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Concentrations and Discrimination of Chemically Related Metals in a Food Chain

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Concentrations of the related elements calcium, strontium, barium, and lead were determined in soil extract, consumer stomach contents, and consumers in lead polluted and unpolluted areas. Discrimination against the nonessential metals relative to the nutritious metal calcium, as the metals were transferred through a trophic pathway was determined. Discrimination of metals varied systematically as a function of degree of nonessential element similarity to calcium. The existence of systematic trends of discrimination may facilitate the assessment of natural levels of some toxic elements (e.g. lead) in organisms.

INTRODUCTION

Considerable research has been conducted in recent years on the movement of trace metals in the environment and factors influencing uptake and location of metals in organisms. This research has been, in part, a response to increasing heavy metal pollution in ecosystems and the recognition that human health and the production of organic matter in ecosystems is influenced by the abiotic and biotic cycles of chemical elements.

Elements which are biotically important can be classified into two main categories: (1) dietary essentials present in macro amounts and, (2) trace elements. The trace elements can be further divided into three groups: (1) dietary essentials, (2) possible essentials and, (3) nonessentials. Some trace elements are often sub-divided into a group known as toxic elements

(Underwood, 1977). In order to understand the behaviour of trace elements in organisms, it must be recognized that most of the required trace elements serve a variety of functions which depend upon their chemical form, combination, and location in the body. The functional forms of these elements and their concentrations must be maintained within certain limits if the functional and structural integrity of tissues is to be preserved and growth, health, and fertility of the organism is to remain unimpaired. An area of research which has not been sufficiently examined is the extent to which nonessential or toxic metal distribution is a function of the degree of chemical and physical similarity to essential nutritious metals.

Theory suggests that toxic metals may be transferred through biological systems, in part, because of the degree in which they are chemically and physically related to nutritious metals (Patterson, 1965). Nutritious metals are, by definition, related to other elements within the same chemical group of the periodic table of elements. For instance, the group I (alkali) metals show most clearly the effect of increasing atomic and mass number on chemical and physical properties. Examples of systematic change in chemical and physical properties with increasing mass are: (1) decrease in solubility and ionization potential and, (2) increase in ionic radii and ionic mobilities. The group II (alkaline earth) metals also form a closely allied series in which the chemical and physical properties of the elements and their compounds vary systematically with increasing atomic number. When these groups of elements, and others, are examined within the periodic table, it is seen that many of the metals in the fourth period are nutrients for organisms. Chemically related metals in each group generally exist under this nutrient row whose physiological effects change in such a manner that the third metal down is usually toxic. Thus, the toxic row of elements usually begins with cesium in the position of the sixth period. The bonding characteristics of these metals within inorganic and biological systems change progressively from strongly ionic bonds in group I to strongly oriented coordinate bonds in group IV.

Various studies illustrate the concept that the distribution of nonessential and toxic metals may depend, in part, upon the similarity of the metals to their chemically related nutritious metal. Strontium, barium, and radium apparently are processed, to some extent, inadvertently along with calcium by organisms and are stored in major reservoirs of calcium (Comar *et al.*, 1956; Garner, 1972). Biochemical mechanisms regulate calcium homeostatically and directly, but operate passively on related nonessential metals as a consequence of environmental trace occurrences and, presumably, as a result of differences in chemical properties (Ericson *et al.*, 1979; Patterson, 1965). Although lead is not a member of the calcium group in the periodic table, it shows similarities to barium and calcium and is partially regulated by calcium metabolism (Settle and Patterson, 1980; Snowden and Sanderson, 1974).

Some research indicates that nonessential metals are discriminated against relative to related nutritious metals as the metals are transferred through biological systems. Alkaline earth metal concentrations were shown to increase in the order calcium > strontium > barium as the metals were transferred through food chains (Hardy *et al.*, 1969). Ratios of strontium/calcium, barium/calcium, cadmium/zinc, and mercury/zinc have been shown to decrease as the metals were transferred across placental membranes (Schulert *et al.*, 1969), and from plants to consumers (Lemons and Kennington, 1976). Competitive uptake by plants from soils occurs for the elements potassium, rubidium, and cesium, and the group calcium, strontium, and barium (Menzel, 1954). Competition between zinc, cadmium, and mercuric ions occurs in serum albumin (Perkins, 1961); competition between cadmium and zinc for metallothionein binding sites has also been demonstrated (Schroeder, 1967).

