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All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy.

Paracelsus
(1493 - 1541)

CONTENTS

GEOTOXIC MATERIALS IN THE SURFACE ENVIRONMENT

ABSTRACT

Knowledge of the natural distribution of toxic substances in the surface geological environment provides a useful baseline for the assessment and eventual use of geological media for the storage and disposal of hazardous wastes. Here we develop data sources and provide insights into the existence and behavior of geotoxic substances in the natural environment.

The composition of the earth is described from the literature on geochemistry and the abundance of major and trace constituents of the silicate crust is described and discussed as well.

The relationship of naturally occurring deposits of potentially hazardous geological materials to the general problem of hazardous waste disposal in geological media is discussed. Three basic types of geotoxic deposits are identified: ore bodies, evaporites, and geothermal and volcanic features. The use of phosphorite ore bodies for fertilizer manufacturing is discussed further as a case in point. The agricultural utilization of phosphatic rocks constitutes an important potential source of geotoxic materials in the human food chain.

We review the toxicology and natural occurrence of several recognized geotoxic elements including arsenic, cadmium, chromium, nickel, lead, selenium, uranium, and vanadium. The behavior of these elements in the environment and in biological systems is examined.

The properties of these eight toxic elements are summarized and presented in a toxicity matrix. The toxicity matrix identifies each of the elements in terms of average crustal abundance, average soil concentration, drinking water standards, irrigation water standards, daily human intake, aquatic toxicity, phytotoxicity, mammalian toxicity, human toxicity, and bioaccumulation factors for fish. Fish are the major aquatic environment contribution to the human diet and bioaccumulation in aquatic ecosystems has been demonstrated to be an important factor in the cycling of elements in aquatic ecosystems. The toxicity matrix is used as a first approximation to rank the geotoxicity of elements for the purpose of focusing future efforts. The ranking from highest to lowest toxicity with respect to the toxicity parameters being discussed is as follows: arsenic, cadmium, lead, selenium, chromium, vanadium, nickel, and uranium. Other rankings may be obtained with the use of different toxicity parameters.

BACKGROUND AND INTRODUCTION

The safe disposal of radioactive and other hazardous wastes is a problem of increasing concern. Determination of acceptably safe methods for disposal of radioactive wastes has proven to be a serious constraint in the development of nuclear power. The predominant methods that have been utilized in the past and proposed for future application involve underground burial of radioactive and chemical toxic wastes. Such burial is intended to minimize environmental and biological impacts by reducing or eliminating the potential release and transport of such materials within the biosphere.

The presence of potentially hazardous levels of naturally occurring geological materials has been recognized in many parts of the world and the effects of many of these deposits have been studied. Although the chemical form of the naturally occurring geological chemical and the hazardous or radioactive waste chemical may differ, there are some useful and constructive comparisons that can be made to place the problem of waste disposal in the proper perspective. One salient difference is that the radioactive species have a finite, albeit often long physical half-life, whereas the naturally occurring geological chemical maintains its toxicity forever unless chemical weathering, biological transformation, or transport removes it from the accessible environment or changes its chemical form.

Recognizing that incorporation of toxic material in the Earth's crust does not present a new or unique phenomenon, we have undertaken a study of geotoxicity impacts to provide useful insights to the problems that result from underground burial of hazardous wastes. The geotoxicity study involves the characterization and evaluation of the potential environmental and biological impacts of toxic material incorporated in the Earth's crust by either man or nature.

Applications for geotoxicity information can be found in the following areas.

- Placement of problems involving underground burial of radioactive and other hazardous wastes into a reasonable perspective.
- Improved understanding of the movement, transport, and environmental impacts of radioactive and chemically toxic materials buried underground. Insights to the hydrogeologic transport and biological impact of radionuclides can be gained by comparison with their stable element analogs in many cases.
- Evaluation of the incremental impact resulting from burial of hazardous waste in identified areas of high existing geotoxicity.
- Improved understanding of the role of geochemistry in health and disease.

With these applications in mind, we summarize our initial efforts toward a study of geotoxicity and develop a preliminary, systematic approach toward the understanding of geotoxic phenomena and their relationship to human health. Such study will identify the most useful and productive areas for continued investigation.

COMPOSITION OF THE EARTH

The chemical composition of the Earth's surface has assumed greater importance in our present technology for several reasons. The requirement for previously exotic and rare trace elements by industry has promoted geochemical exploration for such elements as cadmium, germanium, antimony, and some of the rare earths. Numerous other uses of elements typically occurring in the Earth's crust in the trace element range have arisen from the semiconductor industry and from the manufacture of rubber, plastics, and elastomers.

Knowledge of the surficial geology is also required for the assessment and eventual use of geological media for storage and disposal of hazardous wastes. Armed with the detailed information on the natural distribution and biological consequences of toxic substances in the surface environment, one can realistically determine the effects of repositories of hazardous materials in various portions of the geosphere. Natural deposits of toxic elements have, in a sense, supplied us with many test cases of the behavior of toxic materials in geological media.

The structure of the Earth is generally believed to consist of a heterogeneous silicate crust, a silicate mantle similar to ultrabasic igneous rocks, and an iron-nickel core. The Mohorovicic discontinuity (Moho) separates the crustal region from the mantle and is characterized by a rapid increase in the velocity of seismic waves at approximately 5 to 30 km. The Moho has been described as either a chemical or a physical interface.

Most of the geochemical data we have to utilize for this discussion is related to the silicate crust in which oxygen, silicon, and aluminum are the most abundant elements. The crust of the Earth has a mean depth of 17 km, an average density of 2.8 gm/cm^3, and comprises only 0.4% of the Earth's total mass. It is composed primarily of igneous and metamorphic rocks by volume (95%), with only 4% shales, 0.75% sandstones, and 0.25% as limestone. Where sedimentary and metamorphic rocks occur as a thin veneer, they are usually underlain by igneous basement rocks.

The major oxide compounds that comprise the continental crustal rocks were determined by Poldervaart (1955) and more recently by Ronov and Yaroshevsky (1969), whose data are shown in Table 1. It is obvious from Table 1 that silicon and aluminum compounds dominate the materials of the Earth's crust although locally, carbonates may occur over large areas. The elements that comprise the major portion of the Earth's crust are given as weight and atom percentages in Table 2 (Mason, 1966).

TABLE 1. Major elemental compounds in the continental Earth's crust (Ronov and Yaroshevsky, 1969).

Weight percent										
SiO_2	Al_2O_3	CaO	FeO	Fe_2O_3	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
61.9	15.6	5.7	3.9	2.6	3.1	3.1	2.9	0.8	0.3	0.1

TABLE 2. Major elements in the Earth's crust (Mason, 1966).

Element	Weight percent (g/ton x 10^4)	Atom percent
Oxygen	46.6	62.55
Silicon	27.72	21.22
Aluminum	8.13	6.47
Iron	5	1.92
Calcium	3.63	1.94
Sodium	2.83	2.64
Potassium	2.59	1.42
Magnesium	2.09	1.84

The average weight percentage of a given element in the Earth's crust has been termed a clarke (Mason, 1966). When applied to the concentration of the more rare elements, the clarke of concentration is employed, especially when referring to ore deposits. This term is useful in discussing ore deposits because it compares the average crustal abundance of the element to that which is found in a specific mineral or ore deposit. The concentration clarke for iron required for a commercially extractable ore body is 6, which means that the concentrations need be six times the average crustal abundance of 5% for extractable ore status. On the other hand, manganese has a clarke of 0.1 and a concentration clarke of 350 is required for ore body status. Much of the 10^6 to 10^7 tons of manganese produced in the world per year is obtained from seawater, however, where it is present at 0.002 ppm (Krauskopf, 1967). The extraction technology rather than the concentration clarke is the dominant factor in production in this case.

The abundances of the more widely dispersed or trace elements in average crustal materials (Taylor, 1964); sedimentary rocks, shales, sandstones, and carbonates (Turekian and Wedepohl, 1961); and igneous rocks (Mason, 1966) are shown in Table 3.

During recent biogeochemical studies, data on the occurrence of elements in the alluvium that covers the Imperial Valley of California were obtained by neutron activation analysis (Koranda et al., 1980). These data are shown in Table 4 and can be compared to the soil values given in Bowen (1966) shown in Table 5. The Imperial Valley data are derived from 37 samples collected in the northern part of the area within 8 km of the south shore of the Salton Sea and reflect the composition of the alluvium that has been laid down in the Salton Trough in recent geological time. Colorado River sediments were deposited in the Imperial Valley basin as late as 1910. Physiographically, the data should be considered as soil, but because of the lack of strong morphogenic differentiation in the soil profiles and its relatively recent age, the data are more appropriately considered as geologic materials, namely alluvium.

The composition of soils, which are bioclimatically weathered products of the environment's interaction with parent materials, may differ from the crustal abundance data. Data from Bowen (1966) on soil composition are shown in Table 5. The leaching and removal of soluble constituents as well as the addition of others in agricultural practices or through other natural or anthropic activities can cause the concentrations in the soil to vary from those occurring in the parent materials.

