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ARCHIVES OF
Environmental
Contamination
and Toxicology

Volume 44, Number 2
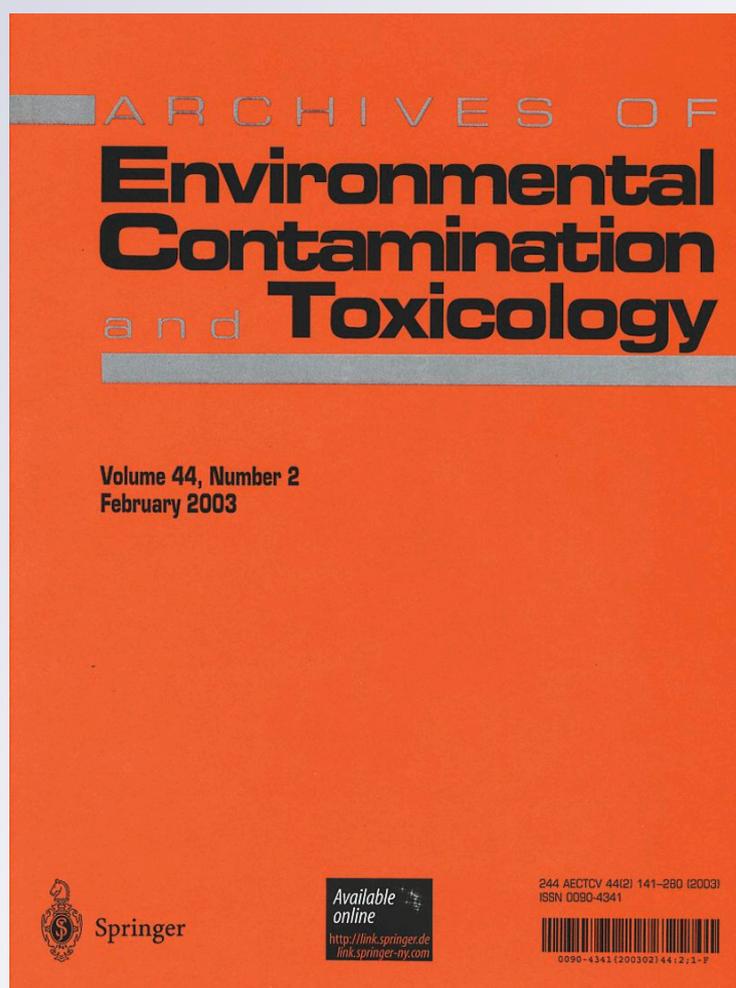February 2003

Available online
http://link.springer.de
link.springer-ny.com

244 AECTCV 44(2) 141–280 (2003)
ISSN 0090-4341

0090-4341(200302)44:2;1-F

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Elevated Levels of Metals and Organic Pollutants in Fish and Clams in the Cape Fear River Watershed

Michael A. Mallin · Matthew R. McIver · Michael Fulton · Ed Wirth

Abstract A study was performed in 2003 to 2004 to assess metal and organic contaminant concentrations at three areas in the lower Cape Fear River system, North Carolina, United States. Sites examined were Livingston Creek along the mainstem of the Cape Fear River near Riegelwood, Six Runs Creek in the Black River Basin, and Rockfish Creek in the Northeast Cape Fear River basin. The results of the investigation showed that levels of metals and organic pollutants in the sediments were lower than limits considered harmful to aquatic life. However, results of fish (adult bowfin) tissue analyses showed that concentrations of arsenic (As), cadmium (Cd), mercury (Hg), selenium (Se), and now-banned polychlorinated biphenyls (PCBs), and the pesticide dieldrin were higher than levels considered safe for human consumption by the United States Environmental Protection Agency and the North Carolina Health Director's Office. Fish tissue concentrations of Hg, Se, and PCBs were also higher than concentrations determined by researchers to be detrimental either to the health of the fish themselves or their avian and mammalian predators. Due to the rural nature of two of the sites, increased concentrations of As, Cd, Se, and PCBs in fish tissue were unexpected. The likely reason the levels are increased in fish and some clams but not in sediments is that these pollutants are biomagnified in the food chain.

M. A. Mallin (✉) · M. R. McIver
Center for Marine Science, University of North Carolina
Wilmington, Wilmington, NC 28409, USA
e-mail: mallinm@uncw.edu

M. Fulton · E. Wirth
Center for Coastal Environmental Health and Biomolecular
Research, National Centers for Coastal Ocean Science, National
Oceanic and Atmospheric Administration, Charleston,
SC 29412, USA

These pollutants will also biomagnify in humans. In these rural areas there is subsistence fishing by low-income families; thus, increased fish tissue metals and toxicant concentrations may present a direct threat to human health.

There is growing concern regarding increased concentrations of metals and various organic compounds (pesticides, herbicides, chemical byproducts, etc.) in fish tissue. This is both a human health issue through fish consumption (Colborn and Thayer 2000; United States Environmental Protection Agency [USEPA] 2000a, b) and an ecological issue through fish disease, reproductive failures, and loss of fish prey items in the environment (Gillespie and Bauman 1986; Woock et al. 1987; Weis and Weis 1989; Long et al. 1995; Macdonald et al. 2000; Evers et al. 2007). In particular, urbanization and industrialization of former natural areas have brought concurrent pollution of inland and estuarine sediments by metals and organic compounds, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides, and herbicides (Sanger et al. 1999a, b; Hyland et al. 2000; Long 2000; Van Metre et al. 2000; Van Dolah et al. 2008). Such contaminants have also entered food chains, concentrated in finfish and shellfish flesh (Fulton et al. 1993; Crutchfield 2000; King et al. 2004), and initiated fish consumption advisories due to increased body burden of toxic substances.

