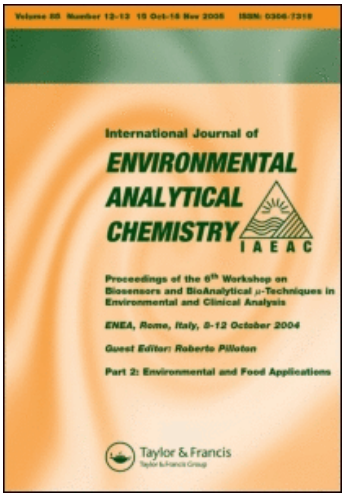

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A Multiresidue Approach for Trace Organic Pollutants: Application to Effluents and Associated Aquatic Sediments and Biota from the Southern Chesapeake Bay Drainage Basin 1985-1992

R. C. Hale[a]; C. L. Smith[a]
[a] Department of Environmental Science, Virginia Institute of Marine Science, College of William and Mary, Gloucester Point, VA, USA

To cite this Article Hale, R. C. and Smith, C. L.(1996) 'A Multiresidue Approach for Trace Organic Pollutants: Application to Effluents and Associated Aquatic Sediments and Biota from the Southern Chesapeake Bay Drainage Basin 1985-1992', International Journal of Environmental Analytical Chemistry, 64: 1, 21 — 33
To link to this Article: DOI: 10.1080/03067319608028332
URL: http://dx.doi.org/10.1080/03067319608028332

Intern. J. Environ. Anal. Chem., Vol. 64, pp. 21–33
Reprints available directly from the publisher
Photocopying permitted by license only

A MULTIRESIDUE APPROACH FOR TRACE ORGANIC POLLUTANTS: APPLICATION TO EFFLUENTS AND ASSOCIATED AQUATIC SEDIMENTS AND BIOTA FROM THE SOUTHERN CHESAPEAKE BAY DRAINAGE BASIN 1985–1992

R. C. HALE and C. L. SMITH

Department of Environmental Science, Virginia Institute of Marine Science, College of William and Mary, Gloucester Point, VA 23062, USA

(Received, 12 August 1995, in final form, 31 January 1996)

Most chemical monitoring approaches target a small subset of the pollutants actually present in environmental samples. As a consequence, significant information is routinely overlooked. A program was developed and applied in the southern Chesapeake Bay drainage basin to obtain a more complete picture of the diverse organic contaminants present. Facilities examined included military, water treatment, creosote and fuel handling, shipyard and papermill installations. Matrices analyzed were aqueous discharges, to assess current releases; sediments, for a more synoptic view; and shellfish, to examine bioavailability and bioaccumulation. Tools used included capillary gas chromatography, electron impact and negative chemical ionization mass spectrometry, retention indices, flame ionization and halogen specific detectors. The approach successfully identified a number of sites in the bay drainage impacted by high concentrations of the so-called "priority" pollutants, such as polycyclic aromatic hydrocarbons, PCBs and chlorinated pesticides. In addition, numerous "non-priority" pollutants (e.g. polychlorinated terphenyls, nitrogen and sulfur heterocyclics, phenolics, ketones and ethers) were identified as major contaminants.

KEY WORDS: Organic pollutants, monitoring, sediment, water, biota, Chesapeake Bay

INTRODUCTION

Thousands of xenobiotic organic chemicals have been released to the aquatic environment. Many are toxic at low concentrations or may accumulate in sediments and organisms. Historically, regulatory and scientific communities have conducted analyses for specific chemicals or abbreviated lists of compounds, such as the "priority" pollutants[1]. Inclusion may be based on the compound's extent of use, persistence or presumed toxicological effects. The outcome is that the majority of pollutants present are not typically sought or identified. Some compounds may be unique to individual facilities. Others may be widely used as minor additives in multicomponent products. Thus, their presence may be unknown to product consumers and responsible regulatory agencies. Failure to institute procedures to detect these diverse compounds may allow their release and dispersion to go unnoticed in the environment. This may result in severe health, environmental and economic consequences.

This undesireable situation occurred in Virginia in the 1970's. The chlorinated insecticide Kepone was manufactured at a site in Hopewell, VA. Concern over disposal practices arose only after health problems were reported in on-site employees. Meanwhile, uncontrolled disposal of large amounts of the pesticide near the plant resulted in wide-spread contamination of the adjacent James River. Subsequently, a moratorium on commercial fishing was imposed in an attempt to minimize exposure of humans to contaminated seafood[2]. While the point source of the Kepone was finally remediated, no adequate treatment was possible for the environmentally disseminated contamination.

Instead of targeting an abbreviated list of chemicals, some investigators have approached environmental monitoring by focusing on properties of potential toxicological relevance. These may include octanol-water partitioning, as an indicator of bioaccumulative potential[3], or acute toxicity[4]. Analytical effort may then be concentrated on compounds exhibiting highest potentials. However, compounds of environmental significance that fail to register highly for the particular indicators chosen may be overlooked. These approaches also typically require additional sample manipulation, increasing potential for analytical losses and in-laboratory contamination.

