Determination of Bioavailable Contaminants in the Lower Missouri River following the Flood of 1993

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The semipermeable membrane device (SPMD) technology was employed to determine the presence of bioavailable organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs), and polyaromatic hydrocarbons (PAHs) in the water of the main stem of the lower Missouri River and three of its tributaries. The SPMDs were deployed in 1994 following the extensive flood of 1993. Specifically, the SPMDs were deployed for 28 days at Wilson State Park, IA; Nebraska City, NE; Parkville, MO; the Kansas River in Kansas City, KS; Napoleon, MO; the Grand River; Glasgow, MO; the Missouri River upstream from the confluence of the Gasconade River; the Gasconade River; and Hermann, MO. Contaminant residues were found at all sites and at higher concentrations than found in the earlier pre-flood sampling. For example, in the present study, dieldrin was found to range from a low of 110 ng/sample in the Gasconade River to a high of 2000 ng/sample at Glasgow, while in the pre-flood sampling, dieldrin ranged from a low of 64 ng/sample at Sioux City to a high of 800 ng/sample at Glasgow. In contrast to the 1992 sampling, residues of PCBs were found at all 1994 sampling sites except the Gasconade River. Samples from Wilson State Park and the Grand River had 3100 and 2700 ng of PCBs/sample, respectively. These two concentrations are about an order of magnitude higher than the other sites and are likely indicative of point source inputs. PAHs were present in SPMD samples from three sites near Kansas City. The contaminant residues sequestered by the SPMDs represent an estimation of the bioavailable (via respiration) contaminants present in the main stem of the lower Missouri River and three of its major tributaries following an extensive flood event.

Introduction

The Missouri River drains 22 million ha over its 3168-km course. Economic and agricultural expansion in the Missouri River basin have led to extensive modification of the Missouri River system. In essence, the lower Missouri River has been transformed from a wide-shallow-meandering stream into a fast-flowing, highly energetic system. Extensive levee systems and dikes are employed to protect accreted land and to maintain a navigation channel. These actions have resulted in a nearly complete reshaping of the Missouri River and extensive modification or loss of fish and wildlife habitats (*1, 2*).

During the spring and summer of 1993, vast areas of land along the lower Missouri River were inundated with floodwaters. The 1993 flood of the Missouri River was categorized as a 500-year flood event and resulted in damages costing billions of dollars. The flood breached many protective levees and destroyed numerous navigation dikes. Consequently, new channels, scour holes, and backwater areas were formed. These areas created extensive new fish and wildlife habitats and present a unique opportunity to restore and enhance fish and wildlife resources along the entire lower Missouri River. The success of these enhancement efforts requires a comprehensive assessment of environmental contaminant issues, particularly in light of the potential for mobilization of agricultural and industrial pollutants resulting from the widespread flooding.

Critically needed environmental data—identities and concentrations of bioavailable, waterborne contaminants—are often unavailable because of the areal extent of nonpoint source discharges, the transient nature of many point source discharges, and the limited analytical approaches for quantitating dissolved pollutants in ambient waters. In addition, few methods have previously existed for the passive determination of time-weighted average contaminant concentrations in aquatic systems.

Recent reports detailing the development and application of semipermeable membrane devices (SPMDs) for passive in-situ monitoring of aquatic contaminants (*3, 4*) describe an innovative approach for determining bioavailable contaminants in a wide array of aquatic systems. The theory and operation of the SPMD samplers are similar in concept to those of passive air monitors and address a number of limitations in widely employed analytical and biomonitoring techniques for waterborne contaminants.

The SPMD sampler (*3*) consists of layflat polymeric tubing, typically polyethylene (PE), containing a thin film of a high molecular mass (≥600 Da) neutral lipid such as triolein. The PE membrane used in SPMDs is commonly referred to as nonporous, even though transient cavities with diameters of about 10 Å are formed by the random thermal motions of the polymer chains. This free volume allows dissolution of neutral organic molecules into the membrane and diffusional jump transport (*5*) through the nonporous polymer (*6*). This process mimics the diffusional transfer of organic contaminants through the respiratory membranes of aquatic organisms (*7*).