TABLE 3. Concentrations of elements in crustal rocks.[a]

	Parts per million				
Element	Average crustal abundance	Granite	Shales	Sandstones	Carbonates
Boron	10	2	100	35	20
Fluorine	625	700	740	270	330
Sodium	28,300	24,600	9,600	3,300	400
Magnesium	20,900	2,400	15,000	7,000	47,000
Aluminum	81,300	74,300	80,000	25,000	4,200
Silicon	277,200	339,600	73,000	368,000	24,000
Phosphorus	1,060	390	700	170	400
Sulphur	260	175	2,400	240	1,200
Chlorine	130	50	180	10	150
Calcium	36,300	9,900	22,100	39,100	302,300
Scandium	22	3	13	1	1
Titanium	4,400	1,500	4,600	1,500	400
Vanadium	135	16	130	20	20
Chromium	100	22	90	35	11
Manganese	950	230	850	--	1,100
Iron	50,000	13,700	47,200	9,800	3,800
Cobalt	25	2.4	19	0.3	0.1
Nickel	75	2	68	2	20
Copper	55	13	45	--	4
Zinc	70	45	95	16	20
Gallium	15	18	19	12	4
Germanium	1.5	1	1.6	0.8	0.2
Arsenic	1.8	0.8	13	1	1
Selenium	0.05	--	0.6	0.05	0.08
Bromine	2.5	0.5	4	1	6.2
Rubidium	90	220	140	60	3
Strontium	375	250	300	20	610
Yttrium	33	13	26	40	30
Zirconium	165	210	160	220	19
Niobium	20	20	11	--	0.3
Molybdenum	1.5	7	2.6	0.2	0.4
Ruthenium	0.01	--	--	--	--
Rhodium	0.005	--	--	--	--
Palladium	0.01	0.01	--	--	--
Silver	0.07	0.04	0.07	--	--
Cadmium	0.2	0.06	0.3	--	0.03
Indium	0.1	0.03	0.1	--	--
Tin	2	4	6	--	--
Antimony	0.2	0.4	1.5	--	0.2
Tellurium	0.01	--	--	--	--
Iodine	0.5	--	2.2	1.7	1.2
Cesium	3	1.5	5	--	--
Barium	415	1220	580	--	10
Lanthanum	30	120	92	30	--

TABLE 3. (Continued.)

Element	Parts per million				
	Average crustal abundance	Granite	Shales	Sandstones	Carbonates
Cerium	60	230	59	92	11.5
Praesodymium	8.2	20	5.6	8.8	1.1
Neodymium	28	55	24	37	4.7
Samarium	6	11	6.4	10	1.3
Europium	1.2	1	1	1.6	0.2
Gadolinium	5.4	5	6.4	10	1.3
Terbium	0.9	1.1	1	1.6	0.2
Dysprosium	3	2	4.6	7.2	0.9
Holmium	1.2	0.5	1.2	2	0.3
Erbium	2.8	2	2.5	4	0.5
Thulium	0.5	0.1	0.2	0.3	0.04
Ytterbium	3.4	1	2.6	4	0.5
Lutetium	0.5	0.1	0.7	1.2	0.2
Hafnium	3	5.2	2.8	3.9	0.3
Tantalum	2	1.6	0.8	--	--
Tungsten	1.5	0.4	1.8	1.6	0.6
Rhenium	0.001	0.0006	--	--	--
Osmium	0.005	0.0001	--	--	--
Iridium	0.001	0.006	--	--	--
Platinum	0.01	0.008	--	--	--
Gold	0.004	0.002	--	--	--
Mercury	0.08	0.2	0.4	0.03	0.04
Thallium	0.5	1.3	1.4	0.8	--
Lead	13	49	20	7	9
Bismuth	0.2	0.1	--	--	--
Thorium	7.2	52	12	1.7	1.7
Uranium	1.8	3.7	3.7	0.45	2.2

[a] From Taylor (1964); Turekian and Wedepohl (1961); and Mason (1966).

TABLE 4. Trace elements in surface soils of the Imperial Valley (Koranda *et al.*, 1980).

Element	Frequency[a] (%)	Mean concentration (μg/g dry weight)	Concentration range Maximum	Concentration range Minimum
Sodium	100	7,193	15,590	4,504
Magnesium	100	20,087	32,950	14,170
Aluminum	100	49,239	64,890	10,210
Chlorine	87	2,443	18,200	2
Potassium	100	18,477	20,500	15,560
Calcium	100	35,340	47,309	5,430
Scandium	100	9.4	10	7.2
Titanium	90	3,057	4,501	101
Vanadium	87	75	101	30
Chromium	10	49	61	42
Manganese	100	468	540	422
Iron	100	26,689	30,700	20,500
Cobalt	100	10	11	8
Nickel	13	35	42	31
Zinc	100	89	117	68
Gallium	83	19	30	12
Arsenic	100	9.1	16	6.3
Rubidium	100	116	132	92
Strontium	100	258	341	218
Zirconium	100	134	259	72
Molybdenum	93	2.5	10	4.9
Indium	50	1.6	12	0.1
Antimony	100	0.9	1	0.7
Cesium	100	6.8	8.1	4.9
Barium	100	511	649	437
Lanthanum	100	32	37	21
Cerium	100	64	71	56
Neodymium	100	29	32	25
Europium	100	0.8	0.9	0.7
Hafnium	100	5.1	7.2	4.3
Thorium	100	10.3	11.6	8.8
Uranium	100	2.9	3.5	2.2

[a] Frequency of detection in sample series.

TABLE 5. Average crustal abundance of elements compared to their occurrence in surface soils.

Element	Parts per million		
	Crustal average[a]	Soil average[b]	Range of soil concentration
Lithium	20	30	7-200
Beryllium	2.8	6	0.1-40
Boron	10	10	2-100
Carbon	200	20,000	--[c]
Nitrogen	20	1,000	200-2,500
Oxygen	466,000	49,000	--
Fluorine	625	200	30-300
Sodium	28,300	6,300	750-7,500
Magnesium	20,900	5,000	600-6,000
Aluminum	81,300	71,000	10,000-300,000
Silicon	277,200	33,000	25,000-350,000
Phosphorus	1,050	650	--
Sulfur	260	700	30-900
Chlorine	130	100	--
Potassium	25,900	14,000	400-30,000
Calcium	36,300	13,700	7,000-500,000
Scandium	22	7	10-25
Titanium	4,400	5,000	1,000-10,000
Vanadium	135	100	2-500
Chromium	100	100	5-3,000
Manganese	950	850	100-400
Iron	50,000	38,000	7,000-550,000
Cobalt	20	8	1-40
Nickel	75	40	10-1,000
Copper	55	20	2-100
Zinc	70	50	10-300
Gallium	15	30	0.4-300
Germanium	1.5	1	1-50
Arsenic	1.8	6	2-100
Selenium	0.05	0.2	0.01-2
Bromine	2.5	5	1-10
Rubidium	90	100	20-600
Strontium	375	300	50-1,000
Yttrium	33	50	25-250
Zirconium	165	300	60-2,000
Niobium	20	--	--
Molybdenum	1.5	2	0.2-5
Ruthenium	0.01	--	--
Rhodium	0.005	--	--

TABLE 5. (Continued.)

Element	Parts per million		
	Crustal average[a]	Soil average[b]	Range of soil concentration
Palladium	0.01	--	--
Silver	0.07	0.1	0.01-5
Cadmium	0.2	0.06	0.01-0.7
Indium	0.1	--	--
Tin	2	10	2-200
Antimony	0.2	--	2-10
Tellurium	0.01	--	--
Iodine	0.5	5	--
Cesium	3	6	0.3-25
Barium	425	500	100-3,000
Lanthanum	30	30	1-5,000
Cerium	60	50	--
Lead	13	10	2-100
Bismuth	0.2	--	--
Thorium	7.2	5	0.1-12
Uranium	1.8	1	0.9-9

NOTE: Elements from praseodymium to thallium not determined for soils.

[a] From Mason (1966).

[b] From Bowen (1966).

[c] Indicates values not well known.

The basic sources of geochemical data describing the composition of the surface environment are used whenever generic information is required, or when specific data on the actual geological milieu under discussion is lacking. A detailed assessment justifies the actual measurement of the chemical composition of the medium being considered for waste disposal or for other engineering use. The composition of the Earth's crust may vary widely from the generalized values shown in the tables in the case of ore bodies, salt deposits or evaporites, and geothermal and volcanic features such as hot springs, mud volcanos, fumaroles, and some local outcrops. For example, areas underlain by serpentinite are known for their high metal content in both the parent materials and the soils derived from the formation (Soane and Saunder, 1959). It is our intent here to relate these naturally occurring deposits of potentially toxic geological materials to the general problem of hazardous waste disposal in geological media.

GEOTOXIC DEPOSITS

Naturally occurring deposits of toxic substances in geological media are typically three basic types:

(1) outcrops, ore bodies, and undisturbed geological strata in contact with the surface environment;

(2) evaporites, salt lakes, playas; and

(3) geothermal features such as steam vents, solfataras, fumaroles, mud volcanos, and various kinds of volcanic ejecta.