Although the above-mentioned studies suggest that discrimination or concentration of nonessential or toxic metals may partially depend upon the metals' similarity to chemically related nutritious metals, none of the studies, or others of which we are aware, have demonstrated whether, and to what extent, distribution of metals is due to qualitative or quantitative differences between the chemical and physical properties of the metals. In this study, we examine whether lead and other metals are transferred through a food chain and selected physiological systems as a function of degree in which they are chemically and physically related to the nutritious element calcium. We also examine whether the degree of chemical similarity between elements may be useful for determining if, and how, lead levels in certain organisms are elevated above natural levels.

METHODS

Changes in concentrations of physically and chemically related metals were determined as the metals were transferred through food chains. Because of chemical similarities between the alkaline earth metals, elements chosen for analysis were calcium, strontium, barium, and lead. Lead was included because it is a toxic metal and follows calcium through metabolic pathways (Patterson, 1965; Snowden and Sanderson, 1974).

Study site descriptions

Two locations which are similar with respect to soil, vegetative, and animal communities were chosen for sampling purposes. The Idaho National

Engineering Laboratory (INEL), Idaho, site is located at approximately 43°40' N latitude and 112°41' E longitude. The climate is typical of the cold desert biome of the western United States. The site is sparsely vegetated, and dominant plants are *Artemisia*, *Agropyron*, and *Chrysothamnus*. Existing levels of metals of interest are not significantly elevated above natural levels due to the activities of man, as the site is located considerable distances from urban and industrial sources of pollution (anonymous, 1975). The second location, near the Anaconda smelter in Montana, is located approximately 2.4 km northwest of Anaconda and 34 km northwest of Butte. Climate and vegetation are similar to that of the INEL site. Smelter operations have increased environmental levels of zinc, cadmium, lead, arsenic, and fluorides (Munshower, 1972).

Sample collection

Soil samples and mammal specimens (*Peromyscus maniculatus*) were collected from 10 sampling stations within each study location. A stratified random sampling technique was used, following the method of Poole (1974), to insure adequate sampling and still maintain the randomness essential to objective sampling. At each sampling point, 5 subsamples of soil were randomly taken from within 10 m of the point, and later mixed together in a mixermill to yield one homogeneous sample. Because previous studies (Munshower, 1972; Wallace *et al.*, 1971) showed that most elements are concentrated in the upper soil layers, soil samples were selected from the 0–10 cm layer. Soil was gathered with small stainless steel trowels, and mammals were collected with snaptraps. All samples were placed in clean double polyethylene bags and stored in a deep freeze until analyzed. Clean polyethylene gloves were worn to avoid sample contamination.

Samples and standard preparation

Standard stock solutions of calcium, strontium, barium, and lead were prepared from pure spectroscopic grade salts and dissolved in dilute distilled nitric acid. Standards of known concentration were made by further dilution of these stock solutions with 1 N ammonium acetate for soil samples and 5 N distilled nitric acid for stomach content and animal tissue samples. Standard concentrations were prepared to cover the ranges of element concentrations in samples to be analyzed.

Recommended procedures for extracting elements from soil were followed (Jackson, 1958). Eighty ml of 1 N ammonium acetate were added to 20 g soil samples in clean polyethylene bottles. Solutions were mechanically agitated for 60 minutes, poured into test tubes and stoppered,

and centrifuged for 10 minutes. The supernatant was decanted for elemental analysis. Ash weight of soil was determined as follows. Soil was placed in numbered platinum crucibles, weighed for wet weight, placed in a drying oven for 24 hours at 90°C, weighed for dry weight determination, and placed in a muffle furnace at 500°C for 24 hours. Samples were then weighed for ash weights.

Animal tissue (bone) and stomach contents were prepared for element analysis in the following manner. Element abundances in animals were determined by analysis of femur. The skin surrounding the legs, abdomen, and lower back was cut. The leg was flexed out of the skin and the remaining skin was cut away; the foot was cut off and discarded. The skinned leg was cut from the body at the pelvic cradle and muscles and ligaments were cut away from the femur, which was scraped clean for elemental determination. The stomach contents were collected from each animal by carefully cutting out the stomach and making a slit so that the contents could easily be collected. All bone and stomach content samples were placed in numbered platinum crucibles and weighed for wet weight. Drying was achieved by placing samples in a drying oven for 24 hours at 90°C. Samples were then weighed for dry weights, ashed in a muffle furnace for 24 hours at 500°C, and weighed for ash weights. Samples were next dissolved in hot distilled 5 N nitric acid, left for one hour, and centrifuged for 10 minutes. The supernatant was decanted for elemental analysis.