It is well documented that mercury (Hg) contamination is widespread (Evers et al. 2007; Peterson et al. 2007), and thus Hg is probably the best known contaminant that regulatory agencies focus on in terms of fishery closures to protect human health. Such Hg advisories are widespread, particularly in coastal wetland areas. In eastern North Carolina, United States (the location of the present study), there is an Hg fish consumption advisory throughout the

Coastal Plain, where blackwater swamps and streams are abundant. At least eight freshwater fishes, including black crappie, bowfin, catfish, chain pickerel, largemouth bass, yellow perch, and warmouth, are included in the advisory; in saltwater areas along the North Carolina coast the advisory covers 17 species. In the sediments of blackwater swamps and rivers, Hg transforms to the toxic methyl mercury form by a bacterially mediated process. One such lowland basin is the lower portion of the Cape Fear River watershed (Fig. 1), which is the largest watershed within the State of North Carolina (North Carolina Department of Environment and Natural Resources [NCDENR] 2005). In addition to Hg, the United States Environmental Protection Agency (USEPA 2000a, b) has listed numerous pollutants that can be harmful to humans if regularly consumed in fish and shellfish. Within the North Carolina Estuarine Research Reserve system, arsenic (As) and Hg have been found to exceed human consumption standards in selected estuarine fish samples (Cooksey et al. 2008). In selected estuarine creeks in South Carolina, inorganic As, total DDT, total polychlorinated biphenlys (PCBs), and the pesticide dieldrin have on occasion been found to exceed human consumption standards in oyster tissue (Sanger et al. 2008). This survey was conducted to examine potentially toxic concentrations of metals, PCBs, polycyclic aromatic hydrocarbons (PAHs), DDT, and various other pesticides in sediments, fish tissue, and clam tissue representing three major areas of the lower Cape Fear watershed.

The USEPA and the State of North Carolina have no official standards for sediment concentrations of metals and organic pollutants in reference to protection of invertebrates, fish, and wildlife. However, academic and government researchers (Long et al. 1995; MacDonald et al. 2000) have produced guidelines based on extensive field and laboratory testing that were published by the USEPA in their National Coastal Condition Report II (USEPA 2004). There are no federal standards for fish or clams concerning metals or organic pollutant body burdens that may pose a physiological or ecological risk to the fish, although some suggested academically derived guidelines have been published (e.g., Lemly 1993; Evers et al. 2007). As mentioned, the USEPA (2000a, b) has risk guidelines for four metals and several organic pollutants concerning human consumption based on four meals per month. In addition, the North Carolina Division of Water Quality has human health screening guidelines for four metals, and the North Carolina Health Director has human health guidelines for Hg, selenium (Se), and total PCBs, points at which a consumption advisory would be issued (NCDENR 2001). These stream-sediment levels of concern and USEPA human consumption standards were compared with our data to assess the ecosystem and human health concerns

that these contaminants pose in these Coastal Plain stream systems.

As a working hypothesis, we assumed that Hg would be increased throughout the system due to regional power plant emissions and because one of the sites was near potential local sources. We also postulated that copper (Cu) and zinc (Zn) would be increased because they are used as feed supplements for swine and poultry in concentrated animal-feeding operations (CAFOs; see later text). However, we predicted that due to the relatively rural nature of two of our Coastal Plain sites, other potentially toxic metals would be found there in low concentrations. We also assumed that certain common pesticides would be in increased concentrations due to high agricultural use of the lower (and upper) Cape Fear basin but that other organic contaminants associated with urbanization and industrialization, such as PCBs and PAHs, would be in low concentrations in the rural sites.

Site Description

The Cape Fear River basin is the most industrialized watershed in the State of North Carolina, with approximately 244 National Pollutant Discharge Elimination System (NPDES) dischargers using the river or its tributaries, principally in the Cape Fear River main stem, which arises in the Piedmont province and enters the Coastal Plain as a fifth-order stream. This stream is often considered a "brownwater" river due to the clay-suspended sediments that color the water brown after large Piedmont rainfalls. In 2000, the watershed's population stood at approximately 1,835,000 (NCDENR 2005), most of which was located in the Piedmont. There is extensive land devoted to crop agriculture in both the Piedmont and Coastal Plain areas of the Cape Fear watershed. In the Coastal Plain province, the Cape Fear River is joined by two fifth-order tributaries, the Black River and the Northeast Cape Fear River (Fig. 1), both of which are darkly stained "blackwater" rivers; within these two basins there are approximately 5,000,000 head of swine and numerous poultry housed and reared in CAFOs, which produce and discharge vast amounts of nutrients and fecal bacteria in waste (Mallin 2000; Mallin et al. 2001). This waste may also potentially contain metals, such as Cu and Zn, which are additive components in these types of feed operations. Our plan was to sample three freshwater areas within the Coastal Plain representing the three major tributaries.

