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A screening-level assessment of lead, cadmium, and zinc in fish and crayfish from Northeastern Oklahoma, USA

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A screening-level assessment of lead, cadmium, and zinc in fish and crayfish from Northeastern Oklahoma, USA

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Abstract The objective of this study was to evaluate potential human and ecological risks associated with metals in fish and crayfish from mining in the Tri-States Mining District (TSMD). Crayfish (*Orconectes* spp.) and fish of six frequently consumed species (common carp, *Cyprinus carpio*; channel catfish, *Ictalurus punctatus*; flathead catfish, *Pylodictis olivaris*; largemouth bass, *Micropterus salmoides*; spotted bass, *M. punctulatus*; and white crappie, *Pomoxis annularis*) were collected in 2001–2002 from the Oklahoma waters of the Spring River (SR) and Neosho River (NR), which drain the TSMD. Samples from a mining-contaminated site in eastern Missouri and from reference sites were also analyzed. Individual fish were prepared for human consumption in the manner used locally by Native Americans (headed, eviscerated, and scaled) and analyzed for lead, cadmium, and zinc. Whole crayfish were analyzed as composite samples of 5–60 animals. Metals concentrations were typically higher in samples from sites most heavily affected by mining and lowest in reference samples. Within the TSMD, most metals concentrations were higher at sites on the SR than on the NR and were typically highest in common carp and crayfish than in other taxa. Higher concentrations and greater risk were associated with fish and crayfish from heavily contaminated SR tributaries than the SR or NR mainstems. Based on the results of this and previous studies, the human consumption of carp and crayfish could be restricted based on current criteria for lead, cadmium, and zinc, and the consumption of channel catfish could be restricted due to lead. Metals concentrations were uniformly low in *Micropterus* spp. and crappie and would not warrant restriction, however. Some risk to carnivorous avian wildlife from lead and zinc in TSMD fish and invertebrates was also indicated, as was risk to the fish themselves. Overall, the wildlife assessment is consistent with previously reported

This study was conducted by the Columbia Environmental Research Center (CERC) of the U.S. Geological Survey (USGS) and cooperating organizations and government agencies. All field and laboratory procedures conformed to the "Guidelines for the use of fishes in research" of the American Fisheries Society (AFS), Institute of Fishery Research Biologists (AIFRB), and American Society of Ichthyologists and Herpetologists (ASIH) Use of Fishes in Research Committee (AFS, AIFRB, and ASIH 2004), and with all USGS and CERC guidelines for the humane treatment of test organisms during culture and experimentation. Use of trade names does not constitute USGS or U.S. government endorsement.

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biological effects attributed to metals from the TSMD. The results demonstrate the potential for adverse effects in fish, wildlife, and humans and indicate that further investigation of human health and ecological risks, to include additional exposure pathways and endpoints, is warranted.

Keywords Metals · Mining · Fish · Crayfish · Ecological risk · Native Americans

Introduction

The Tri-States Mining District (TSMD) occupies some 2500 mi^2 (6475 km^2) of Jasper, Newton, and Lawrence Counties, Missouri; Cherokee County, Kansas; and Ottawa County, Oklahoma. The TSMD was mined for zinc (Zn), lead (Pb), and other metals from the mid-1800s through the 1960s, with peak production occurring during World War II (Pope, 2005). Sites contaminated to varying degrees by wastes from historical mining, ore processing, and smelting are widely distributed in the area. Metals from these sites, which can be toxic to fish, wildlife, and humans, have contaminated soils, surface waters, groundwater, stream sediments, and biota in the watersheds of the Spring River (SR) and Neosho River (NR), which drain most of the TSMD (Allen & Wilson, 1992; Allert, Wildhaber, Schmitt, Chapman, & Callahan, 1997; Barks, 1977; Brumbaugh, Schmitt, & May, 2005; Czarneski, 1985; Davis & Schumacher, 1992; May, Wiedemeyer, Brumbaugh, & Schmitt, 1997; McCormack and Burks, 1987; Neuberger, Mulhall, Pomatto, Sheverbush, & Hassenein, 1990; Pita & Hyne, 1975; Pope, 2005; Proctor, Kisvarsanyi, Garrison, & Williams, 1974; Schmitt et al., 1993, Schmitt, Wildhaber, Allert, & Poulton, 1997; Smith, 1988; Spruill, 1987; Wildhaber, Schmitt, & Allert, 1997, 2000; Yoo & Janz, 2003). Effects on human health from exposure to mining-derived metals have been documented (Neuberger et al., 1990), as have effects on aquatic organisms and wildlife (Beyer et al., 2004; Schmitt et al., 1993, Schmitt, Whyte, Brumbaugh, & Tillitt, 2005; Wildhaber et al., 2000; Yoo & Janz, 2003). Remediation of contaminated sites in the TSMD has been initiated by the US Environmental Protection Agency (USEPA) under "Superfund" (i.e. the Comprehensive Environmental Response, Compensation, and Liability Act and its Amendments).

Northeastern Oklahoma comprises the lands of ten Native American tribes, whose lands adjoin both the SR and NR. Locally procured fish and crayfish are often important in the Native American diet (Bridgen, 2005; Harris & Harper, 1997). Traditional cooking involves boiling or steaming fish with intact skin and bones, and the cooking liquids are often consumed. Although metals contamination in TSMD rivers and streams has been well documented (e.g. Pope, 2005), concentrations in fish as consumed by local inhabitants were unknown in 2001 because human health risk is typically evaluated on the basis of fillet samples (USEPA, 1990, 2000a). Metals in aquatic organisms are not homogeneously distributed (Crawford & Luoma, 1993; Goldstein & DeWeese, 1999; Schmitt & Finger, 1987; Settle & Patterson, 1980). Consequently, the methods used to prepare fish or other aquatic organisms prior to cooking can affect final concentrations. In addition to fish, Native Americans may also consume locally procured crayfish, frogs, turtles, waterfowl, and indigenous vegetation, and may be exposed to contaminants through other pathways such as contact with water and sediments. Native Americans have therefore been recognized as a subpopulation at comparatively greater risk from contaminants due to the proportionally large amounts of fish and other aquatic organisms in the diet, methods used to prepare the organisms, and proximity to contaminated sites (Bridgen, 2005; Harris and Harper, 1997; USEPA, 2000a, 2000b; Van Oostdam et al., 1999).

Our study had two primary objectives: (1) to obtain preliminary information on metals concentrations in aquatic organisms (crayfish and several species of fish) important in the diets of Native Americans and wildlife; and (2) to conduct a screening-level evaluation of the potential hazards associated with Pb, Zn, and cadmium (Cd) in these organisms to fish, wildlife and humans, to determine whether more comprehensive human health and ecological risk assessments were warranted. We collected samples of crayfish and several species of fish from the Oklahoma waters of the TMSD; prepared the organisms as they would be by local inhabitants and measured the metals concentrations in the organisms; and evaluated the risks represented by the metals to fish, wildlife, and humans based on current standards and criteria and the results of other studies reported in the scientific literature. Data from previous studies in the TSMD and elsewhere were also incorporated into the assessment to place the current findings in perspective.

Materials and methods

Collection sites and species

Metals in the SR and NR and its tributaries originate primarily from mine openings, tailings, and chat located in Missouri, Kansas, and Oklahoma (e.g. Pope, 2005; Spruill, 1987). Within Oklahoma, sources are concentrated primarily in the watershed of Tar Creek (TC), which joins the NR in Miami, near the upper end of Grand Lake of the Cherokees (Grand Lake; Fig. 1). Metals also originate near the headwaters of Elm Creek, a tributary of the NR; and from several SR tributaries in Oklahoma (Fig. 1). Fish collection sites (n = 6) were selected to represent the expected range of exposure conditions present in the Oklahoma waters of the SR and NR and at the upper end of Grand Lake (Fig. 1). Three sites were located on the SR upstream of Grand Lake, and one each was located at the confluence of the SR and NR (within Grand Lake) and in the lower reaches of TC. One site on the NR (Site 3) was just upstream of known TSMD pollution sources (Fig. 1). For fish, the collection target at each site was four specimens of each of three primary species: common carp (*Cyprinus carpio*, henceforth carp), largemouth bass (*Micropterus salmoides*), and channel catfish (*Ictalurus punctatus*). Alternate species were substituted as necessary when these species could not be obtained; spotted bass (*Micropterus punctulatus*), white crappie (*Pomoxis annularis*, henceforth crappie), or both were the alternates for largemouth bass, and flathead catfish (*Pylodictis olivaris*) was the alternate for channel catfish. Fish from reference sites and from a contaminated site outside the TSMD were also analyzed for comparison. Reference fish included pond-raised largemouth bass from our laboratory [U.S. Geological Survey, Columbia Environmental Research Center, Columbia, Missouri (CERC); Site 7] and channel catfish from a commercial fish farm (Osage

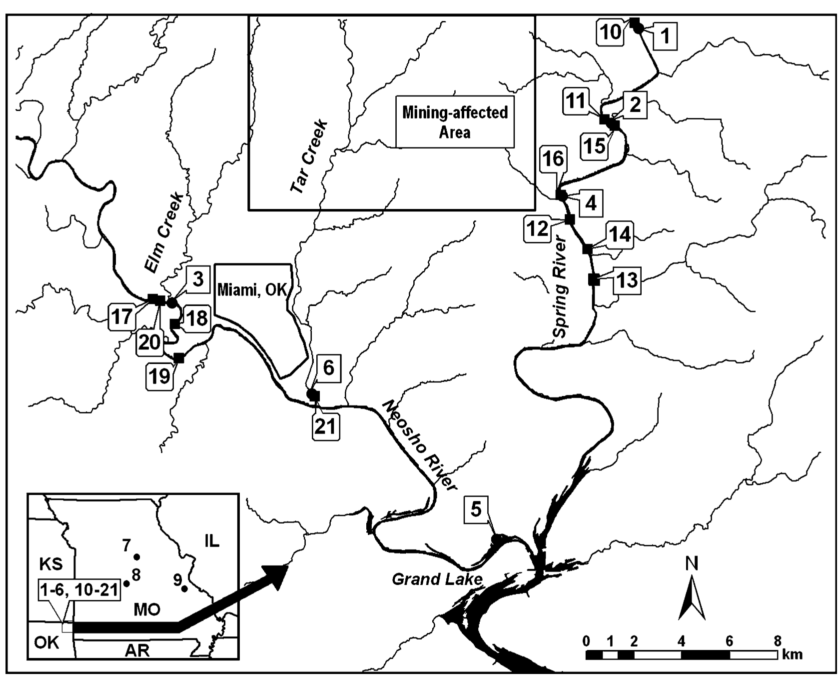

Fig. 1 Map of northeastern Oklahoma showing the locations of fish (1–6; circles) and crayfish (10–21; squares) collection sites on the Spring and Neosho Rivers. Also shown is the general boundary of area most affected by mining and the reference (7, 8) and contaminated (9) sites in Missouri. Additional mining-affected areas are drained by the Spring River in Kansas and Missouri, upstream (north and northeast) of the area shown in detail

Catfisheries, Osage Beach, Missouri; Site 8; Fig. 1; Table 1). The contaminated site outside the TSMD was on the Big River (BR; Site 9) in St. Francois County, Missouri (Fig. 1; Table 1). The BR is heavily contaminated by mine tailings from the Old Lead Belt (Brumbaugh et al., 2005; Dwyer, Schmitt, Finger, & Mehrle, 1988; Gale, Adams, Wixson, Loftin, & Huang, 2004; Schmitt, Dwyer, & Finger, 1984, 1993, 2005; Schmitt & Finger, 1987) and the Missouri Department of Health and Senior Services (MDHSS) has issued a fish consumption advisory due to Pb (MDHSS, 2005). Crayfish (mixture of *Orconectes virilus* and *O. neglectus neglectus*), which are eaten by Native Americans and are important in the diets of many species of fish and riparian wildlife, were collected from areas near fish collection Sites 1–4 and 6. Crayfish were not obtained at Site 5, which is in the upper part of Grand Lake (Fig. 1; Table 1), or from the BR; however, historical crayfish data for the BR were available (Schmitt & Finger, 1982).

Field methods

Fish were collected by electrofishing. They were processed on a measuring board covered with a clear polyethylene bag. Each fish was weighed, measured, scaled (not catfish), headed, eviscerated, washed thoroughly in tap water, wrapped in aluminum foil (dull side in), and frozen immediately in dry ice. Between fish samples, all contact surfaces were thoroughly cleaned with tap water, dissecting instruments were washed with laboratory detergent and rinsed with tap water and acetone, and the polyethylene bag on which the fish had been processed was replaced. Crayfish were collected by hand or with baited traps, placed in acid-cleaned 2-oz glass jars, and frozen (–20 °C). All samples were stored frozen (–20 °C) until prepared for analysis.