Analytical procedure

A Jarrell-Ash 3.4 m Ebert emission spectrograph with a spark discharge was used for element determinations. Modification of the sample electrode and vacuum cup technique has made the sensitivity and precision of this method very competitive with other analytical techniques for trace metals (Lyon, 1980). Approximately 2 ml of sample were pipetted into the sample cups. Because of differences in relative sensitivities between various spectral lines, soil and tissue samples were diluted as necessary by addition of 1 N ammonium acetate and 5 N distilled nitric acid, respectively. Sodium nitrate was added to each sample to give a concentration of 1 mg sodium per ml of sample solution. The addition of sodium nitrate in this concentration improves both the precision and the accuracy of this method by preserving the sample electrode shape, improving line intensities, and reducing background and band emissions. Vanadium was added as an internal standard to give a concentration of 5 mg per ml of sample solution. The densities of the appropriate analytical and internal standard lines were read with a microphotometer for each sample and standard. After the working curves were constructed the concentrations of the elements were

determined in the usual fashion (Ahrens and Taylor, 1961). Two determinations were made for each sample, and were averaged to give the sample value. For some lead determinations, atomic absorption spectrophotometry procedures were used. The atomic absorption spectrograph was custom made from commercially available parts. The analytical line used for lead was 2833 Å. Absorbance units for samples and standards were averaged from two and three determinations, respectively.

National Bureau of Standards (NBS) orchard leaves were analyzed in similar fashion to stomach contents in order to provide a measurement of accuracy and to provide a comparison between analytical methods. Seven determinations were made per element for each analytical technique; these were averaged to give the measured values. Calibrated reference standards for soil and mammal samples were not available from NBS. Comparison of NBS reported and measured element concentrations is given in Table I; no significant differences between NBS reported and measured concentrations were detected by use of the t-test.

TABLE I

Comparison of measured and NBS reported values for NBS standards ($\mu\text{g/g}$ dry weight)^a

	NBS reported values Orchard leaves		Measured values Orchard leaves
Ca	20,900 \pm 300	Ca	20,300 \pm 2,400
Sr	37	Sr	39 \pm 4
Pb	45 \pm 3	Pb	48 \pm 4 ^b
			49.2 \pm 4 ^c

^a Measured values are mean of seven replicas \pm standard deviation (SD)

^b Emission spectrograph

^c Atomic absorption

RESULTS AND DISCUSSION

The data in Table II show the element concentrations, reported in ash, for the INEL site samples. Total body burdens for elements were calculated from element concentrations in bone tissue according to standard methods described in ICRP (1959). Concentration factors for the elements are shown in Table III. Concentration factors are defined in this study as the concentration of an element in a tissue or organism of a higher trophic level divided by the concentration of that element in soil or tissue of a lower trophic level. The alkaline earth metals show a tendency to accumulate as

the metals are transferred from soil to stomach contents (plant) and soil to total body. Although the metals appear to accumulate through the trophic pathway, the nonessential alkaline earth metals and lead have smaller concentration factors than the nutritious metal calcium. Further, concentration factors decrease as the metals increase in atomic number and mass.

TABLE II

Alkaline earth metal concentrations for INEL site samples (mean $\mu\text{g/g}$ ash \pm SD)

Element	Soil	Stomach content	Total body burden ^a
Ca	1,318 \pm 63	85,422 \pm 5024	19,488 \pm 760
Sr	12.6 \pm 1.2	745 \pm 108	106 \pm 34
Ba	13.8 \pm 1.4	148 \pm 3	18.2 \pm 3.7
Pb	0.50 \pm 0.18	1.7 \pm 0.17	0.13 \pm 0.05

^a Body burdens calculated from ICRP (1959) Table 12.

TABLE III

Alkaline earth metal concentration factors for INEL site samples

Element	Soil \rightarrow stomach contents	Stomach Contents \rightarrow total body	Soil \rightarrow total body
Ca	64.8	0.22	14.8
Sr	59.1	0.14	8.5
Ba	10.8	0.12	1.3
Pb	3.5	0.07	0.26

Most researchers report metal concentrations in terms of the concentration of an individual metal in a sample. Because of differences among the physiological activities of chemically related metals, this traditional manner of reporting metal abundances may obscure important relationships. For example, when element concentrations are expressed as ratios of strontium/calcium, barium/calcium, and lead/calcium (Table IV), it is seen that respective element ratios are smaller for consumers compared to soil or plants. Nonessential and toxic metals apparently are discriminated against with respect to their chemically related nutritious metal calcium as the metals are transferred through the food chain.