In the Cape Fear main stem area, we sampled just off the river proper in Livingston Creek (coordinates N 34.35180, W78.20128), a third-order stream with two NPDES dischargers along it and no CAFOs located upstream of the collection area (NCDENR 2005). This is a tidal freshwater

Fig. 1 Location of the three sampling sites in the lower Cape Fear River watershed, North Carolina, United States. Triangles represent sampling sites, *SSEP* sutton steam electric plant, *IP* international paper
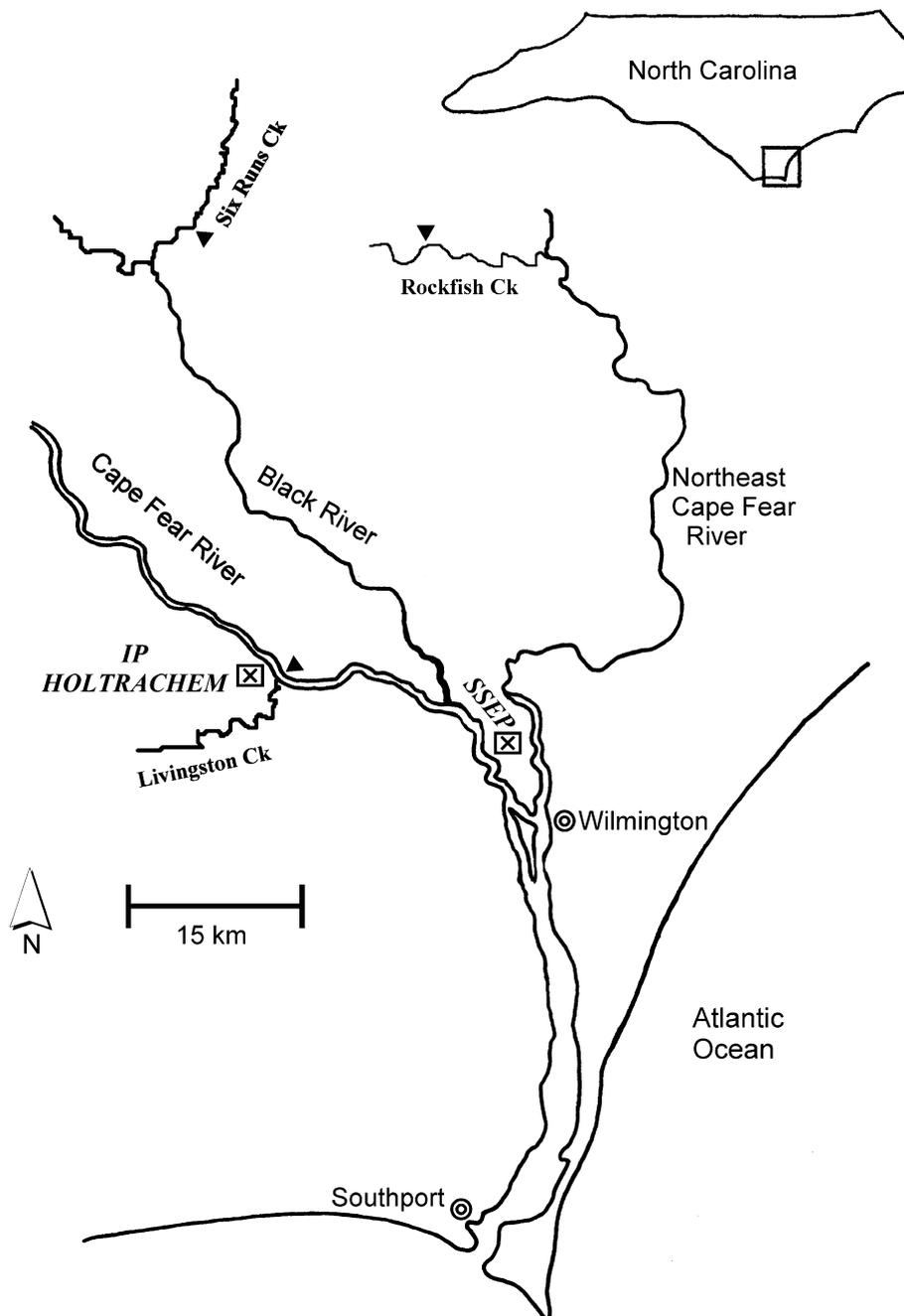
area. Just upstream of this creek on the river is a pulp and article mill, and near that site was a now-defunct company called "HoltraChem," which used Hg as a key component in its production of chlorine and caustic soda. This plant was closed in 2000 and at times had tons of Hg on site. To represent the Black River, we sampled Six Runs Creek (coordinates N34.79357, W78.31192), a fourth-order stream that drains a watershed containing three NPDES dischargers and 131 CAFOs, and contains approximately 8.5% wetlands coverage (Mallin et al. 2001). To represent the Northeast Cape Fear River, we sampled Rockfish Creek (coordinates N34.72000, W77.94030), a fourth-order

stream whose watershed contains four NPDES discharges and 74 CAFOs and contains approximately 16.7% wetlands coverage (Mallin et al. 2001).

Methods

Field Collections

Sediments were collected for contaminant analysis by researchers from the University of North Carolina Wilmington's Center for Marine Science in Livingston

Creek (mainstem Cape Fear), Six Runs Creek (Black River basin), and Rockfish Creek (Northeast Cape Fear River basin). Samples were collected using a petite ponar grab at Livingston Creek (by boat) and at Six Runs Creek (from a bridge, upstream side). At these two sites, three grab samples were taken as follows: the top layer of sediment (approximately 3 cm) was scooped using a stainless steel spoon; the top layer was put into a stainless steel bowl; and mixed. Jars (polypropylene [8 oz. metals] and polystyrene [4 oz. Hg]) were filled and put on ice. The samples at Rockfish Creek were collected by scooping the top layer of sediment (approximately 3 cm) directly into each jar and then mixed as described previously.