Laboratory methods

Each fish was briefly thawed, cut into sections with a stainless steel knife, and ground twice in a stainless steel meat grinder. A 100 g subsample was freeze-dried, then further homogenized in a blender; 0.25 g was digested (6 mL of concentrated HNO_3 and 1 mL of 30% high-purity H_2O_2 in a sealed, Teflon®-lined vessel) in a microwave oven at 200 °C. The digestate was transferred to a low-density polyethylene bottle and diluted to 100 mL with ultra-pure H_2O for analysis. Frozen crayfish in glass jars were analyzed as composite samples of 12–60 animals representing each site. They were freeze-dried to a constant weight, then ground in their jars to a coarse powder with an acid-cleaned glass rod; 0.25 g was digested and diluted as described for fish samples. Percent moisture in fish and crayfish was determined from weight loss during lyophilization. All processing equipment was disassembled and cleaned (tap water and detergent; dilute acid; de-ionized water; acetone) between samples.

Digestates were analyzed by inductively coupled plasma mass spectrometry. Quality control (QC) measures incorporated at the digestion stage for each group of samples included tissue blanks, certified reference materials, replicates, and fortified samples (spikes). Instrumental QC included periodic analyses of calibration check solutions, laboratory control solutions, duplicates, analysis spikes, and interference checks (dilution percent difference and a synthetic interference solution). Limits of detection (LOD) were 0.5–1.0 $\mu g\ g^{-1}$ dry weight (dw) for Zn, 0.008–0.030 $\mu g\ g^{-1}$ for Cd, and 0.01–0.24 $\mu g\ g^{-1}$ for Pb. Elemental concentrations and detection limits were converted to wet weight (ww) values for reporting and statistical analysis using the individually determined moisture content of each sample. Additional information on the analytical procedures and QC is reported by Brumbaugh et al. (2005).

Dataset composition and statistical analyses

Carp (total $n = 25$) were collected at all Oklahoma sites (Sites 1–6) and from the BR (Site 9); no reference fish were analyzed. Channel catfish ($n = 20$) were also obtained from all six Oklahoma sites and the commercial source (Site 8, $n = 12$). Flathead catfish ($n = 4$) were collected only at Sites 1 and 2. Largemouth bass were obtained from Sites 1, 5, 6, and 9 ($n = 11$) and from our laboratory (Site 7, $n = 12$). Spotted bass ($n = 9$) were collected at Sites 2, 4, 5, and 9. No reference spotted bass were analyzed, but both

Table 1 Fish and crayfish collection sites[a] in Missouri (MO) and Oklahoma (OK), and sampling dates

Site type and no.[a]	Water body and location	County and (State)[b]	Date	Latitude, longitude
Fish				
1	Spring R. at state line	Ottawa (OK)	10/15/01	36°59′50.5″ N, 94°42′37.4″W[c]
2	Spring R. at Blue Hole	Ottawa (OK)	10/15/01	36°57′41.0″ N, 94°43′20.6″ W[c]
3	Neosho R. above Elm Creek	Ottawa (OK)	10/16/01	36°53′25.0″ N, 94°55′38.5″ W[c]
4	Spring R. at Promenade Bridge	Ottawa (OK)	10/16/01	36°56′01.1″ N, 94°44′40.9″ W[c]
5	Neosho R. at Twin Bridges (Grand Lake)	Ottawa (OK)	10/16/01	36°47′56.0″ N, 94°45′18.5″ W[c]
6	Tar Creek at Neosho R.	Ottawa (OK)	10/17/01	36°51′25.7″ N, 94°51′39.2″ W[c]
7	USGS-CERC[e] (reference)	Boone (MO)	10/22/01	38°54′41.5″ N, 92°16′58.0″ W[c]
8	Osage Catfisheries (reference)	Camden (MO)	10/23/01	38°07′38.9″ N, 92°40′54.5″ W[c]
9	Big R. at St. Francois State Park	St. Francois (MO)	12/07/01	37°57′23.1″ N, 90°32′29.5″ W[c]
Crayfish				
10 (1)	Spring R. at KS/OK line	Ottawa (OK)	06/25/02	36°59′58.7″ N, 94°42′44.1″ W[c]
11 (2)	Spring R. above Blue Hole	Ottawa (OK)	06/26/02	36°57′46.1″ N, 94°43′32.5″ W[c]
12 (4)	Spring R. at I-44 Bridge	Ottawa (OK)	06/27/02	36°55′29.7″ N, 94°44′27.9″ W[c]
13 (4)	Spring R. below I-44 Bridge	Ottawa (OK)	06/27/02	36°54′08.1″ N, 94°44′12.3″ W[c]
14 (4)	Spring R. below I-44 Bridge	Ottawa (OK)	06/27/02	36°54′49.7″ N, 94°43′57.5″ W[c]
15 (2)	Spring R. at Blue Hole	Ottawa (OK)	06/24-25/02	36°57′38.2″ N, 94°43′14.2″ W[c]
16 (4)	Spring R. at Devil’s Promenade Bridge	Ottawa (OK)	06/25/02	36°56′02.5″ N, 94°44′44.2″ W[d]
17 (3u)	Neosho R. above Elm Creek	Ottawa (OK)	07/15/02	36°53′30.1″ N, 94°56′11.7″ W[c]
18 (3d)	Neosho R. below Elm Creek	Ottawa (OK)	07/15-16/02	36°52′56.4″ N, 94°55′33.5″ W[c]
19 (3d)	Neosho R. above Coal Creek	Ottawa (OK)	07/16/02	36°52′10.6″ N, 94°55′25.3″ W[c]
20 (3u)	Neosho R. above Elm Creek	Ottawa (OK)	10/01/01	36°53′28.1″ N, 94°55′59.2″ W[c]
21 (6)	Tar Creek at Neosho R.	Ottawa (OK)	11/01/01	36°57′14.9″ N, 94°57′31.8″ W[d]

[a]Numbers in parenthesis indicate the fish site to which the crayfish samples were assigned for statistical analysis and reporting; 3u and 3d were near fish Site 3 but upstream and downstream, respectively, of Elm Creek, a possible source of metals to the Neosho River

[b]All USA

[c]From global positioning system, datum = WGS 84

[d]Estimated from map

[e]US Geological Survey, Columbia Environmental Research Center, Columbia, MO

Micropterus species (i.e., bass) were obtained at Sites 5 and 9. Crappie ($n = 12$) were collected at Sites 3–6; no reference crappie were available nor were any obtained at Site 9. Information on the size and age of the fish is presented elsewhere (Brumbaugh et al., 2005; Schmitt et al., 2005).

A total of 21 composite crayfish samples, each containing 5–60 animals, were collected from 12 locations (Sites 10–21; Fig. 1; Table 1). The samples were assigned to the nearest fish station for statistical analysis and reporting. Crayfish from the NR near Site 3 were obtained both upstream and downstream of the mouth of Elm Creek, a source of contaminants (Fig. 1; Table 1). These were considered separate stations (3u and 3d, respectively) for statistical analysis and reporting.

Arithmetic species and species-station means and standard errors were computed and tabulated, and concentrations were log-transformed (base-10) prior to statistical analysis. A value of one-half the LOD was substituted for censored values (i.e. those < LOD) as necessary in all computations. The dw carcass metals concentrations of the fish analyzed in this study differed significantly among species (Brumbaugh et al., 2005). Separate one-way ANOVAs in which site was considered a fixed effect were therefore conducted for each species. Results for flathead catfish were not tested statistically because of the small sample size. Differences among individual sites were tested with Fisher’s protected LSD, and differences among groups of sites were evaluated as planned non-orthogonal contrasts using single degree-of-freedom F-tests. Unless stated otherwise, a nominal significance level of $p = 0.05$ was used to interpret statistical results. All statistical analyses were conducted using the Statistical Analysis System (SAS, 1999).

Evaluation of human health risks

Human exposure to dietary metals was evaluated by estimating the quantities of the most contaminated crayfish, carp, catfish (flathead or channel), and centrarchids (largemouth bass, spotted bass, or crappie) from the TSMD and BR that would have to be consumed per day and per week by ''average-size'' adults (70 kg) and children (14.5 kg; USEPA, 2000a) to achieve various rate-based toxicity thresholds (Table 2). We also estimated the number of 227 g (8-oz, uncooked weight) fish and crayfish meals per month that could be safely consumed by adults and children without reaching these thresholds. Criteria (all ww) included the Tolerable Daily Intake (TDI), Provisionally Tolerable Daily Intake (PTDI), or Provisionally Tolerable Weekly Intake (PTWI) rates for Pb and Cd established by the World Health Organization (WHO, 1992; 1995) and the U.S. Food and Drug Administration (USFDA; all summarized by Van Oostdam et al., 1999). The WHO-TDI for dietary Pb is 3.57 μg/kg body weight/day for both children and adults; the PTWI is 25 μg/kg body weight/week (Table 2). The USFDA-PTDI is 6 μg/day of Pb for children aged 0–6 year, but there is no USFDA value for adults (Van Oostdam et al., 1999). The WHO-PTDI for Cd is 1.0 μg/kg body weight/day (about 400–500 μg/week), but there is also no USFDA value for Cd; however, the (US) Agency for Toxic Substances and Disease Registry has determined a minimum risk level (MRL) for chronic oral Cd ingestion of 0.2 μg/kg/day (Table 2). The MRL is the estimated daily exposure to a hazardous substance that is likely to be without an appreciable risk of adverse non-cancer health effects (ATSDR, 2002).

The USEPA has also established reference dose (RfD) values based on body weight for some pollutants (Table 2). The RfD represents an estimate of daily oral exposure that is likely to be without an appreciable risk of adverse health effects over a lifetime (USEPA, 1992, 1994a, 2000a). Cadmium is considered a probable human carcinogen; the RfD is 1.0 μg/kg body weight/day (USEPA, 1994a, 2000a), which is identical to the WHO-PTDI (Table 2). An RfD has not been established for Pb, which is recognized and evaluated as a developmental toxin (USEPA, 2000a) with a model that estimates blood Pb in children based on concentrations in fish together with other Pb sources (yard soil, drinking water, etc.; USEPA, 1994b) for which we had no data.

In contrast to Pb and Cd, for which there are no known physiological requirements, Zn is an essential element that is required by many enzymes and for critical biochemical processes including RNA and DNA synthesis. As such, the recommended daily allowance (RDA) is 0.16 mg/kg/day, or 8–13 mg/day for adults, 5–9 mg/day for children, and 2–3 mg/day for infants (ATSDR, 1999; Table 2). At about two-fold higher intake rates, Zn is considered toxic; the RfD is 0.3 mg/kg/day (USEPA, 1992).

We also compared metals concentrations to available concentration-based criteria. Draft maximum allowable concentrations (ML) for contaminants in fish and shellfish have been proposed by the Codex Alimentarius Commission of the WHO and the Food and Agricultural Organization of the United Nations (FAO; Table 2). The proposed ML for Pb is 0.2 μg g^{-1} for fish muscle and 0.5 μg g^{-1} for crustaceans (FAO/WHO, 1999). An ML for Cd in fish muscle of 0.05–0.10 μg g^{-1} (depending on species) has also been proposed (FAO/WHO, 1998); for crustaceans the proposed value is 0.05 μg g^{-1} except for lobsters and certain ''brown meats of crabs'', for which it is 0.10 μg g^{-1} and which we used to evaluate Cd in fish and crayfish. The USEPA (2000a) has established screening values (SVs) for Cd of 4.0 μg g^{-1} for recreational fishers and 0.491 μg g^{-1} for subsistence fishers, the latter presumably for Native Americans (USEPA, 2000a; Table 2).

