic acid are extremely cyto- and genotoxic

(Richardson et al., 2008). One L of drinking water is adjusted to pH < 0.5, 350 g sodium sulfate is added, and the sample is extracted with methyl tert-butyl ether (MTBE). The iodo-acids partition into the organic phase where they are derivatized with the addition of diazomethane, thus converting the iodo-acids into methylated iodo-acids prior to GC/NCI-MS analysis.

Nanomaterials are defined as carbon- or metallic-based, dendrimers, and bio-inorganic composites with particle sizes in the nm range (1-100 x 10^{-9} m). Nanomaterials can be considered as new chemicals because their physicochemical properties are very different at this extremely small scale. They have relatively large specific surface areas and at the very low end of the scale, quantum effects can override their general physicochemical properties (Motzer, 2008). While the number of consumer products containing nanomaterials is soaring, methods for their detection in the environment are lacking, with few papers published on the subject. Although the first method was developed to detect naturally occurring C_{60} and C_{70} fullerenes in geologic samples (Heymann et al., 1995), this method could probably be adapted to water samples. Their method requires the sample to be slurried by sonication for 4 hr with adequate amounts of toluene before extraction on a Soxhlet apparatus. A preparatory liquid chromatography column (19 x 300 nm) coupled to a photo diode array (PDA) detector facilitated the separation of the fullerenes from the organic solution using a methanol and toluene mobile phase with a flow rate of 10 mL min^{-1}. Extraction efficiencies were >90% for C_{60} and C_{70}. The second method, reported by Buchard and Ma (2008), is a simple LLE procedure for extracting

C_{60}, C_{70}, and [6, 6]-phenyl C_{61}-butyric acid methyl ester (PCBM) from environmental waters. In this method, water samples are stirred for 13 days and then allowed to settle for 1 hr before sampling. An aliquot was collected from which three sub-aliquots were extracted with toluene. An aliquot of toluene phase was analyzed by HPLC-UV. One consideration when trying to extract fullerenes from environmental waters, is that at neutral pH, fullerenes are negatively charged, thereby facilitating their formation of stable colloidal suspensions, but negating their ability to partition into organic solvents for extraction. Therefore, something needs to be added to the water suspensions to facilitate the break up of the nano-colloidal suspensions. Bouchard and Ma (2008) showed that the addition of $Mg(ClO_4)$ destabilized the colloidal suspensions thereby enhancing the partitioning of the carbon-based nanomaterials into the toluene.

11.3.1.2 Solid Phase Extraction

Because many hydrophilic ECs do not partition into an organic solvent, resulting in poor extraction efficiencies, SPE rather than LLE should be used. SPE offers lower solvent consumption, shorter processing times, automation options, and simpler procedures than LLE. Since direct sampling in the field is an option for SPE, the need for transport and storage of large sample volumes of water to the laboratory can be avoided (Osemwengie and Steinberg, 2001; Primus et al., 2001). Field-portable SPE can reduce the possibility of degradation of target analytes during sample holding times after sample collection.

Solid-phase extraction is commercially available in three basic formats: thin flat discs (47 and 90 mm), small cylindrical cartridges (usually < 6 mL reservoirs), and 96-well plates. Each type of format can employ a wide-variety of sorbents such as silica based (e.g., C_{18}), hydrophilic lipophilic balanced (HLB), mixed cation exchange (MCX), and mixed anionic exchange (MAX). SPE sorbents are selected for their ability to retain the ECs of interest, based upon a variety of physico-chemical properties of both the SPE phase and the analytes (e.g., pK_a and K_{ow}). For example, C_{18} is used as a universal extraction sorbent, with a pH range from 2 to 8, and its retention mechanism is primarily governed by hydrophobic interactions between the analytes and the carbonaceous moieties of the C_{18} alkyl chains (Poole, 2003). Other less commonly used SPE sorbents include weak cation-exchange (WCX), weak anionic-exchange (WAX), strong MAX, anion or cation exchange sorbents without mixed mode sorbents, and C_8 (Benito-Peña et al., 2006; Kasprzyk-Hordern et al., 2007). The ion exchange cartridges are useful not only for extraction and concentration, but also for sample clean up. For example, SPEs can be used to separate humic and fulvic acids from basic ECs, or separate neutral lipids from charged analytes. EC extraction is completed by first cleaning and conditioning the SPE cartridge with the solvent which will be used for the extraction solvent (e.g., methanol), followed by a neutral solvent of the same composition as that of the sample (e.g., water). Once the cartridge is prepared, 0.1 to 2 L of sample is passed through the SPE cartridge, at approximately 7 to 10 mL min^{-1}, using either gravity, vacuum-induced, or syringe-push flow, after which the cartridge is dried for a varying amount of time, and finally extracted using various solvents or solvent mixtures dependent on

the p*K*a's and polarities of the analytes of interest (Poole, 2003).