Tissues (fillets and liver) from adult bowfin, *Amia calva*, a native fish species and tissue from a nonnative but long-established clam (*Corbicula spp.*), were collected from all three sites and analyzed for metals and selected organic contaminants. The target organisms were chosen for analysis because their living habitat or feeding modes are most likely to concentrate potential contaminants. Bowfin feed on crustaceans and insects as young, are largely piscivorous as adults, and have an average life span of approximately 10 years (Rohde et al. 2009). It was assumed that their livers would likely concentrate toxins. Clams are filter feeders and concentrate pollutants associated with suspended particles and benthic particles, including benthic microalgae. The fish, 2 adult fish/site, were collected from a boat using electroshocking. They were immediately placed on ice until return to the laboratory. Whole fish were wrapped in clean aluminum foil, sealed in ziplock bags, labeled, and frozen. They were then shipped frozen overnight to the Estuaries and Land Use Branch, Center for Coastal Environmental Health and Biomolecular Research, National Oceanic and Atmospheric Administration (NOAA), National Ocean Service in Charleston, SC, for analysis. Clams were collected by hand (10 to 20/site), placed unshucked into ziplock bags, and shipped overnight on ice to the NOAA Marine Ecotoxicology laboratory in Charleston for metal and organic pollutant analysis.

Contaminant Analysis of Tissues and Sediments

Sample Preparation

Sediments and tissues (fish and clams) were frozen and stored at $-40°C$ until analysis. Fish were removed from the freezer and allowed to partially thaw at $4°C$, and the fillets (skin off) were weighed. Livers were dissected and weighed. After dissection, each fillet or liver was then well homogenized using a ProScientific homogenizer in 500-ml Teflon containers. Clams were shucked and the wet tissue composited and homogenized as described previously. The homogenized tissue sample was divided into an organic

(precleaned glass container) and an inorganic (precleaned polypropylene container) aliquot, and samples were stored at $-40°C$ until extraction or digestion.

Inorganic Analysis (Digestion for All Inorganic Analytes Except Hg)

Sediments were dried and ground to a fine powder. Approximately 0.2–0.3 g dried sediment was then digested in Teflon vessels using concentrated nitric acid using 900 W CEM MDS-2100 microwaves. Tissue samples were aliquoted (2–3 g wet mass) into Teflon-lined digestion vessels and 10 ml of concentrated nitric acid along with 2 ml of hydrogen peroxide were added. The samples were digested using 900 W CEM MDS-2100 microwaves. Digested samples were brought to a fixed volume (50 ml) with deionized water in graduated polypropylene centrifuge tubes and stored until analysis. Appropriate dilutions of tissue samples were performed so that values for each element would fall within the instrumental calibration.

Inorganic Instrumental Analysis (Except Hg)

Instrumental analysis was performed using either inductively coupled plasma mass spectrometry (ICP-MS) or graphite furnace atomic absorption (GFAA) spectroscopy. Instruments were calibrated with a five-point curve using certified reference standards. The Perkin Elmer Elan 6100 ICP-MS was used for the analysis of the following elements with their respective masses in parentheses: Li (6, 7), Be (9), Al (27), V (51), Cr (52, 53), Fe (54, 57), Co (59), Mn (55), Ni (60, 61), Cu (63, 65), Zn (64, 66, 68), As (75), Se (77, 82), Cd (111, 112, 114), Sn (117, 119, 120), Sb (121, 123), Ba (132, 136, 137), Tl (203, 205), Pb (206, 207, 208), and U (235, 238). The Perkin-Elmer 5100 Zeeman HGA GFAA spectrometer was used to analyze for Ag at a wavelength of 328.1 nm with pyrolysis and atomization temperatures of 1100 and $2100°C$, respectively.

Hg Analysis

A separate aliquot of each tissue homogenate was used for Hg analysis. Approximately 0.5 g wet sediment or tissue was weighed directly into a nickel (Ni) combustion boat. The sample boats were then loaded into an autosampler and analyzed on a Milestone DMA-80 Analyzer. Samples were thermally decomposed in a continuous flow of oxygen with Hg vapors being trapped on a gold amalgamator and subsequently desorbed for quantification using atomic absorption spectrophotometry at 254 nm. The DMA-80 Analyzer was calibrated with two five-point curves (low, high) using matrix-matched standard reference materials.

Quality Control

One sample per batch (i.e., approximately every nine samples) was analyzed in duplicate to assess precision. Control samples included solvent blanks, spiked solutions, and standard reference materials.

Organic Analysis

Extraction for PAHs, Pesticides, and PCBs

An aliquot (approximately 5 g tissue [wet] or 10 g sediment [wet]) was weighed into a glass mortar bowl and mixed with 28–33 g ashed (450°C) anhydrous sodium sulfate to form a dry powder. The dried homogenate was then poured into a precleaned 33-ml accelerated solvent extraction (ASE) vessel. A measured aliquot (250 μl) of an internal standard mixture containing carbon-13-labelled compounds were added to each sample. The samples were then extracted with 1:1 methylene chloride and acetone (for sediments) or 100% methylene chloride (for tissues) on an ASE (Schantz et al. 1997). After extraction, the residual water was removed by passing the extract through phase separation filter article containing a small amount of sodium sulfate. After drying, the extracted sample was concentrated to 1000 μl on an automatic concentrator (TurboVap). Lipid and other high molecular weight components were then removed by size-exclusion chromatography (SEC). The mobile phase was methylene chloride at 5 ml/min. After SEC, the volume was decreased to approximately 1000 μl and solvent exchanged into hexane. The extract was split into two equal aliquots (approximately 500 μl each) for cleanup as described in the following sections. Samples were further cleaned of interferences using solid-phase extraction (SPE) columns (silica and/or cyanopropyl, 1 g, 3 ml Phenomenex). After SPE, a recovery standard was added to each sample to allow for analyte quantitation and internal standard percent recovery determinations.