In the present study a broad-spectrum screening methodology was designed to address concerns over the input and presence of diverse organic contaminants in the environment. It was implemented for seven years at 92 facilities discharging to Virginia waterways. These waterways form part of the drainage for the southern Chesapeake Bay, an area under increasing anthropogenic pressure (Figure 1).

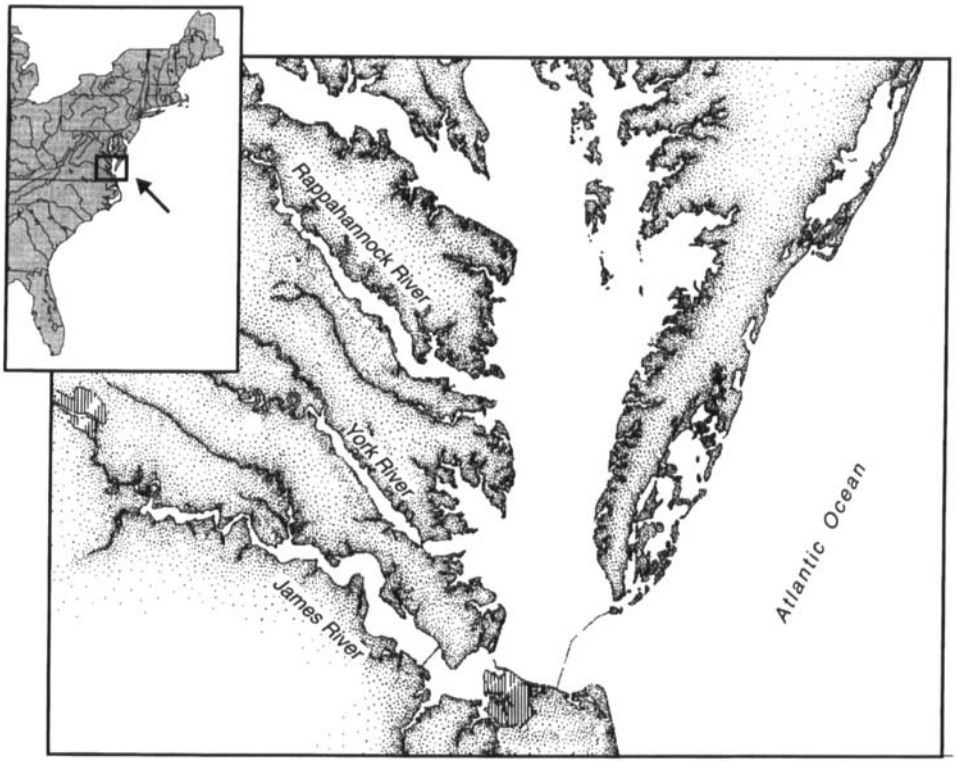

Figure 1 Map of the southern Chesapeake Bay.

Three substrate classes were examined to provide information on present and past contaminant sources and tissue burdens in exposed aquatic organisms. Aqueous effluents were examined from selected sites; including commercial, municipal and federal facilities. Sediments were also collected near these outfalls. Nonpolar organics possess limited water solubility and often associate with particulate matter[5]. Thus, sediments may concentrate and integrate aqueous organic releases over time. They also may serve as an additional exposure route for associated biota[6]. Finally, tissues from molluscs, where available, were analyzed for bioaccumulated chemicals. These organisms have been shown to be valuable environmental monitors[7].

METHODS

Solvents used were high purity grade (Burdick and Jackson). All glassware and utensils were cleaned to eliminate laboratory contamination by detergent washing, high temperature oven treatment and solvent rinsing, as described elsewhere[8].

Sample collection

Grab or 24-h composite effluent samples from pre-selected facilities were collected immediately prior to their discharge to waterways. These were extracted within 72 hours of collection. Surficial sediment samples were taken with a Smith-MacIntyre grab. Oysters (*Crassostrea virginica*) or clams (*Rangia* sp.) were collected with a dredge from the vicinity of the discharge. After a 24-h depuration period in clean water, shellfish were shucked and soft tissues drained of excess moisture. Biota and sediments were frozen and effluent water refrigerated until analysis.

Initial sample treatment and extraction

A flow chart of the analytical procedure is provided in Figure 2. Water samples were extracted by a base/neutral and acid approach. Initially, 1–1 water samples were spiked with 25 ug 1,1'-binaphthyl, perinaphthenone and 2,4,6-tribromophenol and 1.0 ug of decachlorobiphenyl, dissolved in acetone. Sample pH was initially raised to 12, with 6 M NaOH, and then sequentially extracted in separatory funnels with three aliquots (100 ml, 50 ml, 50 ml) of methylene chloride. Sample pH was then decreased to < 2 with 6 M HCl and the water re-extracted.

Large detrital material and macro-organisms were removed from the sediment. Sediment and biota were homogenized and then lyophilized. Material was rehomogenized and a surrogate standard containing 25 ug of 1,1'-binaphthyl and perinaphthenone and 1.0 ug of decachlorobiphenyl, dissolved in methylene chloride, added to representative subsamples. These were extracted in soxhlets for 24–48 h with methylene chloride. Subsequent reductions of extract solvent volumes were conducted on a rotary evaporator or in a thermostatted water bath under a stream of purified nitrogen.