As part of the USGS Environmental and Contaminants Research Center's continuing research (*3, 4, 8—11*) into the efficacy of the SPMD approach for assessment of the contamination of a variety of ecosystems and as an extension of our pre-flood assessment of contaminants in the lower Missouri River (*12*), we used these samplers to determine the post-flood presence of contaminants residues in the Missouri River.

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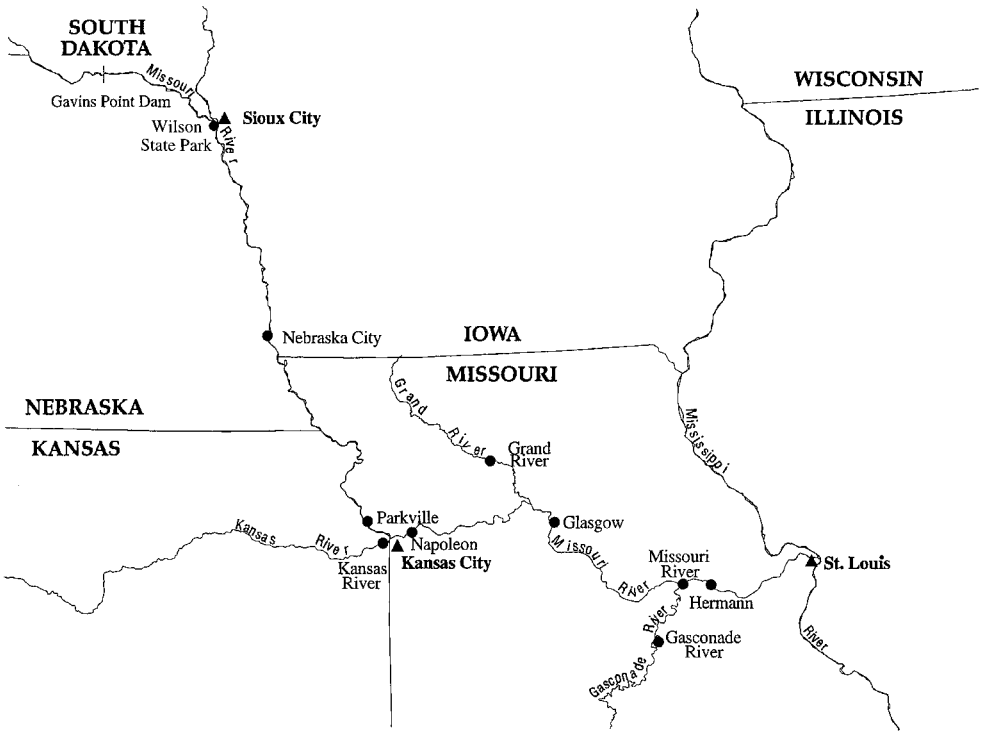

FIGURE 1. Black circles indicate SPMD deployment sites in the lower Missouri River.

Experimental Section

Materials. The SPMDs employed in this research were purchased from Environmental Sampling Technologies (EST), a division of CIA Laboratories, Inc. (St. Joseph, MO).

SPMD Deployment. The SPMDs obtained from EST were deployed at 10 sites in the lower Missouri River basin during July 1994 (Figure 1): Wilson State Park, IA; Nebraska City, NE; Parkville, MO; the Kansas River in Kansas City, KS; Napoleon, MO; the Grand River; Glasgow, MO; the Missouri River upstream from the confluence of the Gasconade River; the Gasconade River; and Hermann, MO. The Nebraska City, Parkville, Glasgow, and Hermann sites were the same as in the 1992 study (*12*). Two replicate SPMD samples (each SPMD sample consisted of two 152-cm PE tubes, each containing 2.0 mL [1.82 g] of triolein) were deployed at each of the 10 sites. As in the previous study, SPMDs were maintained inside stainless steel mesh cages (25 × 25 × 92 cm long) suspended about 1 m below the surface. Following a 28-day exposure (average water temperature, 25 °C), the SPMDs were recovered, placed in airtight metal cans (on ice), and immediately transported to EST for sample processing.