It is important to recognize the assumptions inherent in our approach. We tacitly assumed that fish or crayfish represent the only route of Pb, Cd, and Zn exposure; i.e., other potentially important sources such as other metals-rich foods (organ meats, certain vegetables, and for Native Americans, wildlife and indigenous plants), smoking,

Table 2 Criteria[a] used to evaluate the risks of lead, zinc, and cadmium in fish and crayfish to humans and wildlife

Criterion[a]	Units	Lead	Cadmium	Zinc	Source
Human health					
TDI/PTDI	μg/kg body wt/day	3.57[b]	1.0	nv	WHO (1992, 1995)
PTWI	μg/kg body wt/week	25[b]	400–500[c]	nv	WHO (1992, 1995)
PTDI	μg/day	6[d]	nv	nv	USFDA
MRL	μg/kg body wt/day	nv	0.2	nv	ATSDR (2002)
ML (fish)	μg g^{-1} wet-wt	0.2	0.05–0.10	nv	FAO/WHO (1998)
ML (crustaceans)	μg g^{-1} wet-wt	0.5	0.05–0.10	nv	FAO/WHO (1998)
RfD	μg/kg body wt/day	nv	1.0	300	USEPA (1994a, 2000a, 2000b)
SV (recreational fishers)	μg g^{-1} wet-wt	nv	4.0	nv	USEPA (2000a)
SV (subsistence fishers)	μg g^{-1} wet-wt	nv	0.491	nv	USEPA (2000a)
RDA	μg/kg body wt/day	nv	nv	160	ATSDR (1999)
Ecological risk					
NOAEL-TRV (avian)	mg/kg body wt/day	1.68	1.47	14.5[e]	USEPA (2003a, 2003b; Sample et al., 1996)
NOAEL-TRV (mammal)	mg/kg body wt/day	4.7	0.77	16.0[e]	USEPA (2003a, 2003b; Sample et al., 1996)

[a]TDI, tolerable daily Intake; PTDI, provisionally tolerable daily intake; PTWI, provisionally tolerable weekly intake; MRL, minimum risk level; ML, maximum allowable concentration; RfD, reference dose; SV, screening value; RDA, recommended daily allowance; NOAEL, no observed adverse effect level; TRV, toxicity reference value; WHO, World Health Organization; USFDA, US Food and Drug Administration; FAO, Food and Agricultural Organization of the United Nations; ATSDR, (US) Agency for Toxic Substances and Disease Registry; USEPA, US Environmental Protection Agency; nv, no value

[b]For children and adults

[c]For adults; no value for children

[d]For children; no value for adults

[e]Interim value; consensus value pending

drinking water, and the inhalation or ingestion of particulates were not included, nor were the effects of multiple contaminants (USEPA, 2000a). For inhabitants of mining districts and Native Americans, particulates and drinking water represent significant routes of metals exposure (Harris & Harper, 1997; Hettierachchi, Pierzynski, Oihme, Sonmez, & Ryan, 2003). Because these other sources were not included, our screening-level assessments were based on maximum measured concentrations from our data and previous studies. We also assumed that all of the metals in the organisms as analyzed reach the human consumers, which may vary depending on preparation methods and consumption habits (USEPA, 2000a). This assumption may be appropriate for Native Americans to a greater extent than for the general public because traditional preparation involves boiling or steaming fish and crayfish and the consumption of the cooking liquids. Metals concentrations in fish muscle are not greatly affected by processing and cooking (Zabik & Zabik, 1996). Crayfish may be more problematic, however; metals concentrate preferentially in the hepatopancreas, antennal (green) gland, exoskeleton, and digestive tract (Crawford & Luoma, 1993; Knowlton, Boyle, & Jones, 1983; Roldan & Shivers, 1987), and the extent to which metals in these parts of the animals are consumed by Native Americans is not documented.

Evaluation of risk to fish and wildlife

Risk to wildlife was evaluated with a procedure analogous to that used to assess potential human health effects. Food ingestion rates, toxicity, uncertainty factors, and consensus-based toxic reference values (TRVs) for avian and mammalian wildlife (Table 2) were employed to assess Pb, Cd, and Zn in TSMD fish and invertebrates (USEPA, 1993, 1997, 1999, 2003a, 2003b). The TRVs are similar to TDI/PTDI and RfD values in that they are rates expressed in units of toxicant mass per unit of body weight per day (mg/kg/day). The TRVs are based on either the no-observed-adverse-effect-level (NOAEL) or lowest-observed-adverse-effect-level (LOAEL) for each metal as reported in the scientific literature. We estimated daily contaminant intake rates using the measured Pb, Cd, and Zn concentrations in fish or crayfish and the food intake rates and body weights of representative mammals and birds, which were compared with the TRVs either directly or as a ratio. The ratio, or hazard quotient (HQ), was obtained by dividing the daily intake rate by the TRV, with HQ values >1.0 indicating risk. Maximum concentrations are typically compared to LOAEL-based TRVs whereas mean concentrations are evaluated against the NOAEL-based values when information on other exposure pathways (incidental sediment ingestion, drinking water, etc.) is incorporated into the analysis (USEPA, 1993). Such analyses are also typically based on concentrations in whole fish, which are generally greater than in the headed, scaled, and eviscerated fish carcasses we analyzed. As such, and without data describing other exposure pathways, we used concentration maxima and NOAEL-based TRVs, with the understanding that this approach indicates only whether harmful effects are possible, not whether they are probable (Sample & Suter, 1999).

Weight-normalized food intake rates (kg food/kg body wt/day) in homeotherms decrease with body weight and are therefore greater in small than in large animals (USEPA, 1993). Risk associated with dietary exposure therefore tends to be greatest in small mammals and birds, with all other factors being equal. We used ingestion rates and body weights representative of a range of avian and mammalian wildlife to model food chain exposure. Values for great blue heron (*Ardea herodias*) and mink (*Mustela vison*) were chosen to represent large, adult fish-eating birds and mammals, respectively; and American robin (*Turdus americanus*) and short-tailed shrew (*Blarina brevicauda*) represented small birds and mammals. A scenario in which the receptor is a shrew-sized carnivorous mammal or robin-sized wetland bird (such as a red-winged blackbird, *Agelaius phoeniceus*; killdeer, *Charadrius vociferus*; or spotted sandpiper, *Actitis macularia;* or nestlings of larger species such as great blue heron) consuming a diet composed entirely of the most contaminated organisms from the study area, typically yield the most conservative wildlife risk estimates (i.e. greatest potential hazards).

There is no analogous procedure with which to evaluate risk to fish. Consequently, measured concentrations were compared with benchmark values from the scientific literature. Maximum concentrations in fish and crayfish from previous investigations in the TSMD (Allen & Wilson, 1992; Allert et al., 1997; Wildhaber et al., 1997) and the BR (Gale et al., 2004; Schmitt & Finger, 1982) were incorporated into the human health, wildlife, and fish analyses for comparison.

Results

Metals in fish and crayfish—2001–2002

Moisture content in crayfish was highly variable (60.6–92.8%, mean = 80.5%) but did not differ significantly among sites (Table 3). Excess site water, which was present in some samples but not decanted prior to lyophilization to prevent loss of metals, was the cause of this variation. Moisture content was also anomalously low in two samples collected in 2001, which may have been caused by water loss during freezer storage. Consequently, dw concentrations of Pb, Cd, and Zn in crayfish differed significantly among rivers and sites, but on a ww basis only Cd differences were significant (Table 3). On a ww basis, Zn concentrations only approached significance ($p = 0.08$) and Pb differences were not significant (Table 3). Dry-weight concentrations of all three metals were also significantly greater in crayfish from the SR than in the NR, but on a ww basis only the Cd differences were significant (Table 3). Maximum ww concentrations were 1.01 μg g^{-1} Pb (Site 3d, NR), 0.37 μg g^{-1} Cd (Site 2, SR), and 62.6 μg g^{-1} Zn (Site 3u, NR; Fig. 2). In the NR, the ww concentrations of Pb, Zn, and Cd in crayfish obtained upstream of the confluence of Elm Creek (Site 3u) did not differ significantly from those collected downstream (Site 3d); however, the dw zinc concentrations were significantly lower downstream (Table 3).

Table 3 Moisture content and dry-weight (dw) and wet-weight (ww) concentrations of lead, cadmium, and zinc in crayfish from sites on the Spring River, Neosho River, and Tar Creek (TC)[a]

River, site	n	Moisture	Lead (μg g^{-1})		Cadmium (μg g^{-1})		Zinc (μg g^{-1})	
		(percent)	dw	ww	dw	ww	dw	ww
Spring	3[b]	81.8 ± 1.8 A	2.87 ± 0.19 A	0.50 ± 0.05 A	1.58 ± 0.10 A	0.26 ± 0.03 A	176.5 ± 7.1 A	31.7 ± 3.1 A
1	2	79.3 ± 2.8 a	2.23 ± 0.34 a	0.45 ± 0.01 a	1.18 ± 0.08 ab	0.24 ± 0.02 a	159.5 ± 6.5 ab	32.8 ± 3.1 a
2	5	81.9 ± 2.5 a	3.24 ± 0.31 a	0.56 ± 0.06 a	1.75 ± 0.16 a	0.30 ± 0.03 a	199.6 ± 10.9 a	35.5 ± 4.4 a
4	4	84.3 ± 3.7 a	3.15 ± 0.19 a	0.50 ± 0.13 a	1.49 ± 0.04 a	0.24 ± 0.06 a	170.5 ± 1.3 a	26.8 ± 6.4 a
Neosho	3[b]	78.6 ± 2.1 A	1.58 ± 0.25 B	0.37 ± 0.09 A	0.29 ± 0.01 B	0.06 ± < 0.01 B	107.5 ± 9.4 B	24.1 ± 4.7 A
3u	3	74.3 ± 6.9 a	1.54 ± 0.52 b	0.47 ± 0.27 a	0.31 ± 0.01 b	0.08 ± 0.02 b	110.5 ± 24.2 b	31.7 ± 15.5 a
3d	6	80.1 ± 1.0 a	1.90 ± 0.08 ab	0.39 ± 0.08 a	0.30 ± 0.01 b	0.06 ± < 0.01 b	77.0 ± 2.6 c	15.2 ± 0.6 a
6 (TC)	1	81.3 a	1.29 b	0.24 a	0.24 b	0.05 b	135.0 ab	25.2 a
ANOVA								
$F_{(5, 15)}$		0.90 ns	3.70 **	0.67 ns	234.36 **	18.91 **	26.12 **	2.43 *[c]
R^2		0.23	0.55	0.18	0.99	0.86	0.90	0.45

[a]Shown are arithmetic station and river means (unweighted) ± standard errors, numbers of observations (n). Also shown are results of one-way analysis-of-variance (ANOVA) as F-values, coefficients of variation (R^2), and degrees-of-freedom for differences among sites and between rivers (**$p \le 0.01$; *$0.01 < p \le 0.05$; ns $p > 0.05$). Within each group, means followed by the same letter (lower case letters for site means, upper case for river means) are not significantly different ($p > 0.05$). Metal concentrations were log-transformed for statistical analysis

[b]Number of means

[c]$p = 0.08$

In contrast to crayfish, the moisture content of fish carcass samples was relatively consistent and did not differ significantly among species or sites (Table 4). Moisture in individual fish samples ranged from 70.6% in a carp from Site 1 to 81.6% in a channel catfish, both from Site 1 (SR; data not shown). Species means differed by < 2%, and site means within species varied by only 2–5% (Table 4).

Carcass Pb concentrations were generally greatest in carp, intermediate in channel catfish, and lowest in centrarchids (largemouth bass, spotted bass, and crappie) and flathead catfish (Table 4; Fig. 2). Lead concentrations in carp ranged from minima of 0.06–0.09 μg g^{-1} ww at Sites 1 (SR), 3 (NR-ref), and 5 (NR) to 4.96 μg g^{-1} in one fish from Site 9 (BR; Fig. 2), but concentrations varied greatly among the Oklahoma sites; maxima were 1.15 μg g^{-1} at Site 1 (SR) and 1.23 μg g^{-1} at Site 3 (NR-ref), but one sample from each of these two sites contained only 0.07–0.08 μg g^{-1}. Because of this variability, differences among sites for Pb in carp were not significant ($p = 0.06$; Table 3); however, no reference carp were analyzed.

Lead concentrations in channel catfish ranged from minima of 0.01–0.07 μg g^{-1} at all Oklahoma sites except Site 2 (SR) to 0.91 μg g^{-1} at Site 1 (SR; Fig. 2). Only one channel catfish was obtained at Site 2; it contained 0.15 μg g^{-1} Pb (Fig. 2). In contrast to carp, Pb in channel catfish differed significantly among locations; concentrations in the commercially obtained reference fish (Site 8) were significantly lower than at all Oklahoma sites except Site 3 (NR); and concentrations at Site 1 (SR) were significantly higher than those from Sites 3 and 4 (Table 4). Collectively, Pb concentrations were significantly higher (by two-fold) in channel catfish from the SR than the NR (Table 4). Concentrations in flathead catfish from Sites 1 and 2 were lower than those in channel catfish (Table 4).