An Agilent 6890/5973 N gas chromatographer/mass spectrometer operating in negative chemical ionization mode was used to analyze the samples for selected pesticides. For DDTs and PCBs, quantitation was performed on an identical instrument operating in electron impact ionization mode. Both instruments use programmable temperature vaporization with large volume injection ports. An injection volume of 25 μl was used for each instrumental analysis. A 30 m × 0.25 mm × 0.25 μm DB-5MS column was used in both GCs. The data was collected in selective ion monitoring mode and quantified against a calibration curve with at least five levels. For PAH determinations, a Varian 4000 GC/MS/MS equipped with a 5% phenyl high-resolution capillary column (30 m × 0.25 mm × 0.25 m)

was used for quantitative analysis. The instrument was calibrated with a six-point curve using NIST certified reference standards (NIST SRM2260). Two 2-μl injections were made in the direct injection mode.

Quality Control

Spiked blank, reagent blank, and appropriate standard reference materials were included with each set of samples to ensure the integrity of the analytical method and corresponding analytical results.

Results

Results of Sediment Analyses

At all three sites the sediment concentrations of As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, and Zn were safely below accepted concentrations based on protecting the health of benthic organisms (Long et al. 1995; MacDonald et al. 2000) and for protection of aquatic life in freshwater and estuarine systems (Table 1). Common sediment standards are not available for aluminum, Sb, Be, Co, Fe, Li, Mn, Sn, and other metals examined. Likewise, all three sites had sediment concentrations of total PCBs, total PAHs, and total DDTs that were lower than the sediment guidelines (Table 1). Sediment concentrations of individual pesticides and other organic pollutants were lower than the laboratory detection limits.

Table 1 Selected metals and organic pollutant concentrations (as μg/g or ppm) in sediments from three sites in the lower Cape Fear River basin in 2004

Metal	Livingston Creek	Rockfish Creek	Six Runs Creek
As	<0.909	<0.896	<0.909
Cd	<0.0895	<0.0913	<0.0900
Cr	1.94	5.56	5.91
Cu	<6.10	<6.22	<6.13
Pb	5.38	1.69	4.30
Hg	0.00196	0.00257	0.00496
Ni	<1.07	<1.10	2.51
Se	<0.163	<0.160	<0.163
Ag	<0.262	<0.268	<0.264
Zn	<15.6	< 15.9	32.2
Total PCBs	0.0049	0.0064	0.0036
Total PAHs	0.00827	0.01307	0.0344
Total DDTs	0.0	0.00060	0.0

Results of Fish and Clam Tissue Analyses

The data showed that bowfin and, on occasion, freshwater clams in the lower Cape Fear River basin contain metals and organic contaminant concentrations higher than levels considered safe for human consumption. As in bowfin and clam samples from Livingston Creek exceeded the recommended USEPA (2000b) concentration range (0.008–0.016 µg/g) for cancer risk (Table 2). Cadmium (Cd) in bowfin livers from Livingston Creek exceeded the recommended USEPA (2000b) concentration range (0.35–0.70 µg/g) for noncancer health risk, although liver concentrations in the other two creeks approached the standard (Table 2). Hg in all fish tissues examined exceeded the recommended USEPA

(2000b) concentration ranges (0.12–0.23 µg/g) for noncancer health risk (Table 2; Fig. 2), and Se in bowfin livers from Rockfish Creek, Livingston Creek, and Six Runs Creek exceeded USEPA (2000b) recommended concentration ranges (5.9–12.0 µg/g) for noncancer health risk (Table 2).

Some metals appeared to concentrate strongly in the liver tissue, whereas others did not (Table 2). Cu concentrated in liver tissue by a factor of approximately two orders of magnitude compared with filets; Se concentrated in the livers by approximately one order of magnitude; Zn concentrated in the liver by a factor of between $4\times$ and $10\times$; and cadmium (Cd) and lead (Pb) concentrated in the liver by an indeterminable factor, although As, Hg, and Ni showed no such liver concentration.

Table 2 Selected metals concentrations (µg/g, or ppm) in bowfin filets and livers and clam tissue from Livingston Creek, Six Runs Creek, and Rockfish Creek, as mean ± 1 SD

Metal	Tissue	Livingston Creek	Six Runs Creek	Rockfish Creek
As[a]	Bowfin filet	**0.0095 ± 0.0003**[b]	0.0063 ± 0.0030	0.0059 ± 0.0005
As[a]	Bowfin liver	0.0033 ± 0.0006	0.0039 ± 0.0011	0.0034 ± 0.001
As[a]	Clam tissue	**0.0078 ± 0.0005**	0.0039	0.0039
Cd	Bowfin filet	BDL	BDL	BDL
Cd	Bowfin liver	**0.551 ± 0.162**	0.247 ± 0.234	0.287 ± 0.107
Cd	Clam tissue	0.230 ± 0.020	0.178	0.192
Cr	Bowfin filet	0.399 ± 0.037	0.434 ± 0.01	0.473 ± 0.096
Cr	Bowfin liver	0.292 ± 0.019	0.574 ± 0.025	0.429 ± 0.024
Cr	Clam tissue	0.511 ± 0.118	0.294	0.323
Cu	Bowfin filet	0.403 ± 0.155	0.0847 ± 0.120	0.495 ± 0.195
Cu	Bowfin liver	72.0 ± 2.37	116 ± 22.9	69.9 ± 68.6
Cu	Clam tissue	5.16 ± 0.10	2.61	3.34
Hg	Bowfin filet	**1.77 ± 0.39**	**0.742 ± 0.66**	**1.44 ± 0.94**
Hg	Bowfin liver	**1.38 ± 0.07**	**1.35 ± 1.58**	**1.53 ± 1.53**
Hg	Clam tissue	0.05 ± 0.006	0.02	0.08
Ni	Bowfin filet	0.54 ± 0.76	BDL	0.12 ± 0.18
Ni	Bowfin liver	0.04 ± 0.005	0.07 ± 0.056	0.04 ± 0.001
Ni	Clam tissue	0.59 ± 0.45	0.44	0.24
Pb	Bowfin filet	BDL	BDL	BDL
Pb	Bowfin liver	0.19 ± 0.11	0.15 ± 0.17	0.26 ± 0.09
Pb	Clam tissue	0.21 ± 0.02	0.08	0.11
Se	Bowfin filet	0.46 ± 0.04	0.37 ± 0.14	0.48 ± 0.06
Se	Bowfin liver	**25.0 ± 1.95**	**34.6 ± 26.8**	**19. 5 ± 19.4**
Se	Clam tissue	0.43 ± 0.03	0.27	0.36
Zn	Bowfin filet	3.96 ± 0.03	2.19 ± 0.14	5.86 ± 1.50
Zn	Bowfin liver	30.40 ± 1.76	28.1 ± 2.97	29. 9 ± 5.09
Zn	Clam tissue	29.3 ± 0.55	21.7	20.8