Residue Enrichment and Analysis. The sample processing employed by EST has been previously described (*12*). The final extracts (about 5 mL in hexane) were sealed in amber glass ampules (flushed with high-purity nitrogen prior to sealing). The ampules were forwarded to the Mississippi State Chemical Laboratory (Starkville, MS) for residue enrichment and analysis. The samples were fractionated as previously described (*12*) and analyzed using a high-resolution capillary gas chromatograph equipped with an electron capture or a flame ionization detector. Quantitation of organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs), and polyaromatic hydrocarbons (PAHs) was accomplished using a five-point external standard curve. The method quantitation limits (MQLs) were 10 ng/SPMD sample for each OC pesticide and total PCBs and 250 ng/SPMD sample for PAHs.

The presence of selected organochlorine analytes, i.e., dieldrin, toxaphene, and total PCBs, were confirmed by mass spectral (MS) analysis, employing full-scan electron impact MS. The presence of 4,4′-DDE, dieldrin, and the BHCs was also determined employing selected ion monitoring. Reagent blanks and SPMD controls did not contain measurable levels of any organochlorine compounds.

Quality Control. Field blank SPMDs (one for each of the 10 sample sites) accompanied the SPMD sampler arrays and were open to the atmosphere during deployment and recovery. These field blanks were processed and analyzed exactly as deployed SPMD samplers. Laboratory procedural blanks, treated as samples, were also analyzed with each sample set. Samples containing OC, PCB, and PAH residues exceeding the field blanks were considered positive for OCs, PCBs, and PAHs and were subsequently blank-corrected.

Performance evaluation materials (PEMs) similar in all respects to the purified SPMD dialysates were produced by fortifying two 5-mL volumes of hexane with contaminants. The OCs were spiked at 40 ng/mL for one PEM and the PAHs at 10 μg/mL for the second PEM. The PEMs were provided to Mississippi State Chemical Laboratory as blind samples.

Results and Discussion

The results of the analysis of the PEMs are given in Tables 1 (OCs) and 2 (PAHs). Recoveries of the fortified OC and PAH residues present in the PEMS were generally excellent. The results of analysis of the SPMD samples from the lower Missouri River and tributaries are presented in Tables 3 (OCs and PCBs) and 4 (PAHs). On the basis of total OC pesticide concentrations, the sites in the main stem of the river can be ranked from lowest to highest as follows: Wilson State Park, Nebraska City, Hermann, Parkville, Napoleon, Missouri River at the Gasconade River, and Glasgow. This ranking is similar but not identical to that determined from the pre-flood sampling conducted in 1992 (*12*), i.e., Sioux City (equated with Wilson State Park) lowest and Glasgow highest (Figure 2). The total of the OC pesticide residues found in the Missouri River following the flood were, however, significantly higher at all sites. This is likely the result of mobilization of soil- and sediment-associated OC pesticide residues.