TABLE IV

 μg of element per $10^6 \mu\text{g}$ of calcium for INEL site samples

Element	Soil	Stomach contents	Total body
Ca	1,000,000	1,000,000	1,000,000
Sr	9,559	8,721	5,470
Ba	10,470	1,741	934
Pb	379	20.6	6.8

A comparison of the degree of discrimination against strontium, barium, and lead relative to calcium can be made by examining observed ratios (O.R.) for the elements (Comar *et al.*, 1956). The O.R. is defined as:

$$\text{O.R.} = \frac{\text{nonessential element/calcium}_{(\text{sample})}}{\text{nonessential element/calcium}_{(\text{precursor})}} \quad (1)$$

where sample refers to element concentrations in a higher trophic level and precursor refers to element concentrations in a lower trophic level. An O.R. value of 1 indicates that there is no discrimination against the nonessential metal relative to calcium. A value of less than 1 indicates discrimination against the nonessential metal.

TABLE V

Alkaline earth metal observed ratios for INEL site samples

Element	Soil \rightarrow stomach contents	Stomach contents \rightarrow total body	Soil \rightarrow total body
Sr/Ca	0.912	0.627	0.572
Ba/Ca	0.166	0.536	0.089
Pb/Ca	0.054	0.328	0.017

Table V shows O.R. values for the INEL samples. It is interesting to note that although the concentrations of available strontium and barium in soil extract are approximately the same (Table II), the barium/calcium O.R. from soil to plant and soil to body is smaller than the strontium/calcium O.R. by a factor of 5.5 and 6.4, respectively. Likewise, although the concentration of lead in soil extract is less than that of strontium and barium, the lead/calcium O.R. from soil to plant and soil to animal is approximately 3.1 and 5.2 times smaller, respectively, than the barium/calcium O.R. Once strontium, barium, and lead are in the plants, the differences in uptake into

the body are less dramatic. The barium/calcium and lead/calcium plant to body O.R. values are, respectively, approximately 85% and 50% of the strontium/calcium O.R. Most discrimination against the nonessential and toxic metals therefore appears to occur between the soil and plants. The data also indicate that O.R. values decrease in the order strontium/calcium > barium/calcium > lead/calcium as the metals are transferred from one trophic level to another. These data are instructive because they demonstrate that not only are the nonessential and toxic metals discriminated against relative to their nutritious chemical analog calcium, but that the degree of discrimination increases as element atomic number and mass increases.

Element concentrations for Anaconda samples (Table VI) are, with the exception of lead, similar to those from the INEL site (Table II). In general, the ratios of strontium/calcium, barium/calcium, and lead/calcium in

TABLE VI

Alkaline earth metal concentrations for Anaconda site samples (mean $\mu\text{g/g}$ ash \pm SD)

Element	Soil	Stomach contents	Total body burden ^a
Ca	1,368 \pm 192	90,122 \pm 20,259	19,412 \pm 433
Sr	11.9 \pm 1.8	704 \pm 75	99.6 \pm 4.3
Ba	7.9 \pm 0.5	110 \pm 20	15.1 \pm 2.3
Pb	7.0 \pm 0.7	649 \pm 223	13.4 \pm 1.5

^a Body burdens calculated from ICRP (1969) Table 12.

TABLE VII

μg of element per 10^6 μg of calcium for Anaconda site samples

Element	Soil	Stomach contents	Total body
Ca	1,000,000	1,000,000	1,000,000
Sr	8,698	7,812	5,131
Ba	5,774	1,229	778
Pb	5,116	6,416	690

Anaconda samples decrease as the metals move through successive steps of the food chain (Table VII); this confirms the trend previously determined from INEL data (Table IV) that organisms discriminate against nonessential alkaline earth metals and lead in favor of calcium. The concentrations of lead in soil and plants, and the ratios of lead/calcium are elevated because of previously discussed lead pollution resulting from the Anaconda

smelter. Lead contamination of plants from a source such as the Anaconda smelter is primarily in the form of external contamination of leaf and vegetative surfaces (Hirao and Patterson, 1974; Little, 1973; Patterson, 1965). In fact, a comparison of washed and unwashed leaf samples from randomly collected plants in the Anaconda area, utilizing the method of Little (1973), indicated that approximately 85% of the measured lead content of plants was in the form of external surface deposits.