Although LLE can be used for a variety of hydrophilic ECs as discussed above, much of the current work uses SPE for the extraction of these compounds from water. Snyder et al. (1999) were one of the first to report the use of SPE for hormones and steroids detection in source waters. What makes their method interesting is that it is an *in situ* (field) extraction technique utilizing 90-mm styrenedivinylbenzene SPE discs, which allow for very large volumes (5 L) of water to be extracted. A stainless steel mesh filter at the head of the tubing prevents large particles from entering with the SPE disc encompassed between two glass fiber filters. Once the extraction is complete, the SPE discs are removed, frozen, and shipped to the laboratory for recovery of the hormones and steroids. The resulting organic extract is analyzed using a HPLC-fluorescence detector and radioimmunoassay (Snyder et al., 1999). A more recent analytic procedure using SPE (HLB sorbent) and LC-MS/MS was developed for parabens, alkylphenolic compounds, phenylphenol, and bisphenol A (Jonkers et al., 2009). Water samples at neutral pH, were extracted using SPE (HLB sorbent) cartridges. The cartridges were dried and the analytes were eluted using 3 mL methyl-*tert*-butyl ether/2-propanol (1:1) followed by 3 mL methanol. The eluent was evaporated to approximately 250 µL before adding another 250 L methanol:water (1:1) to bring the final volume to 500 µL before analysis by LC-MS/MS.

Osemwengie and Steinberg (2001) also used an *in situ* SPE extraction technique for

concentrating natural musks and synthetic musks (e.g., tonalide, galaxolide, cashmeran, versalide) from natural waters. A proprietary sorbent [a mix of polystyrene and poly(methyl methacrylate)], packed between polyethylene frits was used. After extraction of ~60 L of water, the cartridges were returned to the laboratory for extraction and clean-up, using gel permeation chromatography, and analysis by GC-MS.

Ternes et al. (2001) used SPE C_{18} to extract nine neutral pharmaceuticals (e.g., diazepam, caffeine, glibenclamide, omeprazole, phenylbutazaone) from water. Briefly, this method calls for the extraction of 500 mL of filtered, pH adjusted (7.0 to 7.5) water, and subsequent elution with 3 x 1 mL of methanol. The extracts were further concentrated to 20 µL, brought back up to 1 mL with a phosphate buffer, and stored at < -20^{o}C until analysis by LC-electrospray-triple stage quadrupole mass spectrometry (LC-ESI-QqQ MS).

These early SPE papers used a variety of familiar sorbents (C_{18}, polyvinylstyrenes), but recently several proprietary sorbents have been developed that are better suited for the emerging contaminants. Since 2004, the most frequently used SPE sorbents used for extracting ECs from water matrices are HLB and MCX sorbents. De Alda and Barcelo (2001), who were among the first to report using the HLB-type sorbent, compared on- vs. off-line SPE extraction, and the recoveries of several estrogens, progestrogens and their synthetic counterparts (e.g., ethynyl estradiol, diethylstilbestrol, norethindrone, levonorgestrel) from three types of SPE sorbents,

namely, HLB, C_{18} and a polydivinyl benzene resin-GP (general phase) cartridge. Each type of sorbent has its merits dependent upon the amount of interfering substances in the water samples and the limit of detection (LOD) required (de Alda and Barcelo, 2001). Öllers et al. (2001) proposed a method for the simultaneous extraction of neutral and acidic pharmaceuticals and a few pesticides from water utilizing HLB cartridges. Their methodology involves filtration of a 1 L water sample adjusted to a pH of 3, followed by sample enrichment onto the cartridge, and elution of the analytes with 6 mL of 50:50 ethyl acetate and acetone mixture. Neutral compounds were assayed by GC-MS, followed by the addition of diazomethane to derivatize the acidic pharmaceuticals before a second GC-MS analysis.

