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Food Chain Analysis of Exposures and Risks to Wildlife at a Metals-Contaminated Wetland

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Abstract. A food chain analysis of risks to wetland receptors was performed in support of a baseline ecological risk assessment at the Milltown Reservoir Sediments Superfund site in Montana. The study area consisted of over 450 acres of primarily palustrine wetland contaminated with metals from mining wastes transported from upstream sources (average of 465 mg/kg for Cu in sediments, and 585 mg/kg in soils). The food chain analysis focused on several species of terrestrial and semi-aquatic animals indigenous to montane wetlands of the northern Rocky Mountains. Receptors consisted of mice, voles, muskrats, beaver, various waterfowl species, osprey, bald eagles, and deer. Samples of aquatic and terrestrial invertebrates, small mammal tissues, fish tissue, aquatic and terrestrial vegetation, soils, sediment, and surface water were collected and analyzed for As, Cd, Cu, and Zn. A linear multimedia food-chain model was constructed to estimate daily intakes of the metals for each receptor, with assumed values for ingestion of aquatic and terrestrial food items, ingestion of local surface water, and incidental ingestion of soils and/or sediments. Evaluation of health risks to the receptors was performed by comparison of exposures expressed as daily intakes to a suite of toxicity values. The range of values consisted of the lower end of chronic toxicity data found in toxicology databases or the literature for the same or similar species, modified to account for extrapolation uncertainties. Daily intakes of chemicals of concern were below or within the range of toxicity values for all receptors. The weight of evidence from the food chain analysis and earlier bioassessment and ecological studies suggest that the health of the wetland receptors is at minimal risk due to the presence of elevated metals in sediments, upland soils, water, or food items at the site.

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Food chain analysis of wildlife exposures to metals has received increasing attention over the past few years (Hunter *et al.* 1987; Ma and Van der Voet 1993; MacIntosh *et al.* 1994), particularly with the recent emphasis of the U.S. Environmental Protection Agency (USEPA) on assessing ecological risks at hazardous waste sites (*USEPA* 1991, 1992). At sites contaminated with mining wastes, elevated concentrations of metals have been observed in a variety of wildlife species, including plants (Hunter *et al.* 1987), invertebrates (Hunter *et al.* 1987; Reporter *et al.* 1989), and small mammals (Hunter *et al.* 1987; Ma *et al.* 1991; Pascoe *et al.* 1994a). Whether these elevated metals concentrations pose a risk of adverse impacts to the exposed organisms, or to higher trophic organisms that feed on them, has been an ongoing concern. Frequently, the lack of available information on the potential transfer of metals within a food web precludes definite conclusions on the potential for adverse impacts. Recent compilations of factors for estimating exposures of wildlife to environmental contaminants (*USEPA* 1993a, 1993b, 1994), coupled with methodological guidance on assessing ecological risks (*USEPA* 1992), lay the groundwork for increasing accuracy in food web analyses and consequent risk estimates (e.g., see MacIntosh *et al.* 1994).

In the upper Clark Fork River (CFR) basin of Montana, an ecological risk assessment was performed to determine baseline risks to aquatic and terrestrial habitats of a metals-contaminated wetland. The Milltown Reservoir Sediments Site, a National Priority List (NPL) "Superfund" site, includes the Milltown Reservoir wetland as one of the operable units. Milltown Reservoir is a riverine and palustrine wetland ecosystem located at the confluence of the Blackfoot and Clark Fork Rivers, five miles (eight km) east of Missoula in western Montana (Figure 1). Contaminant problems at the site are characterized by large volumes of metal-containing sediments and the presence of elevated concentrations of As, Cd, Cu, and Zn in wetland soils, surface water, and groundwater (Pascoe and DalSoglio 1994).

Since the construction of Milltown Dam in 1906-1907 below the confluence of the rivers, the reservoir has accumulated over 120 million cubic feet (4 million cubic meters) of river-borne

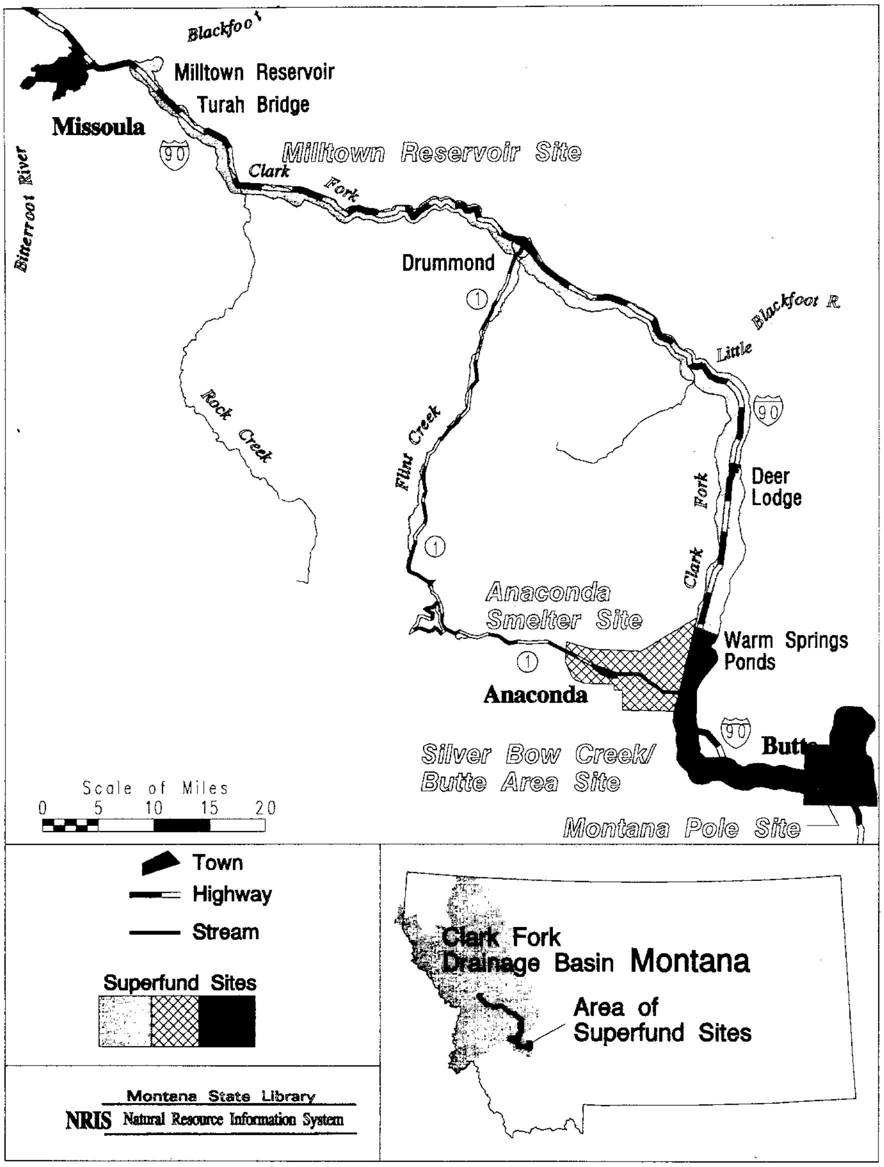

Fig. 1. Site location in the Clark Fork River Basin

sediment. A significant portion of the sediment was deposited during a major flood in 1908, which transported waste materials from upstream mining areas near Butte and Anaconda (Figure 1). Thus, metals contamination at Milltown Reservoir and any consequent ecological impacts are related to contaminants originating in distant areas of the watershed (Moore and Luoma 1990).