OUTCROPS AND ORE BODIES

Toxic minerals and elements are often developed in mining operations producing lead, cadmium, mercury, iron, managanese, gold, nickel, and other elements. One unique use of ore bodies is the utilization of phosphorites or phosphatic rock as fertilizer in agriculture. The phosphatic rock is mined, crushed, washed with phosphoric acid to raise the phosphorus content to 40% (in the case of treble super phosphate), and then pelletized. The fertilizer is used on crop fields, especially high-yielding row crops, at rates up to 400 lb/acre. Analyses of the rock ore and the applied fertilizer are shown in Table 6. One of the major concerns from the standpoint of human health and food chain relationships in the phosphate fertilizer is cadmium at 92 ppm, which is 460 times the average crustal abundance (Bouwer and McKloveen, 1978). All of the elements discussed here occur in phosphatic fertilizer, which constitutes a relatively unevaluated source of

TABLE 6. Trace elements in phosphate ore and phosphate fertilizer (Koranda *et al.*, 1980).

	Parts per million		
Element	Gay Mine ore composite, Idaho	Conda Mine ore washed composite, Idaho	Phosphate fertilizer, Imperial Valley, California
Sodium	4,918	3,426	4,397
Magnesium	1,977	3,208	5,160
Aluminum	6,778	5,594	7,136
Potassium	2,729	2,633	2,210
Calcium	27,050	26,280	14,315
Scandium	2	3	4.1
Titanium	681	4,923	--[a]
Vanadium	857	463	861
Chromium	475	316	461
Manganese	105	68	210
Iron	3,981	3,202	4,786
Cobalt	1.5	1.9	2.7
Nickel	110	92	104
Zinc	882	629	966
Arsenic	14.9	8.2	10.8
Selenium	2.7	12.1	2.8
Rubidium	10.4	9.9	13.4
Strontium	849	940	516
Zirconium	102	137	50
Molybdenum	10.5	10.1	19.6
Silver	4.5	6.1	1.9
Cadmium	81	89	92
Indium	4	--	--
Antimony	3.5	2.3	3.3
Iodine	2.5	1.3	--
Chlorine	49.5	136.5	40.6
Cesium	1.1	0.8	1.1
Barium	114.1	91.6	89
Lanthanum	54.9	75.1	93.5
Cerium	21.4	32.7	35.6
Neodymium	41.7	70.6	36.3
Samarium	6.4	10.6	6.1
Europium	1.1	1.9	1
Terbium	1.1	1.8	1
Dysprosium	7.6	14.2	7.5
Ytterbium	5.5	9.2	7
Lutetium	1.6	2.6	2.2
Hafnium	1.2	1.9	0.9
Tantalum	0.2	0.2	--
Thorium	1.3	2.1	2.1
Uranium	64	79.7	105.8

[a] Not detected.

toxic elements in man's food chain. In the Imperial Valley, 140,000 ton of this fertilizer are used per year and it is used widely in Central California and other parts of the Western U.S. as well.

EVAPORITES

Evaporite deposits are derived from the evaporation of marine salt or terrestrial saline waters in salt pans, playas, salinas, lagoons, and relict seas, such as the Salton Sea of Southern California (Stewart, 1963). The internal drainage of desert basins in the Basin and Range Province of the Western U.S. often creates shallow modern evaporite deposits in the playas and ephemeral lakes that occupy the centers of the basins. The concentrations of salts such as halite, sylvite, and polyhalite in these areas are toxic to almost all species of plants. Since Cambrian time, thick and extensive evaporite deposits of marine origin have been laid down in various regions such as Michigan, Montana, and Wyoming. They are found also in Central Europe (Stewart, 1963). Modern evaporite deposits are being formed continually in arid and semiarid climates, such as those around the Mediterranean Sea and the Western U.S. They are often deposited in the rain shadows of high north-south trending mountain chains in the Northern Hemisphere. Mono Lake in California, the Great Salt Lake in Utah, and the surrounding deposits are examples of contemporary evaporite formation.

Evaporite deposits are dominated by chlorides, sulfates, carbonates, and borates, which are precipitated in a relatively orderly sequence from the crystallizing salt solution. Carbonates are deposited first. The sequence is never completely ordered because some factor in the depositional and evaporating environment usually varies and the crystallization process normally does not go to completion. The primary elements and compounds found in evaporites are the same as in seawater, namely, sodium, chlorine, sulphate, magnesium, calcium, potassium, and carbonate in that order of abundance. Trace elements prominent in evaporite deposits are strontium (30 ppm), boron (10 ppm), silicon (8 ppm), and fluorine (4 ppm) (Stewart, 1963).

GEOTHERMAL AND VOLCANIC MATERIALS

Volcanic and geothermal materials may contain rather high concentrations of the toxic elements discussed here, as well as others with toxic potential at concentrations much higher than typical crustal values. The recent 1980 eruptions of Mount St. Helens in Washington released large quantities of tephra or ash into the environment (Fruchter _et al._, 1980). Table 7 contains analytical data on the two eruptions from the mountain and

TABLE 7. Elemental concentrations in Mount St. Helens ash from the 18 May 1980 eruption (Koranda, 1980).

	Micrograms per gram dry weight or percent by weight			
Element	Yakima[a]	Richland[a]	Pullman[a]	0.1 N nitric acid extracted[b]
Potassium	6135	6800	9240	64.5
Calcium	2.3%	2.5%	1.9%	1238
Titanium	3150	4100	2522	--[c]
Manganese	620	550	456	21.3
Iron	3.1%	3.2%	2.3%	545
Copper	29	28	38	5.4
Zinc	50	58	49	1.7
Gallium	20	21	19	--
Rubidium	19	23	36	--
Strontium	580	490	398	2.7
Yttrium	10	8	12	--
Zirconium	80	99	151	--
Lead	7	5	9	0.8
Boron	--	--	--	0.7
Arsenic	--	--	--	0.7
Cadmium	--	--	--	0.2
Cobalt	--	--	--	0.4
Nickel	--	--	--	0.6
Phosphorus	--	--	--	369
Uranium	--	--	--	2.4
Vanadium	--	--	--	1.3
Magnesium	--	--	--	459
Sodium	--	--	--	215

[a] Analyzed by x-ray fluorescence analysis.

[b] Extracted from Yakima ash sample and analyzed by inductively coupled argon plasma emission spectroscopy.

[c] Not detected.

one laboratory analysis of the availability of trace elements in the tephra (Koranda, 1980). The volume of ejecta released by the Mount St. Helens eruption of 18 May 1980 was large, estimated at 4 km^3, and if the concentrations of lead, arsenic, cadmium, vanadium, and uranium are extrapolated to the total mass of ejecta, the inventory of released toxic elements appears large and significant. The depositional area is also very large, and except at adjacent locations, the ash loading is relatively light. The major immediate health concern from resuspension of the ash deposits appears to be in the free silica content of the ash rather than in the concentrations of major or trace elements (Fruchter et al., 1980).

Volcanic ejecta, ranging in size from tephra to bombs, and lava flows constitute local and at times intense sources of toxic elements. Andesitic volcanic materials may be highly enriched in toxic elements. Table 8 shows the concentrations of these elements in magmatic sulfides (Rankama and Sahama, 1950).

Geothermal features such as fumaroles and the surrounding encrustations may have high concentrations of lead, nickel, chromium, vanadium, arsenic, and cadmium. The high concentrations of metals in these features undoubtedly are related to the high levels of sulfides being emitted from the vents. The metals are either sublimed from the fumarolic gases or dissolved from the surrounding rocks by the emitted acids. A high concentration of 1.64% nickel was found in fumarolic encrustations at the Shirane Volcano in Japan (Shima, 1957). In New Zealand, on White Island, which is an andesite volcano, lead at 1%, vanadium at 0.03%, and arsenic at 0.3% were found in the fumarolic deposits.

Some geothermal fluids are low in total dissolved solids, but other brines are a strong and mobile source of potentially toxic elements that may enter surface water systems from either natural or man-developed geothermal sites (Ireland, 1980). Considerable variation occurs in the brine composition both from one field to another and between wells in a single field. Some examples that were obtained from five California geothermal wells in the Imperial Valley (Pimental et al., 1978) are shown in Table 9.

TABLE 8. Concentrations of trace elements in magmatic sulfides (Rankama and Sahama, 1950).

Element	Parts per million	Element	Parts per million
Iron	539,000	Tellurium	2
Sulfur	404,000	Tungsten	2
Nickel	31,400	Platinum	2
Copper	10,900	Bismuth	2
Zinc	8,500	Ruthenium	1
Phosphorus	2,500	Antimony	1
Cobalt	2,100	Thallium	1
Manganese	800	Indium	0.7
Selenium	200	Iridium	0.4
Lead	100	Rhodium	0.3
Arsenic	60	Gold	0.2
Tin	50	Osmium	0.1
Vanadium	40	Chromium	0.02
Molybdenum	20	Mercury	0.02
Cadmium	20	Rhenium	0.02
Silver	10		
Germanium	10		
Palladium	4		
Gallium	2		

TABLE 9. Trace elements in geothermal brines from Imperial Valley wells (Pimental et al., 1978).