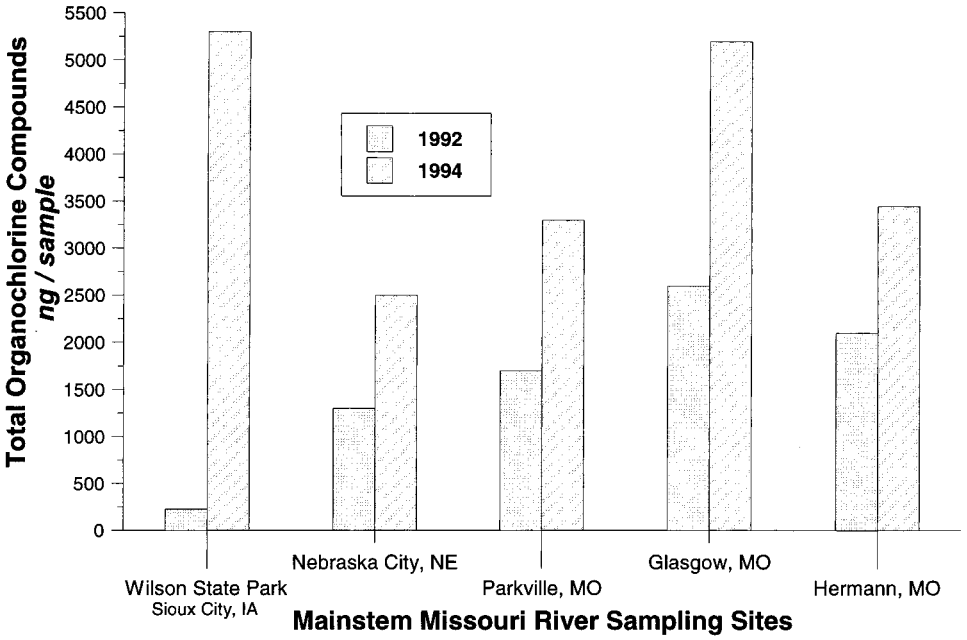

FIGURE 2. Total organochlorine compounds present at the mainstem Missouri River sampling sites.

TABLE 1. Performance Evaluation Materials (% Recoveries)

compd	recovery (%)	compd	recovery (%)
α-BHC	87	dacthal	NA[a]
β-BHC	80	dieldrin	99
δ-BHC	98	endrin	122
cis-chlordane	91	heptachlor	NA
trans-chlordane	87	heptachlor epoxide	94
2,4′-DDD	96	lindane	102
2,4′-DDE	105	methoxychlor	NA
2,4′-DDT	84	mirex	108
4,4′-DDD	104	*cis*-nonachlor	94
4,4′-DDE	99	*trans*-nonachlor	95
4,4′-DDT	95	oxychlordane	92

[a] NA, not analyzed.

TABLE 2. Performance Evaluation Materials (% Recovery)

compd	recovery (%)	compd	recovery (%)
naphthalene	37	benz[*a*]anthracene	91
acenaphthylene	80	chrysene	66
acenaphthene	61	benzo[*b*]fluorathene	82
fluorene	73	benzo[*k*]fluoranthene	89
phenanthrene	68	benzo[*a*]pyrene	96
anthracene	78	indeno[1,2,3-*cd*]pyrene	68
fluoranthene	61	dibenzo[*a,h*]anthracene	94
pyrene	57	benzo[*g,h,i*]perylene	78

Concentrations of individual OC pesticides generally followed the same trend as totals (Table 3). Dieldrin (the OC pesticide found at the highest levels in all samples) concentrations ranged from a low of 1000 ng/sample at Wilson State Park and Nebraska City to a high of 2000 ng/sample at Glasgow. Dieldrin concentrations from the 1992 SPMD deployment (*12*) ranged from a low of 64 ng/sample at Sioux City to a high of 800 ng/sample at Glasgow (*12*). A similar analysis for *cis*- and *trans*-nonachlor (combined) concentrations reveals a low of 116 ng/sample at Wilson State Park and a high of 248 ng/sample at Glasgow. Previous values (*12*) were 4 ng/sample at Sioux City and 135 ng/sample at Glasgow. In general, all OC pesticides were found at higher concentrations in the 1994 samples (Table 3) than in samples from the pre-flood (1992) SPMD deployment (*12*). A notable exception is toxaphene. Residues of this complex OC pesticide were found to range from a low of 100 ng/sample (Sioux City) to a high of 880 ng/sample (Glasgow) in the 1992 Missouri River samples, compared to 220 ng/sample at Nebraska City and 450 ng/sample at Glasgow in the 1994 samples.

During the 1994 SPMD deployment, three major tributaries of the Missouri River (the Kansas River, the Grand River, and the Gasconade River) were also sampled. An examination of the data in Table 3 reveals the highest total—OC pesticide—residues were found in SPMD samples from the Grand River, followed by the Kansas River, with the Gasconade River having the lowest OC pesticide residues. The OC pesticide residues present in these three streams are indicative of the land use practices in their basins, i.e., the Kansas River flows through both agricultural and urban settings, the Grand River through predominately agricultural areas, with the Gasconade River being a relatively clear and cool Ozark stream with only minimal agricultural-based impacts.