A comprehensive ecological risk assessment was performed for the Milltown Reservoir wetland as part of the Superfund remediation process (Pascoe and DalSoglio 1994). *In situ* and laboratory toxicity tests were performed to evaluate responses of wetland plants and invertebrates to the presence of mining waste metals. Potential impacts to primary consumers, such as waterfowl and herbivorous mammals, and higher trophic organisms were evaluated by a food chain analysis, described herein. The analysis integrates extensive field data on metals and As concentrations in environmental media and biota at the wetland, and supplements the previous characterization of ecological risks for the site (Pascoe *et al.* 1994b).

Methods

Food Chain Model

The typical food chain model in risk assessment consists of predicting chemical exposures, such as intake rates or body burdens, for higher trophic level organisms from measurements of chemical concentrations in environmental media and food sources. The food chain study at Milltown Reservoir was conceived as two phases, with the first phase consisting of a deterministic risk analysis using single point estimates of site-wide chemical concentrations and exposure estimates. If the first phase suggested potential risks to individuals from exposures to metals at the site, then a probabilistic analysis of exposures and risks was planned as a second phase. As described below, exposures of receptor species to site chemicals were modeled from the results of field measurements of As, Cd, Cu, and Zn in several food source groups: aquatic and terrestrial invertebrates, aquatic vegetation, above- and below-ground terrestrial vegetation, fish, goose eggs, and small mammals; and in surface water, sediments, and soils that may be inadvertently consumed during typical foraging activities.

Receptor Species

Species for exposure modeling were selected to include herbivores, carnivores, and omnivores representing primary and higher trophic consumers inhabiting the wetland. Game species were included because of their importance to local hunters. Five receptor groups were identified for modeling: small mammals, semi-aquatic mammals, waterfowl, predatory birds, and deer.

Small mammals were the herbivorous deer mouse (*Peromyscus maniculatus*) and meadow vole (*Microtus pennsylvanicus*), and the masked shrew (*Sorex cinereus*). The insectivorous diet of the shrew places it at a higher trophic level than the other small mammals and its energy dynamics results in a high food intake per unit body weight. Because of these characteristics, the shrew has been the focus of recent ecotoxicology studies (Hunter *et al.* 1987; Dodds-Smith *et al.* 1992).

Wetland semi-aquatic mammals were the muskrat (*Ondatra zibethicus*), mink (*Mustela vison*), and beaver (*Castor canadensis*). Muskrat and beaver are herbivores, whereas mink are opportunistic carnivores and consume aquatic invertebrates, fish, and small mammals. Deer were the common mule deer (*Odocoileus hemionus*).

Waterfowl species were the mallard (*Anas platyrhynchos*), Canada goose (*Branta canadensis*), and American coot (*Fulica american*), which consume a variety of aquatic invertebrates and aquatic and terrestrial plants. Predatory birds were the bald eagle (*Haliaeetus leucocephalus*), which consumes a mix of fish, small mammals, and probably waterfowl from the wetland; and the osprey (*Pandion haliaetus*), which consumes primarily fish.

Estimation of Exposures and Chemical Intakes

Sample collection for the food-chain analysis was performed over the 1990 through 1992 field seasons at a 450 acre portion of the wetland. The field study designs and methods for collection, preparation, and analysis of samples followed USEPA and ASTM guidelines; details are provided in technical reports (*ManTech* 1992; *USFWS* 1993) and summarized herein.

The 450 acre wetland was divided into twelve sampling units based on existing topography (Figure 2); ten units were located in the contaminated portion of the site (Units 2-4 and 6-12), and two (Units 1 and 5) in uncontaminated areas used as onsite reference locations (Pascoe and DalSoglio 1994). Sediment sampling locations were selected to represent the range of chemical concentrations and physical and chemical characteristics of the wetland sediments. The sediment station located in the Blackfoot River arm of the wetland (Station MR-01) was selected as an uncontaminated reference location (Figure 2). Reference areas for biota sampling were the Lee Metcalf National Wildlife Refuge on the Bitterroot River and the Ninepipes National Wildlife Refuge on the Flathead River, MT (*ManTech* 1992).

Surface soil samples (6 cm) were collected throughout the twelve sampling units using stainless steel trowels and mixing bowls (*ManTech* 1992; Page *et al.* 1982; Klute 1986). Sediments were sampled by Ponar grab or polypropylene scoop, with each sample a composite of at least ten grabs of the upper 6 cm of sediment surface (*USFWS* 1993). Data are presented in dry weight. Data on surface water quality are averages taken from U.S. Geological Survey monitoring studies (Lambing 1991) conducted over 1985-1990 at Turah Bridge (see Figure 1).

Resident small mammals (meadow voles and deer mice) were collected from four of the units (Units 2, 3, 4, and 6), which were considered representative of the range of chemical concentrations at the site (Pascoe *et al.* 1994a). Qualitative observation of stomach contents indicated a diet of plant materials typical of the site. Only the carcass data on metals and As concentrations are used in the present food chain analysis. Concentrations of metals and As in internal organs have been reported previously (Pascoe *et al.* 1994a).

Aquatic and terrestrial plants were collected from the twelve units of the site. Whole specimens were collected for analyses of above- and below-ground tissues. Plant tissues were thoroughly cleaned of surface soil and visible contamination, then dried prior to digestion. Aquatic and terrestrial invertebrates were also collected throughout the site. Chemical concentration data for vegetation and invertebrates are presented on a dry-weight basis. Fish were collected by netting and electroshocking from three areas representative of the reservoir (*ARCO* 1992). Chemical concentration data are presented on a wet-weight basis.

Metals were analyzed in environmental media and tissue samples by ICP and atomic absorption spectroscopy. Analytical procedures and quality control measures followed USEPA guidelines for conducting studies at Superfund sites (*USEPA* 1988), and are summarized in Linder *et al.* (1994) and described in detail in technical reports prepared for USEPA Region 8 (*USFWS* 1993; *ManTech* 1992; *ARCO* 1992).

Because of a lack of correlation between concentrations of metals and As in terrestrial biota and concentrations in soils from the same sample units (Pascoe *et al.* 1994a), primarily due to insufficient sample numbers for statistical analyses on a sampling unit basis and the heterogeneity of chemical concentrations in soils across the site (Linder *et al.* 1994), chemical concentrations as site-wide averages were used to model their trophic transfer. Receptors were assumed to be exposed to chemicals throughout the site on a random basis. Given the limited habitat in upland areas of the site and the presence of the dam at the downstream end, it was assumed that receptors never foraged off the site and that exposures occurred continuously twelve months per year over the lifetime of the organism. Waterfowl were assumed to be present seven months of the year.