Lead concentrations in centrarchids from the Oklahoma sites (1–6) were also comparatively low (< 0.01–0.09 μg g^{-1}), but were 0.57–1.45 μg g^{-1} in bass from the BR (Site 9; Fig. 2). Concentrations in BR largemouth and spotted bass were significantly higher than in both species from all Oklahoma sites, but differences among the Oklahoma sites were small in both species (Table 4). Concentrations in largemouth bass from Site 1 (SR) were significantly greater than in the laboratory-raised largemouth bass (Site 7; Table 4). Concentrations were uniformly

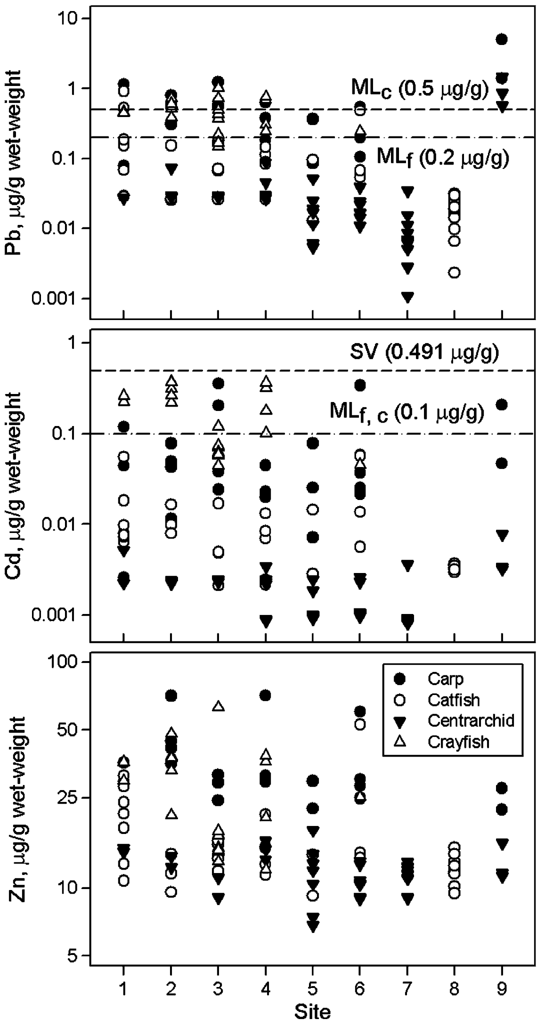

Fig. 2 Concentrations of lead (Pb), cadmium (Cd), and zinc (Zn) in fish of three taxa and in crayfish from sites in Oklahoma (1–6) and Missouri (7–9). Also shown are draft maximum allowable concentrations (ML) for Pb and Cd in fish (f) and crustaceans (c; FAO/WHO, 1998, 1999) and the Cd screening value (SV) for subsistence fishers (USEPA, 2000a); there are no SVs for Pb or Zn and no MLs for Zn. Censored values for Cd are plotted as 50% of the limit-of-detection

low in crappie; differences among the Oklahoma sites only approached significance ($p = 0.06$), with concentrations at Site 4 (SR) slightly greater than those at Sites 3, 5, and 6 (all NR; Table 4). Nevertheless, Pb concentrations in crappie from the SR averaged significantly (and more than two-fold) greater than those from the NR (Table 4). Crappie were not obtained from either the BR or reference sites for comparison.

Carcass Cd concentrations were greatest in carp, lowest in centrarchids, and intermediate in channel and flathead catfish (Fig. 2; Table 4). In carp, Cd concentrations were highly variable; minima at the Oklahoma sites were <0.003–0.022 µg g^{-1}, but were as great as 0.356 µg g^{-1} in one carp from Site 3 (NR) and 0.338 µg g^{-1} in one from Site 6 (NR-TC; Fig. 2). Differences among sites were not statistically significant (Table 4).

Minimum Cd concentrations in channel catfish from the Oklahoma sites were <0.002–0.009 µg g^{-1} except for Site 2 (SR), where only one fish was obtained; it contained 0.06 µg g^{-1} (Fig. 2). Maximum concentrations in channel catfish were 0.055–0.057 µg g^{-1} at Sites 1 (SR) and 6 (NR-TC), respectively. Concentrations in the commercially obtained reference channel catfish (Site 8) were uniformly low (<0.004 µg g^{-1}; Fig. 2). In contrast to carp, Cd concentrations in channel catfish differed significantly among locations (Table 4). The greatest Oklahoma concentrations (Sites 1, 2, and 6) differed significantly from reference fish (Site 8; Table 4). Overall, Cd concentrations in channel catfish from the SR and NR were not significantly different, but were significantly greater than reference fish (Table 4). Concentrations in flathead catfish were within the range of those for channel catfish from Sites 1 and 2 (0.07–0.08 µg g^{-1}).

Cadmium concentrations were comparatively low (<0.001–0.008 µg g^{-1}) in all centrarchid samples, including bass from the BR (Fig. 2). Only one (of 12) pond-raised largemouth bass contained detectable Cd (0.004 µg g^{-1}). Differences among sites were statistically significant in largemouth bass, marginally significant ($p = 0.07$) in spotted bass, and not significant in crappie (Table 4). No reference crappie or spotted bass were analyzed, however. Regardless, only two spotted bass contained detectable Cd—one each from Sites 5 (NR, 0.002 µg g^{-1}) and 9 (BR, 0.008 µg g^{-1}; Fig. 2). Concentrations in largemouth bass from Site 1 (SR) were significantly greater than all others except the BR (Site 9), and concentrations in spotted bass from Site 9 were significantly greater than most from Oklahoma (Table 4). Only two crappie samples contained

Table 4 Moisture content (percent) and concentrations of lead, cadmium, and zinc (all μg g^{-1}, wet-weight) in fish carcass samples from Oklahoma (Sites 1–6) and from reference sites (Ref, Sites 7 and 8) and the Big River (BR, Site 9) in Missouri[a]

Species, river or type, and site	*n*	Moisture	Lead	Cadmium	Zinc
Common carp	25	75.4 ± 0.4	0.63 ± 0.20	0.076 ± 0.19	34.5 ± 2.7
All SR	3[b]	75.1 A	0.49 A	0.039 A	41.4 A
1 (SR)	4	74.7 ± 1.7 a	0.57 ± 0.27 a	0.043 ± 0.027 a	32.4 ± 2.0 a
2 (SR)	4	75.3 ± 1.3 a	0.51 ± 0.12 a	0.045 ± 0.014 a	48.0 ± 7.8 a
4 (SR)	3	75.3 ± 0.7 a	0.40 ± 0.13 a	0.029 ± 0.008 a	43.9 ± 13.6 a
All NR	3[b]	75.6 A	0.32 A	0.096 A	29.4 A
3 (NR)	4	76.4 ± 0.09 a	0.51 ± 0.26 a	0.155 ± 0.078 a	27.4 ± 1.8 a
5 (NR)	3	74.6 ± 1.3 a	0.18 ± 0.09 a	0.037 ± 0.021 a	27.2 ± 2.4 a
6 (NR-TC)	5	75.8 ± 0.5 a	0.28 ± 0.10 a	0.096 ± 0.061 a	33.7 ± 6.7 a
9 (BR)	2 (1[b])	75.8 ± 1.0 aA	3.18 ± 1.79 aA	0.127 ± 0.080 aA	24.8 ± 2.7 aA
ANOVA		–	–	–	–
$F_{(6,\ 18)}$		0.30 ns	2.14 *[e]	1.00 ns	2.11 ns
R^2		0.09	0.42	0.25	0.41
Channel catfish	35	77.4 ± 0.4	0.11 ± 0.03	0.010 ± 0.002	16.2 ± 1.5
All SR	3[b]	77.8 A	0.20 A	0.014 A	17.9 A
1 (SR)	5	78.6 ± 1.3 a	0.37 ± 0.16 a	0.020 ± 0.009 ab	24.6 ± 2.3 a
2 (SR)	1	78.3 a	0.15 ab	0.016 ad	14.0 ab
4 (SR)	5	76.6 ± 1.0 a	0.09 ± 0.02 b	0.007 ± 0.002 cde	15.1 ± 1.7 ab
All NR	3[b]	76.4 A	0.10 B	0.014 A	17.6 A
3 (NR)	4	78.1 ± 0.4 a	0.04 ± 0.01 bc	0.007 ± 0.003 cde	14.2 ± 1.0 ab
5 (NR)	2	73.8 ± 2.5 a	0.05 ± 0.04 ab	0.009 ± 0.006 abcde	11.6 ± 2.4 b
6 (NR-TC)	3	77.4 ± 0.9 a	0.20 ± 0.14 ab	0.025 ± 0.016 ab	26.8 ± 13.0 a
8 (Ref)	12 (1[b])	77.5 ± 0.4 aA	0.02 ± < 0.01 cC	< 0.003 ± < 0.001 eB	12.1 ± 0.4 bB
ANOVA	31	–	–	–	–
F	6	1.58*	8.60 **	4.33 **	4.99 **
R^2	25	0.28	0.67	0.51	0.45
Flathead catfish[c]	4	77.3 ± 0.7	< 0.03 ± < 0.01	0.008 ± 0.001	11.1 ± 0.7
1 (SR)	2	76.1 ± 0.1	< 0.03 ± < 0.01	0.007 ± < 0.001	11.7 ± 1.0
2 (SR)	2	78.5 ± 0.5	< 0.03 ± < 0.01	0.009 ± 0.001	10.5 ± 1.0
Largemouth bass	21	77.5 ± 0.4	0.08 ± 0.07	0.002 ± < 0.001	10.9 ± 0.5
1 (SR)	2 (1[b])	77.3 ± 0.1 abB	0.03 ± < 0.01 bB	0.004 ± 0.001 aA	14.7 ± 0.3 aA
All NR	2[b]	75.7 B	0.03 B	0.001 B	8.4 C
5 (NR)	2	76.6 ± 0.1 ab	0.01 ± < 0.01 c	0.001 ± < 0.001 b	7.1 ± 0.3 c
6 (NR)	4	74.9 ± 0.8 b	0.02 ± < 0.01 bc	0.001 ± < 0.001 b	9.8 ± 0.5 b
7 (Ref)	12	78.5 ± 0.2 aA	0.01 ± < 0.01 cB	0.001 ± < 0.001 bB	11.3 ± 0.4 abB
9 (BR)	1 (1[b])	78.5 aA	1.45 aA	0.003 ± 0.001 abB	11.3 abB
ANOVA	20	–	–	–	–
F	4	12.05 **	13.96 **	4.70 *	13.12 **
R^2	16	0.75	0.78	0.54	0.77
Spotted bass	9	77.1 ± 0.4	0.19 ± 0.10 –	0.003 ± 0.001 –	14.1 ± 0.7
All SR	2[b]	76.7 A	0.04 B	0.002 B	13.6 A
2 (SR)	3	76.7 ± 0.6 a	0.04 ± 0.02 b	0.002 ± < 0.001 b	12.8 ± 0.5 a
4 (SR)	3	76.7 ± 0.7 a	< 0.03 ± < 0.01 b	< 0.002 ± < 0.001 b	14.3 ± 0.5 a
5 (NR)	1 (1[b])	77.7 aA	0.05 abB	0.002 abB	18.0 aA
9 (BR)	2 (1[b])	78.1 ± 0.8 aA	0.71 ± 0.14 aA	0.006 ± 0.002 aA	13.7 ± 2.0 aA
ANOVA	8	–	–	–	–
F	3	0.90 ns	34.35 **	4.56 *[d]	2.43 ns
R^2	5	0.35	0.95	0.73	0.59
White crappie	12	75.9 ± 0.4	0.03 ± 0.01	0.002 ± < 0.001	12.7 ± 0.7
4 (SR)	3 (1[b])	77.6 ± 0.4 aA	0.05 ± 0.02 aA	0.002 ± 0.001 aA	15.7 ± 0.5 aA

Table 4 continued

Species, river or type, and site	n	Moisture	Lead	Cadmium	Zinc
All NR	2[b]	75.4 cB	0.02 B	0.002 A	11.5 B
3 (NR)	2	76.1 ± 0.7 ab	< 0.03 ± < 0.01 b	< 0.002 ± < 0.001 a	10.1 ± 1.0 b
5 (NR)	4	75.7 ± 0.4 bc	0.02 ± < 0.01 ab	< 0.001 ± < 0.001 a	12.3 ± 0.8 b
6 (NR-TC)	3	74.4 ± 0.3 c	0.03 ± 0.01 ab	0.001 ± < 0.001 a	12.1 ± 0.8 b
ANOVA	11	–	–	–	–
F	3	8.52 **	3.72 *[e]	1.70 ns	6.49 *
R^2	8	0.76	0.58	0.39	0.70

[a]SR, Spring River; NR, Neosho River; TC, Tar Creek. Shown are arithmetic station and river means (unweighted) ± standard errors and numbers of observations or means (n); and results of one-way analysis-of-variance (ANOVA) as F-values (**$p \le 0.01$; *$0.01 < p \le 0.05$; ns $p > 0.05$), degrees-of-freedom, and coefficients of variation (R^2). Within taxa, means followed by the same letter (lower case letters for site means, upper case for river means; ranked alphabetically from largest to smallest) are not significantly different ($p > 0.05$); metals concentrations were log-transformed for statistical analysis

[b]Number of means

[c]Flathead catfish not analyzed statistically due to small n

[d]$p = 0.07$

[e]$p = 0.06$

detectable Cd—one each from Sites 4 (SR, 0.003 μg g^{-1}) and 6 (NR-TC, 0.002 μg g^{-1}).

Carcass Zn concentrations were also greatest in carp and lowest in centrarchids (Fig. 2). In carp, Zn concentrations ranged from 22 μg g^{-1} at Sites 5 (NR) and 9 (BR) to 71 μg g^{-1} at Sites 2 and 4 (both SR; Fig. 2). Site means ranged from 25 μg g^{-1} (Site 9, BR) to 48 μg g^{-1} (Site 2, SR; Table 4). Differences among sites were not significant in carp (Table 4), but no reference carp were analyzed.