Extract purification

Shellfish and sediment extracts were subjected to size exclusion chromatography (SEC) on an ABC Laboratories Autoprep 1002A to remove large molecular weight biogenic

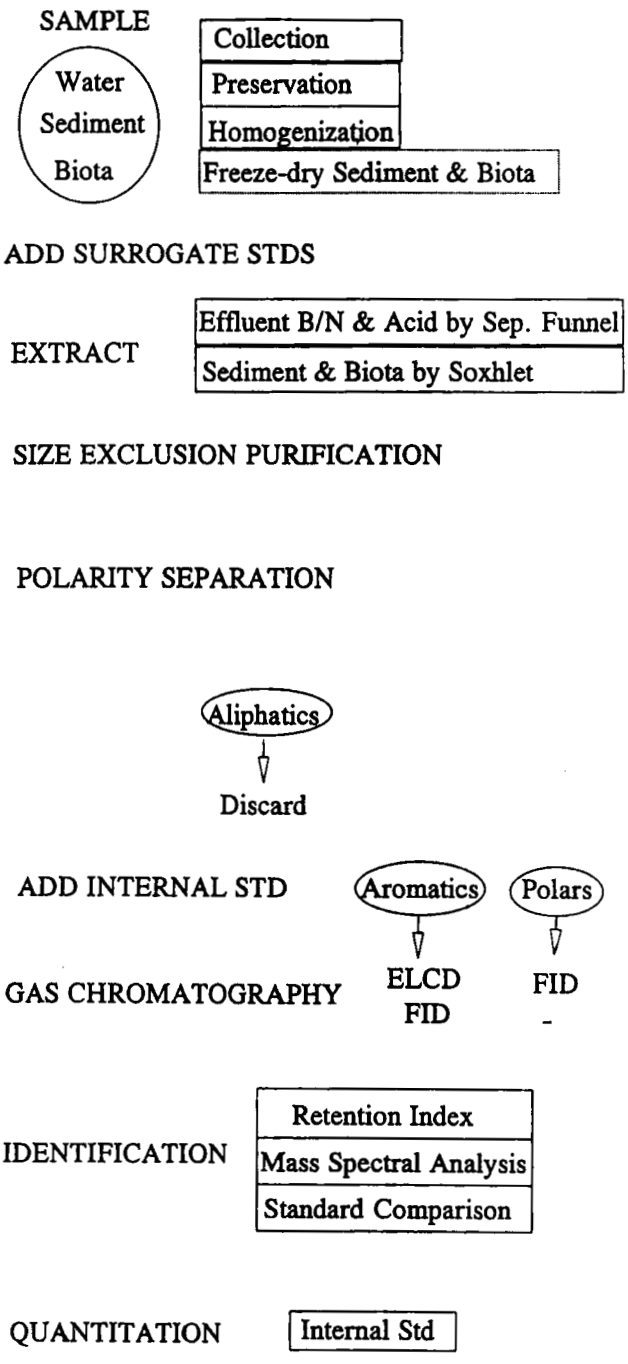

Figure 2 Flow chart of procedures for the analysis of effluent, sediments and biota. Only the aromatic fractions of biota extracts were analyzed by GC or GC/MS. Further details are available in the text.

molecules. The column (2.5 cm × 65 cm) was slurry-packed with 100 g of Bio-Rad Biobeads SX-8 in methylene chloride. This column was later replaced with a 60 g column of Biobeads SX-3 resin, to improve lipid separation. The latter column was eluted with a 1:1 mixture of methylene chloride:cyclohexane[8]. Retention characteristics were verified periodically by elution of standards. Sulfur in sediment extracts was removed by passage over copper wool, previously activated with 3 M HCl.

Polarity fractionation

The post-SEC extract was separated into aliphatic, aromatic, and one or more polar fractions. This decreased gas chromatographic (GC) interference by co-extracted polar biogenic compounds and reduced the complexity of the remaining fractions of interest. Presence in a particular fraction also provided clues to a compound's functional groups. Acidic water extracts were not subjected to polarity fractionation. Analysis of fractions more polar than the aromatic from biota extracts was discontinued since co-eluting polar biogenic interferences severely impacted GC column performance and lifetime. The polar compounds also showed limited bioaccumulation.

Appropriate SEC-purified extracts were placed on a 10 g column of pre-extracted, activated silica gel (100–200 mesh), topped with 1 g sodium sulfate. Each column was eluted with 25 ml of hexane and the fraction (S1) containing aliphatics discarded. It was then eluted with 50 ml of a 4:1 hexane:methylene chloride mixture. This fraction (S2) contained predominantly aromatic compounds (e.g. PAHs, PCBs and chlorinated pesticides). A relatively polar fraction (S3), containing carbazoles and phenolics, was collected for sediments with 40 ml methylene chloride. Two additional fractions of increasing polarity (S4 and S5) were obtained with 40 ml of 1:9 acetone:methylene chloride and then 40 ml of 100% methanol. These contained azaarenes, ketones and additional oxygen containing aromatics.