	Milligrams per liter				
Element	Salton Sea well	Westmoreland well	Brawley well	Heber well	East Mesa well
Arsenic	11	--	2.6	0.1	0.16
Boron	350	63	140	14	5.4
Barium	433	--	363	3.8	2.2
Copper	4	0.07	0.11	0.53	0.03
Fluorine	9	2.24	--	1.6	2
Iron	2300	0.3	65	22	2.2
Lithium	211	48	100	9.5	6.3
Magnesium	1200	2.8	190	2.7	0.42
Nickel	4	--	--	--	0.03
Lead	100	3.6	1.1	1.9	0.09
Selenium	--	--	--	--	1.2
Strontium	500	--	340	53	38
Zirconium	660	0.04	14	0.83	0.07

NATURALLY OCCURRING GEOTOXIC ELEMENTS

The following elements will be considered as a primary focus in this discussion of naturally occurring geotoxic materials:

- arsenic
- cadmium
- chromium
- nickel
- lead
- selenium
- uranium
- vanadium

There are other rather toxic elements in the Earth's crust such as indium and thallium, which are known to be toxic at low concentrations, but the eight elements above have been chosen as examples of naturally occurring elements with a known history or a strong potential for causing toxic reactions under the appropriate conditions in man or animals.

They have been chosen for review because there is a considerable amount of information on their occurrence, availability, and toxicology.

ARSENIC

Arsenic is widely dispersed throughout most rock types, usually at the parts per million level. It is often associated with sulfides, pyrites, or apatite. Commercial arsenic is obtained as a by-product from the smelting of lead, copper, silver, and gold ores. Arsenic is found in the following types of natural deposits or ore bodies.

- Skarn deposits
- Polymetallic deposits (lead, zinc, and cadmium)
- Realgar-orpiment deposits (rare)

Arsenic is used in geochemical surveys as an indicator of gold, silver, copper, lead, and cobalt. It is mobile in the surface environment and is found in soil, stream, groundwater, and vegetation surveys.

In the natural environment, four oxidation states are possible for arsenic: the -3 state, the metallic (0) state, and the +3 and +5 valence states. The metallic state is common for the element in certain types of mineral deposits. The +3 and +5 states are common in a variety of complex minerals and in dissolved salts in natural waters. The -3 state is present in gaseous AsH_3 (arsine), which may form under some natural conditions. The element most commonly associated with arsenic in nature is sulfur (Boyle and Jonasson, 1973).

There are about 100 arsenic-bearing minerals known to occur in nature. The principal arsenic minerals are arseno-pyrite (FeAsS), niccolite (NiAs), cobaltite (CoAsS), tennantite ($Cu_{12}As_4S_{13}$), enargite (Cu_3AsS_4), native arsenic (As), orpiment (As_2S_3), realgar (AsS), prousite ($AgAsS_3$), scorodite [(Fe,Al) $(AsO_4) \cdot 2H_2O$], bendantite [$PbFe_3(AsO_4)(SO_4)(OH_6)$], olivinite ($CU_2AsO_4OH$), mimetite [$Pb_5(PO_4,AsO_4)_3Cl$], arsenolite [$As_2O_3$], and erythrite [$Co_3(AsO_4)_2 \cdot 2H_2O$]. Arsenic also occurs in minor quantities in practically all the common sulfides and in a great variety of secondary oxidation products, particularly in sulfates and phosphates (Boyle and Jonasson, 1973).

In aquatic systems, arsenic has an unusually complex chemistry, with oxidation-reduction, ligand exchange, precipitation, and adsorption reactions all taking place. Pollution control is poorly understood for these reasons. Wagemann (1978) examined the typical concentrations of major and minor ionic constituents in freshwater systems in an attempt to find the possible controls on total dissolved arsenic in freshwater. He selected four metals (barium, chromium, iron, and calcium) as possible controlling factors and studied their metal arsenates more closely in the laboratory. Ionic barium, at typical freshwater concentrations, was the most likely freshwater constituent capable of holding total dissolved arsenic to rather low concentrations.

There has been much discussion as to the natural concentrations of various species of arsenic and their interconversion. It is now generally recognized that arsenite and arsenate interconvert via the mono- and di-methylarsonic acids.

Andreae (1978) analyzed seawater from the Southern California coast and terrestrial waters from several locations in the U.S. for four arsenic species: arsenite, arsenate, monomethylarsonic acid, and dimethylarsonic acid. Generally, arsenate was dominant. However, speciation of arsenic in natural waters is significantly influenced by biota.

These results were confirmed by the work of Waslenchuk and Windom (1978) in estuaries and Waslenchuk (1979) in rivers. Waslenchuk and Windom (1978) found that in estuaries the only detectable species was arsenate, which remained in solution as freshwater and saltwater mixed. Complexes occurred between arsenic and low-molecular- weight, dissolved organic matter. These complexes presumably prevented adsorptive and coprecipitative interactions with the sediments and allowed the arsenic to travel to the ocean in a dissolved form. Arsenic that enters the estuary associated with particulates, however, apparently remains so and accumulates in the sediments.

Waslenchuk (1979) found that the levels of dissolved arsenic in rivers in the Southeast U.S. are controlled by the availability of arsenic, by rainwater dilution, by the extent of complexation with dissolved organic matter, and perhaps by the metabolic activity of aquatic plants. Arsenic complexation by dissolved organic matter prevents adsorptive interactions between the arsenic and solid-phase organic and inorganic materials. However the particulate arsenic load may be as important as the dissolved load with respect to material transport in rivers. It appears further that those biologically mediated reactions that result in arsenic species disequilibria in the ocean and lakes have a negligible effect on arsenic speciation in rivers.

Cycling of arsenic in the aquatic environment is dominated by adsorption and desorption to sediments, when not controlled by organic matter. Arsenic may be sorbed to clays, aluminum hydroxide, iron oxides, and organic material (Ferguson and Gavis, 1972; Jackson et al., 1978). In some areas where phosphate minerals occur, arsenate may isomorphously substitute for phosphate (Hem 1970). Under most conditions, coprecipitation or sorption of arsenic with hydrous oxides of iron is probably the prevalent process in the removal of dissolved arsenic. In soils and underground aquifers, pH is also an important factor.

Reay (1972) studied the arsenic levels in the arsenic-rich Waikato river in New Zealand and related bioaccumulation of arsenic by aquatic plants to the total amount transported by the river. By estimating total biomass production and the amount of arsenic transported by the river, the author estimated that only 3 to 4% of the annual arsenic input to the river was bioaccumulated, with much of the balance being discharged to the sea and the remainder settling out with sediment at impoundments.

It is known that arsenic occurs naturally in high concentrations in various parts of the world, for example in Southwest Britain and some parts of Switzerland as well as in New Zealand. However, the long-term effects on fauna and humans appears not to have been studied to any great extent and results are inconclusive.

The concentration of arsenic in granites, basalts, limestone, and sandstone is approximately 1 ppm, in shale 13 ppm, and in soils 6 ppm. The arsenic concentration in seawater averages 3.7 ppb and in freshwater 0.5 ppb. The average concentration in plants is about 1 ppm. The amount of arsenic cycled naturally is 6 to 19 x 10^9 g/y and from mining it is 47 x 10^9 g/y.

CADMIUM

Cadmium generally accompanies zinc and lead in its natural state. It is commercially obtained from zinc ores as a by-product. Zinc and cadmium typically occur in the following deposits.

- Sphalerite shales (copper or Kupferschiefer types)
- Concretions of sphalerite in carbonate rocks
- Skarn-type deposits
- Massive sulfide deposits

Cadmium is often associated with lead, copper, zinc, silver, gold, barium, arsenic, and manganese. In geochemical surveys it is found in soils, sediments, surface waters, and vegetation.

During the past 15 y much research has been done to determine the hazard of cadmium exposures. Of the trace elements, only lead and mercury have received more attention by researchers.

Cadmium exists in nature in the +2 valence state. The ionic radius of the +2 ion is estimated to be 0.97 Å, making it one of the larger divalent ions. Cadmium is a relatively rare element that is concentrated in zinc-bearing sulfide ores (zinc to cadmium ratio is usually 100:1 to 200:1) and, consequently, is found in virtually all zinc-containing products. It occurs at an average concentration of 0.2 ppm in the Earth's crust, and most freshwaters contain less than 1 ppb cadmium. Cadmium levels in seawater average 0.15 ppb. The chemistry of cadmium in surface waters and groundwaters has been reviewed by Hem (1972).

In natural waters, cadmium can be found in several chemical forms; for example, as simple hydrated ions, as metal-inorganic complexes, or as metal-organic complexes. An understanding of the chemical speciation of cadmium in any given situation can be based on theoretical calculations of hydrolysis, oxidation/reduction, and organic complexation. Cadmium forms complexes with OH^- such as $CdOH^+$, $Cd(OH)_2$(aq.), $Cd(OH)_3^-$, and $Cd(OH)_4^{-2}$. However, almost all of the soluble cadmium ions are in the divalent cation form up to about pH 9. The solubility of cadmium decreases as pH increases due to formation of solid $Cd(OH)_2$. Patterson et al. (1977) studied the removal of dissolved cadmium by hydroxide and carbonate precipitation. A comparison of experimentally determined $Cd(OH)_2$ solubility with the calculated solubility curve showed that even at the optimal pH for precipitation, the equilibrium solubility of cadmium is still approximately 1 mg/liter. Cadmium is always found in the +2 valence state in water and redox potential normally has little direct effect on cadmium. Under reducing conditions and in the presence of sulfur, however, cadmium may react to form the insoluble sulfide. Under acidic conditions, CdS is more soluble. In the sediments, in anaerobic digestion of waste water, and in other reducing environments where sulfur is available, the solubility of cadmium may be controlled by formation of CdS (Holmes et al., 1974).