Zinc concentrations in channel catfish ranged from 9.2 μg g^{-1} at Site 5 (NR) to 52.8 μg g^{-1} at Site 6 (NR-TC; Fig. 2). Site means ranged from 12–15 μg g^{-1} at Sites 2–5 and the reference fish (Site 8) to 25–27 μg g^{-1} at Sites 1 and 6 (Table 4). In contrast to carp, Zn in channel catfish differed significantly among locations; sites with the greatest concentrations (1 and 6) differed from the lowest (5 and 8; Table 4). As a group, Zn concentrations in channel catfish from the SR and NR were not significantly different, but both were significantly greater than the reference fish (Site 8; Table 4). Concentrations in flathead catfish from Sites 1 and 2 were lower than those in channel catfish from these sites (Table 4).

Zinc concentrations in centrarchids were only slightly lower than those in catfish and spanned a comparatively narrow range—from 6.8 μg g^{-1} in largemouth bass to 18 μg g^{-1} in spotted bass, with both extremes at Site 5 (NR, Fig. 2). Site means for all centrarchids were 7.1–18.0 μg g^{-1}; differences among sites were statistically significant in largemouth bass and crappie, but not in spotted bass (Table 4). Overall, Zn concentrations in largemouth bass from the SR were significantly greater than those from the BR (one fish) and the reference site (8); the latter were not significantly different but were in turn significantly greater than those in largemouth bass from the NR (Table 4). Concentrations in crappie from the SR were also significantly greater than those from the NR, but Zn in spotted bass did not differ significantly among sites (Table 4).

Metals in fish and crayfish-previous studies

Maximum concentrations (ww and dw) of metals in crayfish collected in 2001–2002 were lower than (Pb, Cd) or comparable to (Zn) most previously reported values for crayfish from contaminated parts of the SR system (Table 5). Wildhaber et al. (1997) reported concentrations as high as 5.21 μg g^{-1} (ww) Pb, 1.64 μg g^{-1} Cd, and 119.4 μg g^{-1} Zn in crayfish from mining-contaminated SR tributaries in Kansas and Missouri; these were two-fold (Zn) to five-fold (Cd) greater than 2001–02 values (Table 5). Wildhaber et al. (1997)

Table 5 Concentrations[a] (all μg g^{-1} wet-weight) of cadmium, lead, and zinc in crayfish (*Orconectes* sp.) from the Spring-Neosho River system of Missouri (MO), Kansas (KS), and Oklahoma (OK), USA, and from the Big River in Eastern Missouri, as reported by this and previous investigations. Within rivers, sites are listed upstream to downstream. Values in *italics* were used to assess potential hazards to humans, wildlife, or both

Source of information and river or stream	Location or reach	Lead	Cadmium	Zinc
This study				
Neosho River	Above Miami, OK (Sites 3u, 3d)	*1.01*	0.12	*62.6*
Tar Creek	Miami, OK (at Neosho River, Site 6)	0.24	0.04	25.2
Spring River	Sites 1, 2, and 4	0.76	*0.37*	47.9
*Wildhaber et al. (*1997*)*				
Cottonwood River	Emporia, KS[b]	< 1.07	0.10	21.5
Neosho River	Neosho Rapids-Chetopa, KS[b]	0.68	0.12	44.9
Spring River	Waco, MO	< 1.13	0.07	31.0
Spring River	Crestline, KS	1.73	0.25	40.9
Center Creek	Joplin, MO (at Spring River)	*5.21*	1.09	*119.4*
Spring River	Belleville-Lawton, KS	1.07	0.35	48.0
Turkey Creek	Galena, KS (at Spring River)	3.54	0.70	102.2
Shoal Creek	Galena, KS	3.43	*1.64*	74.0
Spring River	Riverton, KS	1.06	0.18	36.9
Spring River	KS/OK line (Site 1)	*2.80*	*0.39*	*67.4*
Spring River	Baxter Springs, KS	1.24	0.21	59.2
Spring River	Quapaw, OK (Site 4)	1.33	0.19	35.8
*Allen and Wilson (*1992*)*				
Cow Creek	Lawton, KS (at Spring River; R)	0.30	0.02	23.0
Spring River	Empire Lake (Riverton, KS)	2.70	0.63	56.0
Spring River	Baxter Springs, KS	3.20	0.30	55.0
*Schmitt and Finger (*1982*)*				
Big River	Irondale, MO[b]	0.39	0.12	24.0
Big River	Desloge, MO (upstream of Site 9)	*38.65*	*0.41*	*55.2*

[a]Indicated concentrations from this study are maxima; all others represent individual composite samples

[b]Reference site

also reported concentrations as great as 2.80 μg g^{-1} (ww) Pb, 0.39 μg g^{-1} Cd, and 67.4 μg g^{-1} Zn in crayfish from the SR at the state line (our Site 1; Table 5). Maximum concentrations in crayfish from the uncontaminated SR tributaries sampled by Wildhaber et al. (1997) were 1.73 μg g^{-1} Pb, 0.25 μg g^{-1} Cd, and 44.9 μg g^{-1} Zn (Table 5). Crayfish obtained from the BR in the early 1980s contained as much as 38.65 μg g^{-1} (ww) Pb, 0.41 μg g^{-1} Cd, and 35.9 μg g^{-1} Zn, however (Schmitt & Finger, 1982; Table 5).

Concentrations of Pb, Cd, and Zn in 2001 fish carcass samples from the TSMD were generally similar to or less than those reported for whole fish of the same or similar species in previous studies. Allen and Wilson (1992) analyzed whole fish of several species obtained from the Kansas reach of the Spring River in the late 1980s. Their highest metals concentrations, which were in carp, were 1.00 μg g^{-1} (ww) Pb, 0.50 μg g^{-1} Cd, and 120 μg g^{-1} Zn (Table 6). Concentrations in whole channel catfish, largemouth bass, and crappie analyzed by Allen and Wilson (1992) were lower than those in carp and were similar to the 2001 carcass concentrations in those species (data not shown). Concentrations of Pb in our fish from tailings-contaminated waters of the BR were similar to those reported previously (Dwyer et al., 1988; Schmitt & Finger, 1987; Schmitt et al., 1984, 1993), but there are no previously reported concentrations for carp from the BR. Gale et al. (2004) recently reported Pb concentrations as high as 0.960 μg g^{-1} (ww) in longear sunfish (*Lepomis megalotis*) fillets, 0.185 μg g^{-1} in bass (*Micropterus* spp.) fillets, and 42.09 μg g^{-1} in whole longear sunfish, however.

Risks of metals in fish and crayfish to humans

The maximum ww metals concentrations in crayfish obtained from the Oklahoma waters of the TSMD in 2001–2002 were 1.01 μg g^{-1} Pb (Site

Table 6 Range of lead, cadmium, and zinc concentrations (all μg g^{-1} wet-weight) in common carp from sites in Missouri (MO), Kansas (KS), and Oklahoma (OK) as reported by this and previous investigations. Values shown in *italics* were used to assess potential hazards to humans, wildlife, or both

Sample type and collection location	Lead	Cadmium	Zinc
Individual headless, scaled, eviscerated fish carcasses			
Neosho R., Spring R., and Big R.[a]			
Neosho R., OK	0.06–*1.23*	0.007–*0.356*	22.4–60.2
Spring R., OK	0.08–1.15	< 0.003–0.118	28.6–*71.0*
Big R., MO	1.39–*4.96*	0.047–*0.207*	22.2–*27.5*
Composite samples of whole fish			
Neosho R. system, KS[b]			
Cottonwood R. @ Cottonwood Falls	< 0.50–0.50	0.20–0.35	62.0–64.0
Neosho R. @ Neosho Rapids	0.20–0.30	0.11–0.25	44.0–64.0
Neosho R. @ Humboldt	< 0.50–0.50	0.17–0.17	52.0–59.0
Neosho R. @ Oswego	0.20–0.20	0.37–0.38	45.0–65.0
Neosho R. @ Chetopa	< 0.50–0.60	0.17–0.26	41.0–60.0
Spring R., KS[c]			
Spring R. @ Empire Lake	0.20	0.08	75.0
Spring R. @ Baxter Springs	0.30–*1.00*	0.10–*0.50*	71.0–*120*
Central U.S. rivers[d]			
Verdigris R. @ Oologah Lake, OK	0.18–0.31	0.220–0.270	72.7–101
Arkansas R. @ Keystone Lake, OK	0.14–0.17	0.083–0.092	62.3–73.5
Canadian R. @ Eufaula Lake, OK	0.23–0.28	0.109–0.141	76.2–150
Red R. @ Lake Texoma, OK	0.10–0.11	0.045–0.067	54.1–81.7
Kansas R. @ Bonner Springs, KS	0.08–0.14	0.140–0.239	57.2–75.1
Missouri R. @ Hermann, MO	0.05–0.07	0.084–0.111	37.8–48.7

[a] This study

[b] From Allen et al. (2001)

[c] From Allen and Wilson (1992)

[d] From Schmitt (2004)

3u), 0.37 μg g^{-1} Cd (Site 2), and 62.6 μg g^{-1} Zn (also Site 3u; Fig. 2). The TDI/PTDIs for both Pb (3.6 μg/kg/day) and Cd (1.0 μg/kg/day) would be reached by eating 2.7–3.6 g/kg/day of this crayfish; a 70-kg adult would reach the TDI/PTDI for Pb by eating about 250 g (0.5 lb) of crayfish per day or for Cd by eating 210 g (0.46 lb) per day, or roughly 3–4 lb/week or 23–31 meals/month (Table 7). A 14.5-kg child would reach the TDI/PTDI for Pb after eating only about 40–50 g/day (0.6–0.8 lb/week), or 5–6 meals/month (Table 7). Based on the RfD for Cd (1.0 μg/kg/day), the USEPA (2000a) would recommend that a 70-kg adult consume no more than four 8-oz crayfish meals per month. For Zn, the RfD of 300 μg/kg/day (USEPA, 2000b) would be reached by consuming 4.8 g/kg/day of the most contaminated 2001–2002 crayfish, which would represent 41 meals/month for adults and 9 meals/month for children (Table 7).

Crayfish collected from the Kansas reach of the SR in 1988 by Allen and Wilson (1992) contained as much as 3.2 μg g^{-1} (ww) of Pb, 0.63 μg g^{-1} of Cd, and 56.0 μg g^{-1} of Zn (Table 5). Crayfish obtained from this reach in 1994 by Wildhaber et al. (1997) contained up to 2.8 μg g^{-1} of Pb, 0.39 μg g^{-1} of Cd, and 67.4 μg g^{-1} of Zn (Table 5). About 1.3–2.6 g/kg/day of these more recently collected crayfish could be eaten before reaching the TDI/PTDIs for Pb and Cd, respectively, or 90–180 g/day (0.2–0.4 lb/day; 11–22 meals/month) for a 70-kg adult and 19–37 g/day (0.02–0.04 lb/day; 2–5 meals/month) for a 14.5-kg child (Table 7). These crayfish would also be in the USEPA (2000a) four-meal-per-month category. An adult would need to consume 312 g/day (38 meals/month) and a child 65 g/day (8 meals/month) to reach the RfD for Zn, however (Table 7). The most contaminated crayfish from SR tributaries in Kansas (Shoal Creek, Turkey

Table 7 Amounts of the most contaminated crayfish and fish of several taxa obtained in 2001–2002 and previous studies from sites in the Tri-States Mining District (TSMD) and from the Big River that would need to be consumed by adults or children of the indicated body weights to reach the Tolerable or Provisionally Tolerable Daily Intake or Provisionally Tolerable Weekly Intake for lead (Pb) and cadmium (Cd)[a], or the chronic effect reference dose (RfD) for zinc (Zn)[b]