Kolpin et al. (2002) describes five different methodologies utilizing combinations of SPE (HLB cartridges) and LLE (using methylene chloride as the extraction solvent) with subsequent analyses either by LC-MS or GC-MS (with derivatization of the acidic compounds before analysis) to characterize 95 ECs in US streams. Togola and Budzinski (2007) developed two extraction methods using both HLB and C_{18} sorbents for 18 different pharmaceuticals (7 basic compounds and 11 acidic drugs) including carbamazepine, aspirin, caffeine, gemfibrozil, and naproxen. However, they later further refined their method to using only HLB sorbent (Togola and Budzinski, 2008). After the same pre-extraction procedures (filtering, pH adjustment < 2), the waters were extracted at a rate of 12 to 15 mL min^{-1}, the cartridge is dried for 1 hr under N_2, before extraction with 3 mL ethyl acetate, 3 mL ethyl acetate/acetone (50:50, v/v), and 3 mL

ethyl acetate/acetone/ammonium hydroxide (48:48:2 v/v/v). The extracts were evaporated, taken up in 100 μL ethyl acetate, and MSTFA is added to derivatize the acidic compounds (e.g., aspirin, ibuprofen, diclofenac, naproxen, gemfibrozil, and clofibric acid) before analysis by GC-MS. An optimized method using SPE (MCX sorbent) was developed for 21 pharmaceuticals from corticosteroids (e.g., cortisone, dexamethasone, hydrocortisone, prednisone) and β-blockers (e.g., atenolol, metoprolol, propanolol) classes by Piram et al. (2008). In this method, 400 mL water is acidified with formic acid before loading onto MCX cartridges. The corticosteroids are eluted with 1 mL methanol/water/formic acid (70:30:0.1, v/v/v) and the β-blockers are eluted in a second stage with methanol/ammonia (95:5, v/v). The subsequent eluants are evaporated to dryness and taken up in acetonitrile/water (25:75, v/v) before analysis by LC-MS/MS.

Antibiotics [e.g., fluoroquinolones (FQs), macrolides (MCs), sulfonamides (SAs), tetracyclines (TCs)] are EC classes of interest due to their possible adverse effect on the environment by promoting the development of antibiotic-resistant bacteria in waters receiving wastewater effluents (Miyabara et al., 1995; Schwartz et al., 2003; Schwartz et al., 2006). Hirsch et al., (1998) were among the first to describe the extraction and detection of multiple classes of antibiotics (e.g., MCs, SAs, TCs, trimethoprim, chloramphenicol, and penicillins) in water. Their early methodology compared a lyophilization procedure with SPE C_{18} sorbent. The resulting extract was analyzed by LC-MS/MS (using a QqQ). Other researchers have successfully reported the use of SPE sorbents for recovery of antibiotics from water. Reverté et

al. (2003) describe a SPE (HLB sorbent) extraction method for the recovery of ciprofloxacin, enrofloxacin, and 4 TCs from water. In their method, 100 to 250 mL water samples are pH adjusted to < 3, the analytes were eluted with 5 mL of methanol, the eluate was evaporated to dryness, and re-dissolved in methanol/water (50:50, v/v) before analysis by selected-ion monitoring (SIM) LC-MS. A watershed scale field study was conducted by Yang and Carlson (2003) to determine contamination occurring due to TCs and SAs used in animal production to treat and prevent disease, and promote growth. The compounds were found in manure and waste lagoons from confined animal feed operations (CAFOs). Because TCs are unstable in acid solutions, the pH of the waters is adjusted to < 3 just immediately before extraction with 5 mL methanol (1% trifluoroacetic acid) to remove the TCs and SAs. Separate water samples are extracted at neutral and pH < 3 to recover the SAs. Subsequently, all eluants are evaporated to 50 µL before analysis by SIM LC-MS. Batt and Aga (2005) describe a SPE methodology using HLB sorbents to extract 13 antibiotics of various classes (FQs, SAs, TCs, MCs) from water, which is initially adjusted to pH <3 and then Na_2EDTA added to chelate metal ions competing with the sorbent, followed by extraction of the analytes from the SPE sorbent with 10 mL acetonitrile. The eluate is reconstituted in 1 mL of deionized water, before analysis by LC-MS/MS. A SPE method to enrich 4 different classes [TCs, SAs, MCs, and ionophore polyethers (IPs)] of 19 veterinary antibiotics from water samples was developed by Kim and Carlson (2006). TCs, SAs, and MCs are used as both human and veterinary drugs to treat disease and prevent infection, while the IPs are used to promote growth and efficiency of feed conversion in

animal production. Their methodology is a modification of that of Yang and Carlson (2003) with optimization of the SPE method for the IPs. As a result no pH adjustments or additives to the methanol and water used for cartridge conditioning or eluting solvent (methanol) are required.

