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Uptake and Trophic Transfer of Barium in a Terrestrial Ecosystem

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At an industrial site in central Virginia, organochlorine solvents and inorganic compounds with the potential to adversely affect wildlife have been released into the environment as a consequence of past industrial activities and practices. In the course of a ecological risk assessment for the site, soil, surface water, vegetation, insect, fish, and small mammal tissues were analyzed to ascertain whether these contaminants were bioavailable and present in the food chain. Although organochlorine solvents were found in the soil, none were found higher in the food chain. Of the inorganic compounds for which chemical analyses were performed, only barium was found at above detection limits at several level trophic levels. Four hypotheses were formed to investigate the behavior of barium in the terrestrial ecosystem at this site, as follows:

(1) Barium has high assimilation efficiencies and low depuration rates in mammalian receptors.
(2) Barium exhibits high bioaccumulation and / or bioconcentration factors and a potential for biomagnification.
(3) Barium has a low toxicity that would allow its accumulation in various terrestrial receptors without adverse effects that could hinder such accumulation, and/or
(4) Barium is being released from a persistent source that would provide the chronic exposure required to force its steady accumulation in terrestrial receptors.

To assess these hypotheses, measured tissue concentrations in a variety of terrestrial receptors were applied to a food chain model in order to estimate site-specific intake and loss dynamics and bioaccumulation potential of this element in a terrestrial food chain. Extant literature data on the occurrence of barium in soil, plant, and animal tissues, as well as information on barium ecotoxicology, are also provided to assist with this assessment.

MATERIALS AND METHODS

The site is located in central Virginia, on the banks of the James River, near Lynchburg, Virginia. Plant communities represented at the site are those typical of the Eastern Piedmont Province mesic uplands and floodplains with varying degrees of disturbance and development. Areas in the floodplain contain different associations than the mesic forest reflecting the higher soil-moisture content. Floodplain forest dominants typically include silver maple (*Acer saccharinum*) and sycamore (*Platanus occidentalis*). The floodplain forest contains numerous patches of grassland habitat and forest edge habitat that have been created by construction, development, and landscaping activities at the site.

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Ground-dwelling small mammals living in areas with known metal contamination of soil generally show elevated body burdens of metals (Ma et al. 199; Pascoe et al. 1994). Small mammals were trapped at 3 sampling units from July 18 to July 22, 1994. in the floodplain habitats of the site. A total of 100 Sherman live traps (7.6 by 7.6 by 25.4 cm) were baited with a mixture of rolled oats and peanut butter and deployed among the three sampling units (approximately 30 traps per unit). Traps were set in late afternoon or early evening and checked the following morning. All traps remained in-place at each sampling unit for four consecutive nights. Trapping resulted in a total collection of 11 white-footed mice (*Peromyscus leucopus*) and 7 hispid cotton rats (*Sigmodon hispidus*). Specimens were identified, weighted, sacrificed by induced hypoxia; frozen whole in sealed, cleaned, glass containers; packed in dry ice; and shipped to the laboratory for analysis. Soil and vegetation samples were collected concurrently (time and location) with each small mammal sample; additional soil and surface water samples were also collected in each sampling unit. Vegetation samples were taken from a variety of potential small mammal food items, including: various grasses partridge pea (*Cassia fasiculata*), cattails seed pods (*Typhus* sp.), *Lespedza* sp., vineweed pods and flowers blackberry fruit, wooley mullin seed pods Queen Ann's Lace, wild onion, buckhorn plantain seed heads, Phlox flowers, and horse nettle flowers.

One terrestrial insect sample was also obtained, consisting of a composite of several ground-dwelling beetles and termite larvae. Thirteen individual sunfish (*Lepomis* sp.) specimens were caught in two onsite ponds and, because of their small size, pooled into four samples. Small mammal, insect, and fish samples were analyzed for total body barium content by Savannah River Laboratories, Charleston, South Carolina. Soil, water, and vegetation samples were analyzed for barium by Babcock and Wilcox Laboratories. Lynchburg, Virginia. Concentrations below the limit of detection entered calculations as one-half the detection limit.

A 1000 iteration Monte Carlo analysis using a Latin hypercube strategy (implemented using CrystalBall® Version 3.0 added in to Excel® Version 5.0) was used to compute values and associated distributions for depuration, BCF, and BAF parameters based on the models given below. Parameter distributions are presented as: normal = [norm(mean, standard deviation)], lognormal = [lognorm(mean, standard deviation], and triangular = [tri(minimum value, likeliest, maximum value)]. A sensitivity analysis of the various parameters was performed using features included with the CrystalBall® software.