Samples from the 1994 SPMD deployment, with the exception of the Gasconade River sample, all contained quantifiable levels of PCBs. No PCBs were present at quantifiable levels in any of the 1992 (pre-flood) SPMD samples. Of particular note are the PCB residues (Table 3) present in the Missouri River at Wilson State Park (3100 ng/sample) and in the Grand River (2700 ng/sample). These values are an order of magnitude higher than concentrations determined at other sampling sites and may be indicative of point source inputs near the SPMD sampling arrays.

As with PCBs, no PAHs were found in the 1992 SPMD samples but were at quantifiable levels in SPMDs from the 1994 study (Table 4). The highest total concentration of PAHs was in the sample from the Kansas River. This is not surprising considering that the Kansas River flows through a heavily industrialized area in Kansas City. Samples from the Parkville and Napoleon sites also contained several PAHs, with the Napoleon SPMDs containing higher levels of PAHs than those from the Parkville site. The PAHs found at all three sites (chrysene, fluoranthene, perylene, phenanthrene, and pyrene) are ubiquitous contaminants found in runoff from urban and industrialized areas (*12, 13*).

TABLE 3. Organochlorine Compounds in SPMD Samples

analyte	total ng/SPMD sample[a]									
	Wilson State Park	Nebraska City, NE	Parkville, MO	Kansas River	Napoleon, MO	Grand River	Glasgow, MO	MO River at Gasconade	Gasconade River	Hermann, MO
aldrin	32	36	43	24	34	39	38	40	<10	26
HCB	21	29	32	24	35	15	34	33	<10	30
α-BHC	13	<10	<10	<10	<10	<10	<10	<10	<10	<10
cis-chlordane	<10	180	240	210	340	140	340	290	41	300
β-BHC	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
cis-nonachlor	28	32	58	53	53	50	68	68	<10	70
δ-BHC	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
dieldrin	1000	1000	1900	380	1800	1800	2000	1800	110	1600
endrin	13	13	20	260	16	20	25	22	<10	23
lindane	15	12	<10	17	14	22	<10	18	<10	<10
trans-chlordane	110	150	190	150	250	140	280	270	21	220
heptachlor epoxide	200	170	230	93	230	260	280	270	20	210
2,4′-DDT	25	38	55	<10	55	56	38	57	<10	44
oxychlordane	41	<10	16	<10	<10	49	25[b]	44	<10	33
4,4′-DDD	80	100	100	110	130	50	120	130	48[b]	20
4,4′-DDE	90	80	90	50	110	240	110	120	17	85
4,4′-DDT	90	68	88	31	93	<10	75[b]	100	20	42
toxaphene	370	220	330	420	310	310	450	410	<10	320
trans-nonachlor	88	100	130	110	170	110	180	180	24	150
total PCBs	3100	270	170	360	370	2700	300	280	<10	240

[a] Average of duplicate SPMD samples. [b] Value of one sample.

TABLE 4. Polyaromatic Hydrocarbon Compounds in SPMD Samples

compd	total ng/SPMD sample[a]				
	Parkville, MO	Kansas River	Napoleon, MO	Gasconade River	Hermann, MO
2,6-dimethylnaphthalene	<250	440[b]	300[b]	<250	<250
2,3,5-trimethylnaphthalene	<250	540	<250	<250	<250
C2-naphthalenes	<250	440[b]	<250	<250	<250
C3-naphthalenes	<250	540[b]	250	<250	<250
phenanthrene	<250	520	460	<250	<250
1-methylphenanthrene	<250	1300	550	<250	<250
C1-phenanthrenes	<250	1300	550	<250	<250
fluoranthene	820	2400	1500	<250	<250
pyrene	920	2600	1700	<250	1000[b]
chrysene	650	1300	670	<250	<250
perylene	300	560	410[b]	<250	<250
benzo[*b*]fluoranthene	<250	470	<250	<250	<250
benzo[*e*]pyrene	<250	380[b]	<250	<250	<250

[a] Average of duplicate SPMD samples samples. [b] Value of one sample.