GC Analysis

Separation

GC analyses were conducted with a Varian 3400 or 3700, on DB-5 (J&W) fused silica columns (film thickness 0.25 um, O.D. 0.32 mm and length 30 or 60 m). Carrier gas was helium at 2 to 3 ml/min. Sample injections (1–2 ul) were made in the splitless mode at an injector temperature of 300°C. Nonchlorinated compounds were detected with a flame ionization detector (FID) held at 320°C. Initial column temperature was 75°C and was maintained for 2 minutes, then programmed at 6°C/ min to 310°C and held there for 10 min. A DB-5 column and an OIC 4420 electrolytic conductivity detector (ELCD) were used for the separation and detection of halogenated compounds. The ELCD was operated in the halogen-specific mode and maintained at 850°C. Initial GC column temperature was 90°C, with a one minute hold. It was then programmed at 4°C per minute to 310°C and held there for 10 min. Column effluent to the ELCD was purged for the first two minutes of each run to eliminate solvent. All data were collected on a Hewlett Packard 3350A Laboratory Automation System.

Compound identification

Initial identifications were based on GC/FID for nonhalogenated and GC/ELCD for halogenated compounds, in conjunction with relative retention index (RRI) libraries. The RRI system has proven to be a powerful tool for analyte identification and tracking[9-10]. Greatest attention was focused on the aromatic fraction, as the compounds therein are generally of most environmental concern due to their greater toxicity and bioaccumulative potential. RRI libraries for aromatic fractions were generated by examination of standards or previous mass spectral analysis of compounds in environmental extracts. The aromatic compound RRI approach has been described previously[9]. Marker compounds were naphthalene, biphenyl, phenanthrene, pyrene, chrysene, perylene and benzo(ghi)perylene and were assigned numerical RRIs (1000–7000). If absent in a given extract, the retention time of the missing marker was estimated by that of a standard injected daily. RRIs of extract components were then interpolated from those of the markers. The RRI library was augmented as new identifications were made.

A halogenated RRI was created using GC/ELCD data. This retention standard consisted of 2-chloronaphthalene, alpha-BHC, 2,4'-DDD and decachlorobiphenyl[11]. Components were assigned values from 1000 to 4000. With the exception of decachlorobiphenyl, these are typically absent in environmental samples, so retention times of the marker peaks were determined by coinjection or estimated from daily standard injections.

All RI-based identifications were manually reviewed. Polar fractions and aromatic fractions with unusual chromatographic patterns were further examined by mass spectrometry (MS) after initial GC separation. A DuPont 492-B, in the electron ionization (EI) mode, was used for nonhalogenated compounds. An Extrel ELQ 400–2 MS, in the electron capture negative chemical ionization (ECNCI) mode, was employed for halogenated analytes. Methane was used as the moderator gas. GC conditions were similar to those described above.

Quantitation

The internal standard approach was used. Concentrations in biota and sediment were expressed on a dry weight basis. The FID was used for quantitation of all nonhalogenated analytes and a terphenyl standard was added to the desired fractions immediately prior to GC injection. FID response is relatively consistent for compounds containing minimal non-hydrocarbon substitutions[12]. This approach was adequate here as the main goal was to identify compounds present, estimate relative concentrations and prioritize sites of greatest environmental concern.

ELCD was used for the quantitation of chlorinated and brominated species encountered. Its response is a function of the degree of halogenation and is less affected by the position of halogens than the widely used electron capture detector[13]. PCBs were detected as individual congeners, where resolvable with the GC column used. Pentachlorobenzene generally served as the internal standard.

Quantitation limits (QLs) were 1 ug/l or less for hydrocarbons and halogenated compounds in water. This was adequate for the effluents, but may be high for surface waters. QLs for compounds containing oxygen, sulfur or nitrogen substitution were higher, between 1 and 5 ug/l. QLs for sediment and biota were ten-fold higher due to the smaller mass of matrix extracted. Blanks were run with each set of samples extracted.

Recoveries of PAHs, pesticides, PCBs and heterocyclic compounds from laboratory-amended matrices were 38% to 129%. On account of the preparative steps involved, recovery of compounds more volatile than phenanthrene and some polar compounds were typically about 50%. Most recently, deuterated PAHs and PCB congeners absent from commercial Aroclors have been added to samples as surrogates, prior to extraction. This permits the analyst to more closely follow method losses. Table 1 lists representative surrogate standard recoveries from some effluents, sediment and biota samples.

RESULTS AND DISCUSSION

Chromatography-based techniques using MS, FID and ELCD are capable of extracting considerable information on the presence of environmentally significant organic chemicals from samples. This power is typically not fully utilized in monitoring studies, despite availability of the technology.