Measurements of contaminant residues in abiotic environmental media (surface water and soil) and receptors (vegetation, insects fish, small mammals) were used to estimate bioconcentration (BCF) and bioaccumulation (BAF) factors for barium, as follows: BCF = C_i / EC_{sw} and BAF = C_i / EC_{ss} where: EC_{ss} = environmental concentration of contaminant in surficial soil, ppm; EC_{sw} = environmental concentration of contaminant in surface water, ppm. In the BCF expression, C_i is the barium concentration in fish tissue and in the BAF expression it is the barium concentration in vegetation, insect, or small mammal tissues. The distributions for EC_{sw} EC_{ss} and C_i were lognorm(mean, standard deviation) with values as shown in Table 1.

The following equation was used to estimate barium dose to white-footed mouse and hispid cotton rat from three pathways: (a) consumption of contaminated food items (plants and insects), (b) consumption of surface water, and (c) incidental ingestion of soil, as follows:

$$D = \left[(Q_i \times EC_{sw}) + \sum_{j=1}^{k} (C_{ij} \times F_{ij})) + (EC_{ss} \times F_{ss}) \right] \times W_i^{-1} \tag{1}$$

where: D = estimated applied daily dose, mg/kg-d; C_{ij} = contaminant concentration in jth food item of ith receptor diet, mg/kg; F_{ij} = fraction of jth food item in diet of ith receptor, unitless; R_i = food intake rate of jth receptor, wet diet, kg/d; Q_i = water intake rate of ith receptor, wet diet, L/d; F_{ss} = dietary fraction of incidentally ingested soil, unitless; W_i = body weight of ith receptor, kg; k = number of food items, unitless.

Water and food intake rates were estimated using allometric relationships based on body weight as follows: $Q_i = 0.099 \times W^{0.90}$ and $R_i = 0.054 \times W^{0.9451}$ (EPA 1993). Body weights for white-footed mice and hispid cotton rats were determined from site captures and were taken as norm(0.0307 kg, 0.006 kg) for mice and norm(0.102 kg, 0.013 kg) for hispid rats.

Barium absorption has been estimated to be approximately 5% in adult humans (Harrison et al. 1967). Owen (1990) estimated a mean absorption value of 0.1, while ICRP (1973) reported that approximately 72% of ingested barium is eliminated via fecal excretion following oral exposure. These data suggested an ingestion absorption factor (α_{ing}) distribution of tri(0.05, 0.1, 0.28).

White-footed mice are omnivorous, feeding on nuts, seeds, fruits, beetles, caterpillars, and other insects (Burt and Grossenheider 1964). Hispid cotton rats are also omnivorous, consuming vegetation, insects and small animals including ground-nesting bird eggs and chicks (Burt and Grossenheider, 1964). Based on this information and site-specific field observations, primary food items in both species were assumed to consist of equal portions of vegetation and insects, including some incidental ingestion of soil. Incidental ingestion of soil was assumed to be a constant 0.025 of the total dietary fraction for both species (EPA 1993: Garten 1980). This allowed the insect dietary (F_{insect}), vegetation dietary (F_{veg}). and incidental soil (F_{ss}) fractions for both species to be fixed at 0.5, 0.475, and 0.025, respectively.

Depuration rates for small mammals for a given contaminant can be estimated using measured tissue residue levels, estimates of applied daily dose, and estimates for a barium absorption factor. The depuration rate for mice and rats was then estimated with the following equation:

$$k_{el}^* = (D \times \alpha_{ing}) / C_i \qquad (2)$$

where: k_{ei}^* = estimated contaminant-specific depuration rate for the Rh receptor, d^{-1}; α_{ing} = estimated ingestion absorption factor for barium, unitless; C_i = measured contaminant whole body burden in ith receptor, ppm.

RESULTS AND DISCUSSION

Site soils exhibited a mean barium concentration of 104.2 ppm ± 9.5 mean standard error (SE) (Table I), below the reported range of means of 265 to 835 ppm (10 to 3000 ppm total range) for barium in soils of the United States (Kabata-Pendias and Pendias 1984). Barium in soils may be mobilized to various extents under oxidizing and acid, neutral, alkaline, or reducing conditions and, once mobilized, is easily precipitated as soluble sulfates and carbonates (Kabata-Pendias and Pendias 1984). Although the chemical analyses were for total recoverable metals, it is most likely that barium was present in soils at the site as either sulfates or carbonates.