Gardiner (1974), in his study of the speciation of cadmium in natural water, found that a substantial portion of the total cadmium in river and lake water will be present as the divalent cadmium ion, the concentration of which will be inversely related to the pH and the concentration of organic material in the water. Humic substances usually account for most of the complexation, followed in importance by carbonates. O'Shea and Mancy (1978), in their study of the effects of pH and hardness on cadmium speciation, found that the effects of pH and hardness were insignificant in trace metal-inorganic interactions. Hardness and pH were quite important, however, in trace metal-humic acid interactions. Increasing the pH increased the exchangeable cadmium while an increase in hardness led to a most pronounced decrease in the humic acid interaction. Metals responsible for hardness apparently inhibit the exchangeable interactions between metals and humic materials in ways that are not yet fully understood.

Guy and Chakrabarti (1976), in their study of metal-organic interactions in natural water, found that humic acids in solution and other natural complexing agents can maintain cadmium ions in a bound form at a pH as low as 3. The release of cadmium from sediments is, therefore, apparently controlled by a combination of ion exchange and complex formation whereby the stability of the metal-organic complex determines the amount of metal solubilized.

Suzuki et al. (1979) in their study of a polluted Japanese river indicated that organic material is mainly responsible for the accumulation of cadmium in organically polluted river sediments. These results suggest that suspended solids of high organic content play a dominant role in the transport of cadmium in aquatic ecosystems.

Gardiner (1974) in a laboratory study found that concentration factors for mud varied between 5,000 and 50,000 depending on the type of solid, its state of subdivision, the concentration of metal ion and complexing ligands present, as well as the temperature, pH, and hardness of the water. It appeared further that humic material was the major component of sediment responsible for adsorption.

In contrast, Perhac (1974b) found that most of the cadmium in the bottom sediments of an unpolluted Tennessee stream was associated with carbonates and (to a lesser extent) iron oxides and therefore hypothesized that cadmium occurs in cation lattice sites within the carbonate minerals.

Ramamoorthy and Rust (1978), in their study of Ottawa River sediments, found that although the sediment was composed mainly of well-sorted sand, it was an efficient sink for heavy metals including cadmium. They discovered that this was because of the significant amount of organic material added to the sediments by the commercial use of the river for logging. Both sorption and desorption were controlled by the nature of total heavy metal loading, the sediment type, and the surface water characteristics.

The adsorption of cadmium on soils and silicon and aluminum oxides was studied by Huang et al. (1977). The results of this laboratory study indicate that adsorption is strongly pH dependent, increasing as conditions become more alkaline. When the pH is below 6 to 7, cadmium is desorbed from these materials. Cadmium has considerably less affinity for the absorbents tested than do copper, zinc, and lead and thus might be expected to be more mobile in the environment than these materials.

Another relevant observation of Huang et al. (1977) was that addition of anions to the dissolved cadmium caused an increase in adsorption. Humic acid was most effective in this regard.

Cadmium is strongly accumulated by most organisms in polluted waters. Cadmium is accumulated in the tissues of aquatic marine organisms. Fish accumulate cadmium most readily in the liver, kidneys, and intestines and to a lesser extent by the gills and the remainder of the body.

The influence of hardness on uptake of cadmium by a microcosm containing an alga, a rooted plant, snails, catfish, and guppies was studied by Kinkade and Erdman (1975). They found that initial uptake of cadmium was faster in hard than in soft water, but that the total concentration of cadmium was greater in the organisms that were placed in soft water. The relative bioaccumulation factors descended in the following order: rooted plant → alga → guppies → snails → catfish.

Cadmium is readily accumulated through both food and water by freshwater organisms, and either source of uptake can result in the development of toxic symptoms by fishes.

CHROMIUM

Chromium is widely dispersed in all rock types, having the highest concentration in mafic or ultramafic igneous rocks. The ore mineral is chromite, and most commercially useful deposits of the ore occur in ultramafic rocks as ore bodies, lenses, or other inclusions. Chromium is evident in all ecological phases except water. Nickel and cobalt are used as indicators of chromium in geochemical surveys in which stream sediments and waters are sampled.

Chromium is a transition element and occurs in nature principally as the trivalent ion Cr^{+3}, although valence states ranging from -2 to +6 have been reported. The two main forms of chromium are Cr^{+3} and Cr^{+6}. Chromium ore is always found in conjunction with other metals as an oxide (such as ferrochrome). The two largest deposits are in South Africa and the Soviet Union. Zimbabwe, which was long considered a large and important source, has declined recently in importance because of the deposits being worked out. Chromium is found in concentrations of about 10 to 100 ppm in the crust and about 0.001 to 0.8 ppm in river waters. The principal chromium-bearing minerals belong to the chromite spinel group with the general formula $[(Mg,Fe)O(Cr,Al,Fe)_2O_3]$. Depending on the degrees of substitution in the Cr, Al, Fe series, the chromites contain from 13 to 65% Cr_2O_3.

Chromite is generally resistant to chemical weathering. Because of its high specific gravity, it can be mechanically concentrated in laterites or heavy mineral placers. The chromium-bearing silicates release chromium, which is then incorporated into shales and schists. Little chromium becomes solubilized, and thus geological precipitates and evaporites normally have a low chromium content.

Trivalent chromium is the most stable form under redox conditions normally found in natural waters and sediments, and when in solution at pH greater than 5, Cr^{+3} quickly precipitates due to formation of the insoluble hydroxide or oxide.

Hexavalent chromium Cr^{+6} is a strong oxidizing agent and is always found in aqueous solution as a component of a complex anion. The anionic form varies according to pH and may be chromate $(CrO_4)^{-2}$, hydrochromate $(HCrO_4)^-$, or dichromate $(Cr_2O_7)^{-2}$. Dichromate concentration is not significant unless pH values are well below those observed in most natural waters. Thus, hexavalent chromium present in most natural waters (pH ∿6.5) will be in the form of the chromate ion $(Cr0_4)^{-2}$. All of the anionic forms are quite soluble and thus are quite mobile in the aquatic environment (Towill et al., 1978).

Schroeder and Lee (1975) in a laboratory study on the transformation of chromium in natural waters, found that Cr^{+3} and Cr^{+6} are readily interconvertible under natural conditions. Their results indicated that Cr^{+6} can be reduced by Fe^{+2}, dissolved sulfides, and certain organic compounds with sulfhydryl groups, while Cr^{+3} can be oxidized by a large excess of MnO_2 and at a slower rate by O_2 under natural water conditions. Moreover, if aquatic conditions favor Cr^{+6}, then chromium will accumulate as soluble forms in waters ; if however Cr^{+3} is favored, then the accumulation will occur in the sediments. The environmental accumulation of Cr^{+3} in the sediments can be explained by the hydrolysis of Cr^{+3} complexes to insoluble hydroxide forms, especially $Cr(OH)_3$.

Hexavalent chromium is not absorbed to any significant degree by clays, ferric hydroxide, or ferric and manganese oxides (Kharkar et al., 1968). The Cr^{+6} may, however, have some affinity for organic materials in natural waters. It appears that while Cr^{+3} is only weakly absorbed on inorganic solids, it is adsorbed more strongly than Cr^{+6}, but the sorption of Cr^{+3} may be ancillary to precipitation of $Cr(OH)_3$.

Chromium is accumulated in aquatic and marine biota to levels much higher than in ambient water. Levels in biota, however, are usually lower than levels in sediments.

Namminga and Wilhm (1977) studied heavy metal partitioning between water, sediments, and chironomid larvae (a benthic invertebrate). They found an average chromium concentration of 1.1 ppb in water, 7.64 ppm in sediments, and 2.96 ppm in chironomids. Bioconcentration factors for chironomids to water are thus about 3,000 and for chironomids to sediments, about 0.39. Rehwoldt et al. (1975) found similar relationships among water, sediments, and biota in the Danube River.

Baptist and Lewis (1969) studied the transfer of radiolabeled Cr^{+3} in an estuarine food chain consisting of phytoplankton, brine shrimp, postlarval fish, and mummichog. In general, the food chain was a more efficient pathway for uptake of chromium than direct uptake from seawater.

Distribution of chromium in water, sediment, seston, phytoplankton, mollusks, annelids, and fish in Narragansett Bay, Rhode Island, was studied by Phelps et al. (1975). The highest concentrations of chromium were found in the sediments, followed by the seston. Phytoplankton concentrated chromium to a greater extent than other organisms, with the lowest levels being found in bottom-feeding fish.

NICKEL

Nickel is also widely dispersed in most rock types, but is primarily in mafic and ultramafic igneous rocks. The major nickel deposits are

- massive sulfide lenses,
- veins and lenses of sulfides and arsenides, and
- lateritic nickel-cobalt deposits (garnierite).

Nickel is a good self-indicator of deposits in geochemical surveys, with elevated local concentrations being seen in soils, sediments, water, and vegetation. Precipitates at spring mouths may also indicate the presence of nickel in the region.

Nickel is a naturally occurring element that is found in the Earth's crust at an average concentration of 75 ppm. Nickel is normally divalent in its compounds, which are predominantly ionic in character. It is siderophilic and will alloy itself with metallic iron whenever this phase is present. Nickel is only slightly miscible in iron, and the two phases separate at low temperatures. The Earth's core is thought to be a nickel-iron alloy with an iron to nickel ratio of approximately 11:1. The weathering of nickel-rich bedrock gives rise to iron-, nickel-, and silica-rich solutions. Ionic nickel is very stable in aqueous solutions and is capable of migration over long distances. The high affinity of nickel for sulfur accounts for its occurrence in magmatic or metamorphic segregates of sulfide bodies. These sulfide segregates compose the large nickel ore body at Sudbury, Ontario, which provides the world's largest mining production of nickel.