One of the most widely used human antibiotics in the U.S. is azithromycin (annual sales in 2007 were $1.3 billion dollars, equivalent to over 45 million prescriptions; see http://drugtopics.modernmedicine.com/drugtopics/data/articlestandard/drugtopics/102008/500218/article.pdf). Only a few methods have been published on its extraction and detection. Koch et al. (2005) used methyl-*tert*-butyl ether added to 10 mL of water prior to vortexing and centrifugation. The supernatant is transferred to a glass tube, dried, reconstituted in mobile phase, and subsequently analyzed by LC-MS/MS. Jones-Lepp (2006) published a SPE method (HLB sorbent) in which 500 mL of water sample is acidified to pH < 3, passed through the HLB cartridge before extracting the analytes with either methanol (1% acetic acid) or a methanol/MTBE (10:90, v/v) mixture, and analysis (and analyzed) by LC-MS/MS. Focazio et al. (2008) added this compound to their list of analytes being monitored in a large survey of US waters, using the methodologies reported by Kolpin et al. (2002), while Loganathan et al. (2009) used a modification of the method developed by Jones-Lepp (2006).

Other classes of ECs demanding attention are the perfluorinated surfactants including

perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA). Analogous to the persistence of many historic contaminants such as polychlorinated biphenyls (PCBs), perfluorinated compounds are ubiquitous in the environment throughout the world (Giesy and Kannan, 2001) due to their multiple uses as surfactants and surface protectors in a variety of consumer goods. Tseng et al. (2006) report an optimized SPE method in which a water sample at pH 3 is extracted using a C18 SPE cartridge prior to LC-MS analysis. Loganathan et al. (2007) used a SPE (HLB sorbent) and LC-MS/MS methodology to detect PFOS and PFOA in wastewater.

Comment [Fan,Xiaoh2]: No reference

A recent European Union (EU) survey of a variety of ECs in European river waters used a simple SPE (HLB sorbent) extraction procedure followed by LC-MS/MS detection for the analysis of a variety of ECs compromising pharmaceuticals, PFOS, PFOA, steroids and hormones (Loos et al, 2006). A 400 mL unfiltered water sample is passed through SPE and the analytes eluted with 6 mL of methanol. It is assumed that the eluent was further concentrated before LC-MS/MS analysis. Isotopically-labeled compounds were used to correct for extraction losses inherent in the method. Gros et al. (2009) reported a simplified SPE (HLB sorbent) extraction followed by a more sophisticated analytical detection approach using LC-quadrupole-linear ion trap mass spectrometry (LC-QtrapMS) and automated library searching for the detection and identification of 73 pharmaceutical residues (covering a wide range of pharmaceutical classes) in both surface and wastewaters. Their SPE methodology was optimized by comparing both MCX and HLB type sorbents, and a combination thereof with and without

sample acidification and with and without the addition of Na_2EDTA. They concluded that the optimum conditions were: no acidification, Na_2EDTA addition, and HLB sorbent.

11.3.1.3 Other Extraction Techniques

Other extraction techniques including two types of microextraction techniques have been used. The first involves equilibrium liquid–liquid–liquid microextraction (LLLME) rather than exhaustive LLE to extract SAs from small volumes (µL) of water (McClure and Wong, 2007). Unlike in solid-phase microextraction (SPME), the extract phase of LLLME does not come into contact with the sample solution. Instead, LLLME uses a disposable polypropylene hollow fiber to extract SAs into a few µL of an organic phase and subsequently into another phase before analysis. The risk of carryover and cross contamination is essentially eliminated due to the disposable nature of the sampling apparatus. The second method is an SPME technique which uses hollow fibers to extract compounds from an aqueous sample by absorption in the case of liquid coatings, or adsorption in the case of solid coatings, and is similar to LLLME. Moeder et al. (2000) were among the first to use SPMD fiber coatings, and the resultant SPME extracts were derivatized prior to GC-MS analysis. Basheer et al. (2005) describe a modified SPME procedure, termed polymer-coated hollow fiber microextraction (PC-HFME), in which SPME fibers were coated with a new polymer having a large number of functional groups (-OH) more compatible with polar compounds, such as the estrogens. Using PC-HFME, they extracted diethylstilbestrol, estrone, 17β-estradiol and 17β-ethynylestradiol from spiked reservoir and tap

water samples. The extracts were derivatized and analyzed using GC-MS. Some obvious advantages of SPME are small sample size and solvent volume while disadvantages include interferents (e.g., surfactants, humic and fulvic acids) competing for limited bonding sites and extended equilibrium times necessary for ensuring representative extraction efficiencies.