The wide spectrum organic pollutant monitoring program has been used in Virginia since the mid-1980s at 92 sites. The diversity of compounds detected is illustrated in the partial listing of pollutants identified in Table 2. The majority of the compounds observed in the effluents provided EI mass spectra indicative of highly alkylated, nonaromatic chemicals. In contrast, most compounds detected in sediments and biota had large molecular ions, allowing apparent molecular weights to be assigned. PAHs, chlorinated pesticides and PCBs were the dominant compounds identified in sediment and biota. As noted previously, only the aromatic fractions of biota samples were examined, due to biogenic interferences in the polar fractions. Often no shellfish were available near outfalls. This may be due to the action of toxic chemicals, decreasing regional shellfish stocks, or unsatisfactory salinity or other physical conditions. Representative findings from several specific facility classes are discussed below to further illustrate the utility of the approach.

Shipyards

Samples associated with 13 separate shipyard outfalls were examined. Oil/water separator discharges were targeted at several sites. Historically, separators were regulated based on the release of total oil and grease, rather than individual organic compounds. Examination of effluents revealed the presence of mg/l concentrations of

Table 1 Mean % recovery (standard deviation) of surrogate standards from representative effluents, sediment and biota.

MATRIX	*BINAPHTHYL*	*PERINAPH*	*DCB*	*TBP*	*N*
Water	81 (12)	80 (18)	124 (42)	72 (26)	24
Sediment	94 (19)	67 (21)	97 (33)	na	31
Biota	78 (4.4)	na	91 (19)	na	16

BINAPHTHYL = 1,1'-binaphthyl; PERINAPH = perinaphthenone; DCB = decachlorobiphenyl; TBP = 2,4,6-tribromophenol; N = number of samples reported; na = standard not added to this matrix.

Table 2 Listing of individual or classes of pollutants detected in three matrix classes collected from discharging facilities and associated waterways. Biota extracts were not typically analyzed for polar compounds, such as N- and O-containing pollutants, due to the presence of biogenic interferences. These heterocyclic chemicals also typically possess low bioaccumulation potential.

	Effluent	*Sediment*	*Biota*
PAHs	x	x	x
PCBs		x	x
PCTs		x	x
Octachlorodibenzodioxin		x	
Chlorinated dibenzofurans		x	x
Chlorinated phenols	x	x	x
Chlorinated biphenyl ethers		x	x
Chlorinated isocyanates	x	x	
Chlorinated anilines	x		
DDE, DDD, DDT		x	x
Chlordane		x	x
BHC		x	x
HCH		x	x
Methoxychlor		x	x
Dieldrin		x	x
Aldrin		x	x
Endrin		x	x
Permethrin		x	x
Mirex		x	x
Endosulfan		x	x
Triclosan			x
Bromacil	x		
Brominated biphenyl ethers	x	x	x
Xylenols	x	x	
Cyclohexanone		x	
Cyclohexanol		x	
Aromatic ketones	x	x	
Aromatic acids	x		
Thiophenes	x	x	x
Nonylphenols	x	x	x
Cumylphenols		x	
Carbazole(s)	x	x	x
Quinoline(s)	x	x	
Indole(s)	x	x	
Tolyltriazoles	x	x	
Caffeine	x	x	
Biphenyl	x	x	x
Biphenyl ether	x	x	
Alkylbenzenes	x	x	x
Alkylnaphthalenes	x	x	x
Misc. pulp-mill cpds	x	x	x

several low molecular weight aromatic compounds, specifically naphthalene and alkylated analogs. Also present were more polar compounds such as carbazoles and phenolics. The latter included not only xylenols, but also nonylphenols, at mg/l concentrations. Nonylphenols are degradation products of detergents, often added to separators to breakup oil/water emulsions. They have been reported by several researchers in environmental samples and are toxic to aquatic organisms[14,15]. They have recently been found to be estrogenic[16].

Sediments near these shipyard outfalls were grossly contaminated. More than 200 individual compounds were detected in some samples. Concentrations of compounds in sediment aromatic fractions ranged from 6.5 to 153 mg/kg. Alkylated and nonalkylated PAHs were dominant components. Polar compounds similar to those in the effluents were detected. In addition, aromatic ketones and azaarenes were often present. Both of these groups have been reported previously in aquatic sediments[17,18]. The ketones may be oxidative degradation products of PAHs, while azaarenes were probably present in the original petroleum-related materials released. Their higher polarities, compared to the more abundant PAHs, may result in enhanced water solubilities and attendant bioavailabilities. Sediment concentrations of these heterocyclics were often 10% of those of the associated PAHs.

ELCD analysis of sediments from several sites showed the presence of not only elevated concentrations of PCBs, but also an incompletely resolved group of chromatographically late-eluting peaks. MS analysis in both the EI- and NCI-modes suggested a polychlorinated terphenyl (PCT) structure. Standards were obtained and the presence of Aroclor 5460 confirmed at the mg/kg level in some cases. A potential use for Aroclor 5460 was in investment casting[19]. A more detailed discussion of the occurrence of this PCT formulation in sediments near shipyards and elsewhere in the Chesapeake Bay region has been published previously[20]. Aroclor 5460 has also been reported in sediments from Antarctica, the Mediterranean and the U.S. Great Lakes region[21-23].