Nickel is divalent in aquatic systems. Under reducing conditions and in the presence of sulfur, the insoluble sulfide is formed. Under aerobic conditions and pH below 9, the compounds that nickel forms with hydroxide, carbonate, sulfate, and naturally occurring organic ligands are sufficiently soluble to maintain aqueous Ni^{+2} concentrations above 10^{-6} M (60 µg/liter). Above pH 9, precipitation of the hydroxide or carbonate inhibits nickel mobility.

Hydrolysis of aqueous nickel to the hydroxide $Ni(OH)_2$ is significant only under basic conditions. Patterson et al. (1977) compared the precipitation behavior of nickel carbonate and nickel hydroxide in the context of treatment of nickel-bearing waste effluents. Although precipitation as the hydroxide was found to be the more efficient treatment, the lowest nickel concentration attained at pH values below 9 was 15 mg/liter. This level is quite high with regard to its toxicity and indicates that precipitation is not an effective control of nickel under most conditions.

In natural waters, humic acids alter the solubility and precipitation behavior of nickel. Rashid and Leonard (1973) exposed nickel carbonate to humic acid and found that complexation with humic acid solubilized much of the nickel. Sorption of nickel hydrous iron and manganese oxides and organic material probably exerts the major control on the mobility of nickel in the aquatic environment. Nickel, however, is a highly mobile metal and is sorbed only to a small extent, except in the presence of organic compounds. Lee (1975) presented cogent evidence for the importance of hydrous iron and manganese oxides in controlling nickel concentrations in aquatic environments.

However, Perhac (1972, 1974a) found that almost all of the nickel transported by two Tennessee streams was in the dissolved form. The reason for this discrepancy is probably the fact that about 90% of the solids in the streams studied by Perhac were dissolved solids, so that there were very few suspended particles available for coprecipitation/ sorption reactions.

The partitioning of nickel to dissolved and particulate fractions is undoubtedly related to the abundance of suspended material, competition with organic material, and concentrations of iron and manganese.

Suspended organic matter may be a good adsorbent for nickel. Rashid (1974) used colloidal humic substances to adsorb nickel and found that of the nickel thus bound, only 26% could be extracted by ammonium acetate.

Nickel is bioaccumulated by some aquatic organisms, but most concentration factors are less than 10^3. Tong (1974) showed that nickel does not bioaccumulate in lake trout *Salvelinus namaycush*. In a study of the accumulation of iron, zinc, lead, copper, and nickel by algae collected near a zinc smelting plant, it was found that nickel exhibited the lowest concentration factor for all metals tested (Trollope and Evans, 1976). In general, nickel is not accumulated in significant amounts by aquatic organisms.

LEAD

Lead occurs in a variety of deposits, usually those that also contain zinc, cadmium, and copper. The best indicators of lead deposits are zinc, cadmium, silver, copper, barium, arsenic, and antimony. The natural compounds of lead are rather insoluble and geochemical surveys of surface water are not effective. Spring precipitates, however, may indicate the presence of regional lead deposits.

The average concentration of lead in the Earth's crust is approximately 13 ppm, which is equivalent to one-half ounce of lead per ton of rock. Lead is a major constituent of more than 200 identified minerals. Most of these minerals are rare, and only three are found in sufficient abundance to form ores : galena (PbS), the simple sulfide ; angelesite ($PbSO_4$), the sulfate ; and cerrusite ($PbCO_3$), the carbonate. By far the most abundant is galena, which is the primary constituent of the sulfide ore deposits from which most lead is presently mined. Lead ore is commonly present together with ores of copper, zinc, silver, arsenic, and antimony in complex vein deposits, but lead ore also may occur in a variety of igneous, metamorphic, and sedimentary rocks.

The tendency for lead to form complexes with naturally occurring organic materials (e.g., humic and fulvic acids) increases its adsorptive affinity for clays and other mineral surfaces. However, natural compounds of lead are not usually mobile in normal groundwater or surface water because the lead leached from ores becomes adsorbed by ferric hydroxide or tends to combine with carbonate or sulfate ions to form insoluble compounds (Hem 1976a).

An outstanding characteristic of lead is its tendency to form complexes of low solubility with the major anions of natural environmental systems. The hydroxide, carbonate, sulfide, and (more rarely) the sulfate of lead may act as solubility controls. Throughout most of the natural environment, the divalent form Pb^{+2} is the stable ionic species of lead. The more oxidized solid PbO_2, in which lead has a +4 charge, is stable only under highly oxidizing conditions and probably has very little significance in the aquatic environment. If sulfur activity is very low, metallic lead can be a stable phase in alkaline or near neutral reducing conditions.

Hem (1976b) calculated the fields of stability for solid species of lead based on the available thermodynamic data. Although his figures are useful in depicting equilibrium behavior, they are limited in that they do not take into account environmental interactions with organic compounds and other trace elements and, therefore, may be misleading with respect to fate and transport in normal surface waters. Hem (1976a) also modelled the equilibrium distribution between lead in solution and lead adsorbed on cation exchange sites in sediments. In general, this model suggests that in most natural environments, sorption processes would more effectively scavenge dissolved lead than would precipitation.

Lead exists mainly as the divalent cation in most unpolluted waters and becomes sorbed to particulate phases and organic material in polluted waters.

Sorption processes appear to exert a dominant effect on the distribution of lead in the environment. Several investigators have reported that in aquatic and estuarine systems, lead is removed to the bed sediments in close proximity to its source, apparently due to sorption onto the sediments (Helz et al., 1975; Valiela et al., 1974). Different sorption mechanisms have been invoked by different investigators and the relative importance of these mechanisms varies widely with such parameters as geological setting, pH, Eh, availability of ligands, dissolved and particulate iron concentration, salinity, composition of suspended and bed sediments, and initial lead concentration.

The adsorption of lead to soils and oxides was studied by Huang et al. (1977). The data indicate that adsorption is highly pH-dependent, but above a pH of 7, essentially all of the lead is in the solid phase. It should be noted that at low pH, lead is negatively sorbed (repelled from the adsorbent surface). The addition of organic complexing agents increases the affinity for adsorption. Therefore, the tendency for lead to be adsorbed probably reflects the fact that lead is strongly complexed by organic materials in the aquatic environment (Ramamoorthy and Kushner, 1975).

Sorption processes appear to be effective in reducing dissolved lead levels and result in enrichment of bed sediments. It appears that under most conditions, adsorption to clay and other mineral surfaces, coprecipitation/sorption by hydrous iron oxides, and incorporation into cationic lattice sites in crystalline sediments are the important sorption processes.

Several authors, notably Jenne (1968), Lee (1975), and Hohl and Stumm (1976) have hypothesized that the sorption of heavy metals by hydrous iron and manganese oxides is a major control on the mobility of these pollutants in the aquatic environment.

Bioconcentration of lead has been demonstrated in a variety of organisms ; however, some microcosm studies indicate that lead is not biomagnified. Lu et al. (1975) studied the fate of lead in three ecosystems differing only in their soil substrate. The ecosystems contained algae, snails, mosquito larvae, mosquito fish, and microorganisms. Lead was concentrated most by the mosquito larvae and least by the fish. Body burdens and aqueous lead concentration appeared to be strongly correlated to the percentage of organic matter and cation exchange capacity of the soils, indicating that the availability of lead in the systems was controlled by adsorption to the soils. Since pH was the same for all three soils, precipitation/dissolution of inorganically bound lead was probably not responsible for the differences in lead availability and uptake.

Merlini and Pozzi (1977a) measured lead uptake in pumpkinseed sunfish (*Lepomis gibbosus*) exposed to ^{203}Pb at pH 6 and 7.5. Fish in water at a pH of 6 accumulated three times as much lead as fish kept at pH 7.5. Gill, liver, and fin accumulated the most lead and muscle the least. The authors attributed the increased lead uptake at low pH to the increasing concentration of divalent lead with decreasing pH. In another experiment, Merlini and Pozzi (1977b) found a direct correlation between lead accumulation by pumpkinseed sunfish and the concentration of ionic lead in water at various concentrations of total lead. Results suggest that the conditions existing in the majority of natural waters render most lead unavailable for accumulation by aquatic animals.

Patrick and Loutit (1976) studied uptake of lead by benthic bacteria and subsequent transfer to tubificid worms. The concentration factor for bacteria was approximately 360. Concentration of lead by tubificids was 0.77 times the amount fed them in the bacteria, indicating that the tubificids can clear lead more easily than the bacteria. The fact that the bacteria could concentrate lead indicates that lead in the sediments can be remobilized by bioaccumulation.

Based on available information, it appears that fish accumulate very little lead in edible tissues ; however, oysters and mussels are capable of accumulating high levels of lead. Decreasing pH increased the availability of divalent lead. Lead can be methylated by microorganisms present in lake sediments. The volatile compound resulting from biomethylation, that is, tetramethyl lead, probably leaves the sediments and is either oxidized in the water column or enters the atmosphere. Biomethylation represents a process that enables lead in the bed sediments to be reintroduced to the aqueous or atmospheric environment.