BDL below analytical detection limit

[a] Arsenic concentrations are estimated as inorganic As computed as 2% of total As. Concentrations are for total Hg and are assumed to represent 100% methyl mercury

[b] Concentrations in *bold* exceed USEPA consumption guidelines based on four meals per month. As concentrations in *bold* are for cancer risk; the other values in *bold* are for noncancer health risk
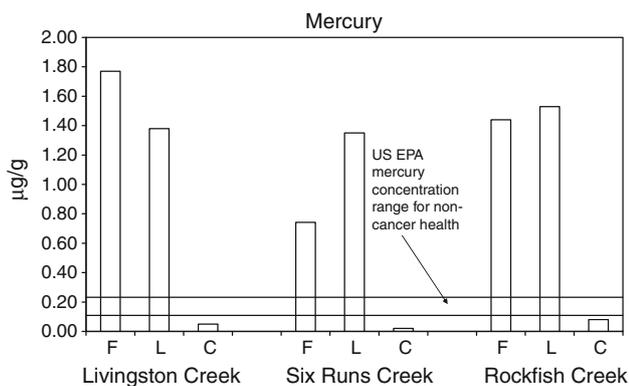
Fig. 2 Concentration of Hg in fish and clam tissue in three areas of the lower Cape Fear River watershed, NC. *F* filets, *L* liver, *C* clam tissue

Concentrations of PCBs exceeded USEPA (2000b) levels considered safe for human consumption (0.023–0.047 μg/g) in bowfin filets or bowfin livers at all three locations (Table 3; Fig. 3). Concentrations of total PAHs were lower than the analytical detection limit for all samples. Concentrations of total DDTs were lower than the safe consumption level in all three areas. Concentrations of the pesticide dieldrin exceeded USEPA (2000b) levels associated with human cancer risk (0.00073–0.0015 μg/g) in bowfin filets, and bowfin livers at all three sites (Table 3; Fig. 4). Lindane had measurable concentrations in fish liver tissue at all three sites and in filets in Livingston Creek, but concentrations were lower than the health-risk range. Lindane concentrations were lower than detection limits for

fish filets at the other two sites and for clam tissue at all three sites (Table 3). Concentrations of a variety of other pesticides including aldrin, chlorpyrifos, chlordane, endosulfan, heptachlor and mirex were mostly lower than detection limits in both bowfin and clam tissues. With the exception of dieldrin and lindane, most toxicants did not appear to concentrate in liver tissue compared with fish filets compared with the liver concentration expressed by some of the metals (Tables 2, 3).

Discussion

Metal concentrations in sediments from three widely separated areas of the lower Cape Fear River basin were lower than concentrations considered harmful to the health of benthic invertebrates; however, bowfin and some clam tissue in these streams showed levels unsafe for human consumption for As, Cd, Hg, and Se. The increased concentrations of some of the metals (As, Cd, and Se) in tissue were surprising due to the remoteness of two of these sites from presumed urban or industrial sources that have been associated with increased sediment concentrations elsewhere (Sanger et al. 1999a). We assume the levels are increased in the fish and clams but not sediments because these pollutants become more concentrated (biomagnify) as they move up the food chain (from water and sediments to algae and insects or from crustaceans to higher organisms). The disparity in findings between the sediments and tissue is troubling because as it implies that fish harvested

Table 3 Selected organic contaminant concentrations (μg/g, or ppm) in bowfin filets and livers and clam tissue from Livingston Creek, Six Runs Creek, and Rockfish Creek, as mean ± one standard deviation

Metal	Tissue	Livingston Creek	Six Runs Creek	Rockfish Creek
Total PCBs	Bowfin filet	**0.0119 ± 0.0095**	**0.0132 ± 0.0067**	0.0043 ± 0.0036
Total PCBs	Bowfin liver	<u>**0.0423 ± 0.0090**</u>	0.0049 ± 0.0008	<u>**0.0344 ± 0.0087**</u>
Total PCBs	Clam tissue	0.0087 ± 0.0034	0.0037	0.0098
Total PAHs	Bowfin filet	BDL	BDL	BDL
Total PAHs	Bowfin liver	BDL	BDL	BDL
Total PAHs	Clam tissue	BDL	BDL	BDL
Total DDTs	Bowfin filet	0.0060 ± 0.0013	0.0111 ± 0.0051	0.0090 ± 0.0002
Total DDTs	Bowfin liver	0.0043 ± 0.0061	BDL	0.0066 ± 0.0000
Total DDTs	Clam tissue	0.0022 ± 0.0002	0.0008	0.0025
Dieldrin	Bowfin filet	**0.0011 ± 0.0001**	**0.0009 ± 0.0013**	**0.0081 ± 0.0014**
Dieldrin	Bowfin liver	**0.0032 ± 0.0028**	**0.003 ± 0.0006**	**0.0512 ± 0.0206**
Dieldrin	Clam tissue	BDL	BDL	0.0007
Lindane	Bowfin filet	0.0008 ± 0.0006	BDL	BDL
Lindane	Bowfin liver	0.0022 ± 0.0012	0.0001 ± 0.0002	0.0003 ± 0.0001
Lindane	Clam tissue	BDL	BDL	BDL