Soil to body O.R. values reflect the discrimination against metals that occurs as the metals are transferred from soil to plant and from plant to consumer. Calculations of barium/calcium and lead/calcium soil to body O.R. values for Anaconda samples yield values of approximately 0.13 for both barium and lead. Data from INEL samples (Table V) suggest that in unpolluted environments, O.R. values for lead/calcium should be less than those of barium/calcium. The adventitious contamination of lead on plants bypasses the physiological mechanisms of plants which purify calcium of lead, thereby increasing lead/calcium O.R. values; this consequently increases the body burden of lead in consumers. Although lead levels are elevated due to pollution of the Anaconda habitat, the data (Table VII) further demonstrate the strong tendency of discrimination against increasingly heavy metals. For example, the lead/calcium ratio of plants is 5.2 times greater than the barium/calcium ratio. The discriminatory mechanisms of consumers against lead relative to calcium have, nevertheless, reduced the lead/calcium ratio to approximately 88% of the barium/calcium ratio.

Although organisms utilize and retain strontium, barium, and lead less effectively than calcium, it is not certain whether this is due to qualitative or quantitative differences between the chemical and physical properties of the metals. Observed ratio values quantify the degree of discrimination against nonessential metals relative to calcium as the metals are transferred through the food chain or biological membranes. Therefore, a comparison of O.R. values with a measure of element chemical and physical similarity to calcium should indicate whether, and to what extent, degree of discrimination is a systematic function of quantitative differences between the metals.

The differences of behavior among calcium, strontium, barium, and lead in biological systems is undoubtedly due to many factors. These may include differences in solubility and diffusion constants, differential abilities of biological chelating agents to chelate the various elements, differences in binding capacity of proteins for the elements with different ionic and effective radii, and specificity of transport systems or hormone regulation. The relative importance of these factors cannot, of course, be ascertained in a general study of this type.

However, studies have shown that certain physical and chemical para-

meters of related elements seem to be more important regarding elemental distribution than others. Distribution of elements and biological fractionation of isotopes are influenced by mass differences when element movement depends upon diffusion (Bowen, 1960; Passow *et al.*, 1961). When enzyme or transport systems control element movement, ionic and hydrated or effective radii differences become important (Passow *et al.*, 1961; NRC, 1972). When movement depends upon solubility, solubility constants are of obvious importance (Nelson and Rust, 1966). Because of the above considerations, the following parameters for calcium, strontium, barium, and lead were used to measure the degree of similarity between the elements. These parameters were mass, solubility of the chloride, ionic radius, and effective radius. Parameter values for each element were obtained from Durrant and Durrant (1962).

The degree of similarity (C_j) of element (j) to calcium, using (i) parameters for each element, equals

$$C_j = \sum_{i=1}^m \hat{N}_{ij} m^{-1}, \quad (2)$$

where $j = 1$ to k number of elements; $i = 1$ to m number of parameters. The individual parameters (i) of each element (j) were normalized to give values (\hat{N}_{ij}) between 1 and 10, according to

$$N_{ij} = \frac{9(N_{ij} - N_{i\ell})}{\max(N_{ij}) - \min(N_{ij})} + 1 \quad \text{for each } i, \text{ and all } j, \quad (3)$$

where $N_{i\ell}$ = i th parameter of calcium, N_{ij} = i th parameter of element j ; $\max(N_{ij})$ = maximum (N_{ij}), and $\min(N_{ij})$ = minimum (N_{ij}).

The degree of similarity for each element to calcium (C_j) therefore has a value between 1 and 10, a value close to 1 indicating similarity to calcium, and a value close to 10 indicating maximum dissimilarity. The similarity values (C_j) calculated for a given metal are relative values, and are dependent upon the choice of other metals included in the array. If it is necessary to incorporate an additional element into the array after C_j calculations have been performed for a previously selected array of elements, the C_j values for all elements have to be recalculated.

The degree of similarity for each element to calcium was plotted against O.R. values from the INEL site samples (Figure 1). The data suggest that O.R. values, in an unpolluted ecosystem, systematically decrease as the degree of element similarity to calcium decreases. Results from other studies were examined to determine whether these observed trends would be repeated. Concentrations of calcium, strontium, barium, and lead in soil moisture and herbivores from another ecosystem (Hirao and Patterson,