Estimated daily intakes were calculated by the following equation:

$$\mathrm{DD} = \frac{((\mathrm{C}_{\mathrm{f(Ab\&Be)}} \cdot \mathrm{FC}) + (\mathrm{C_S} \cdot \mathrm{SC}) + (\mathrm{C_W} \cdot \mathrm{WC} \cdot \mathrm{CO})) \cdot \mathrm{AB}}{\mathrm{BW}} \tag{1}$$

where:

- DD = daily dose in mg/kg body weight
- $\mathrm{C}_{\mathrm{f(Ab\&Be)}}$ = chemical concentration (mg/kg) in plant (Ab: above ground plant parts; Be: below ground plant parts) or animal food items
- FC = feed consumption rate (kg/day)
- $\mathrm{C_S}$ = chemical concentration in soil or sediment (mg/kg)
- SC = soil or sediment consumption rate (kg/day)
- $\mathrm{C_W}$ = chemical concentration in water (μg/L)
- WC = water consumption rate (L/day)
- CO = conversion factor for μg to mg (10^{-3})
- AB = absorption of metals and As (fraction)
- BW = body weight (kg).

Intake parameters (i.e., FC, SC, WC, and BW) were either taken from recent compilations by USEPA (1993a, 1993b, 1994) as primary sources for small mammals and predatory birds, or estimated by allometric equations based on body weight (*USEPA* 1993b; Calder and Braun 1983; Nagy 1987). Where values were unavailable from USEPA, additional studies were used as supplements (Beyer and Miller 1990; Beyer *et al.* 1994; Nolet *et al.* 1994; Terres 1980; Nowak 1991). Sources of specific parameter values are identified in the **Results** section.

Water ingestion rates were assumed to be 20% of body weight for small mammals; 5% of body weight for waterfowl; 10% of body weight for deer, beaver, and mink; and 5% of body weight for muskrat (*USEPA* 1993a, 1993b). Mink were assumed to consume 20% of their fish intake as minnows, which were more highly contaminated than larger fish in the reservoir (see **Results**).

An absorption fraction (AB) is used to compare absorption of chemicals by receptors in the field with absorption during laboratory feeding and gavage studies from which toxicity values are derived. Gastrointestinal absorption and elimination of metals and As in food items and ingested environmental media was previously calculated at less than 0.1% of intake for small mammals at the wetland (Pascoe *et al.* 1994a). Conservatively assuming that only 10% of metals and As are absorbed

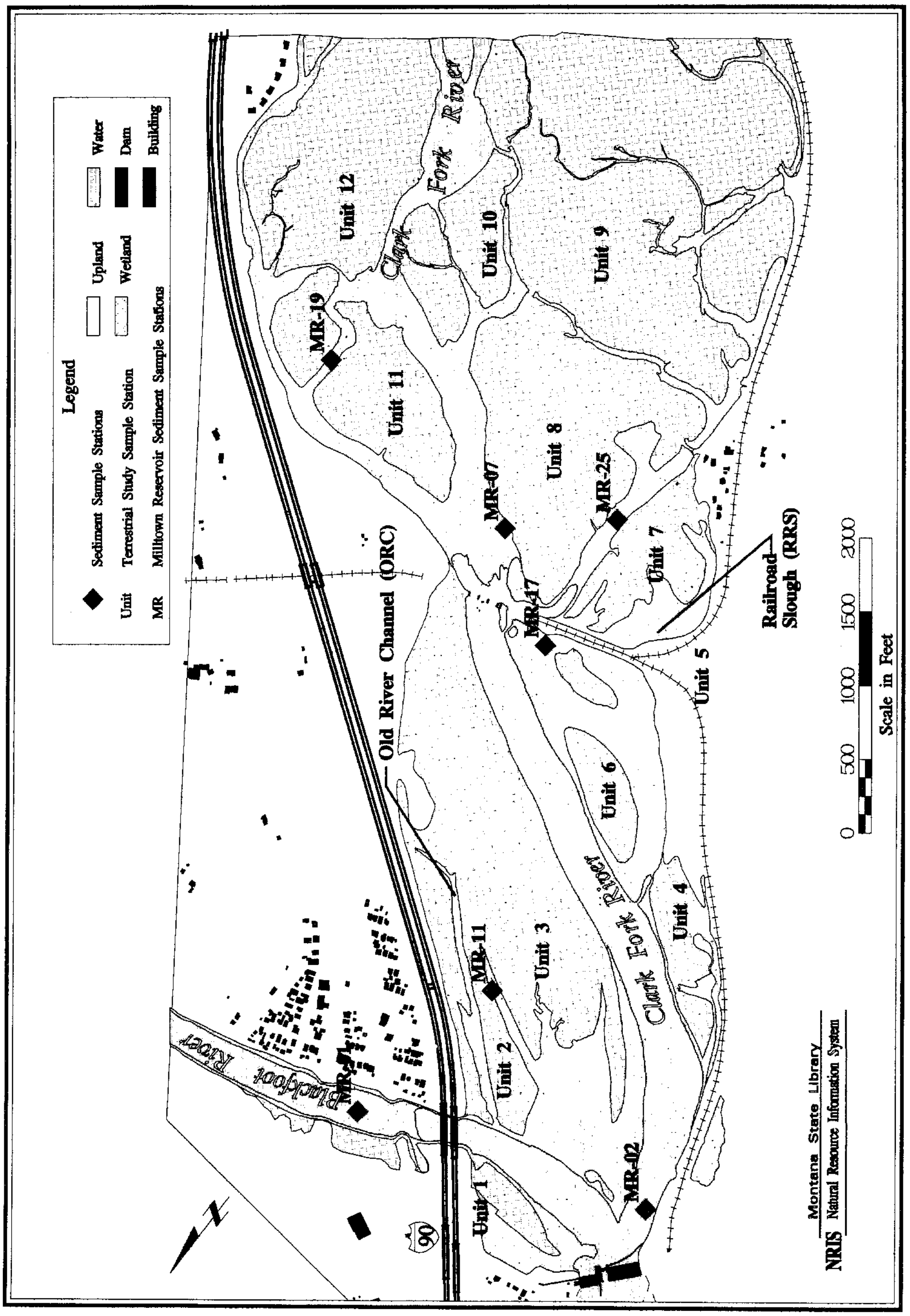

Fig. 2. Locations of wetland sampling units and sediment sampling stations in the Milltown Reservoir operable unit

during laboratory feeding and gavage studies, then comparison with the measured 0.1% absorption-elimination factor for small mammals at the site results in an absorption fraction (AB) of 1% for the food chain model. The absorption fractions of metals and As for beaver, muskrat, and mink were assumed to be greater than for small mammals, at 2.5% (Friberg *et al.* 1986). A conservative estimate of 10% was used as an absorption fraction for deer, waterfowl, and predatory birds.