On the horizon is a novel extraction technique utilizing molecularly-imprinted polymers (MIPs) that are target class specific imprinted with specificity for either a single analyte or a class of analytes. Once only in the realm of the research laboratory, there are now several commercially-available MIP sorbents. Meng et al. (2005) developed a re-useable (up to 5 extractions) non-specific MIP to extract 17β-estradiol, diethylstilbestrol, estriol, and estrone from wastewater but a limitation is the difficulty in completely removing the target analytes from the MIP template. This is especially problematic at the low levels at which most pharmaceuticals and hormones are found in the environment (ng L^{-1}), making accurate quantitation of the target compound difficult. This problem was solved by Watabe et al. (2006) who developed a MIP template to extract only 17ß-estradiol (E2) from river water. The MIP template used a similarly structured analog of 17β–estradiol namely, 6-ketoestradiol (KE2), which has a different chromatographic retention time than that of 17β-estradiol. Gros et al. (2008) developed a method that uses a commercially available MIP template (MIP Technologies, Lund, Sweden) to selectively extract eight β-blockers from waste water. Comparing MIP and SPE (HLB) extracts, they found that while recoveries were similar, the MIP extract yielded a lower overall detection limit due to the

specificity of the MIP template.

11.3.2 Detection Techniques

As discussed above, most detection techniques for ECs are based on mass spectrometry, which has become the preferred method in environmental analysis due to the inherent complexity of most environmental samples. For example, early attempts at measuring estrogens in the environment used HPLC-fluorescence detection, but numerous interferences made identification of the targeted estrogens difficult (Snyder et al., 1999). In later work, he utilized the mass accuracy and specificity of a mass specific detector for the same analytes with the additional benefit of being able to characterize other pharmaceuticals in the same lake water matrix (Vanderford et al., 2003).

A variety of mass spectrometers [quadrupole, ion traps (ITMS), time-of-flight (TOF), triple quadrupole (QqQ), magnetic sector, and orbitrap] are now used as detectors coupled to either GCs or LCs. Selection of the type of mass analyzer for environmental analyses depends on the separation technique used (GC or LC), information needed, mass accuracy necessary, and specificity dictated by regulation. A better understanding of mass spectrometry and its application to environmental analysis can be gained from McLafferty 1980, Busch et al. 1988, Barcelo 1996, Grayson 2000, and Herbert and Johnstone 2003.

11.4 Analytical Difficulties

Environmental samples, especially surface water samples containing WWTP effluents, can be extremely complex. Even with state-of-the-art mass spectrometers, positive identification of chemicals can be difficult to nearly impossible to achieve. Problems of co-eluting chemicals, chemicals with common mass-to-charge ratios, and matrix effects such as ion suppression and shifting retention times can all lead to misidentification of compounds. Jones-Lepp et al. (2004) observed shifting retention times during the LC-MS analysis of the illicit drugs methamphetamine and methylenedioxymethamphetamine (MDMA or Ecstasy) in POCIS extracts. Identification and quantitation of the drugs was made possible by the use of collision-induced dissociation (CID) and the method of standard addition to the extracts. Azithromycin has also been shown to share a common product ion with some surfactants requiring CID to prevent misidentification.

Sample cleanup is often essential in isolating chemicals of interest from the rest of the sample. Methods for isolating ECs in environmental samples are limited, but generally involve modifications to common techniques such as SPE, LLE, and dialysis among others. Co-extracted chemicals in environmental samples can be structurally similar to those of interest, making their removal difficult. For example, steroidal hormones share similar ring systems with many naturally occurring sterols (e.g., cholesterol). Many standard cleanup methods are not applicable to EC analyses as the background interferences they were designed to remove are now

part of some EC chemical lists. Besides the sample cleanup problems, laboratory and field contamination issues are different for ECs than for historic contaminants such as pesticides. Soaps, deodorants, cleaning supplies, insect repellants, plasticizers from computer cases, foams, and many other items can all be sources of the chemicals which are part of many EC monitoring programs. Knowledge of a chemical's use and good laboratory practices are essential in preventing accidental contamination of samples.

In addition to the analytical difficulties posed by the complexity of environmental samples, the availability of authentic pure standard materials is limited. Many proprietary chemicals, degradation products, and metabolites of ECs are only available from the original manufacturer or through custom synthesis. Surrogate chemicals, such as isotopically-labeled analogs of targeted ECs, and certified reference materials to be used in QC programs, are not available for many ECs. As demand for these materials and potential for new regulatory action increase, additional ECs will become available from commercial sources to be used in environmental monitoring studies.

11.5 Conclusions

The field of emerging contaminants research is ever-changing as new chemicals are developed and new threats to the environment are recognized. Pharmaceuticals, personal care products, natural and synthetic hormones, plasticizers, and flame retardants are currently the center of

attention due to their constant release into surface-, ground-, and ultimately drinking water.

Water sample collection methods for these ECs are similar to most common sampling techniques. Sample preservation or special handling is generally not required but the use of products containing these ECs during collection must be avoided to prevent contamination. Grab samples have the advantages of being easy to collect and relatively inexpensive. Passive sampling techniques are now favored in EC monitoring studies due to their ability to concentrate trace levels of ECs, catch EC pulses into the environment, and selectively sample dissolved chemicals (not bound to particulate matter).