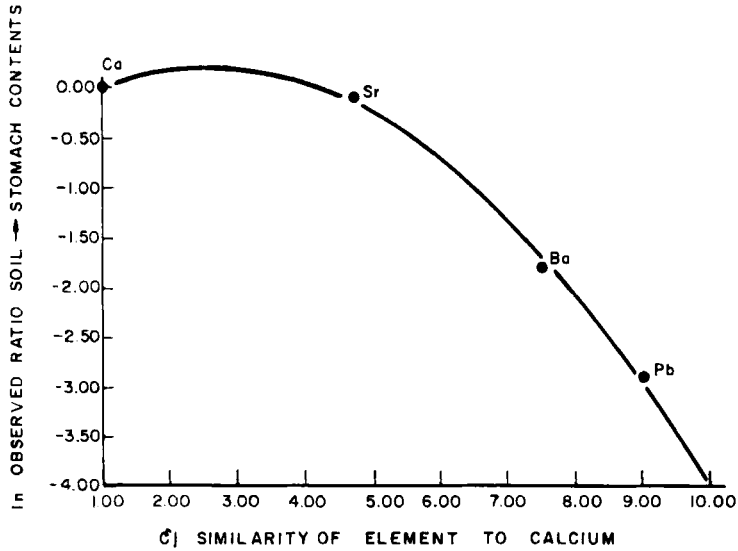
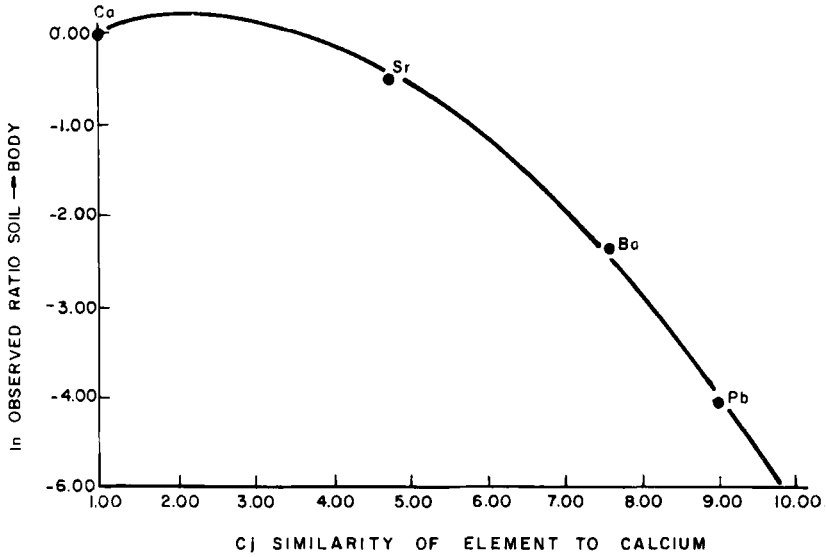


FIGURE 1 Observed ratios vs. element similarity to calcium for INEL site samples.

1974) were recalculated to give O.R. values and were plotted against element similarity values to calcium (Figure 2A). Likewise, data from an alkaline earth metal study (Schulert *et al.*, 1969) which measured the ratio of strontium/calcium, barium/calcium, and beryllium/calcium in rat placenta and fetus after intravenous injection of these elements were recalculated to give the ratio of nonessential element to calcium in the fetus divided by the ratio of nonessential element to calcium in the placenta. These O.R. values were plotted against element similarity to calcium (Figure 2B). The results of the original study indicated that the placenta acts as a discrimination barrier to the passage of nonessential or toxic elements. Thus, the ratio of nonessential or toxic element to calcium was greater in the placenta compared to the fetus. To provide an additional check, data from a third study (Domanski *et al.*, 1969) were recalculated to give O.R. values; these values were plotted against alkaline earth element similarity to calcium (Figure 2C). This study provided data (from rats) for the urinary clearance-rate of nonessential alkaline earth metals divided by the urinary clearance-rate of calcium. Since the study examined the excretion of elements, the expected trend, if real, would be for the nonessential element to calcium ratio to increase systematically as element similarity to calcium decreases. The trend of systematic change of O.R. values as element similarity to calcium decreases, as evidenced by data from the literature, supports the conclusion that discrimination against chemically related alkaline earth metals and lead is a systematic function of quantitative differences between the metals and calcium.

The fact that calcium, as it moves through food chains, increasingly becomes purified of nonessential metals as the metals are more dissimilar to calcium, may be useful for better determining whether existing lead levels in organisms are natural or elevated due to man's activities. A notable problem with lead pollution studies is that an adequate method of determining organism natural body burden of lead does not exist. (A thorough discussion of the difficulty of determining natural levels of lead is beyond the scope of this paper; excellent references can be found in Settle and Patterson (1980) and Patterson (1965).)

As used historically, the term natural has been applied to tissue concentrations and absorption levels of lead ranging from acute toxicity levels to levels that were in existence during an organism's prehistoric times. Estimates of natural levels of lead absorption in humans have ranged from 0.3 to 129 μg of lead per day, and estimates of natural body burdens in humans have varied by 100-fold differences (Settle and Patterson, 1980). The absence of a valid determination of natural body burden of lead has meant that health effects and toxic thresholds for total body burdens of lead are not readily defined.