Toxicity Values

Toxicity values for As, Cd, Cu, and Zn were compiled as daily doses or intake rates in mg per kg body weight per day (mg/kg-day). Rather than derive a single toxicity value as a reference for each chemical and receptor species, toxicity data are presented as suites of values for each of the five receptor groups, with values representing the low end of the range of toxicity data from studies of the same or similar species in the group (*ARAMDG* 1994). Where literature toxicity data consisted only of concentrations of the chemicals in laboratory feed sources, daily doses of the chemicals were estimated for the study organism using the appropriate exposure parameter values (food ingestion rate, body weight) as described under **Results.** Toxicity data associated with internal organ concentrations were also identified for Cd. Sources for the toxicity values consisted of toxicology databases, reviews, and original research publications, and are listed in **Results.**

Preference in toxicity data was given to the no-observed-adverse-effect level (NOAEL) for sensitive endpoints for the receptor species or a related species that could serve as a surrogate. Where NOAELs were unavailable, toxicity data included low-observed-adverse-effect-levels (LOAELs) and low-observed-effect-levels (LOELs). LOAELs and LOELs are defined as the lowest doses where adverse health effects and effects on enzymes without other symptomology, respectively, are observed. NOAELs, LOAELs, and LOELs can be adjusted by uncertainty factors ranging from 0.1 to 10 to extrapolate between species, and from 1 to 10 to adjust a LOAEL to a surrogate NOAEL or to adjust from an acute test to represent chronic toxicity, as recommended by USEPA (1986) and CalEPA (1994).

Assessment of Risk

Assessment of potential risks to wetland receptors was performed by comparison of exposures, expressed as daily intake or dose, to the suite of toxicity values, also expressed as daily intake (*USEPA* 1986, 1992). An exposure estimated to be less than a daily intake is interpreted as presenting no risk to the health of exposed individuals or populations. An exposure that exceeds the suite of toxicity values may indicate potential risk to that receptor and would support a more thorough evaluation of the toxicity database and method of extrapolation, and a probabilistic-based quantitation of exposures to more accurately characterize risk.

Results

Chemical Concentration Data

Summaries of the concentrations of metals and As in environmental media and biota throughout the wetland are provided in Tables 1 and 2. Sample data collected from reference locations are provided for comparison with the contaminated areas of the wetland, and were not used in the food chain analysis.

Aquatic invertebrates collected for chemical analyses included damselfly (suborder Zygoptera), water boatman (family Corixidae), dragonfly (suborder Anisoptera), midges (family Chironomidae), amphipods, and snails (order Gastropoda); terrestrial invertebrates included grasshopper and earthworm (*ManTech* 1992). Aquatic vegetation consisted of emergent species, primarily cattails (*Typha latifolia*), arrowhead (*Sagitaria sp.*), and pondweed (*Potamogeton sp.*); and floating vegetation such as duckweed and periphyton. Terrestrial vegetation included willow (*Salix sp.*), Azolla, mint (*Mentha piperata*), equisetum, tansy (*Tanacetum vulgare*), clover (*Melilotus sp.*), butter 'n eggs (*Linaria vulgaris*), umbelliferae, and smartweed (which were all grouped as *forbs* in calculating intakes); and a variety of grasses. The number of floating aquatic vegetation and terrestrial grass samples were limited to two and four, respectively, with high variability in chemical concentrations (Table 2).

Over 100 fish samples were collected from three locations in the reservoir to provide data on chemical concentrations for both the ecological and human health risk assessments (Sherman and Pascoe 1993). Data on whole body concentrations of metals and As were combined for rainbow trout (*Oncorhynchus mykiss*), brown trout (*Salmo trutta*), whitefish (*Prosopium williamsoni*), largemouth bass (*Micropterus salmoides*), yellow perch (*Perca flavescens*), and bull trout (*Salniems confluentus*) (*ARCO* 1992). These species were assumed to be food sources for mink, osprey, and bald eagle. Minnows were also collected from the wetland (*ManTech* 1992) for use in modeling a food source for mink.

Comparison for concentrations of As, Cd, Cu, and Zn in terrestrial and aquatic biota with those in soil and sediment on a site-wide basis provides estimates of invertebrate, plant, and small mammal uptake factors for these chemicals (Table 3). The uptake, or partitioning, factors were greatest for Cd overall, and for all chemicals were greater for below ground plant tissues compared to above ground tissues. A relational trend in soil uptake factors was observed for all four chemicals, in the order of earthworms > below-ground vegetation > grasshoppers > above-ground vegetation > small mammals.

Table 1. Summary of site-wide chemical concentrations in environmental media at the Milltown Reservoir wetland

Media	n	As	Cd	Cu	Zn
Sediment (mg/kg)[a]	6	45.3	5.5	464.7	1426.2
		(11.8)	(4.1)	(212.8)	(1381.2)
Reference area	1	5.8	0.09	29.9	52
Soil (mg/kg)[b]	46	67.1	7.3	584.7	1949.5
		(31.4)	(3.7)	(279.9)	(1410.6)
Reference area	10	7.7	1.9	17.9	49.3
		(3.1)	(0.8)	(4.5)	(15.4)
Surface water (μg/L)[c]	34	14	0.8	78	149
		(5–110)	(<1–4)	(5–500)	(10–1100)

Values are arithmetic means, with standard deviations in parentheses except where noted

[a] Data from USFWS (1993). Reference sediments were collected from Station MR-01 in the Blackfoot River arm of the reservoir (see Figure 2)

[b] Data for soils collected from Units 2,3,4,6,7,8,9,10,11,12 (*ETI* 1991; *ManTech* 1992). Reference soils were collected from Units 1 and 5 (see Figure 2)

[c] Data are averages and ranges for total recoverable metals from the USGS monitoring station at Turah Bridge immediately upstream of Milltown Reservoir (Lambing 1991)

NA: Not available

<: Less than detection limit value

Table 2. Summary of site-wide chemical concentrations in biota at the Milltown Reservoir wetland