Because of improvements in EC detection, interest in and understanding of ECs in the environment has skyrocketed. The advent of reasonably priced sophisticated mass spectrometry systems coupled to gas or liquid chromatographs has allowed a greater number of laboratories to gain the needed instrumentation to undertake EC analyses. As knowledge of these ECs increases and new regulations are implemented, sampling and analytical methods for ECs will become commonplace but the cycle will continue as new classes of ECs are identified

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product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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Table 11.1 Review of extraction and detection methods for the analysis of select emerging contaminants

Analyte(s) class(es)	Aqueous matrix	Extraction Method[a]	Detection Method[b]	Reference
Pharmaceuticals, hormones, illicit drugs, surfactants, plasticizers, pesticides, personal care products	Surface water, wastewater	SPMD POCIS	GC-MS LC-MS LC-MS/MS	Alvarez et al., 2005 Alvarez et al., 2007 Alvarez et al., 2009 Jones-Lepp et al., 2004
Nonyl-, octyl- phenols Bisphenol A, 17□-estradiol, 17□-ethynylestradiol	Surface water	LLE	GC-MS w/derivatization	Mol et al., 2000
Alkylphenol ethoxylate nonionic surfactants, flame retardants, plasticizers, fecal sterols, disinfectants	Surface water, stormwater overflows, domestic and industrial wastewater	CLLE	GC-MS	Zaugg et al., 2006
Nonylphenols, bisphenol A, p-	Surface water,	LLE	GC-MS	ASTM D 7065-06

tert-octylphenol, nonylphenol menoethoxylate, nonylphenol diethoxylate	wastewater			
Nonylphenol, nonylphenol ethoxylate, nonylphenol diethoxylate, octylphenol	Surface water, wastewater, sea water	SPE (C_{18})	LC-MS/MS	ASTM D 7485-09
Iodo-disinfection byproducts	Drinking water	LLE	GC/NCI-MS w/ derivatization	Richardson et al., 2008
C_{60} and C_{70} fullerenes, [6,6]-phenyl C_{61}-butyric acid methyl ester	Surface water	LLE	HPLC-UV	Bouchard and Ma, 2008
Steroids, hormones	Surface water	SPE (styrenedivinylbenzene) field sampler	HPLC-fluorescence and radioimmunoassay	Snyder et al., 1999
Parabens, alkylphenols, phenylphenol, bisphenol A	Surface water, wastewater	SPE (HLB)	LC-MS/MS	Jonkers et al., 2009

Musks, synthetic musks (e.g., tonalide, galaxolide)	Surface water, wastewater	SPE[polystyrene/ poly (methyl methacrylate)]	GC-MS	Osemwengie and Steinberg, 2001
Nine neutral pharmaceuticals (e.g., diazepam, caffeine, glibenclamide, omeprazole)	Surface water	SPE (C_{18})	LC-MS/MS	Ternes et al., 2001
Carbamazepine, ibuprofen, diclofenac, ketoprofen, naproxen, clofibric acid, triazines, acetamides, phenoxy acids	Drinking water, surface water, wastewater	SPE (HLB)	GC-MS (two step analysis, derivatization for acidic compounds)	Öllers et al., 2001
Estrogens, progestrogens	Surface water, sediments	SPE (HLB, C18, polydivinylbenzene resin-GP)	LC-DAD-MS	de Alda and Barceló, 2001
95 compounds: veterinary and human antibiotics, prescription drugs, non-prescription drugs,	Surface water	LLE SPE (HLB)	GC-MS LC-MS	Kolpin et al., 2002

phthalates, insecticides, nonylphenols, polynuclear aromatic hydrocarbons				
7 basic pharmaceuticals and 11 acidic drugs: carbamazepine, aspirin, caffeine, gemfibrozil, naproxen	Surface water, wastewater	SPE (HLB)	GC-MS w/derivatization	Togola and Budzinski, 2007
21 pharmaceuticals: corticosteroids (cortisone, dexamethasone, hydrocortisone, prednisone); □-blockers (atenolol, metoprolol, propanolol)	Wastewater (influent, effluent)	SPE (MCX)	LC-MS/MS	Piram et al., 2008
Antibiotics: macrolides, sulfonamides, tetracycline's, trimethoprim, chloramphenicol,	Surface water	Lypholization and SPE (C_{18})	LC-MS/MS	Hirsch et al., 1998