Qualitative and quantitative comparisons of the OC and PAH residues in SPMD samples from 1994 to those found in the 1992 samples (*12*) reveal the effects of the extensive and long-lasting flood of 1993. In general, concentrations of OC pesticides, PCBs, and PAHs were markedly increased. A similar situation was documented by Goolsby et al. (*14*) for increased levels of herbicide residues (e.g., atrazine, alachlor, cyanazine, metolahlor, etc.) in the Mississippi River resulting from the flood of 1993. Despite the large increase in flow resulting from the flood event, the maximum daily load of atrazine, for example, in the Mississippi River near Thebes, IL, was determined by Goolsby et al. (*14*) to be approximately 70% higher than in pre-flood 1991 samples. The total loading of atrazine to the Gulf of Mexico resulting from the mobilization of these soil-bound herbicide residues by the flood of 1993 was 235% higher than during the same sampling period in 1992 (*14*). Consequently, the record flooding in the Mississippi River Basin did not decrease the levels of herbicides but rather appeared to flush large quantities of soil-bound herbicide residues into the Mississippi River (*14*).

The mechanisms and kinetics of the desorption of soil- and sediment-bound hydrophobic chemicals has recently been critically reviewed by Pignatello and Xing (*15*). These authors report that the desorption of particle-bound chemicals exhibits a bimodal release profile, with a major slow release fraction following a comparatively rapid release. Furthermore, these researchers state that historically contaminated soils or sediments (contact times of months to years) are often enriched in the slow fraction, resulting in a concomitant decrease in the rate of diffusion of contaminants from particles to the aqueous media. Consequently, a return of the contaminant levels in the waters of the Missouri River to pre-flood levels would not be expected to occur quickly.

Zooplankton samples were also collected during deployment of the SPMDs. These samples were analyzed for the identical suite of contaminants as the SPMD samples. No detectable contaminant residues were present in any of the grab samples of zooplankton. This likely results from the low lipid content of these organisms (generally $\leq 2-3\%$) or their short lifetimes.

Using models previously developed (*3*) and applied (*8, 12, 13*), the bioavailable waterborne concentrations of selected OCs and PAHs in the Missouri River water and the water of two of its tributaries were estimated from concen-

TABLE 5. Estimated Concentrations of Typical OC Pesticides and PAHs in the Waters of the Missouri River and Selected Tributaries[a]

	concentrations (pg/L)								
sampling site	dieldrin	*trans*-chlordane	4,4′-DDT	4,4′-DDE	4,4′-DDD	chrysene	fluoranthene	phenanthrene	pyrene
Wilson State Park	3000	190	240	140	180	NA[c]	NA	NA	NA
Nebraska City	3000	260	180	130	230	NA	NA	NA	NA
Parkville	5800	330	240	140	230	2600	3100	ND	3000
Kansas River	1200	260	83	80	250	5200	9100	3200	8600
Napoleon	5500	430	250	180	300	2700	5700	2800	5600
Grand River	5500	240	ND[b]	390	110	NA	NA	NA	NA
Glasgow	6100	490	200	180	270	NA	NA	NA	NA
MO River/Gasconade	5500	460	270	190	300	NA	NA	NA	NA
Gasconade River	340	35	54	27	110	ND	ND	ND	ND
Hermann	4900	380	110	140	46	1800	ND	ND	3300

[a] Values derived using SPMD lipid concentrations on the linear model described previously (*3*). [b] ND, not detected. [c] NA, not analyzed.

trations in the SPMDs exposed in this study. The details of the model development are available (*3*) and will not be presented here. Equation 1 was used to calculate the dissolved (i.e., readily bioavailable) waterborne concentrations:

$$C_L = C_w R_{sc} t / V_L \quad (1)$$

As applied here, C_L is the concentration of the analyte in the lipid, C_w is the concentration of the analyte in water, t is the exposure time in days, V_L is the volume of the lipid, and R_{sc} is the SPMD sampling rate (*12*). For purposes of this discussion, a membrane/lipid partition coefficient (K_{mL}) of 0.1 was used to derive C_L as previously described (*9*). Also, an average fouling impedance of 31% was employed for biofouled SPMDs to correct for the reduction in SPMD uptake (*9, 12*). The sampling rate data for the OC pesticides at one temperature, 26 °C, applicable to the present discussion, have been reported earlier (*16*). Sampling rates for the PAHs will be reported elsewhere (*17*). To facilitate comparison of the 1992 and 1994 results, the SPMDs were deployed in the main stem of the Missouri River at the same sites both years, ensuring equivalent environmental conditions.