Location, collection period, taxon, and metal	Max. conc. ($\mu g\ g^{-1}$ ww)	Site(s)	Daily intake, g/kg/day	Adults (70 kg)				Children (14.5 kg)			
				g/day	lb/day	lb/week	Meals/month[h]	g/day	lb/day	lb/week	Meals/month[h]
TSMD, 2001–2002											
Crayfish, Pb	1.01	3u	3.6	250	0.5	3.8	31	52	0.1	0.8	6
Crayfish, Cd	0.370	2	2.7	189	0.4	2.9	23	40	0.1	0.6	5
Crayfish, Zn	62.6	3u	4.8	336	0.7	5.2	41	70	0.2	1.1	9
Carp, Pb	1.23	3	2.9	205	0.5	3.2	25	43	0.1	0.7	5
Carp, Cd	0.356	3	2.8	197	0.4	3.0	24	41	0.1	0.6	5
Carp, Zn	71.0	2, 4	4.2	296	0.7	4.6	36	62	0.1	0.9	8
Catfish[c], Pb	0.91	1	4.0	277	0.6	4.3	34	58	0.1	0.9	7
Catfish[c], Cd	0.057	6	17.5	1229	2.7	18.9	151	255	0.6	3.9	31
Catfish[c], Zn	52.8	6	5.7	398	0.9	6.1	49	83	0.2	1.3	10
Centrarchid[d], Pb	0.09	2	40.0	2800	6.2	43.1	345	580	1.3	8.9	72
Centrarchid[d], Cd	0.008	1	125.0	8750	19.3	134.8	1078	1813	4.0	27.9	223
Centrarchid[d], Zn	18.0	5	16.7	1166	2.6	18.0	144	242	0.5	3.7	30
TSMD, pre-2000[e]											
Crayfish, Pb	2.80	K[e]	1.3	90	0.2	1.4	11	19	< 0.1	0.3	2
Crayfish, Cd	0.39	K[e]	2.6	180	0.4	2.8	22	37	0.1	0.6	5
Crayfish, Zn	67.4	K[e]	4.5	312	0.7	4.8	38	65	0.1	1.0	8
Crayfish, Pb	5.21	T[e]	0.7	49	0.1	0.7	6	10	< 0.1	0.2	1
Crayfish, Cd	1.64	T[e]	0.6	44	0.1	0.7	5	9	< 0.1	0.1	1
Crayfish, Zn	119.4	T[e]	2.5	176	0.4	2.7	22	36	0.1	0.6	5
Big River, 2001											
Carp, Pb	4.96	9	0.7	51	0.1	0.8	6	11	< 0.1	0.2	1
Carp, Cd	0.207	9	4.8	339	0.7	5.2	42	70	0.2	1.1	9
Carp, Zn	27.5	9	10.9	764	1.7	11.8	94	158	0.3	2.4	20
Centrarchid[d], Pb	1.45	9	2.5	174	0.4	2.7	21	36	0.1	0.6	4
Centrarchid[d], Cd	0.008	9	125.0	8750	19.3	134.8	1078	1813	4.0	27.9	223
Centrarchid[d], Zn	15.7	9	19.1	1338	2.9	20.6	165	277	0.6	4.3	34
Big River, pre-2001											
Crayfish, Pb[f]	38.65	D	0.1	7	< 0.1	0.1	< 1	1	< 0.1	< 0.1	< 1
Crayfish, Cd[f]	0.410	D	2.4	171	0.4	2.6	21	35	0.1	0.5	4
Crayfish, Zn[f]	35.9	D	8.4	585	1.3	9.0	72	121	0.3	1.9	15
Centrarchid, Pb[g]	0.96	F	3.8	263	0.6	4.0	32	54	0.1	0.8	7
Centrachid, Cd[g]	0.118	F	8.5	594	1.3	9.1	73	123	0.3	1.9	15
Centrachid, Zn[g]	29.8	F	10.1	705	1.6	10.9	87	146	0.3	2.2	18

[a]3.57 μg/kg/day or 25 μg/kg/week for Pb; 400-500 μg/week or 1.0 μg/kg/week for Cd [World Health Organization (WHO) 1995]

[b]0.3 mg/kg/day [U.S. Environmental Protection Agency (USEPA) 2000b]

[c]Channel catfish (*Ictalurus punctatus*) or flathead catfish (*Pylodictis olivaris*)

[d]Largemouth bass (*Micropterus salmoides*), spotted bass (*M. punctalatus*), or white crappie (*Pomoxis annularis*)

[e]From Wildhaber et al. (1997); T, tributary; K, Kansas (all upstream of 2001–2002 study area)

[f]From Schmitt and Finger (1982); D, near Desloge, MO (upstream of 2001 site)

[g]Longear sunfish (*Lepomis megalotis*) fillets, from Gale et al. (2004); F, Flat River Creek (BR tributary near Desloge, MO, upstream of 2001 site)

[h]8-oz (227-g) meals

Creek) and Missouri (Center Creek) sampled by Wildhaber et al. (1997) in 1994 contained as much as 5.2 μg g^{-1} (ww) of Pb, 1.6 μg g^{-1} of Cd, and 119.4 μg g^{-1} of Zn (Table 5). Only 0.6–0.7 g/kg/day of these crayfish could be consumed before reaching the TDI/PTDI for Pb or Cd; i.e., by adults after consuming only 44–49 g/day (< 0.1 lb/day, 5-6 meals/month) or by children after 10 g/day (0.1 lb/week, 1 meal/month; Table 7), and the USEPA (2000a) would recommend not more than one meal per month. Adults could consume 176 g/day (22 meals/month) and children 36 g/day (5 meals/month), or 2.5 g/kg/day, of this crayfish before reaching the RfD for Zn (Table 7). The crayfish obtained from the SR mainstem in 1988 by Allen and Wilson (1992) would have been intermediate between the Wildhaber et al. (1997) values. The Cd in crayfish from tributaries reported by Wildhaber et al. (1997) also exceeded the Cd SV for subsistence fishers (0.491 μg g^{-1}; Fig. 2), as did the maximum concentration in crayfish from the SR mainstem reported by Allen and Wilson (1992; Table 5), but no TSMD crayfish exceeded the SV for recreational fishers (4.0 μg g^{-1}; USEPA, 2000a).

Crayfish obtained from the BR during the 1980s contained substantially greater Pb, but less Cd and Zn, than those from the TSMD. As such, human consumption of only 0.1 g/kg/day of BR crayfish would exceed the TDI/PTDI for Pb, which would represent only 6.5 g/day (0.1 lb/week, < 1 meal/month) for adults and 1.4 g/day (< 0.1 lb/week) for children (Table 7). The TDI/PTDI for Cd would be reached by adults eating 2.4 g/kd/day (2.6 lb/week, 21 meals/month) and by children eating 0.5 lb/week (4 meals/month; Table 7). The consumption of crayfish containing this amount of Cd would probably not be restricted according to current guidelines (USEPA, 2000a). For Zn, adults would need to consume 72 meals/month and children 15 meals/month, or 8.4 g/kg/day, to reach the RfD (USEPA, 2000b; Table 7).

Concentrations of Pb in some 2001–2002 crayfish from Sites 2, 3, and 4 exceeded the proposed ML for Pb (0.5 μg g^{-1}; Fig. 2). Crayfish from Sites 1–4 also exceeded the proposed ML for Cd in crustaceans (0.1 μg g^{-1}; Fig. 2). The samples obtained in 1995 by Wildhaber et al. (1997) from the SR at Site 1 and from SR tributaries in Missouri and Kansas also exceed the proposed MLs for both Pb and Cd, as did those obtained from the SR in Kansas by Allen and Wilson (1992) and form the BR by Schmitt and Finger (1982; Table 5). Based on the Wildhaber et al. (1997) data, which indicated two-fold greater metals concentrations in crayfish from contaminated tributaries than in the SR, it is reasonable to suspect that concentrations in crayfish from Tar Creek and other tributaries in northeastern Oklahoma are also greater than those from the SR and NR mainstems.

Metals concentrations in 2001 fish carcasses were greatest in carp (Fig. 2, Table 4). Maximum concentrations of Pb (1.23 μg g^{-1}, Site 3), Cd (0.36 μg g^{-1}, also Site 3), and Zn (71.0 μg g^{-1}, Sites 2 and 4) were similar to those in crayfish (Fig. 2), as were the amounts of each that would have to be consumed to achieve the same toxicity thresholds (Table 7). The TDI/PTDIs for both Pb and Cd would be reached by eating 2.8–2.9 g/kg/day of this carp, and a 70-kg adult would reach the TDI/PTDI for both Pb and Cd by consuming about 200 g/day (0.4–0.5 lb/day, 3 lb/week) of TSMD carp; a 70-kg adult could consume 24 8-oz meals/month. However, children would reach the TDI/PTDIs after eating only 41–42 g/day (0.1 lb/day, 0.6–0.7 lb/week, 5 meals/month) of this fish. The RfD for Zn would be reached by eating 4.2 g/kg/day of the most contaminated carp, or 36 meals/month for adults and 5 meals/month for children (Table 7).

The maximum Pb concentration in catfish (0.91 μg g^{-1}, channel catfish from Site 1) approached the maxima for carp and crayfish, but the maximum Cd concentration was lower (0.057 μg g^{-1}, channel catfish from Site 6). The TDI/PTDI for Pb would be reached by eating 4 g/kg/day, but for Cd it would require 17.5 g/kg/day. A 70-kg adult would reach the TDI/PTDI for Pb by consuming 277 g/day (0.6 lb/day, 34 meals/month) of TSMD catfish, but would have to consume 1.2 kg/day (2.7 lb/day, 151 meals/month) to reach the TDI/PTDI for Cd (Table 7). A child would reach the TDI/PTDI for Pb by eating 57.4 g/day (0.1 lb/day, 7 meals/month) of catfish, but would need to consume 254 g/day (31 meals/month) to reach the TDI/PTDI for Cd (Table 7). The USEPA (2000a) considers the consumption of fish containing < 0.088 μg g^{-1} of Cd to be unrestricted (that is, the consumption of >16 8-oz meals per month by a 70-kg adult is acceptable). The RfD for Zn would be reached by eating 5.7 g/kg/day of catfish, or 49 meals/month for adults and 10 meals/month for children (Table 7).

The maximum concentrations of Pb in centrarchids (0.09 μg g^{-1}, crappie from Site 2), Cd (0.005 μg g^{-1}, largemouth bass from Site 1), and Zn (18.0 μg g^{-1}, spotted bass from Site 5) were low compared to other taxa (Fig. 2). As such, 40–125 g/kg/day of this fish could be consumed before reaching the TDI/PTDI for Pb or Cd and 16.7 g/kg/day would be required to reach the RfD for Zn (Table 7). A 70-kg adult would need to consume 2.8 kg/day (6.2 lb/day, 345 meals/month) of the most contaminated crappie or bass to reach the TDI for Pb and 8.8 kg/day (19.3 lb/day, 1078 meals/month) to reach the PTDI for Cd; and a 14.5-kg child could safely consume 0.6-1.8 kg/day (1.3-4.0 lb/day, 72–223 meals/month; Table 7). As was true for catfish, the USEPA (2000a) would consider the consumption of fish containing Cd at these concentrations to be unrestricted. The RfD for Zn would be reached by an adult after eating 144 meals/month or a child eating 30 meals/month (Table 7).

Based on 2001 concentrations, fish from the BR represent substantially greater risk to humans than those from the TSMD due to their greater Pb content; the Pb TDI/PTDI would be reached by consuming only 0.7 g/kg/day of BR carp (Table 7). A 70-kg adult would reach the TDI/PTDI for Pb after consuming about 51 g/day (0.1 lb/day, 6 meals/month) of carp or 174 g/day (0.4 lb/day, 21 meals/month) of bass (Table 7). Children could consume only 10.5 g/day (< 0.1 lb/day, 1 meal/month) of carp or 36.0 g/day (0.1 lb/day, 4 meals/month) of bass (Table 7). Risks associated with Cd in fish from the BR are lower than those for the most contaminated fish from the TSMD, however; 4.8 g/kg/day of carp and 125 g/kg/day of bass could be consumed before reaching the PTDI for Cd, which represents about 5 lb/week (42 meals/month) of carp and 135 lb/week (>1000 meals/month) of bass for adults and 1 lb/week (9 meals/month) of carp and 28 lb/week (>200 meals/month) of bass for children (Table 7). The USEPA (2000) would recommend not more than 12 meals per month of carp containing >0.2 μg g^{-1} of Cd, but the consumption of bass from the BR would not be restricted due to Cd. Similarly, adults would need to eat 94 carp meals/month or 165 bass meals/month and children 20 carp meals/month or 34 bass meals/month to reach the RfD for Zn (Table 7). In addition, at least one carp from all TSMD sites exceeded the proposed ML for Pb (0.2 μg g^{-1} ww), as did the maximum carcass concentrations in catfish from several Oklahoma and all carp and bass carcass samples from the BR (Fig. 2). Carp from several Oklahoma sites also exceeded the proposed ML for Cd in fish, as did one carp from the BR (Fig. 2).