The barium content range for plants is reported as 1 to 198 ppm (dry weight); being highest in leaves of cereal and legumes and lowest in grains and fruits (Kabata-Pendias and Pendias 1984). Mean concentrations (dry weight) of barium in ferns (exclusive of horsetails or clubmosses) and angiosperms have been reported as 8 ppm and 14 ppm, respectively (Bowen, 1966). Site vegetation exhibited a mean barium concentration of 29.8 ppm ± 13.7 SE (Table 1). Plants may take up barium quite easily from acid soils, but there are few reports on toxic barium concentrations in plants (Kabata-Pendias and Pendias 1984). A range of 1 to 2% (dry weight) barium in plants has been reported as a toxic concentration, while 220 ppm (ash weight) is reported as moderately toxic (Kabata-Pendias and Pendias 1984).

TABLE 1. Summary of Site-Specific Barium Concentrations

MEDIA	Number of Samples	Mean Concentration (ppm)	Standard Deviation	Mean Standard Error
Soils [a]	28	104.2	50.3	9.5
Surface water (total)	33	0.07	0.1	0.02
Surface water (dissolved)	33	0.07	0.1	0.02
Vegetation [a]	13	29.8	49.5	13.7
Terrestrial invertebrates [b]	1	16.0	---	---
Sunfish	4	2.1	1.1	0.5
White-footed mouse	11	1.5	0.6	0.2
Hispid cotton rat	7	2.0	0.9	0.3

[a] At a minimum, a vegetation and a soil sample were collected concurrently with each small mammal sample.

[b] Composite of several individuals of ground-dwelling insect species.

As a group II A element, barium is concentrated by bone, the choroid of the eye, and the lung of mammals (Friberg et al. 1986). Mean concentrations (dry weight) of barium in mammalian tissues, other than bone, range from a low of <0.007 ppm in liver to a high of 0.67 ppm in lung (Bowen 1966). Small mammals resident onsite exhibited a mean whole body barium concentration of between 1.5 ppm ± 0.2 SE and 2.0 ppm ± 0.3 SE for mice and rats, respectively (Table 1). These values are below both the mean concentration (dry weight) of 2.3 ppm barium reported in mammalian tissue and the mean concentration of 6.9 ppm reported in bone (Bowen 1966).

In experimental animals: chronic exposure to bioavailable barium leads to disturbances in cardiovascular function and regulation (Perry et al. 1989) and prolonged contraction of all forms of muscle, probably by direct action on chromaffin cells, possibly by displacing calcium (Underwood 1971). Tardiff et al. (1980) reported an acute oral LD_{50} for barium chloride of 220 ppm in weanlings and 132 ppm in adult rats. They exposed rats to doses ranging from 0 to ≈ 66.3 mg/kg-d in drinking water for up to 13 weeks. Although barium body burden increased with increasing dosage, no compound-related adverse effects were observed. The maximum tolerable level for barium in domestic animals has been estimated to be 20 ppm (NAS 1980). Opresko et al. (1994) report a rat oral NOAEL (for barium chloride) of 5.1 mg/kg-d, a computed white-footed mouse oral NOAEL (for barium chloride) of 13.5 mg/kg-d, and a domestic chicken oral NOAEL (for barium hydroxide) of 20.8 mg/kg-d.

In mice supplied with ≈ 0.8 mglkg-d (as barium acetate) in their basal drinking water, longevity was slightly reduced but weight was not significantly affected; there was no evidence of significant tumorigenisis (Schroeder and Mitchener 1975a). In another similar study, a dose of ≈ 0.3 mg/kg-d in drinking water had no significant effect on the growth of male rats but increased that of older female rats. Proteinuria occurred in males given barium to a greater extent than in the controls (Schroeder and Mitchener 1975b).

In rats supplied with 1, 10, or 100 ppm barium (as barium chloride) in their basal drinking water, those exposed to 10 ppm (average dose of 0.5 mg/kg-d) for 8 months and 100 ppm (average dose of 5.1 mg/kg-d) for 16 months demonstrated a significant increase in systolic blood pressure (Perry et al. 1989). After 4 and 16 months, the barium concentrations in heart, liver, and kidneys of control animals ranged from 0.007 to 0.022 ppm (wet weight); after 16 months, the aortic barium concentration of control rats averaged 0.12 ppm. After 4 months exposure to 5.1 mg/kg-d barium, the average renal barium concentration was 0.21 ppm; at 16 months it has risen to 1.1 ppm. The highest average tissue concentration observed was 1.8 ppm, found in the aortas of the maximally exposed group after 16 months of exposure (Perry et al. 1989).