Biota	n	(mg/kg) As	Cd	Cu	Zn
Invertebrates[a]					
Aquatic					
Damselflies/Water Boatmen Midges/Amphipods, Dragonflies	17	7.7 (12.2)	2.8 (3.1)	49.6 (44.5)	519.9 (442.9)
Reference area	3	<0.02	<0.001	<0.036	20.3 (35.1)
Snails	1	<0.02	0.89	149.0	116.0
Reference area	1	<0.02	<0.001	<0.036	13.0
Terrestrial					
Grasshoppers	14	3.9 (2.1)	1.5 (0.9)	60.5 (28.3)	270.8 (73.9)
Reference area	2	<0.02	<0.001–0.3	<0.036	<0.004–160
Earthworms	6	10.9 (4.0)	27.5 (9.2)	77.2 (30.6)	1060.0 (176.5)
Laboratory control[b]	10	1.7 (0.3)	1.2 (0.4)	<0.036	90.4 (15.1)
Minnows[a]	20	5.7 (11.7)	0.9 (1.9)	7.6 (12.9)	209.3 (51.3)
Fish[c]	101	0.15 (0.09)	0.13 (0.24)	1.6 (1.5)	26.3 (9.3)
Reference areas	6[d]	0.09 (0.12)	0.04 (0.05)	0.61 (0.16)	NA
	7[e]	0.11 (0.05)	0.01 (0.003)	0.60 (0.05)	15.1 (2.0)
Small mammals[f]	10–19	0.07 (0.10)	0.12 (0.15)	3.1 (0.61)	28.4 (4.6)
Goose eggs[g]	9	<0.1	<0.4	4.6 (1.7–14)	59.0 (32.9–93.1)
Vegetation[a]					
Above ground					
Forbs	20	1.1 (1.9)	2.8 (3.5)	2.2 (4.1)	224.1 (173.7)
Reference area	2	0.4–0.5	0.16–0.25	5.4–6.2	11.1–13.4
Grasses	4	6.7 (7.5)	0.9 (0.9)	24.2 (17.1)	153.7 (80.3)
Reference area	1	2.1	0.6	7.0	36.2
Emergent macrophytes	4	3.6 (2.8)	7.9 (8.6)	12.3 (4.0)	122.0 (74.6)
Floating macrophytes	2	18.9–35.2	141–908	NA	NA
Reference area	3	<0.02	<0.001	<0.036	10.7 (18.5)
Below ground					
Forbs	20	9.3 (7.3)	8.3 (3.1)	74.8 (60.6)	408.9 (356.7)
Reference area	2	2.0–2.2	0.62–0.68	9.1–10.6	23.5–32.3
Grasses	4	100.1 (151.2)	8.6 (10.1)	274.3 (320.6)	882.1 (674.7)
Reference area	1	6.4	1.5	14.4	71.8
Emergent macrophytes	12	52.0 (71.3)	34.6 (106.0)	68.1 (130.3)	423.6 (685.5)
Reference area	3	<0.2	0.1 (0.2)	<0.036	<0.004

Values are arithmetic means, with standard deviations in parentheses except where noted
Reference locations were Unit 1 for terrestrial plants and local wildlife refuges for remaining biota (see text)
[a] Data are dry weight for invertebrates, vegetation, and minnows collected from Units 2,3,4,6,7,8,9,10,11,12 (*ETI* 1991; *ManTech* 1992)
[b] Data are dry weight, from laboratory studies of earthworm exposure to artificial soils (*ManTech* 1992)
[c] Data from ARCO (1992) fish sampling program. Values are wet weight for whole body samples of a mix of brown trout, rainbow trout, and whitefish
[d] Brown trout collected from the Big Hole River, MT; values are for whole body, wet weight samples (Farag *et al.* 1995)
[e] Whitefish collected from the Big Hole River and Rock Creek; values are for whole body, wet weight samples (Bergman and Szumski 1994)
[f] Data are wet weight carcass, from small mammal trapping efforts in Units 2,3,4, and 6 (Pascoe *et al.* 1994a; *ManTech* 1992). Range of sample numbers; not all carcasses were analyzed for all chemicals. Reference area data not available
[g] Values are dry weight and are average and range (*USFWS* 1991). Reference area data not available
NA: Not available
<: Value is detection limit

Table 3. Ratios of biota to soil or sediment concentrations of metals and arsenic at the Milltown Reservoir wetland

	n	As	Cd	Cu	Zn
Soil ratios[a]					
Terrestrial invertebrates					
Grasshoppers	14	0.058	0.205	0.103	0.139
Earthworms	6	0.162	3.780	0.132	0.544
Small mammals[b]	10–19	0.001	0.015	0.006	0.015
Vegetation[c]					
Above ground forbs	20	0.016	0.384	0.004	0.115
Below ground forbs	20	0.139	1.137	0.128	0.210
Sediment ratios[a,c]					
Above ground emergent vegetation	4	0.079	1.430	0.026	0.086
Below ground emergent vegetation	12	1.150	6.290	0.150	0.297

[a]Ratios calculated as the average site-wide concentration of chemical in biota divided by the average site-wide soil or sediment concentration
[b]Ratios of small mammal concentrations to soil concentrations derived from sample Units 2, 3, 4, and 6 (Pascoe *et al.* 1994a; *ManTech* 1992)
[c]Ratios not estimated for grasses or aquatic floating plants due to low sample numbers

Exposure Parameters

Exposure parameters for the receptors of concern are presented in Table 4, and values are provided for rates of ingestion of terrestrial and aquatic biota, soil, sediment, and water; frequency and duration of exposure; body weight; and absorption fraction. Daily doses expressed as mg/kg body weight per day were calculated from the chemical concentration data in Tables 1 and 2 and the exposure parameter values in Table 4, and are presented under *Risk Characterization.*

Toxicity Assessment

Toxicology studies on As, Cd, Cu, and Zn are briefly reviewed and toxicity values for each chemical are identified for each of the five receptor groups. Where studies on wetland receptor species of Milltown Reservoir are unavailable, studies are presented on surrogate species. Toxicity values are compiled in tabular form under *Risk Characterization* for comparison with daily doses. Note that in five cases where NOAEL and LOAEL data are available from the same study, the differences between them range from two to five-fold, with an average of 3.5.

Arsenic: All of the studies on As exposures from which dose-response information are adequately summarized were based on inorganic As, usually sodium arsenate. Since speciation data on As in consumable substances from the wetland are unavailable, the food chain model assumes that all exposures to As are to the inorganic form. However, actual exposures at Milltown Reservoir would be to a mix of inorganic forms in soil, sediment, and water, and largely organic forms in food items. Organic forms of As generally pass through the body unutilized and are far less toxic than inorganic forms, partly because of the rapid excretion (Phillips 1990). Also, ingested inorganic As is detoxified by methylation to various organic forms (Marcus and Rispin 1988). Because of the detoxification and rapid excretion of As, chronic poisoning is infrequently seen in wildlife (Eisler 1988a). From these considerations, the assumption in the food chain model that all exposures at the wetland are to inorganic As overestimates exposure to this more toxic form.

Chronic toxicity of As is typically characterized by weakness, paralysis, conjunctivitis, dermatitis, decreased growth, and liver damage (Eisler 1988a). Studies of feeding As to mice over three generations at about 0.5 mg/kg-day in drinking water (5 ppm) and 2 mg/kg-day for feed found reduced litter sizes with no other effects (Eisler 1988a; Schroeder and Mitchener 1971). Rats fed inorganic As for two years at about 10 mg/kg-day (31.25 ppm in diet) resulted in decreased weight, but without effects on histopathology or survival at 20 mg/kg-day (Byron *et al.* 1967). Other chronic feeding studies with rats have found no effects at a daily dose of 2.3 mg/kg-day (*ATSDR* 1992a). Guinea pigs fed arsenic trioxide in diet at about 5 mg/kg-day for 21 days resulted in no observed effects, although greatly elevated tissue levels of As were observed (Eisler 1988a).