penicillin's				
Ciprofloxacin, enrofloxacin, tetracyclines	Surface water, well water, wastewater	SPE (HLB)	LC-MS (SIM)	Reverté et al., 2003
Erythromycin-H2O, roxithromycin, tylosin	Surface water, CAFO wastewater	SPE (HLB)	LC-MS/MS	Yang and Carlson, 2003
13 antibiotics: fluoroquinolones, sulfonamides, tetracyclines, macrolides	Surface water	SPE (HLB)	LC-MS/MS	Batt and Aga, 2005
Tetracyclines, sulfonamides, macrolides, ionophore polyethers	Surface water	SPE (HLB)	LC-MS/MS	Kim and Carlson, 2006
Azithromycin	Wastewater	LLE	LC-MS	Koch et al., 2005
Azithromycin, roxithromycin,	Surface water,	SPE (HLB)	LC-MS/MS	Jones-Lepp 2006

clarithromycin, methamphetamine, MDMA, urobilin	wastewater			
Azithromycin, roxithromycin, clarithromycin, methamphetamine, MDMA	Surface water, wastewater (influent,effluent)	SPE (HLB)	LC-MS/MS	Loganathan et al., 2009
Perfluorooctanesulfonates (PFOSs), perfluorooctanoates (PFOAs)	Surface water, wastewater	SPE (C18)	LC-MS	Tseng et al., 2006
PFOSs, PFOAs	Wastewater	SPE (HLB)	LC-MS/MS	Loganathan et al., 2007
PFOSs, PFOAs, steroids, hormones	Surface water	SPE (HLB)	LC-MS/MS	Loos et al., 2006
PFOSs, PFOAs	Surface water	SPE (HLB)	LC-MS/MS	Gros et al., 2009
Sulfonamides	Surface waters	LLLME	HPLC/UV	Lin and Huang, 2008
Sulfonamides, macrolides, trimethoprim	Surface water	SPME	LC-MS/MS	McClure and Wong, 2007

Estrogens: diethylstilbestrol, estrone, 17β-estradiol, 17β-ethynylestradiol	Reservoir water, drinking water	PC-HFME	GC-MS w/ derivatization	Basheer et al., 2005
diethylstilbestrol, estrone, 17β-estradiol, estriol	Wastewater	MIP	HPLC/UV-vis	Meng et al., 2005
17β-estradiol	River water	MIP	LC-MS	Watabe et al., 2006
8 β-blockers: atenolol, sotalol, pindolol, timolol, metoprolol, carazolol, propranolol, betaxolol	Wastewater	MIP	LC-MS/MS	Gros et al., 2008

[a] Extraction methods: SPMD – semipermeable membrane device, POCIS – polar organic chemical integrative sampler, LLE – liquid-liquid extraction, CLLE – continuous liquid-liquid extraction, SPE – solid phase extraction, HLB – hydrophilic lipophilic blend, MCX – mixed mode cation exchange, LLLME – liquid-liquid-liquid microextraction, SPME – solid phase microextraction, PC-HFME – polymer coated hollow fiber microextraction, MIP – molecularly imprinted polymers.

[b] Detection methods: GC-MS – gas chromatography mass spectrometry, LC-MS – liquid chromatography mass spectrometry, LC-

MS/MS – liquid chromatography tandem mass spectrometry, GC/NCI-MS – gas chromatography negative chemical ionization mass spectrometry, HPLC-UV – high performance liquid chromatography ultraviolent detection, LC-DAD-MS – liquid chromatography diode array detection coupled with mass spectrometry, SIM – selection ion monitoring.

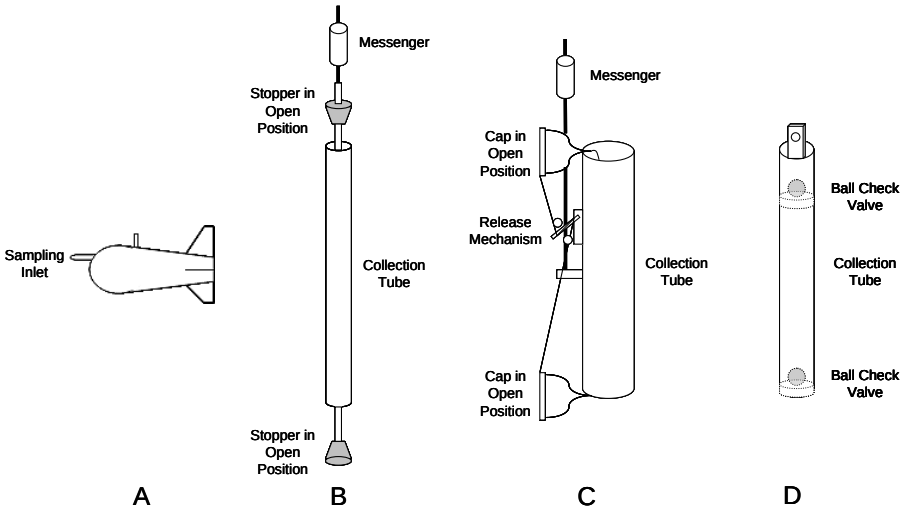

Figure 11.1 Commonly used grab and depth-integrating samplers for collection of surface water samples. A. depth-integrating sampler; B. Kemmerer sampler; C. Van Dorn sampler; D. Double check-valve bailer.