Shellfish were absent from many shipyard sites. When found, nonpolar compounds, e.g. PAHs and PCBs, dominated tissue burdens. Aroclor 5460 was either not detected or present at low ug/kg concentrations in biota examined. This may be due to low bioavailability related to low water solubility or large molecular size.

Fuel handling and creosoting facilities

Major pollutants observed at four fuel-handling facilities were dominated by alkylated PAHs, derived from petroleum products. Contamination near creosoting operations was particularly heavy. It consisted mostly of nonalkylated PAHs, with lesser but significant contributions from oxygen and nitrogen heterocyclics. At the two creosote handling sites examined under this program, methylcarbazoles and benzoquinolines were present in the effluents at ug/l concentrations. Aromatic acids were detected in the acid extracts. Sediment from a creek near one site contained nearly a g/kg of nonsubstituted PAHs. Carbazole at the mg/l level was also found. Halogenated compounds were typically low in sediments from these facilities and shellfish were absent.

In-situ biological effects, such as liver pathologies in finfish, have been detected near one of the creosoting operations[24]. In the laboratory, water-soluble fractions generated from sediment from this site have been shown to compromise resistance of oysters to challenge by disease[25].

Military and other Federal installations

These included U.S. Navy, Army, Marine Corps, Air Force and NASA facilities. A total of 10 outfalls were examined. The effluents themselves emanated from diverse operations. With one exception, concentrations in effluents were low at the time sampled. The exception received infiltration from leaking underground fuel tanks. Dominant compounds were alkylated benzenes and naphthalenes, present in the mg/l

range. Shellfish collected near this site contained low concentrations of mostly nonalkylated PAHs. Thus, it likely that these molluscs were beyond the immediate influence of the effluent sampled.

Sediment here contained 91 mg/kg of resolved aromatic hydrocarbons. Alkylated PAHs were the dominant compounds present, suggestive of a petroleum source. A suite of low chlorinated terphenyls was detected with the ELCD in these sediments. Comparison of extract chromatographic patterns and mass spectra to standards indicated the presence of Aroclor 5432. These compounds were not apparent with the FID, due to the high concentration of hydrocarbons present and the low response of this detector to chlorinated compounds. Sediment collected near another outfall, in an adjacent creek, was also heavily contaminated with Aroclor 5432. Subsequent sampling to determine the extent of contamination revealed sediment concentrations as high as 250 mg/kg.

Shellfish collected downstream from this creek outfall contained Aroclor 5432 components at a concentration of 35 mg/kg. This high accumulation contrasts with shellfish from sites contaminated by the highly chlorinated Aroclor 5460 formulation discussed above. Detailed results and optimized methods for the analysis of PCTs have been previously described[26,27]. A possible use for Aroclor 5432 was as an additive in hydraulic fluids[19]. Aroclor 5432 has recently been shown to be a potent inducer of cytochrome P4501A in the mummichog, *Fundulus heteroclitus*[28]. Aroclor 5460 was observed to be less potent.

Also present in the sediment and effluent from this site was diphenyl ether at 11 mg/kg and 16 ug/l, respectively. This material is used in heat transfer fluids and has been previously reported in the marine environment[29]. In addition, sediment at this particular federal facility was highly contaminated with cumylphenols at a concentration of 103 mg/kg. These have been used in resins, insecticides and lubricants[30].

Sediment from another military site contained 19.3 mg/kg of Aroclor 5460. Sediments from three other federal sites contained relatively elevated total DDT (4,4'-DDT, 4,4'-DDE and 4,4'-DDD) concentrations, ranging from 167 to 331 ug/ kg. A fourth contained 1420 ug/kg. These were the highest DDT-related sediment concentrations observed at any of the 92 sites examined in this study.

Sewage treatment works (STWs)

Effluents from 29 STWs examined generally contained low concentrations of organic pollutants, implying relatively efficient removal of contaminants at the time of sampling. However, petroleum hydrocarbons at ug/l concentrations were occasionally encountered. In some cases considerable polar materials, corresponding to aliphatic and aromatic acids, were detected in the acid extract suggesting release of partially degraded materials.

Outfall-associated sediments were often contaminated with mg/kg concentrations of PAHs and nonylphenols, indicating historic releases or deposition from nearby sources. Many of these treatment facilities were located on industrialized waterways. Shellfish were often absent from these locales. When present, their contaminant burdens generally reflected the diversity of nonpolar chemicals, e.g. PCBs and PAHs, in associated sediments.

Paper and wood product manufacturing

Samples from six different facilities were examined. On-site activities ranged from pulp and paper production to container and siding manufacturing.

Effluent from a softwood pulping and kraft paper operation was very complex and differed considerably from others encountered. As such, it represented a challenge for the analytical protocol. On account of the character of this source, a separate RRI was constructed for pulp and paper-related compounds. Many of the compounds identified were derived from natural products released from wood during pulping[31]. Compounds identified by GC-MS included guiacols, syringaldehydes, dehydroabietic acids, thiophenes and isoborneol. These are common components of pulpmill effluents[32]. ELCD analysis detected several chlorinated compounds, likely produced during bleaching processes. These were examined by GC/MS in the NCI and EI modes. Components included tri- and tetra-chloroguiacol and trichlorosyringol.