SELENIUM

Selenium is widely dispersed in various rock types at low concentrations. It is particularly concentrated in sulfides. Most of the commercially extracted selenium is derived from polymetallic ores such as copper, mercury, and silver. Selenium is a good indicator element for sandstone deposits of uranium, gold-silver selenide ores, and the polymetallic ores containing copper, silver, and mercury. Many western range plants concentrate selenium from the soil and produce concentrations in the thousands of parts per million. For example plants such as locoweed, vetch, or *Astragalus* can concentrate selenium to the point where it causes sickness and mortality in range cattle. On the other hand, deficiency of the same element in northeastern glaciated soils causes poor growth and reproduction, hoof problems, and the so-called white muscle disease in ungulates.

Principal positive oxidation states for selenium are +4 and +6 and in a few unstable compounds, +2. In selenides, selenium assumes the oxidation state of -2. Selenium forms compounds analogous with sulphur compounds including bromides, chlorides, nitrides, oxides, oxy-salts, and sulfides. In the solid state, selenium exists as the Se_8 molecular form, while in the vapor phase, decomposition to the Se_2 form takes place.

Selenium has an average crustal abundance of 0.05 ppm, 0.6 ppm in shales, 0.05 ppm in sandstones, and 0.08 ppm in carbonates. Many sulfide ores are selenium enriched. Selenium forms selenides and sulfo-selenides of silver, copper, lead, and mercury. Minerals that may bear selenium are galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and arsenopyrite (AsFeS). Minerals in which selenium forms an essential component have only been identified in a few deposits. High concentrations (up to 548 ppm) of selenium are found in limonitic concentrations in the basal portion of the Niobrara Formation of Central and Southeastern Wyoming.

The selenium content of rocks varies with different geological formations. Processes contributing to the enrichment of selenium in geological materials include mechanical enrichment, precipitation, adsorption, substitution, and presence of organic materials (Krauskopf, 1955). Highly seleniferous volcanic tuffs have been reported in Wyoming that can contain up to 187 ppm selenium (Rosenfeld and Beath, 1964). Other selenium-bearing rocks include carbonaceous shales, lignites, phosphates, ferruginous sandstones, and limestones. High selenium concentrations also have been associated with uranium-vanadium ores.

Selenium normally does not occur in water in sufficient amounts to produce selenosis in man or animals (Rosenfeld and Beath, 1964). Selenium in water is primarily caused by leaching from seleniferous plants, but these concentrations are usually less than 0.1 ppm. Large amounts of selenium are carried in solution to the sea, but they are largely removed from the aqueous solution by adsorption on precipitated hydroxides of iron and manganese, organic matter, and sulfides. Enrichment of selenium by sedimentary iron ores explains the higher than crustal abundance in these ores. Marine waters typically contain 3 to 6 ppb selenium (Rosenfeld and Beath, 1964).

Selenium in soil may be derived from (1) formations or rock outcrops, (2) rocks lying beneath the soil mantle, (3) weathering of parent rocks and transport by groundwater or surface water, (4) indicator plants, and (5) man-caused enrichment from mining or ore processing. Various selenium compounds in soils differ in their solubility in water. Selenides, selenates, organic selenium compounds, and some elemental selenium may be present in soils ; some are readily adsorbed by the vegetation. The compounds most available for plant absorption are organic selenium compounds and selenates. Selenium content in soils averages 0.2 ppm, but in highly seleniferous areas, surface soils may contain from 1.5 to 20 ppm.

Certain plants accumulate high concentrations of selenium when they grow in seleniferous soil or geological formations. Primary accumulator plants require selenium for their growth and development. Secondary selenium absorbers are different species that accumulate moderately large amounts and thus are an aid in locating seleniferous deposits. Selenium-accumulating plants often play an important role in converting absorbed selenium to soluble compounds that are readily available for absorption by all types of vegetation.

URANIUM

Uranium is widely dispersed in all three major rock types (igneous, metamorphic, and sedimentary), but mainly occurs in the following specific types of deposits.

- Granitic rocks
- Calcite-fluorite-apatite deposits
- Veins, lodes, and igneous dikes (pitchblende)
- Sandstone deposits
- Pyrite-quartz conglomerates
- Carbonatites
- Black shales
- Phosphorites
- Coal and lignite
- Placer deposits

Indicators of uranium are phosphorus, fluorine, cobalt, nickel, and arsenic in soils and sediments. Uranium is, however, a good indicator of its own deposits in all types of geochemical surveys, including radioactivity measurements. Selenium is used sometimes as a uranium indicator, and the presence of darkened or colored carbonate and quartz deposits created by radiation effects is also used.

The average concentration of uranium in the Earth's crust is 1.8 ppm. Granites and shales contain an average of 3.7 ppm, while carbonates have 2.2 ppm and sandstones 0.45 ppm. An estimate for seawater is 0.001 ppm. The total uranium content of the Earth's crust to a depth of 25 km is calculated to be 10^{17} kg and the oceans contain 10^{13} kg.

A few important uranium minerals are uraninite (UO_2), euxenite-polycrase [(Y, Ca, Ce, U, Th)(Na, Nb, Ti)$_2$O$_6$], brannerite [(Y, Ca, Fe, U, Th)$_3$ (TiSi)$_5$O$_{16}$], coffinite ($USiO_4$), autunite [$Ca(VO_2)_2(PO_4)_2 \cdot H_2O$], and uranophane [$Ca(UO_2)_2\ Si_20_7 \cdot H_20$]. Uraninite may occur in pegmatites, but at such low concentration that they are of little economic significance. Pitchblende, found in hydrothermal veins, is the most important ore and is usually associated with sulfides. Near-surface uranium ores are usually oxidized.

Important uranium producers are the sandstone-type Colorado Plateau deposits ; the conglomerates of Blind River, Ontario ; and the reef deposits of the Witwatersand, South Africa. Vein deposits at Great Bear Lake and Lake Athabasca, Canada are also important sources. Low-grade uranium (0.005 to 0.02%) is present in phosphate deposits, bituminous shale, and lignites.

Uranium exists in four oxidation states in solution, but only U^{+4} and U^{+6} are stable. Hexavalent uranium forms the uranyl ion $(UO_2)^{+2}$, which in turn forms complexes with many anions (fluorides, chlorides, bromides, etc.).

The most important oxides of uranium are UO_2, U_4O_9, U_3O_8, and UO_3. At elevated temperatures, uranium and oxygen form extensive solid solutions.

Thermodynamic data show that U^{+4} is less stable than U^{+6}. The U^{+4} species tends to precipitate as insoluble uraninite and coffinite. Uranium in natural waters is usually complexed, and these complexes greatly increase the solubility of uranium minerals in surface water and groundwater (Langmuir, 1978).

Granitic rocks have a relatively high uranium content and are the presumed source rocks for many sedimentary uranium deposits (Langmuir, 1978).

VANADIUM

Vanadium is widely dispersed in most rock types at low concentrations. Basic rocks usually contain the highest concentrations and vanadium is found in a large number of minerals, including sulfides. Vanadium occurs in the following types of deposits.

- Titaniferous magnetite deposits
- Uraniferous sandstones
- Asphalt and other hydrocarbons
- Polymetallic deposits (copper, lead, and zinc)
- Phosphorites and vanadiferous shales
- Sedimentary iron ores
- Petroleum and coal deposits
- Placer deposits containing magnetite

Vanadium is a good indicator of its own presence in the surface environment and is evident in soils and stream sediments. Stream and spring precipitates are enriched in vanadium when it is present in the region.

Vanadium does not naturally occur as a free metal but as relatively soluble salts, commonly in the trivalent state. Important vanadium minerals are patronite (V_2S_5 + nS), carnotite ($K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$), vanadinite [$Pb_5(VO_4)_3Cl$], and descloizite [$4(Pb,Zn)O \cdot V_2O_5 \cdot H_2O$]. Ultramafic rocks (peridotites) and mafic shales contain an average of 200 ppm vanadium; granites contain an average of 16 ppm. Soils in the U.S. may contain 200 ppm with clays usually the highest (300 ppm). Average crustal abundance is 135 ppm.

The most important natural sources of vanadium are marine aerosols, continental dust, and volcanic activity (Duce et al., 1975). An estimate of the total oceanic inventory is 7.5×10^{12} kg, even though only about 0.001% of the vanadium entering the oceans is retained in the soluble form.

Most of the environmental vanadium originates from man's industrial activity, primarily from the combustion of oil to produce electricity. In the coking of coal, there is little emission of vanadium to the air because most of it remains in the coke.

Vanadium exists in four valencies: pentavalent (V_2O_5), tetravalent (VO_2), trivalent (V_2O_3), and divalent (VO). The pentavalent oxide dissolves in alkalies to form vanadates or reacts with halides to form $VOCl_3$, VOF_3, and $VOBr_3$. The VO_2 dissolves in acids to form salts (e.g., $VOSO_4$); trivalent and divalent oxides are insoluble in water and alkalies, whereas divalent vanadium oxide dissolves in acid to form salts.

Vanadium enters the body mainly via the respiratory route and has been found in many human lung samples. The next highest concentration in human tissue is the lower small and large intestines.