Concentrations in *bold* exceed USEPA consumption guidelines based on 4 meals per month. Concentrations in *bold* are for cancer risk. *Underlined* values are for non-cancer risk. *BDL* below analytical detection limit
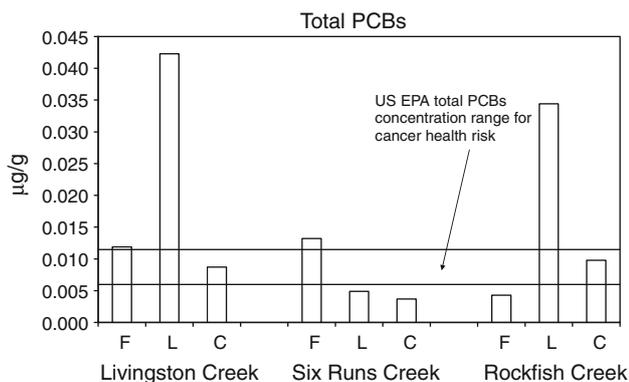
Fig. 3 Concentration of total PCBs in fish and clam tissue in three areas of the lower Cape Fear River watershed, NC. *F* filets, *L* liver, *C* clam tissue
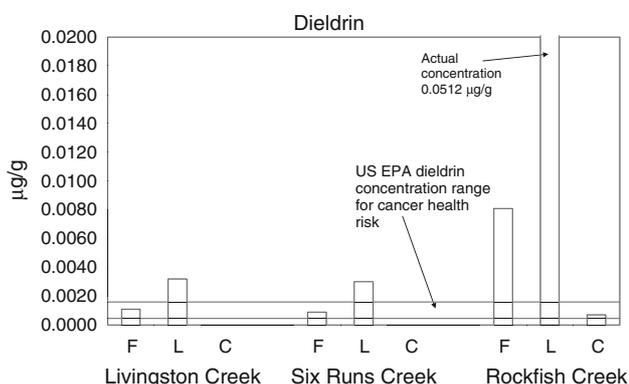
Fig. 4 Concentration of dieldrin in fish and clam tissue in three areas of the lower Cape Fear River watershed, NC. *F* filets, *L* liver, *C* clam tissue

from an area that is believed to be safe (at least for benthic biota) based on sediment chemical analysis (Long et al. 1995; MacDonald et al. 2000) may in fact be unsafe for human consumption. Unfortunately, fish and clam tissue analyses are less easy to collect than sediments, and fewer commercial laboratories perform tissue analyses than sediment analyses.

Based on human-consumption tissue-concentration guidelines, the results lead to serious questions regarding metals concentrations in the Cape Fear River basin. Large doses of As are acutely toxic to humans and animals. Chronic impacts on human health include skin lesions and gastrointestinal, cardiovascular, hematological, and liver and kidney disorders (USEPA 2000b). Sources of As include fossil-fuel power-plant emissions, hazardous waste site leachate, wood preservatives, pesticides and herbicides, and mining and smelting operations (USEPA 2000a). As is also a naturally occurring element in various soils and rocks. As a regional comparison, As in flounder flesh was found at excessive concentrations in two urbanized estuaries, Winyah Bay (3.15 µg/g) and Charleston Harbor

(4.80 µg/g), but were at undetectable concentrations in less developed St. Helena Sound and Port Royal Sound (Matthews 1994).

Chronic exposure to Cd leads to kidney disorders, neurotoxicity, and bone disorders, and in animals, cadmium toxicity includes kidney impacts, immune system disorders, and reproductive and development toxicity (USEPA 2000b). Sources of Cd include mine drainage, waste disposal operations, paints, batteries, plastics, pesticides, and herbicides (USEPA 2000a). In comparison, flounder flesh Cd concentrations in several South Carolina estuaries were lower than consumption advisory standards (Winyah Bay [0.16 µg/g], Port Royal Sound [0.08 µg/g], and St. Helena Sound [0.07 µg/g]) and at undetectable levels in Charleston Harbor (Matthews 1994).

Hg, particularly methyl mercury, is easily and rapidly absorbed by the body and has well known acute and chronic effects (based on consumption of contaminated fish), including neurological impairment and reproductive and developmental problems in humans and animals (USEPA 2000b). In addition to exceeding human consumption body burden guidelines, fish filet and liver Hg concentrations in our samples were well above the whole-fish Hg concentration of 0.16 µg/g, which Evers et al. (2007) used as an adverse level for food-chain health risk to piscivorous birds. In comparison, the median Hg concentration in North Carolina bluegills in 1989 to 1999 was 0.10 µg/g, just lower than the EPA consumption guideline (Chalmers et al. 2010). As previously mentioned, Hg can arrive onsite through airborne sources from coal-fired power plants upwind (Evers et al. 2007). Airborne transport may be the single most import means of Hg impacting stream fish life in the western United States, where conditions for methylation (low pH and high dissolved oxygen concentration) are rare (Peterson et al. 2007). However, in the southeastern United States. Hg body burdens in fish have been on a significantly increasing trend, likely a result of airborne transit (Chalmers et al. 2010). As mentioned previously, a potential local Hg source is the former HoltraChem plant, which was located just upstream of the sampling location in Riegelwood along the Cape Fear River.