Sediments near this site were inundated with raw wood materials, e.g. fibers and bark, spilled during bulk transportation operations. No shellfish were present in this area. Subsequent in-laboratory exposures to effluents showed bioaccumulation of a number of the above mill-related compounds (unpublished). Several of these have been reported to have toxic effects on aquatic organisms[33].

In contrast, most effluent samples associated with nonpulping operations contained relatively low concentrations of organic compounds. The exception was a composite board manufacturing facility. Effluent from this plant contained ug/l levels of alkylated naphthalenes and phenanthrenes. Sediments here were grossly contaminated with PAHs and dibenzothiophenes in the mg/kg range. Nitrogen-containing aromatics, with apparent molecular weights between 279 and 317, were also present at the mg/kg level. Low chlorinated congeners (di- to tetrachlorobiphenyls), indicative of the release of a less chlorinated Aroclor formulation, dominated the PCBs detected in these sediments. All other sites investigated with this methodology contained sediments dominated by PCBs with five or more chlorines.

No shellfish were present here. Teleosts were collected to provide some information on potential xenobiotic bioaccumulation. Sunfish (*Lepomis* sp.) and dace (*Rhinichthys* sp.) from this particular site showed a dominance of low chlorinated PCBs similar to the sediments.

Other facility types

A total of 28 other outfalls were examined during this program, encompassing power generation plants, food processors, specialty chemical manufacturers and the transportation industry. The majority of these effluents contained low concentrations of organics. In contrast, many associated sediments were grossly contaminated by PAHs derived from petroleum sources. These may have been contributed by past or adjacent operations. PCBs and PAHs were elevated in some associated shellfish examined.

In addition to the relatively ubiquitous PAHs and PCBs, facility-specific or unusual compounds were detected in a few sediments. These included two, as yet unidentified, high molecular weight chlorinated compounds associated with a textile dying operation. Researchers have found industry specific pollutants useful in identifying dischargers and tracing the movement of chemicals and particles in the aquatic environment[34].

CONCLUSIONS

The monitoring program described permitted the semi-quantitative determination of a diverse group of chemicals. Each matrix examined had advantages. The widest diversity of organic pollutants was observed in sediments. Burdens detected in aquatic organisms

provided direct evidence of compound bioavailability. Assessment of this matrix is also related to major endpoints of concern, biological effects and human exposure. Routine examination of polar fractions from biota extracts was discontinued due to the presence of interfering biogenic materials. Effluents provided an instantaneous picture of contaminants being released by a specific facility.

Compounds detected in this study included the so-called "priority" pollutants, as well as a number of seldom reported chemicals, e.g. PCTs, ketones, nonylphenols, ethers, and nitrogen heterocyclics. These latter pollutants often occurred at high concentrations. Once a site or chemical was determined by the monitoring approach to be a problem, more extensive field sampling and specific analytical methodologies could be brought to bear. Despite the ability of the approach to identify pollutants, some effluent components remained unidentified. However, mass spectra, chromatographic retention indices and other pertinent sample information were retained. These data gaps may be re-examined and filled as additional information becomes available.

Interestingly, samples from federal government facilities possessed some of the highest and most diverse pollutant loads, particularly in sediments. Some of these chemicals, e.g. the PCTs, bioaccumulated to elevated concentrations in aquatic organisms. Others, such as ethers and phenolics, exhibited lower bioaccumulation potentials.

Data generated with this wide spectrum analysis approach resulted in several follow-up regulatory and research activities. Efficacies of some discharge permit monitoring requirements, e.g. for oil/water separators, have been questioned as a result of the detection of high concentrations of alkylated phenolics in discharges. Additional efforts to locate the ultimate sources of the PCT contamination have been made. In the case of sites with severe Aroclor 5432-contaminated sediments, remediation has been initiated and fishing restrictions proposed to protect human health. Acute toxicities of effluents from several facilities, suggested by the chemical analyses, were confirmed by aquatic bioassays. Subsequently, toxicity reduction plans and best-management practice issues were addressed.

Acknowledgements

Drs. R. Huggett, R. Bieri, C-W. Su, J. Greaves, R. Edstrom and Mr. P. deFur contributed to early stages of this project. Major technical support was provided by E. Harvey, G. Vadas, E. Bush and D. Anderson. The cooperation and assistance of C. Lunsford, D. Grimes and other Virginia Department of Environmental Protection (VA DEQ) staff are also acknowledged. Financial support was provided by the VA DEQ. This is Contribution 2004 from the Virginia Institute of Marine Science, College of William and Mary.