No studies were found on exposures of semi-aquatic mammals to As. The only study on deer exposure reported a lethal dose at 34 mg/kg for an inorganic form (Eisler 1988a). A NOAEL of about 0.08 mg/kg-day was observed in a study of lambs fed inorganic As for three months (Eisler 1988a).

Few studies are available for waterfowl exposures to As. Nine-week exposures of ducklings to sodium arsenate in the diet resulted in a NOAEL of 1.25 mg/kg-day (30 ppm in diet). Higher doses at 12.5 mg/kg-day were related to significant effects on the schedules of bathing, resting, and alertness (Whitworth *et al.* 1991). In a study of 99 pairs of breeding mallards fed sodium arsenate in the diet throughout the reproductive cycle, a NOAEL of 4.2 mg/kg-day (100 ppm in diet) was observed, with a LOAEL of 16.7 mg/kg-day for reduced weight gain, reduced liver weight, delayed egg laying, reduced egg weight, and eggshell thinning (Stanley *et al.* 1994). Overall hatching success was unaffected, despite the other reproductive effects. In another study, duckling mallards fed As in the diet showed decreased growth at 12.5 mg/kg-day (300 ppm in diet), with a NOAEL at 4.2 mg/kg-day (Camardese *et al.* 1990).

No studies were found on chronic exposure of predatory birds to As. A NOAEL of 9.1 mg/kg-day was found in a nine-week feeding study with chickens (*Gallus gallus*) (Eisler 1988a).

Cadmium: No evidence has been found that Cd is biologically essential or beneficial to any species. In mammals, Cd concentrations exceeding 200 mg/kg wet weight in kidney, or 5 mg/kg whole animal, have been considered typical thresholds for life-threatening concentrations (Friberg *et al.* 1986). More recently, a value of 100 mg/kg was recommended as a critical concentration of Cd because of findings of kidney lesions in rats and birds at concentrations of 100-150 mg/kg (Nolet *et al.* 1994). In a study of shrews (*Sorex areneus*) and voles (*Microtis agrestis*) exposed to metals at a contaminated nature reserve (Ma *et al.* 1991), a critical renal load of Cd was estimated at 120 mg/kg (Hunter *et al.* 1987).

In a study of mice, a LOAEL for Cd at about 1 mg/kg-day (10 ppm in drinking water) exposure over three generations was associated with increased malformations and decreased

Table 4. Food chain exposure parameters

Species	Intake rates												Absorption (%)	Exposure frequency (days/yr)	Exposure duration (years)	Body weight (kg)
	Plants (kg/day)				Animals (kg/day)											
	Emergent[a]	Grasses[a]	Forbs[a]	Floating	Aquatic Invertebrates	Fish	Terrestrial Invertebrates	Small Mammals	Goose Eggs	Soil (kg/day)	Sediment (kg/day)	Water (L/day)				
Meadow vole	0	0.006	0.006	0	0	0	0	0	0	0.00025	0	0.008	1	365	0.6	0.04
Deer mouse	0	0.001	0.001	0	0	0	0.0025	0	0	0.00025	0	0.0044	1	365	1	0.022
Shrew	0	0	0	0	0	0	0.013	0	0	0.0000625	0	0.0009	1	365	1	0.0043
Beaver	0.5	0.5	0	0	0	0	0	0	0	0.0235	0.0235	1.8	2.5	365	2	18
Muskrat	0.37	0	0	0	0	0	0	0	0	0	0.012	0.0625	2.5	365	2	1.25
Mink	0	0	0	0	0.03	0.09	0	0.025	0.01	0.0047	0.0012	0.1	2.5	365	2	0.9
Deer	0	1.5	1.5	0	0	0	0	0	0	0.075	0	10	10	365	5	100
Mallard	0.0125	0.0125	0.0125	0.003	0.0065	0	0	0	0	0.00031	0.00031	0.06	10	215	2	1.2
Canada goose	0.025	0.025	0.025	0.0065	0.012	0	0	0	0	0.0041	0.0041	0.165	10	215	4	3.3
American coot	0.0125	0.0125	0.0125	0.003	0.0065	0	0	0	0	0.001	0.001	0.035	10	215	2	0.7
Bald eagle	0	0	0	0	0	0.25	0	0.25	0	0.0035	0	0.16	10	365	3	4.5
Osprey	0	0	0	0	0	0.3	0	0	0	0	0	0.08	10	365	3	1.5

[a] Intake rates are the sum of rates for below-ground and above-ground vegetation, which are assumed to be equivalent

Exposure parameters were taken from the following:

Intake rates: Biota—deer mouse, vole, shrew, beaver, muskrat (*USEPA* 1993a, 1994)

—mink, osprey, bald eagle (*USEPA* 1993a)

—deer, mallard, American coot (*USEPA* 1993a)

Soil and sediment—all species (Beyer and Miller 1990; Beyer *et al.* 1994)

Water—all species (*USEPA* 1993a,b)

Exposure duration: Deer mouse, vole, shrew, muskrat, beaver (*USEPA* 1993a; Nolet *et al.* 1994)

Mallard, goose, coot, bald eagle, osprey (*USEPA* 1993a; Terres 1980)

Mink, deer (*USEPA* 1993a; Nowak 1991)

Body weight: Mammals (*USEPA* 1993a, 1994; Nowak 1991)

Birds (*USEPA* 1993a; Terres 1980)

Absorption: Small mammals (Pascoe *et al.* 1994a)

Semi-aquatic mammals, deer, avian species (Friberg *et al.* 1986)

birth weight and litter size (Schroeder and Mitchener 1971). Additional chronic feeding studies with mice have reported a range of NOAELs from 1 to 57 mg/kg-day (*ATSDR* 1992b). In rats, a NOAEL of 12.5 mg/kg-day for embryotoxic effects was observed in a feeding study over the pregnancy period (Machemer and Lorke 1981). Another study with rats exposed to Cd salts in a feeding study over three months found a NOAEL at about 3.5 mg/kg-day (30 ppm in diet) for changes in behavior, weight, blood chemistry, liver and kidney function, and histopathology (Loeser and Lorke 1977). No studies were found on exposures of semi-aquatic mammals or deer to Cd.

In birds, effects from chronic Cd exposure typically include growth retardation, anemia, and testicular damage (Eisler 1988b). Avoidance of food was observed with American black ducks (*Anas ruripes*) exposed to Cd at 4 mg/kg in the food source (Eisler 1988b). Mallard ducklings fed Cd at 0.8 mg/kg-day (20 ppm in diet) for 12 weeks showed altered blood chemistry and kidney lesions (Eisler 1988b), whereas adults fed up to 8 mg/kg-day showed no effects. No studies were found on exposures of predatory birds to Cd.

Copper: Copper is an essential nutrient as an enzyme component, with dietary requirements for most animals estimated at 8 to 17 mg/kg-day, which is supported by a feeding study of rats with a NOAEL at 7.9 mg/kg-day (*ATSDR* 1992c). In conflict with these recommendations, however, feeding studies with mice have observed a decrease in body weight gain at 4.2 mg/kg-day (Massie and Aiello 1984). In a one-year feeding study with minks, a NOAEL for effects of Cu on reproductive systems, blood chemistry, and weight gain was observed at 7.5 mg/kg-day (50 ppm in diet), with a LOAEL at 15 mg/kg-day (Aulerich *et al.* 1982). No studies were found to develop toxicity values for exposures of deer or birds to Cu.