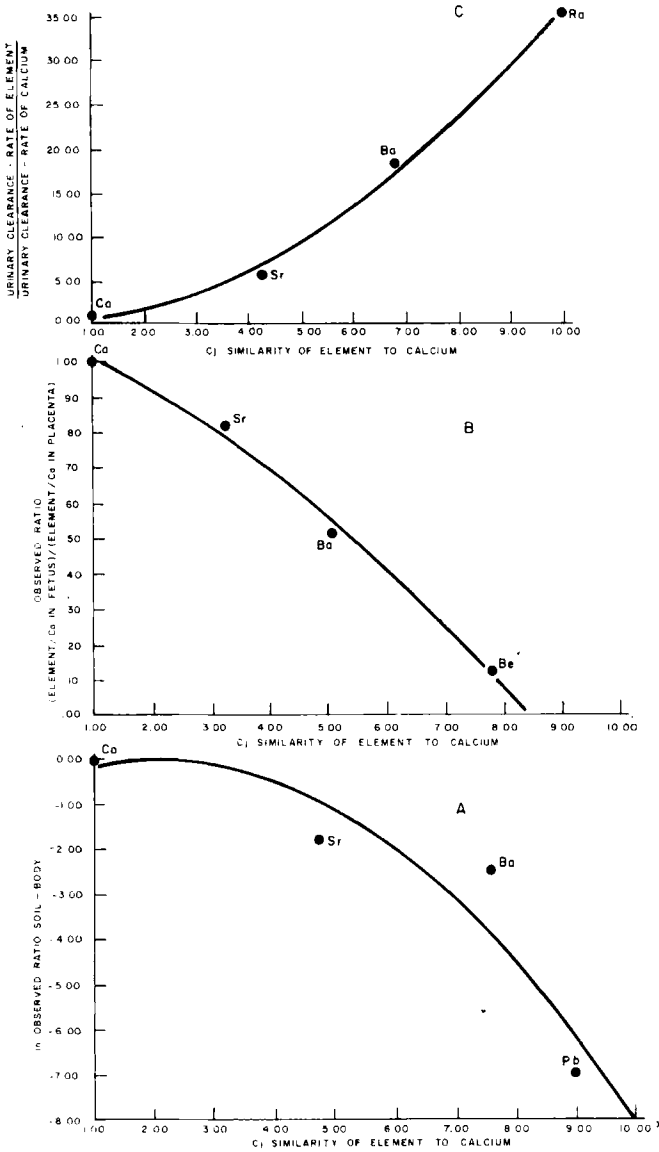


FIGURE 2 Observed ratios vs. element similarity to calcium. (A) Data calculated from Hirao and Patterson, 1974. (B) Data calculated from Schultert *et al.*, 1969. (C) Data calculated from Domanski *et al.*, 1969.

The ambiguity of the term natural results, in part, from the fact that lead pollution exists on a global scale. In fact, gasoline and smelter fume lead were reported in components of a food chain in the Sierra Nevada of California previously thought to be pristine (Hirao and Patterson, 1974). In the case of man, recourse to samples of primitive or prehistoric man is not always suitable when attempting to determine natural lead levels, because these cultures often are or were contaminated with lead for various reasons. In the case of animals, recourse to specimens collected and stored before modern industrial pollution is not always possible because of contamination problems during handling and preservation.

The data which we have examined indicate that calcium is purified of strontium, barium, and lead as the metals are transferred through the food chain, so organisms at the higher ends of food chains possess calcium reservoirs with low barium/calcium and lead/calcium ratios compared to initial values for soil or food. Observed ratio values remain relatively fixed in natural environments (Settle and Patterson, 1980), independent of increases of trace lead concentrations in the environment. However, higher levels of lead in soil or food due to industrial contamination elevate lead O.R. values and increase lead concentrations in consumers. Data (Table V) from an unpolluted environment indicate the lead/calcium O.R. values should be no greater, and probably smaller, than barium/calcium O.R. values. Data from Hirao and Patterson (1974) recalculated to provide barium/calcium and lead/calcium O.R. values support this trend (Figure 2A). Since O.R. values decrease systematically as nonessential alkaline earth metals and lead are more dissimilar to calcium, it should be possible by extrapolation to determine whether existing metal levels in organisms are natural or elevated by examining the trend of O.R. values versus element similarity to calcium.