The estimated ambient concentrations of selected contaminants are presented in Table 5. Interestingly, the DDE/DDT ratio is skewed from that expected based on past usage; i.e., about a 3:1 ratio is generally considered normal (*4*). This is likely the result of mobilization of soil-bound DDT residues. When compared to more pristine sites not significantly affected by agricultural runoff (*18, 19*), all the OC pesticides were at higher concentrations.

The PAH residues (Tables 4 and 5) can generally be ascribed to combustion and industrial activity (*13*). The highest concentrations were found at sites near Kansas City, MO. Total PAH residues at the sites (as calculated here and presented in Table 5) ranged from a low of about 9000 pg/L at Parkville, MO, to a high of about 26 000 pg/L in the Kansas River near its confluence with the Missouri River.

The presence of the OC pesticides in the Missouri River system likely results from past agricultural practices and the mobilization of these residues by the extensive flooding. Even though the use of most OCs and the PCBs found in the SPMD samples have been banned—some for more that 20 years (*20*)—the longevity of the residues may be adversely affecting Missouri River ecosystem quality. The presence of OC pesticides, PCBs, and PAHs serve as a warning for the overall quality of Missouri River water. Furthermore, rather than flushing and the rapid dissipation of contaminants, the flood of 1993 appears to have caused an increase in the levels of waterborne contaminants in the Missouri River system.

The presence of a broad spectrum of contaminant residues is of increasing concern due to their potential endocrine disrupting activity (*20*). Exposure to these chemicals have been reported to result in decreased fertility (*21, 22*) and gender alterations (*23, 24*) in fish, birds, and mammals. The presence of complex mixtures of environmental contaminants and their potential synergistic effects may adversely impact fish and wildlife resources that use the Missouri River and its tributaries. Also, humans may be at risk for increased incidence of cancers (*25*), reduced fertility (*26*), and impaired childhood development (*27*). Clearly, assessment of exposure of fish, wildlife, and humans to the complex mixture of environmental contaminants is of continuing and growing concern (*28*).

To this end, we have initiated studies designed to determine the potential effects of exposure of organisms to complex mixtures of contaminants sequestered by SPMDs deployed in aquatic environments. Specifically, the bioassay procedure involves the measurement of vitellogenin (VTG), an eggyolk phosphoprotein precursor, which is synthesized in the liver of female telosts in response to estrogen from the ovary (*29*). It is subsequently released into the plasma from which it is removed by the ovary. Liver VTG production can be induced in immature female fish as well as male fish by injection of estradiol (*30*−*32*). There is also evidence that VTG production is induced in male fish that have been exposed to environmental contaminants (*33, 34*).

In the current research, four immature rainbow trout (RBT), *Oncorhynchus mykiss*, were each injected with an equal portion of the extracts from SPMD samples deployed at two sites (Napoleon, MO, and the Gasconade River). Three of four fish injected with SPMD sample extract from the Napoleon site exhibited vitellogenin induction as compared to one of four fish injected with SPMD sample extract from the Gasconade River site. These results parallel the analytical results for these samples, i.e., the Napoleon SPMD sample had higher overall levels and a greater number of contaminant residues than the Gasconade River SPMD sample (Table 3). In addition, RBT exposed to laboratory processing controls had no evidence of vitellogenin production, whereas all four fish injected with estradiol (positive control) demonstrated vitellogenin production. These preliminary results indicate that the overall physiological effect of the complex mixture of contaminants sequestered by the SPMDs at the Napoleon site was estrogenic. Long-term exposure of fish and wildlife to such complex mixture of contaminants could result in reproductive perturbations. Research is ongoing to more clearly define the potential adverse effects associated with chronic exposure of organisms to complex mixtures of environmental contaminants.

Acknowledgments

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