Zinc: Zinc is an essential nutrient for higher animals, and toxicity values are generally greater than values for non-essential metals. For example, no effects have been observed in chronic feeding studies at 55 and 104 mg/kg-day for rats and mice, respectively (*ATSDR* 1992d). In a six-month feeding study with ferrets, a LOEL for Zn was found at 142 mg/kg-day (500 ppm in diet), where a decrease in caeruloplasmin oxidase activity was observed with no other effects on blood chemistry or histopathology, and no observed clinical poisoning symptoms (Straube *et al.* 1980). Exposure of minks (*Mustela vison*) to Zn at an estimated daily intake of 16 mg/kg-day (121 ppm in diet) for 73 days resulted in digestive problems, with a NOAEL estimated at 3.5 mg/kg-day (Mejborn 1990).

No studies were found on exposures of deer to Zn. In a study of weanling horses fed Zn in the diet for 15 weeks, a NOAEL was estimated at a dose of 9 mg/kg-day, with a LOAEL for lameness at 35 mg/kg-day (Eisler 1993). Effects on hepatic and renal systems were observed in sheep fed Zn at 18.6 mg/kg-day (*ATSDR* 1992d).

Mallards fed Zn in the diet at an estimated dose of 125 mg/kg-day (3,000 ppm in diet) for 60 days showed leg paralysis and decreased food consumption (Eisler 1993). A study of three-day-old Pekin ducks (*Anas platyrhynchos*) fed Zn at 100 mg/kg-day (2,500 ppm in diet) for 56 days showed degeneration of the pancreas (Eisler 1993). No studies were found on exposures of predatory birds to Zn. In a nine-month study of domestic breeding hens, a NOAEL was estimated at 4 mg/kg-day (94

Table 5. Comparison of small mammal daily dose with toxicity values

Chemical	Receptor species	Calculated daily dose (mg/kg-day)	Toxicity values[a] (mg/kg-day)	Basis of toxicity value[b]	References
Arsenic[c]	Vole	0.092	0.5	Mouse LOAEL, reduced litter sizes	Schroeder & Mitchener 1971; Eisler 1988a
	Deer mouse	0.041	2.3	Rat NOAEL	*ATSDR* 1992a
	Shrew	0.191	5	Guinea pig NOAEL	Eisler 1988a
Cadmium	Vole	0.016	1–57	Range of mouse NOAELs	*ATSDR* 1992b
	Deer mouse	0.016	12.5	Rat NOAEL, reproductive study	Machemer & Lorke 1981
	Shrew	0.282	3.5	Rat NOAEL	Loeser & Lorke 1977
Copper	Vole	0.318	4.2	Mouse LOAEL, decreased weight gain	Massie & Aiello 1984
	Deer mouse	0.226			
	Shrew	2.065	7.9	Rat NOAEL	*ATSDR* 1992c
Zinc	Vole	1.374	104	Mouse subchronic NOAEL	*ATSDR* 1992d
	Deer mouse	1.181	55	Rat subchronic NOAEL	*ATSDR* 1992d
	Shrew	15.630			

[a] Surrogate species toxicity values. Toxicity values are not assigned to the receptor species on the same line, but were selected as representative of lower end NOAELs and LOAELs for the receptor group

[b] All data are from chronic feeding studies, except where noted as subchronic or a multigenerational reproductive study. NOAEL: No Observed Adverse Effect Level; LOAEL: Low Observed Adverse Effect Level, followed by observed effect at LOAEL dose

[c] Daily doses of As are to a mix of inorganic and organic forms; toxicity data are from studies on inorganic As exposures

ppm in diet), with a LOAEL for immunosuppression in young progeny at 7.6 mg/kg-day (Eisler 1993).

Risk Characterization

Comparisons of exposure data to the suites of toxicity values for the five receptor groups are presented in Tables 5-8. In general, daily doses of all chemicals were highest for the masked shrew and muskrat, which reflects the high invertebrate intake rate for the masked shrew per body weight and the high intake of emergent macrophytes by the muskrat.

For mammalian receptors, all estimated daily doses for the metals and As were within the ranges of toxicity values in Tables 5 and 6. Inclusion of uncertainty factors to the toxicity values, however, results in a number of exceedances of the lower range values. For example, assuming that an uncertainty factor of ten is appropriate to account for extrapolation between species and from a LOAEL to a NOAEL, adjustment of the mouse LOAEL for reduced litter size (0.5 mg/kg) results in exceedances by the daily doses of As for most small and semi-aquatic mammals at the site (up to four-fold for the shrew and muskrat). The estimated dose of As to deer is also slightly greater than its surrogate toxicity value (Table 6). Since it is likely that a major portion of the daily dose of As to the wetland receptors is in an organic form in food items, comparisons to a toxicity value for the more toxic inorganic form of As can be considered an overestimation of risk.

Estimated Cu and Cd doses to small and semi-aquatic mammals were below the respective suites of toxicity values (Tables 5 and 6), including consideration of uncertainty factors described above for As. The masked shrew is an exception, where the estimated intake of Cu exceeds the toxicity values when adjusted by uncertainty factors. Cd concentrations in kidneys of voles at the site were previously measured at an average of 0.7 mg/kg wet weight (Pascoe *et al.* 1994a), which is well below the critical toxic level of 120 mg/kg for vole or shrew kidney (Hunter *et al.* 1987; Ma *et al.* 1991). This large difference between the measured concentration of Cd in kidney and the toxic concentration threshold suggests that a similar large difference should be expected between the calculated dose and the surrogate toxicity values adjusted by uncertainty factors. The large difference further suggests that the food chain model may overestimate risks to the shrew. Estimated doses of Cd, Cu, and Zn for semi-aquatic mammals and deer are below their respective suites of toxicity values, except for muskrats where the daily intake of Zn exceeds the mink NOAEL by seven-fold when adjusted by a ten-fold uncertainty factor.

Potential health risks to waterfowl and birds of prey exposed to As, Cu, and Zn at the wetland are not suggested from this food chain model, since estimated intakes for these receptors are below the ranges of toxicity values (Tables 7 and 8), inclusive of uncertainty factors. Although Cd daily intakes for waterfowl were estimated to be below the suite of toxicity values, the average Cd concentration of 9 mg/kg measured in the waterfowl food times at the wetland exceeds a feed avoidance concentration of Cd at 4 mg/kg (Eisler 1988b).

The maximum concentrations of metals and As in sediment and emergent vegetation samples at the site were found in depositional areas of the wetland such as the oxbow of Railroad Slough (RRS) shown in Figure 2, where values ranged from two to four times the site-wide average concentrations. If muskrats consumed only emergent vegetation, water, and sediments from the higher contaminated depositional areas, estimated daily dose of metals and As would be two to three times the site-wide averages. These higher doses are still within the ranges of toxicity values for metals and As for semi-aquatic mammals (Table 6), but exceed the lower ends of the As and Zn ranges, particularly when adjusted with uncertainty factors.