Risks of metals to wildlife based on food chain analysis in model species

In the scenario evaluated here, a robin-sized wetland bird (red-winged blackbird, killdeer, or spotted sandpiper) would exceed the NOAEL-based TRVs for Pb (HQ = 1.1) and Zn (HQ = 7.4) on a 100% diet containing the maximum 2001 TSMD concentrations in carp (Table 8). The TRVs would also be approached or exceeded on a diet of 100% maximally contaminated crayfish or other invertebrate (Table 8). Neither the small mammal (shrew), the larger bird (great blue heron), nor the larger mammal (mink) would exceed any current TRVs (all HQs < 1.0) due to the lower weight-adjusted food intake rates of these species (Table 8). Substitution of the maximum concentrations reported by the most recent previous investigations for the 2001–2002 values did not change these findings appreciably. The greater concentrations of Pb, Cd, and Zn in crayfish (Wildhaber et al., 1997) elevated daily intake rates for all three metals in the small bird (illustrated by the American robin) further above the TRVs for Pb and Zn (HQs = 4.8 for Pb, 12.5 for Zn), and raised the daily intake rate of Cd slightly above the TRV (HQ = 1.1; Table 8). In the fish diet the greater Zn concentrations of the pre-2001 carp also further elevated the HQ in the small bird (to 12.6), but the Cd HQ remained < 1.0 (Table 8). In addition, the greater concentrations of Zn in both carp and crayfish from the earlier studies elevated the daily intake rates over the NOAEL-based TRV in the large bird (great blue heron HQ = 0.2–1.5;

Table 8 Potential hazards of food-borne cadmium (Cd), lead (Pb), and zinc (Zn) to carnivorous wildlife represented by the consumption of the most contaminated fish (carp) and crayfish collected from the TSMD and from the Big River, in eastern Missouri, by this and previous investigations[a, b]

Data source and species	Crayfish						Carp					
	Lead		Cadmium		Zinc		Lead		Cadmium		Zinc	
	DI, mg/kg/day	HQ	DI, mg/kg/day	HQ	DI, mg/kg/day	HQ	DI, mg/kg/day	HQ	DI, mg/kg/day	HQ	DI, mg/kg/day	HQ
TSMD, 2001–2002												
Robin	1.54	0.9	0.56	0.4	*95.2*	*6.6*	*1.87*	*1.1*	0.54	0.4	*107.9*	*7.4*
Heron	0.18	0.1	0.07	< 0.1	11.3	0.8	0.22	0.1	0.06	< 0.1	12.8	0.9
Shrew	0.63	0.1	0.23	0.3	38.8	0.2	0.76	0.2	0.22	0.3	44.0	0.3
Mink	0.22	0.1	0.08	0.1	13.8	0.1	0.27	0.1	0.08	0.1	15.6	0.1
TSMD, pre-2001[c]												
Robin	*7.90*	*4.8*	*1.66*	*1.1*	*181.5*	*12.5*	*2.13*	*1.3*	0.76	0.5	*182.4*	*12.6*
Heron	0.94	0.6	0.20	0.1	*21.5*	*1.5*	0.25	0.2	0.09	0.1	*21.6*	*1.5*
Shrew	3.22	0.7	0.68	0.9	74.3	0.5	0.87	0.2	0.31	0.4	74.4	0.5
Mink	1.14	0.2	0.24	0.3	26.3	0.2	0.31	0.1	0.11	0.1	26.4	0.1
Big River[d]												
Robin	*58.75*	*36.0*	0.62	0.9	*54.6*	*3.8*	*7.54*	*4.6*	0.31	0.2	*41.8*	*2.9*
Heron	*6.96*	*4.3*	0.07	0.1	6.5	0.4	0.89	0.5	0.04	< 0.1	0.3	0.3
Shrew	*23.96*	*5.1*	0.25	0.3	22.3	0.1	3.08	0.7	0.13	0.2	17.1	0.1
Mink	*8.50*	*1.8*	0.09	0.1	7.9	< 0.1	1.09	0.2	0.05	0.1	6.1	< 0.1

[a]Shown are estimated daily intake rates (DI) and hazard quotients (HQ) for small and large carnivorous birds (represented by data for the American robin, *Turdus migratorius* and great blue heron, *Ardea herodias*) and mammals (short-tailed shrew, *Blarina brevicauda* and mink, *Mustela vison*) relative to No Adverse Effect Level (NOAEL)-based Toxicity Reference Values (TRVs) for Pb, Cd, and Zn (HQ = DI / TRV). Daily intake rates that exceed their respective TRVs and HQs > 1.0 are shown in *italics*

[b]NOAEL-based TRVs for birds, Cd = 1.47, Pb = 1.68, Zn = 14.5; for mammals, Cd = 0.77, Pb = 4.7, Zn = 160. TRVs for Cd and Pb are consensus values from USEPA (2003a) and (2003b), respectively; TRVs for Zn are provisional values from Sample et al. (1996); all other wildlife and toxicity data from USEPA (1993)

[c]Pre-2001 crayfish data from Wildhaber et al. (1997); pre-2001 fish data from Allen and Wilson (1992)

[d]Big River crayfish data from Schmitt and Finger (1982)

Table 8). However, the HQ for Pb was < 1.0 for all species evaluated against the lower maximum Pb concentration in the pre-2001 carp (1.0 μg g^{-1}; Tables 6, 8). In contrast to the bird models, the mammalian TRVs were not exceeded by the daily intake rates of either species (shrew, mink) even under these worst-case scenarios (HQs ≤ 0.7; Table 8).

The consumption of fish and crayfish from the BR also appears to represent a risk to wildlife due to Pb and Zn, but not Cd (Table 8). The daily intake of Pb and Zn from the most contaminated BR carp exceeded both TRVs for Pb and Zn in the small bird (robin, HQ = 2.9–4.6), but not in any of the other models. However, the daily intakes of Pb from the most contaminated crayfish (Schmitt and Finger, 1982) exceeded the TRVs for all species (HQs = 1.8–36.0), as did the intake of Zn for the robin (HQ = 3.8; Table 8). It is also important to note that higher concentrations of Pb have been reported in whole fish from the BR (e.g. Gale et al., 2004).

Risk of metals to fish and wildlife based on comparisons with benchmark values

Because Pb does not bioaccumulate (Settle & Patterson, 1980), environmental Pb has historically been perceived as a greater hazard to lower trophic level organisms (such as herbivorous waterfowl) than to predators, including piscivorous wildlife (Eisler, 1988; Henny, Blus, Hoffman, & Grove, 1994, Henny et al., 2000). However, and as reported by many studies cited in a comprehensive review (Jarvinen & Ankley, 1999), Pb exposure and accumulation may affect fish.

Among the studies reviewed, the lowest reported effect concentration was associated with reduced hatchability in third-generation brook trout (*Salvelinus fontinalis*) embryos, which occurred at a whole-body Pb concentrations of 0.4 μg g^{-1} (Holcombe, Benoit, Leonard, & McKim, 1976). Reduced growth at various life stages in brook trout was associated with whole-body concentrations of 4.0–8.8 μg g^{-1} (Holcombe et al., 1976). Carcass Pb concentrations in some TSMD fish exceeded 0.4 μg g^{-1}, and concentrations in fish from the BR (this and other studies cited) exceeded 4.0 μg g^{-1} (Fig. 2). Effects on enzymes involved in heme synthesis have been reported in fish with whole-body Pb concentrations exceeding 1.0 μg g^{-1} and varying with Zn burden (Schmitt et al., 1984, 1993, 2002), which is consistent with the biochemical effects reported by Schmitt et al. (2005) in fish from the TSMD and the BR.

Although biochemical responses to environmental Pb exposure in fish are well documented, effects at higher levels of biological organization are not. Effects on fish behavior and growth have been induced by waterborne Pb exposure in laboratory studies (Alados & Weber, 1999; Burden, Sandheinrich, & Caldwell, 1998; Shafiq-ur-Rehman, 2003; Weber, Russo, Seale, & Spieler, 1991), but concentrations in the fish were not measured in these studies so there is no basis for comparison with our data. Reduced bone strength, which may impair swimming performance and ultimately lower the ability to escape predators, was reported in longear sunfish with fillet Pb concentrations of about 1.0 μg g^{-1} ww (Dwyer et al., 1988). Reduced condition factors were associated with effects on heme synthesis in two species of catfish (Pimelodidae) from a tailings-contaminated stream in Brazil (Moraes et al., 2003) in which the fish community was also found to be depauperate. Muscle Pb concentrations averaged 2.97 μg g^{-1} and 7.55 μg g^{-1} dw (0.59 μg g^{-1} and 1.51 μg g^{-1} ww, assuming 80% moisture) in the two catfish species, which is within the range of carcass concentrations in fish from the BR and TSMD (Fig. 2, Table 4) and of BR fillet concentrations (Gale et al., 2004).

Eisler (1985) indicated that a Cd concentration of 2 μg g^{-1} (ww) in fish is evidence of contamination, 5 μg g^{-1} is potentially hazardous to the fish, and 13–15 μg g^{-1} represents a threat to higher trophic levels. For fish, the review by Jarvinen and Ankley (1999) cited only one laboratory study that evaluated the effects of Cd exposure relative to whole-body concentrations (Spehar, 1976); concentrations >2.8 μg g^{-1} were associated with decreased spawning and number of embryos produced in flagfish (*Jordanella floridae*). All Cd concentrations in fish from the TSMD reported to date (this study; Allen & Wilson, 1992) were below these benchmarks, but concentrations in whole fish as high as 2.76 μg g^{-1} have been reported from the BR (Schmitt et al., 1993).

Farag et al. (1999) induced biochemical, histopathological, and behavioral effects in westslope cutthroat trout (*Oncorhynchus clarki lewisi*) with a diet of invertebrates from the Coeur d'Alene River, Idaho that contained 452–792 μg g^{-1} (dw) of Pb, 29.1–29.9 μg g^{-1} of Cd, and 2119–2336 μg g^{-1} of Zn. Maximum Pb concentrations in crayfish from the SR-NR system (this and other studies cited) are about one tenth of those that induced effects in cutthroat, but historical concentrations in BR crayfish (Schmitt & Finger, 1982) were only about half those in the Coeur d'Alene (Fig. 2). Maximum concentrations of Cd and Zn in crayfish from the BR and the SR-NR system (this and other studies cited) were also at least ten-fold lower than those that induced effects in cutthroat (Farag et al., 1999). However, it is also important to note that the Coeur d'Alene invertebrates contained substantial quantitites of other contaminants, including arsenic, chromium, copper, and mercury (Farag et al., 1999).

Birds and mammals are sensitive to dietary Pb, which accumulates to potentially harmful concentrations in aquatic organisms. In contrast, internal Zn concentrations are generally well-regulated by fish and many other aquatic organisms (Bury, Walker, & Glover, 2003; Crawford & Luoma, 1993; Giesy & Wiener, 1977), and Zn does not bioaccumulate. As illustrated by our data, concentrations in fish and crayfish span only about a factor of two (Fig. 2), which is consistent with previous studies (e.g. Schmitt et al., 1993; Schmitt, 2004). Nevertheless, and as is also true for humans, dietary Zn may be toxic to wildlife at concentrations <2-fold greater than those required for optimal growth; according to Eisler (1993), Zn concentrations in the diets of young chickens and ducks should be 25–38 mg kg^{-1} (μg g^{-1}, dw) to prevent Zn deficiency, 93–120 mg kg^{-1} for adequate to optimal growth, < 178 mg kg^{-1} to prevent marginal sublethal effects, and < 2000 mg kg^{-1} to prevent death. Maximum Zn concentrations in crayfish collected from the SR and NR in Oklahoma during 2001–2002 were 173–227 μg g^{-1} dw (48–63 μg g^{-1} ww), which are about the same as those reported for the SR in Cherokee County by Wildhaber et al. (1997) but lower than maximum concentrations in SR tributaries (102–119 μg g^{-1} ww, 421–429 μg g^{-1} dw). The latter concentrations are within the range associated with sublethal effects in ducks and chickens (Eisler, 1993). Birds and mammals are comparatively resistant to Cd; dietary toxicity thresholds in the studies reviewed by Eisler (1985) were all >100 μg g^{-1}. However, recent studies have shown that Cd can act as an estrogen mimic in rats (e.g. Johnson et al., 2003), indicating that reproductive effects in wildlife may occur at exposure levels previously believed to be safe.

Discussion

Metals in fish and crayfish

Maximum concentrations of Pb in crayfish from the SR-NR system (all studies) were about ten-fold lower than those obtained from the BR during the early 1980s (Schmitt & Finger, 1982), but maximum Cd and Zn concentrations in crayfish from the TMSD were similar to those from the BR. Maximum TSMD concentrations of all three metals in crayfish were also about ten-fold lower than those in invertebrates from tailings-contaminated reaches of the Coeur d'Alene River, Idaho (Farag, Woodward, Goldstein, Brumbaugh, & Meyer, 1998, 1999), but Pb, Cd, and Zn concentrations documented by Wildhaber et al. (1997, 2000) in crayfish and other invertebrates from SR tributaries exceeded those associated with deleterious effects in fish elsewhere (Farag, Boese, Woodward, & Bergman, 1994; Woodward, Brumbaugh, DeLonay, Little, & Smith, 1994). Metals concentrations in 2001–2002 crayfish were also variable; those with the greatest ww Pb and Zn concentrations came from Site 3u (Fig. 2), which is upstream of known metals sources to the NR, but the greatest dw and mean concentrations were at sites on the SR (Table 3). We attribute this variation to the wide range of moisture content in our samples (Table 3), which probably reflected both the inclusion of excess site water and moisture lost during freezer storage in a few samples; and the fact that the Site 3u crayfish were obtained only a short distance upstream of the Elm Creek confluence (Fig. 1, locations 17 and 20). Regardless, data from this and previous studies (Table 5) indicate that crayfish from the most contaminated parts of the TSMD contain greater concentrations of Pb, Cd, and Zn than those from uncontaminated parts of the SR-NR system. Concentrations of Cd and Zn in TSMD crayfish also exceeded those from the BR, but Pb concentrations in BR crayfish were substantially higher (Table 5).