Selenium (Se) is highly magnified in the food chain. Compared with fish and birds, taxa groups lower in the food chain (e.g., phytoplankton, zooplankton, invertebrates) require far higher body burdens of Se before ill effects are seen (Lemly 1993). Increased Se levels in fish tissue cause decreased larval survival; deformations including edema; and eye cataracts (Gillespie and Bauman 1986; Woock et al. 1987). Liver concentrations of Se in our collected bowfin well exceeded concentrations (12 µg/g) suggested by Lemly (1993) to be detrimental to freshwater fish health and reproduction, but filet concentrations in our

study were lower then the 8 µg/g muscle tissue detrimental concentration suggested by Lemly (1993). Chronic exposure to Se in humans in food and water causes symptoms, including skin disorders, hair and nail loss, limb pain, convulsions, and paralysis (USEPA 2000b). A major source of Se is emissions from fossil fuel combustion and leachate from ash ponds associated with coal-fired power plants (Woock et al. 1987; Lemly 1993; Crutchfield 2000). For example, data from North Carolina's Hyco Reservoir, a power-plant cooling reservoir, showed fish muscle and liver Se concentrations ranging from 29 to 68 and 27 to 239 µg/g, respectively, in a bay polluted by ash pond runoff (Crutchfield 2000). Fish in this reservoir suffered deformities and reproductive failure until subsequent Se pollution-decrease actions occurred (Crutchfield 2000). Several coal-fired power plants are located inland along the upper Coastal Plain and in the Piedmont, and one is located 30 km downstream of the Livingston Creek sampling site along the lower Cape Fear River near the head of the estuary (Fig. 1). Se is also is abundant in certain soils, mostly in the southwestern United States.

Determining the potential sources of the four metals in question is important to any mitigation strategies. In these largely rural areas, we surmise that airborne deposition of Hg, As, and Se is the most likely means of distribution to all sites. Although the sampling site at Livingston Creek contains fresh water, this location is strongly impacted by Cape Fear River tides. Thus, movement of pollutants from downstream industrial sources upstream toward this station is also a real possibility. In contrast, tidal influence is low in Rockfish Creek and insignificant in Six Runs Creek. In the rural sites of Rockfish and Six Runs Creeks, there is also the potential for As and Cd contamination to be sourced from pesticides or herbicides presently or formerly used in crop agriculture.

Concentrations of PCBs that exceeded levels safe for human consumption were found in bowfin at all three sites. PCBs were previously used as lubricants, hydraulic fluids, and insulating fluids in electrical transformers, compressors, vacuum pumps, and other equipment. They are closely related to chlorinated hydrocarbon pesticides. PCBs were banned by the USEPA in 1979 but are persistent and bioaccumulate in the food chain (USEPA 2000a). Among fish, increased PCB concentrations lead to decreased hatching success and various larval deformities (Weis and Weis 1989) and serve as endocrine disruptors higher in the food chain (Colborn and Thayer 2000). PCB concentrations in bowfin liver and filets were in the range of the dietary thresholds of fish as prey items (0.01–0.15 µg/g) found to cause toxic effects in aquatic mammal consumers (Kamman et al. 2000). Some studies have indicated that PCBs, through ingestion of contaminated fish, have caused various developmental effects in children, including lower

IQ, birth weight, and other effects, and that various individual PCBs may cause liver problems, cardiovascular toxicity, neurological problems, and cancers (USEPA 2000b). Although banned, PCBs enter the environment through landfills and waste dumps and are spread through airborne deposition as well as by water. However, PCBs in sediments and fish have been strongly linked to various measures of anthropogenic development in estuarine systems (Sanger et al 1999b; King et al. 2004), and at least two of our sites (Rockfish Creek and Six Runs Creek) were in rural areas.

Because considerable land in the Cape Fear River watershed is or has been under crop agriculture, pesticides in the environment should not be unusual. However, the increased levels of dieldrin that we found in the fish and clam samples were surprising. Dieldrin is an organochlorine pesticide previously used to control termites and soil-dwelling insects and was used on corn, cotton, and citrus crops (USEPA 2000a). The USEPA banned many uses of dieldrin in 1974, and the remaining uses were terminated by industry in 1987. In a survey from 1990 to 1993, dieldrin fish body burdens were mostly lower than detection limits in a number of South Carolina estuaries, although Charleston Harbor showed high (0.78 µg/g) average concentrations (Matthews 1994). Dieldrin is known to cause reproductive and developmental toxicity and cancers in animals and neurological toxicity in animals and humans (Weis and Weis 1989; USEPA 2000b). It is obviously persistent in the inland environment and is also a breakdown product of aldrin, another pesticide no longer in use.

As mentioned, the target organisms were chosen for analysis because their living habitat or feeding modes are likely to concentrate potential contaminants. Bowfin and *Corbicula* are not typical sport fishing species, but their ecological niches allow them to serve as sentinel species for contaminant problems. Some fish with relatively similar habitat and predatory feeding modes, such as various catfish, are avidly sought by sport fishermen in this system, along with sunfish and largemouth bass, a top predator that presumably will biomagnify many pollutants. It is important to note that low-income families in this basin fish for sustenance (including bowfin) rather than sport (personal communication; R. Carpenter, North Carolina Division of Marine Fisheries) and the presence of such increased levels of several toxins has direct implications for rural human health.

Our results indicate that several metals, toxicants, and pesticides (including banned ones) were found in increased concentrations in fish tissue in widely separated and largely rural areas of this large Coastal Plain river basin. These concentrations present health implications for human consumers as well as potential impacts to the resident fish communities. Our findings suggest the need for a

widespread survey of these and other potential toxicants in such rural coastal areas focused on fish and shellfish that are primary prey for commercial, sport, and subsistence fishermen.

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