Discussion

The initial phase of the food chain analysis for Milltown Reservoir consisted of screening level exposure modeling and risk assessment. Modeling was based on single point estimates of

Table 6. Comparison of semi-aquatic mammals and deer daily dose with toxicity values

Chemical	Receptor species	Calculated daily dose (mg/kg-day)	Toxicity values[a] (mg/kg-day)	Basis of toxicity value[b]	References
Arsenic[c]	Beaver	0.060	(0.5–5.0)	Small mammal values	see Table 5
	Muskrat	0.222			
	Mink	0.020			
	Deer	0.095	0.08	Lamb NOAEL	Eisler 1988a
Cadmium	Beaver	0.018	(1–12.5)	Small mammal values	see Table 5
	Muskrat	0.163			
	Mink	0.004			
	Deer	0.016	(1–12.5)	Small mammal values	see Table 5
Copper	Beaver	0.664	7.5	Mink NOAEL	Aulerich *et al.* 1982
	Muskrat	0.417			
	Mink	0.148			
	Deer	0.339	(4.2–7.9)	Small mammal values	see Table 5
Zinc	Beaver	0.660	3.5	Mink NOAEL	Mejborn 1990
	Muskrat	2.415	142	Ferret LOEL, effect on enzyme activity	Straube *et al.* 1980
	Mink	0.910			
	Deer	1.438	9	Horse NOAEL	Eisler 1993
			18.6	Sheep LOAEL, hepatic and renal effects	*ATSDR* 1992d

[a]Receptor and surrogate species toxicity values. Toxicity values are not assigned to the receptor species on the same line, but were selected as representative of lower end NOAELs and LOAELs for the receptor group. The values for horse, sheep, and lamb are intended for comparison with deer daily dose

[b]All data are from chronic feeding studies, except where noted as subchronic or a multigenerational reproductive study. NOAEL: No Observed Adverse Effect Level; LOAEL: Low Observed Adverse Effect Level, followed by observed effect; LOEL: Low Observed Effect Level for effect on enzyme activity

[c]Daily doses of As are to a mix of inorganic and organic forms; toxicity data are from studies on inorganic As exposures

Table 7. Comparison of waterfowl daily dose with toxicity values

Chemical	Receptor species	Calculated daily dose (mg/kg-day)	Toxicity values[a] (mg/kg-day)	Basis of toxicity value[b]	References
Arsenic[c]	Mallard	0.107	1.25	Mallard duckling NOAEL	Whitworth *et al.* 1991
	Can. goose	0.088	4.2	Mallard NOAEL, reproductive study	Stanley *et al.* 1994
	Am. coot	0.195	4.2	Mallard duckling NOAEL	Camardese *et al.* 1990
Cadmium	Mallard	0.167	0.8	Mallard duckling LOAEL	Eisler 1988b
	Can. goose	0.130			
	Am. coot	0.288			
Copper	Mallard	0.304	NA		
	Can. goose	0.324			
	Am. coot	0.625			
Zinc	Mallard	1.557	125	Mallard LOAEL, paralysis	Eisler 1993
	Can. goose	1.447	100	Pekin duck LOAEL, pancreatic toxicity	Eisler 1993
	Am. coot	3.001			

[a]Receptor and surrogate toxicity values. Toxicity values are not assigned to the receptor species on the same line, but were selected as representative of lower end NOAELs and LOAELs for the receptor group

[b]NOAEL: No Observed Adverse Effect Level; LOAEL: Low Observed Adverse Effect Level, followed by observed effect

[c]Daily doses of As are to a mix of inorganic and organic forms; toxicity data are from studies on inorganic As exposures

NA: Not available

exposures to site-wide metals and As present in the wetland soils, sediments, water, vegetation, and lower trophic food sources at the site, and risk assessment consisted of comparisons of average daily doses to a suite of toxicity data. The absence of substantial exceedances of the suites of toxicity indices by any chemical dose suggests that major risks to wildlife at the wetland are not expected from the exposures.

This conclusion is consistent with results of biological assessment studies that were performed at the wetland in support of the overall ecological risk assessment program. Although subtle or chronic effects were observed in some of the laboratory and *in situ* toxicity tests (e.g., earthworm and root elongation bioassays), acute or overt expressions of toxicity were not observed (Linder *et al.* 1994). In addition, the assumption that absorption fractions of 2.5% and 10% for exposures of semi-aquatic mammals, deer, and birds to metals and As in consumable substances may be overly conservative, given that an absorption-elimination factor for small mammals was found to be less than 0.1%.

To place the food chain analysis results in perspective with

Table 8. Comparison of predatory bird daily dose with toxicity values

Chemical	Receptor species	Calculated daily dose (mg/kg-day)	Toxicity values[a] (mg/kg-day)	Basis of toxicity value[b]	References
Arsenic[c]	Bald eagle	0.006	9.1	Chicken NOAEL	Eisler 1988a
	Osprey	0.003			
Cadmium	Bald eagle	0.002	(0.8)	Waterfowl value	see Table 7
	Osprey	0.003			
Copper	Bald eagle	0.072	NA		
	Osprey	0.033			
Zinc	Bald eagle	0.456	4	Chicken NOAEL, reproductive study	Eisler 1993
	Osprey	0.527			

[a] Surrogate species toxicity values
[b] NOAEL: No Observed Adverse Effect Level
[c] Daily doses of As are to a mix of inorganic and organic forms; toxicity value is from a study on inorganic As exposure
NA: Not available

the ecology of the wetland, a wildlife survey and vegetation community survey performed during the wetland delineation found a lack of population or community-level impacts in terrestrial habitats at the site (*USFWS* 1991; Linder *et al.* 1994). In the aquatic environment, although metals and As concentrations are elevated in sediment invertebrates of the wetland, no evidence was found of adverse effects on population or reproductive success indices of waterfowl that consume them (*USFWS* 1991; Linder *et al.* 1994). Similarly, muskrat exposures to metals and As at the site are largely driven by their high consumption rate of cattail tubers per body weight. Yet, evidence of a viable muskrat population was also observed at the wetland (Johns 1987; *USFWS* 1991).

Following a weight-of-evidence approach to characterizing risks, the food chain analysis, bioassessment studies, and the ecological surveys support a conclusion that site-wide risks to higher trophic level terrestrial and semi-aquatic organisms from the presence of metals and As at the wetland can be characterized as minor, and that the calculated daily doses to the receptor species on a site-wide basis are conservative. Minor impacts are defined as affecting a specific group of localized individuals within a population, but not affecting other trophic levels or the population itself (Duinker and Beanlands 1986). Results of the muskrat exposure analysis and field observations suggest that higher than average chemical concentrations in sediment depositional areas also pose a minimal risk to wetland wildlife populations. Based largely on the results of the risk analyses, interim remedial plans for the site are limited to monitoring of sediments in depositional areas of the wetland.

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