References

1. US EPA. 1983. Methods for Chemical Analysis of Waters and Wastes. PA-600/4–79–020. 552 p.
2. R. J. Huggett and M. E. Bender, *Environ. Sci. Technol.*, **14**, 918–923 (1980).
3. L. P. Burkhard, D. W. Kuehl and G. D. Veith, *Chemosphere*, **14**, 1551–1560 (1985).
4. L. P. Burkhard, E. J. Durhan and M. T. Lukasewycz, *Anal. Chem.*, **63**, 277–283 (1991).
5. B. Reuber, D. MacKay, S. Paterson and P. Stokes, *Environ. Toxicol. Chem.*, **6**, 731–739 (1987).
6. D. C. Malins, B. B. McCain, D. W. Brown, U. Varanasi, M. M Krahn, M. S. Myers and S-L Chan, *Hydrobiologia*, **149**, 67–74 (1987).
7. J. L. Sericano, E. L. Atlas, T. L. Wade and J. M. Brooks, *Mar. Environ. Res.*, **29**, 161–203 (1990).

8. R. C. Hale, E. Bush, K. Gallagher, J. L. Gundersen and R. F. Mothershead II, *J. Chromatogr.*, **539**, 149–156 (1991).
9. R. H. Bieri, C. Hein, R. J. Huggett, P. Shou, H. Slone, C. Smith and C-W Su, *Intern. J. Environ. Anal. Chem.*, **26**, 97–113 (1986).
10. D. L. Vassilaros, R. C. Kong, D. W. Later and M. L. Lee, *J. Chromatogr.*, **252**, 1–20 (1982).
11. R. D. Edstrom, *PCB Congener Analysis with Hall Electrolytic Conductivity Detection* (Dissertation, Virginia Institute of Marine Science, Gloucester Point, Va. 1989) 128p.
12. H. Y. Tong and Karasek, *Anal. Chem.*, **56**, 2124–2128 (1984).
13. J. Greaves, E. Harvey and R. J. Huggett, *Environ. Toxicol. Chem.*, **10**, 1391–1398 (1991).
14. D. W. McLeese, V. Zitko, D. B. Sergeant, L. Burridge and C. D. Metcalfe, *Chemosphere*, **10**, 723–730 (1981).
15. R. Ekelund, A. Granmo, K. Magnusson and M. Berggren, *Environ. Poll.*, **79**, 59–61 (1993).
16. R. White, S. Jobling, S. A. Hoare, J. P. Sumpter and M. G. Parker, *Endocrinology*, **135**, 175–182 (1994).
17. R. J. Pruell, Extended Abstract presented at the Div. Environ. Chem. ACS Meeting, Anahiem, CA. Sept. 7–12, 1986.
18. E. T. Furlong and R. Carpenter, *Geochim. Cosmochim. Acta.*, **46**, 1385–1396 (1982).
19. A. A. Jensen and K. F. Jorgensen, *Sci. Total Environ.*, **27**, 231–250 (1983).
20. R. C. Hale, J. Greaves, G. G. Vadas, E. Harvey and K. Gallagher, in: *Aquatic Toxicology and Risk Assessment* (M. A. Mayes and M. G. Berron, eds. American Society for Testing and Materials, Philadelphia, 1991) pp. 305–312.
21. R. W. Risebrough, B. W. DeLappe and C. Younghans-Haug, *Mar. Poll. Bull.*, **21**, 523–529 (1990).
22. M. T. Galceran, F. J. Santos, J. Caixach, F. Ventura and J. J. Rivera, *J. Chromatogr.*, **643**, 399–408 (1993).
23. E. T. Furlong, D. S. Carter and R. A. Hites, *J. Great Lakes Res.*, **14**, 489–501 (1988).
24. W. R. Vogelbein, J. W. Fournie, P. A. Van Veld and R. J. Huggett, *Cancer Res.*, **50**, 5978–5986 (1990).
25. F.-L. E. Chu and R. C. Hale, *Mar. Environ. Res.*, **38**, 243–256 (1994).
26. R. C. Hale, J. Greaves, K. Gallagher and G. G. Vadas, *Environ. Sci. Technol.*, **24**, 1727–1731 (1990).
27. K. Gallagher, R. C. Hale, J. Greaves, E. O. Bush and D. Stilwell. *Ecotox. Environ. Safety*, **26**, 302–312 (1993).
28. K. Gallagher, P. A. Van Veld, R. C. Hale and J. J. Stegeman, *Environ. Toxicol. Chem.*, **14**, 405–409 (1995).
29. R. F. Addison, *Mar. Poll. Bull.*, **8**, 237–239 (1977).
30. K. Verschueren, *Handbook of Environmental Data on Organic Chemicals* (Van Nostrand Reinhold, New York 1983), 2nd ed. p. 412.
31. R. Ekman, B. Holmbom and A. Akademi, *Nordic Pulp Paper Res. J.*, **1**, 16–24 (1989).
32. L. R. Suntio, W. Y. Shiu and D. MacKay, *Chemosphere*, **17**, 1249–1290 (1988).
33. T. Andersson, L. Forlin, J. Hardig and A. Larsson, *Can. J. Fish. Aquat. Sci.*, **45**, 1525–1536 (1988).
34. D. S. Carter and R. A. Hites, *J. Great Lakes Res.*, **18**, 125–131 (1992).