Figure 3 shows O.R. values (soil to consumer) from the lead-contaminated Anaconda samples plotted against element similarity to calcium. The lead/calcium O.R. value is not consistent with trends observed in two unpolluted environments (Figures 1-2A) since said value is greater than the barium/calcium O.R. value, and is also greater than expected based upon extrapolation from other metals (i.e. the lead/calcium O.R. is above the line). This type of trend, if detected for organisms in other environments, would suggest that existing lead levels of respective organisms are in fact elevated above natural levels.

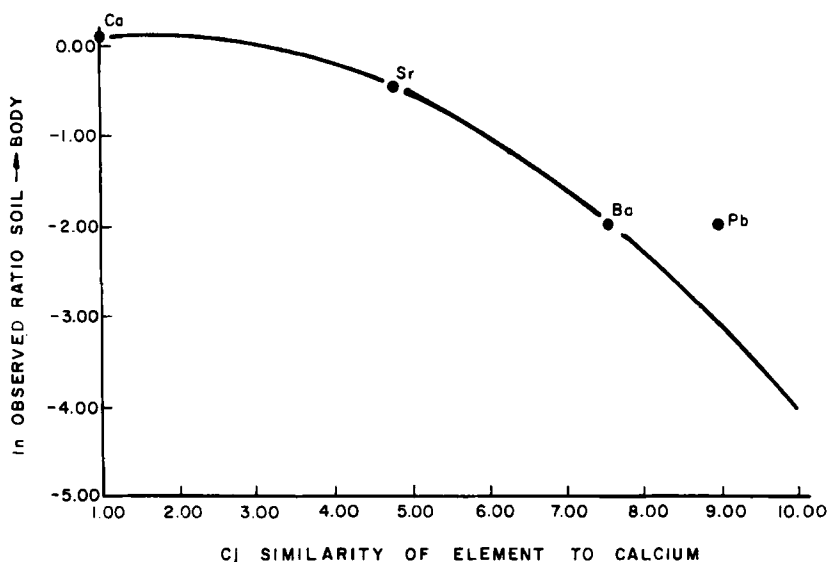


FIGURE 3 Observed ratios vs. element similarity to calcium for Anaconda site samples.

CONCLUSION

It appears that in certain unpolluted environments, uptake of strontium, barium, and lead through food chains varies systematically as a function of degree of similarity to the related nutritious element calcium. The use of systematic O.R. trends may circumvent some of the problems of determining whether metal levels in organisms are elevated above normal.

Contamination which alters O.R. values has consequences for plants and consumers. The abundance of heavy metals in soils constitutes a strong selective force in plant evolution (Antonovics and Bradshaw, 1970; Urquhart, 1971). Sites with relatively high heavy metal content usually have impoverished flora in comparison with surrounding areas, and plant populations seem to be genetically distinct from populations of the same species which exist in areas of low heavy metal content. A general observation has been that evolution of species or races tolerant to heavy metals has occurred only when such habitats have been colonized *in situ*; there is little evidence that species have constitutional tolerance to heavy metals (Antonovics *et al.*, 1971). Few reports exist in the literature which describe that species have been able to colonize soils with a high heavy metal content in the absence of the evolution of tolerant races (McNaughton *et al.*, 1974).

Plants existing in a particular environment are adapted to the natural levels of nutritious elements. It is reasonable to assume that a natural level

for a heavy metal within a plant will be determined by the degree to which its behavior is similar to the chemically related nutritious element within the plant, the existing environmental levels of the nutritious metal, and the nutritional needs of the plant. This implies that under normal levels of both nutritious and heavy metals, that is, levels which were in existence during the period of evolutionary development of the physiological responses to these metals, that there should exist an O.R. value from soil to plant which is within relatively constant limits.

The abundance of nutritious elements such as calcium is under homeostatic control in mammals. The major source of nutrients for mammals is their food, and natural selection has fixed the needs and tolerances of mammals to environmental and dietary levels of the elements. It is unlikely that animals are evolutionarily adapted to metal levels in the environment that vary significantly from those present during the creation of the evolutionary response. It follows that there should also exist, under natural conditions, O.R. values for animals that should be relatively constant and of adaptive significance. Once again, the O.R. values should be, in part, a function of the degree of similarity to the chemically related nutritious element.

Contamination of toxic elements upon plants, which consumers utilize for food, leads to an increase of O.R. values as metals are transferred to consumers. This elevates toxic metal body burdens. Although consumers exhibit intense discrimination against toxic metals (e.g. lead), the O.R. values and body burdens are not reduced to levels comparable with unpolluted areas, or which should exist based upon extrapolation from other related elements. The reason seems to be that deposits of toxic metals on plant surfaces bypass discrimination mechanisms of plants which consumers depend upon, consequently exposing them to elevated levels of metals to which they have no defense.

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