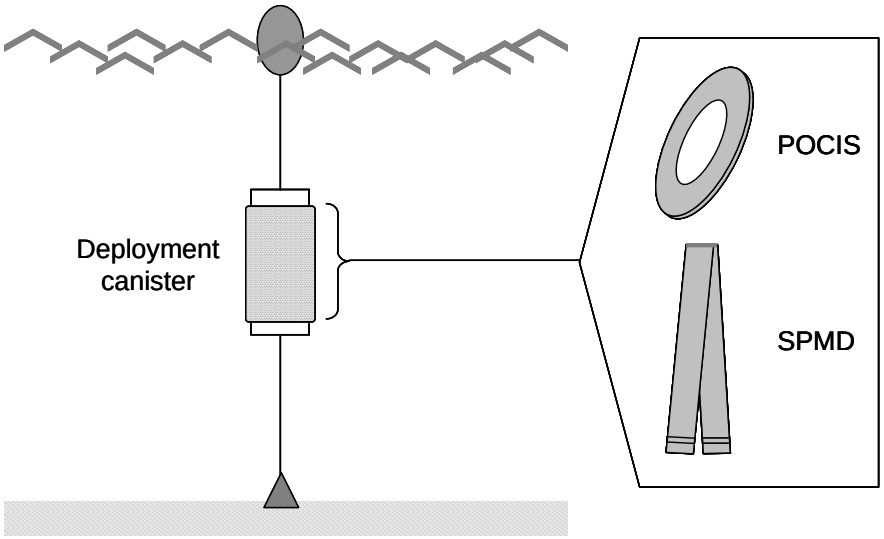

Figure 11.2 A typical apparatus for suspending passive samplers in the water column. Polar organic chemical integrative samplers (POCIS) and semipermeable membrane devices (SPMDs) are commonly housed in this type of protective canister.

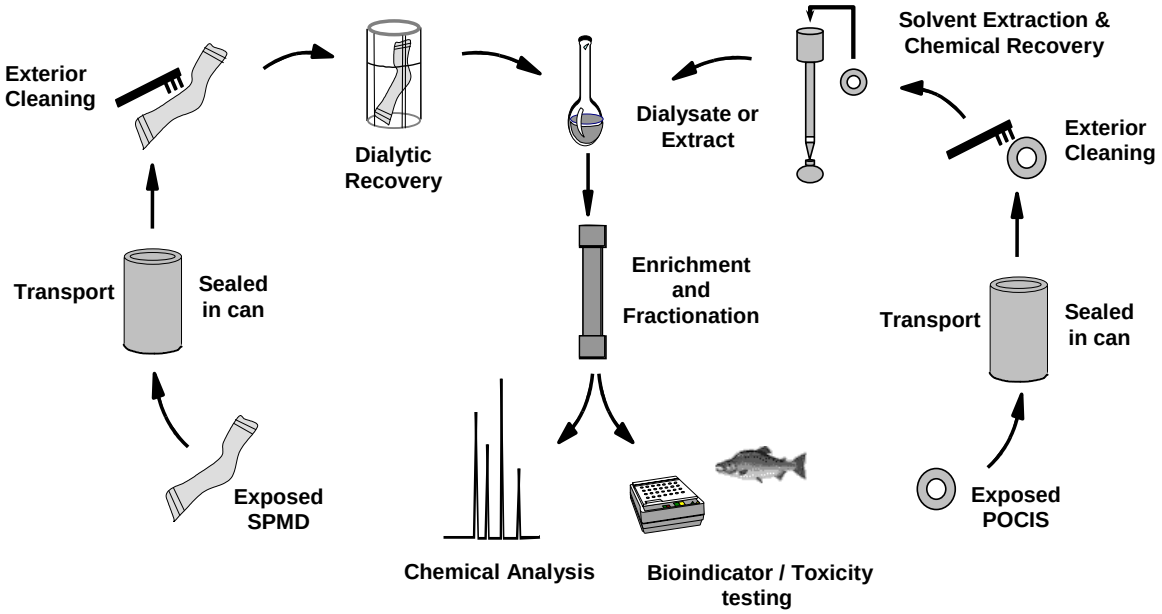

Figure 11.3 General schematic for the processing, analysis, and/or biological testing of passive samplers.