Barium concentrations in plants collected onsite were below the level at which phytotoxic effects might be expected. Doses received by white-footed mice and hispid cotton rats at this site were estimated to be 3.1 mg/kg-d ± 0.1 SE and 2.5 mg/kg-d ± 0.1 SE, respectively. These doses are below the NOAEL values discussed above.

Based on samples of a variety of plant species, a site-specific bioconcentration factor for soil (dry weight) to plants (dry weight) was estimated as 0.4 ± 0.02 SE. This is within the same order of magnitude as an elemental barium soil-to-plant concentration factor of 0.15 for non-reproductive vegetative plant materials (Baes et al. 1984) and the barium biological absorption coefficient of 0.66 (Dobrovolsky 1994). Site-specific BAFs, based on the ratio of barium concentrations in soil to whole body concentrations in various receptors, were computed to be as follows soil/terrestrial insect, 0.2 ± 0.002 SE; soil/white-footed mouse, 0.02 ± 0.0004 SE; soil/hispid cotton rat, 0.02 ± 0.0005 SE. These last two values compare favorably with a maximum average barium BAF of 0.02 calculated using rat data presented by Perry et al. (1989). A site-specific mean bioconcentration factor for a pooled sample of one species of fish was estimated, based on dissolved barium concentrations in surface water of 0.07 ppm ± 0.02 SE and fish whole body concentrations of 2.1 ppm ± 0.5 SE, to be 129.0 L/kg ± 13.5 SE. This is a BCF value much less than that for inorganic mercury (≈ 5500). close to that for copper (≈ 200). and greater than that for either antimony (≈ 1) or arsenic (≈ 44) (EPA, 1986).

The white-footed mouse and hispid cotton rat mean depuration rates were estimated to be 0.4 d^{-1} ± 0.01 SE and 0.2 d^{-1} ± 0.01 SE, respectively. These values indicate that barium is lost from these receptors at a fairly rapid rate. These rates are an order of magnitude higher than those for persistent. lipophilic compounds such as polychlorinated biphenyls, for which a geometric mean k_e value of 0.08 d^{-1} has been reported for mammals (Macintosh et al. 1992). Sensitivity analysis indicated that estimated dose. measured plant tissue concentration, and measured mouse tissue concentration made the greatest contribution (≈ 75%) to variance in the estimate of depuration while, in turn, measured plant concentration made the greatest contribution (≈ 70%) to variance in the estimate of dose.

With respect to the four hypotheses posed for this study, our findings wereas follows:

(1) Estimates of assimilation and depuration support the view that barium is generally poorly bioavailable in this system, that much of the barium ingested is eliminated fairly rapidly (high depuration rates), and that only a small fraction of the total barium dose is eventually sequestered in the organism (low assimilation efficiency).
(2) Barium appears capable of bioconcentration and bioaccumulation in terrestrial and aquatic ecosystems. However. barium bioaccumulation factors are low for all terrestrial receptors examined. In addition, with barium concentrations decreasing by approximately an order of magnitude with each successive increase in trophic level, there is no evidence of biomagnification.
(3) Although barium was detected at all levels in the food chain, it was not found at

concentrations which, based on the limited ecotoxicological data available, could be considered capable of causing adverse effects in plants or wildlife. Such low toxicity would assist its slow accumulation in various terrestrial receptors without adverse effects that could hinder such accumulation.

(4) Barium was not used in any industrial processes at the site; however, the site is immediately adjacent to a large non-operational metal foundry which could have been a historic source for anthropogenic barium. The site overlays a karst formation containing higher than average levels of barium and barite has been mined in the area. Erosion of this material from outcrops and its subsequent deposition in the floodplain could be a primary, and continuing, source for non-anthropogenic barium. This source could provide the chronic exposure required to force its steady accumulation in receptors.

These results suggest rejecting the first two hypotheses and acepting the latter two. On this basis, we conclude that the uptake. transfer, and presence of barium in several trophic levels at this site most likely results from a combination of site-specific conditions and barium's low environmental toxicity. Sensitivity analysis suggests that the depuration, bioaccumulation, and bioconcentration factors calculated in this study are highly dependent on site-specific conditions and thus may be applicable only to receptors at the site. In addition, because the data were generated during a single summer sampling event, their interpretation may be limited to summer conditions only. Thus, while these results are instructive and provide a perspective on barium behavior for this specific ecosystem, their extrapolation to terrestrial ecosystems in general is cautioned.

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