Maximum concentrations of Pb, Cd, and Zn in most 2001 fish carcasses from the TSMD were lower than those in whole fish samples of the same or similar species reported by previous TSMD studies (Fig. 2; Table 6). However, the historical concentrations differ from our maxima by < 2-fold (Cd and Zn greater, Pb lower; Fig. 2; Table 6). Whole carp obtained from the NR in Kansas, upstream of the TSMD, contained < 0.20–0.60 μg g^{-1} (ww) of Pb, 0.11–0.38 μg g^{-1} of Cd, and 45–65 μg g^{-1} of Zn (Allen, Blackford, Tabor, & Cringan, 2001); these concentrations are greater than the lowest concentrations in our carcass samples from the TSMD, but similar to (Cd) or less than (Pb, Zn) our maxima (Fig. 2; Table 6). Metals concentrations in whole channel catfish, largemouth bass, and crappie reported by Allen and Wilson (1992) were similar to 2001 carcass concentrations. Most 2001 carcass metals concentrations from the BR were within the ranges reported for BR fillets by Gale et al. (2004); however, and as noted previously, these authors reported concentrations as great as 42.1 μg g^{-1} Pb, 1.00 μg g^{-1} Cd, and 173 μg g^{-1} Zn in whole sunfish (*Lepomis* spp.). It therefore appears that metals concentrations in whole fish samples from the TSMD differ by only about two-fold from those in the carcass samples we analyzed, and that the carcass concentrations used together with NOAEL-based TRVs reasonably represent metals risk to wildlife associated with the consumption of fish from the TSMD. In contrast, carcass concentrations may underestimate the risks of Pb in fish from the BR to wildlife.

Concentrations of Pb, Cd, and Zn in carp, bass, crappie, and catfish carcasses from our Oklahoma sites were within the ranges reported for whole fish of the same species from the large rivers in the Central U.S. sampled in 1995 by Schmitt (2004). However, Zn concentration in whole carp obtained from impoundments in Oklahoma in 1995 by Schmitt (2004) were as great as 150 $\mu g\ g^{-1}$ (ww), which exceeded even the maximum previously reported concentration in whole carp from the TSMD (Table 6). Concentrations of Pb and Cd in TSMD carp carcasses were greater than those in whole carp from elsewhere in Oklahoma, Kansas, and Missouri, however (Table 6). Comparatively high Zn concentrations in carp from Oklahoma reservoirs may reflect widespread atmospheric pollution from Zn smelters, which operated historically throughout northeastern Oklahoma and adjoining parts of Kansas and Missouri. However, it is also important to note that Zn concentrations > 100 $\mu g\ g^{-1}$ (ww) in whole carp have been reported from sites not directly associated with mining (Schmitt, Zajicek, May, & Cowman, 1999; Schmitt, 2004). Goldstein and DeWeese (1999) reported mean concentrations of only 0.035 $\mu g\ g^{-1}$ (ww) Pb, 0.055 $\mu g\ g^{-1}$ Cd, and 54 $\mu g\ g^{-1}$ Zn (all computed from dw values assuming 75% moisture) in whole carp from rural areas of Minnesota and North Dakota, which may more accurately represent background concentrations. All SR and NR concentrations (this and previous studies, including the NR upstream of the TSMD) exceeded the Pb and Cd concentrations for Minnesota and North Dakota, but TSMD Zn concentrations were similar (Table 6). Overall, these findings support the generally held assumption that Zn concentrations are much more highly regulated by fish than concentrations of Pb and Cd.

Carcass Pb concentrations in carp (1.39–4.96 $\mu g\ g^{-1}$) and bass (0.57–1.45 $\mu g\ g^{-1}$) from the BR were substantially greater than those in whole carp and bass from the large river sites sampled by Schmitt (2004) and were about the same as those in whole carp (4.39 $\mu g\ g^{-1}$) from the Mississippi River downstream of a smelter complex in Herculaneum, Missouri (Schmitt et al., 2002). However, whole channel catfish from Herculaneum contained only slightly greater concentrations of Pb (1.22 $\mu g\ g^{-1}$) than the maximum carcass Pb concentrations in channel catfish samples from Oklahoma (0.91 $\mu g\ g^{-1}$, Site 1; Fig. 2), and carcass Cd and Zn concentrations in carp and catfish from Oklahoma were about the same as those in whole fish of the same species from Herculaneum (Schmitt et al., 2002). Our results therefore confirm previously reported elevated Pb concentrations in fish from the BR, which have not changed appreciably since the 1980s (Dwyer et al., 1988; Gale et al., 2004; Schmitt & Finger, 1987; Schmitt et al., 1984, 1993), and are consistent with the current Pb-based fish consumption advisory for the BR (MDHSS, 2005). We also note that the flathead catfish from the TSMD we analyzed were relatively small for this species (470–651 mm, 0.5–2.5 kg; Brumbaugh et al., 2005), and that greater concentrations (and associate risk) may occur in larger fish; concentrations of 12 $\mu g\ g^{-1}$ (ww) Pb, 0.34 $\mu g\ g^{-1}$ Cd, and 23 $\mu g\ g^{-1}$ Zn were reported in the muscle tissue of a 1-m long flathead catfish from a site on the BR where concentrations in channel catfish fillets were only 0.13 $\mu g\ g^{-1}$ Pb, 0.03 $\mu g\ g^{-1}$ Cd, and 5.1 $\mu g\ g^{-1}$ Zn (Schmitt & Finger, 1982). Collectively, our results and those of the other studies cited indicate that concentrations of Pb and Cd in TSMD fish are elevated relative to other parts of the Midwest, but that Pb concentrations in BR fish are substantially higher.

In addition to being higher, metals concentrations in carp also varied more than in the other fish species we analyzed. Consequently, differences among sites were not statistically significant (Table 4). In addition, both the highest and lowest concentrations of Pb and Cd in carp were in samples from Site 3 (Fig. 2, Table 4), which is nominally upstream of known sources of metals to the NR. Concentrations of Zn in crayfish from Site 3 were also greater upstream of Elm Creek than downstream (Table 3). Brumbaugh et al. (2005) attributed the variation in carp to fish movement caused by severe flooding in the months preceding collection of the fish. However, and as noted for crayfish, some fish from Site 3 were obtained < 1 km upstream of the mouth of Elm Creek.

Uncertainties in the assessment of metals hazards to wildlife and humans

In addition to the previously noted differences between carcass and whole-fish metals concentrations, there are other substantial sources of uncertainty in both the human health and wildlife food chain exposure analyses. First, the wildlife TRVs for Zn are currently not defined as consensus values; the NOAEL-based value we used (from Sample, Opresko, & Suter, 1996) is currently being reviewed pending adoption as consensus values, as has already been done for Pb and Cd (USEPA, 2003a, b). Second, a wide range of body weights characterize the various life stages of the organisms (including humans) evaluated. We selected values believed to be representative for both humans (adults and children) and wildlife (adults only) from available data. For wildlife, the exposure of (and corresponding risk to) smaller, younger animals would exceed that of the adult animals we evaluated, which could be especially problematic for nestling birds fed contaminated fish or crayfish. Third, caveats analogous to those identified for the evaluation of human health risks based solely on food intake also apply for wildlife. As recognized by the USEPA (1993), the incidental ingestion of contaminated sediments by wildlife feeding on aquatic organisms from an area such as the TSMD, along with the inhalation of contaminated dust and any water consumed by the animals either through drinking or while feeding, may represent additional and important routes of exposure; for example, as much as 30% of the diet of sandpipers (*Calidris* spp.) may be composed of sediment (Beyer, Connor, & Gerould, 1994). Although sediment and water contamination are widespread in the TSMD, none of these latter exposure routes have been incorporated into the screening-level analyses presented here. Conversely, it is unlikely that the diet of the organisms evaluated (or those they might represent as surrogates) would be composed of either 100% crayfish or carp (or of other fish or invertebrates contaminated to the same extent) from the most contaminated parts of the TSMD. Fourth, the concentrations of Pb, Cd, and Zn in the crayfish and large fish we analyzed might not accurately estimate the concentrations in other prey organisms such as benthic insect larvae, snails, and smaller fish. Besser, Brumbaugh, May, and Schmitt (2006) reported that metals concentrations in benthic insect larvae from streams draining the New Lead Belt of southeastern Missouri were typically higher than those in crayfish, which were both higher than concentrations in snails. Concentrations of Pb and Cd, but not of Zn, in small fish (largescale stoneroller, *Campostoma oligolepis;* and juvenile longear sunfish) were higher than concentrations in all invertebrates. In addition, it is likely that metals concentrations in bivalve mollusks are higher even still (e.g. Schmitt & Finger, 1982). Consequently, the incorporation of metals concentrations in crayfish and large fish into the risk analysis for small birds and mammals is reasonable. And finally, the risk assessment approaches used here assume that the contaminants evaluated act independently. Lead, Cd, Zn, and other metals co-occur throughout the TSMD, and their cumulative effects are not necessarily independent or additive (e.g. Joselow, 1980; Schmitt et al., 1984, 1993). Regardless of these uncertainties, however, the data in Tables 5 and 6 indicate the potential for adverse effects in humans and wildlife from metals in aquatic organisms in the TSMD, and that a more complete risk assessment is warranted.

In 2002, one year after our fish were collected, the Oklahoma Department of Environmental Quality (ODEQ) initiated a more thorough investigation of Pb, Zn, and Cd concentrations in TSMD fish that corroborated many of our findings (ODEQ, 2003). The ODEQ collected samples representing multiple fish species from the Oklahoma waters of the TSMD in northeast Oklahoma and prepared the fish for analysis as skinless, boneless fillets; as head-on, eviscerated carcasses; and as whole fish. Metals concentrations were greatest in whole fish and head-on carcasses and lowest in fillets of the same species. Our concentrations in headless carcasses were typically greater than ODEQ fillet concentrations but less than the ODEQ values for head-on carcasses and whole fish. The ODEQ (2003) data also indicated that metals concentrations were generally greater at sites on the SR than on the NR. Based on these findings and application of the risk model for Pb (USEPA, 1994b), the ODEQ recommended that only fillets of fish from the Oklahoma waters of the TSMD be eaten.

Summary and conclusions

Our results and those of a subsequent study (ODEQ, 2003) corroborated those of previous investigations showing that metals from historical mining activity in the TSMD have been transported to the SR and NR and accumulated by aquatic organisms important to Native Americans. Comparatively high concentrations of metals were evident in fish and crayfish from both the SR and the NR. Within the TSMD, concentrations were generally greater in samples from the SR than in the NR, but there was considerable variability within and among sites. Overall, concentrations of Pb in TSMD fish and crayfish were greater than those from reference sites, but were lower than in the BR and other historical mining areas. Nevertheless, data from this and other studies indicate that concentrations of Pb and Cd in carp, catfish, and crayfish from some TSMD sites are sufficiently high to represent a potential health risk to human consumers and to possibly warrant consumption advisories. Based on USEPA and WHO recommendations and subject to previously discussed caveats, the human consumption of carp and crayfish prepared in the manner described here (i.e. headed and eviscerated) from the most contaminated TSMD sites could warrant restriction due to Pb or Cd. Channel catfish consumption might also be restricted due to Pb, but Cd concentrations in catfish were lower than in crayfish and carp and would probably not warrant restriction. Concentrations of both metals were low in bass and crappie, and their consumption would also probably not be restricted. Concentrations of Zn were comparatively high in carp and crayfish, but would probably not warrant restriction. The consumption of carp and other fish from the BR is currently restricted due to Pb by the MDHSS (2005); and the ODEQ (2003) recommends the consumption of only fillets of fish from the Oklahoma waters of the TSMD, also due to Pb.

Risk to fish and to carnivorous wildlife was evaluated by comparing concentrations in fish and crayfish to benchmark values from the scientific literature. Risk to wildlife was also evaluated using an approach based on food chain analysis, which is analogous to the procedures used to assess human health risk. The conclusions of these assessments were essentially identical; i.e., mining-derived metals in aquatic organisms may also represent risk to carnivorous wildlife in the TSMD. Preliminary analysis indicates some risk to birds from the consumption of Pb and Zn contaminated fish and invertebrates, but not Cd. This assessment is also consistent with recent reports of biochemical effects in fish (Schmitt et al., 2005; Yoo & Janz, 2003) and of Zn poisoning in TSMD waterfowl (Beyer et al., 2004). Collectively, the results of this and the other investigations cited indicate that fish in the TSMD are also exposed to comparatively high concentrations of Pb, Cd, and Zn and possibly other elemental contaminants from mining. Further studies should seek to resolve some of the uncertainties associated with other routes of wildlife exposure and to more thoroughly document contaminant effects in fish and wildlife.

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