Vanadium uptake by plants and animals is variable and depends somewhat on its availability in soils. Seafood is generally higher in vanadium than other foods (Hopkins and Mohr, 1971). Only about 1% of the ingested amount is absorbed from the human intestine and that quantity absorbed is rapidly excreted (60% in 24 h). Because of its low absorption and rapid excretion, vanadium is less toxic than many other trace metals.

No data in the pertinent literature suggests that vanadium is carcinogenic or mutagenic to man. Occupational exposures to the element may result in irritation of the mucous membranes of the respiratory tract, resulting in the possiblity of severe chronic bronchitis.

THE TOXICITY OF ELEMENTS FROM GEOCHEMICAL SOURCES

DISCUSSION OF ELEMENTAL TOXICITY

The relationship of essential, nonessential, and toxic trace elements in the soil and parent materials of a region to the health and prevalent diseases in man and animals of that region has received increased attention during the past two or three decades (Kovalsky, 1974; Lag and Bolviken, 1974; Fortescue, 1974). Numerous reports have directly addressed the subject of naturally occurring toxic elements and their relationship to animals and man (Cannon, 1974; Gough et al., 1979). Continued research on the interrelationships of endemically high or low concentrations of trace elements (including those of anthropic origin) and disease states (geomedicine) may reveal how important the local occurrence of geotoxic materials are to the general welfare of man (Warren, 1974; Gould and Warren, 1980). The weakening philosophy that all or most disease states have a microbial origin may eventually be reevaluated in view of the data being obtained in modern research in the embryonic science of geomedicine.

Some of the elements discussed here have the ability to cause toxic effects in animal food chains and in human nutrition, especially where the elements are derived from water or food. Of the eight elements, naturally occurring arsenic and selenium have the most notable physiological effects in animals and man. Examples of water contamination with arsenic have occurred in Chile (Borgono and Greiber, 1971) and Alaska (Hawkins et al., 1980) where the local population became intoxicated from water supplies that contained elevated levels of arsenic derived from a local geochemical source. Selenium toxicity has occurred throughout the Western U.S. in range cattle that typically acquire the element from several accumulator species of range vegetation (Gough et al., 1979).

Many of the eight elements discussed here reach man in significant quantities from various anthropic activities that can and usually do overwhelm any natural pathways. Lead and cadmium are examples of elements with strong anthropic sources, and the inventory of lead and cadmium released by automobile exhaust and industrial outfall, respectively, exceed releases from any other known sources. Recent research by Burau et al. (1980) has shown that endemic geochemical sources of cadmium can occur and may affect regional agricultural products. Natural arsenic, selenium, and uranium deposits (often associated with each other) may produce locally elevated concentrations of those elements in soils, sediments, and surface water. This is, in fact, the basis of geochemical prospecting techniques widely used in obtaining commercial deposits of these and other elements.

Undoubtedly it can be demonstrated that under typical cultural conditions, all or most of the elements considered here reach man primarily as the result of technological, agricultural, and other anthropic activities rather than from local geochemical sources. Of the eight elements, five are known carcinogens (chromium, nickel, selenium, cadmium, and lead). The physiologically essential elements in the series are arsenic, chromium, nickel, selenium, and perhaps vanadium (Mertz, 1981).

Stimulatory effects have been observed when vanadium has been added to the diet of animals. The requirements for essentiality of any element are as follows (Dulka and Risby, 1976).

- The presence of the element in the newborn or fetus.
- Homeostatic regulation of the element.
- Existence of a metabolic pool of the element, specifically influenced by hormonal or physiological processes.
- Presence of a metallo-enzyme in which the element occurs.
- Occurrence of a deficiency syndrome that can be eliminated by the ingestion of trace amounts of the element.

It is possible that essentiality can be demonstrated in one class or taxon of organisms and not in others. For example, vanadium is essential to ascidians and marine invertebrates, but may not be required by other animals, including mammals.

In relating the biological effects of one material to another, it should be understood that rigorous and precise comparisons are impossible. This is particularly the case in comparing toxic materials that are essential metabolites in low concentration to those apparently having no threshold levels for exhibiting harmful effects. Also, it must be realized that different toxins may exhibit different physiological effects, and it is somewhat tenuous to compare the severity of such effects to each other. For example, it is difficult to relate a kidney poison to a carcinogen, except perhaps at the extreme effect of death itself.

The approach adopted in this study is that harm or detriment, in itself, can be a useful scale and that at relatively low doses (which for geotoxic exposures are of overriding importance), relative comparisons, although not rigorous, can provide useful insights and perspectives on detriment.

In the case where radiation effects are related to chemical effects, many believe that any comparison is invalid because many stable elements have been shown to be essential metabolites at low dosage, while radiation is reputed to have no threshold for harmful effect. It should be pointed out however, that the latter observation is, as yet, theoretical. In fact, radiation also has been reported to exhibit stimulatory effects at low doses (hormesis) (Luckey, 1980). Therefore, considering our present state of knowledge in this regard, it may be concluded that relating low-dose detriment of radiation to chemical toxins can be considered a valid approach.

Toxicity of the eight elements considered here can be described in a concise way by the lethal dose from oral ingestion (oral LD_{50}) determined in small mammals in laboratory experiments. Table 10 shows the oral LD_{50} concentrations for the eight elements. Two of the elements have large oral LD_{50} values (nickel and uranium), and these values depend largely on the compound or elemental form administered. Generally arsenic, selenium, and cadmium have the lowest oral LD_{50} values and the highest toxicity. As was noted, arsenic and selenium have caused health problems in man and animals from low chronic exposures to elevated natural levels.

Anthropic sources of these elements may deliver inventories to the environment far greater than any other known sources of geochemical deposits, although many geochemical sources are extremely large. Metallic emissions from all industrial and technological sources in 1970 for the eight elements are shown in Table 11 (Dulka and Risby, 1976). The largest source is automotive lead, which far outweighs all other metallic releases to the environment. The emission of lead by autos, although decreasing for various economic and technological reasons, is affecting the health of the urban population despite predictions by petroleum industry scientists made when alkyl lead compounds were first introduced (Warren, 1974; Zook, 1978). In 1972 the total lead use was 1.44×10^6 ton, of which 19.3% was on-highway fuel anti-knock lead and batteries (Osweiler and VanGelder, 1978). The major route of exposure is apparently inhalation of lead particulates that, coupled with the lung absorption of approximately 50%, produces physiologically significant lead concentrations in the blood of city dwellers, especially children (Poole and Smythe, 1980; Warren, 1974). Additional lead intake occurs from the use of processed foods and tobacco (Settle and Patterson, 1980).

The eight elements discussed here can be arranged in two groups.

- Group I -- Toxic essential elements: arsenic, selenium, chromium, and nickel
- Group II -- Toxic nonessential elements: cadmium, lead, uranium, and vanadium

Two of the most toxic elements, arsenic and selenium, are found in the essential group. The window of beneficial concentration for both of these elements is rather narrow, and a few parts per million in either direction from the optimum will produce either toxicity or deficiency symptoms. Selenium is a good example of the narrow optimal range of a toxic required element. At 0.1 ppm (dry weight) in the diet, nutritional needs are met in grazing sheep and cattle (Underwood, 1971). Intake of more

TABLE 10. The oral LD_{50} values for eight toxic elements in small mammals.[a]

Element	Oral LD_{50} (mg/kg)	Animal
Arsenic	1-25	Rat
Cadmium	72	Rat
Chromium	1870	Rat
Nickel	2000	Rat
Lead	150	Rat
Selenium	6	Rat
Uranium	400	Rat
Vanadium	23	Mouse

[a] From National Research Council (1972), (1974a), (1974b), (1975), (1977); Environmental Protection Agency (1977); Maynard and Hodge (1949); and Nraigu (1980).

TABLE 11. Metallic emissions in 1970 (Dulka and Risby, 1976).

Element	Tons per year	Percent of total metallic emissions
Arsenic	10,600	1.6
Cadmium	2,160	0.3
Chromium	18,136	2.7
Nickel	7,310	1.1
Lead	16,563[a]	
	197,437[b]	34.7
Selenium	986	0.1
Vanadium	20,300	3.1

[a] Off highway use.

[b] Highway use.

than 4 ppm of selenium in the diet results in toxicity symptoms, and rats eating 8 to 10 ppm in the diet died after a few weeks. A daily intake of 1 mg selenium by man is not harmful to an adult human whose average body burden is on the order of 15 mg. Selenium concentration may be high in Western U.S. grains, but it is unlikely that a population subsisting on the output of grain from a seleniferous area would obtain a toxic dose under normal dietary conditions. The maximum concentration of selenium that man can consume in the diet without toxic effects is between 3 and 7 ppm and water containing 0.5 ppm is dangerous (Bowen, 1966). The drinking water standard (Environmental Protection Agency, 1976) is 0.01 ppm, which is lower than for arsenic. Chronic selenium toxicosis was observed in Mexico and Columbia (Leonidas and Hernan, 1970) and was the result of exclusive subsistence on locally produced crops and water in a seleniferous area.

Both selenium and arsenic are cumulative in the appropriate chemical forms and at relatively low concentrations. Arsenic concentrations in drinking water as low as 0.8 ppm ingested for 12 y caused cutaneous lesions in 30% of the population of Antofagasta, Chile (Borgono and Greiber, 1971). Bowen (1966) gives the probable lethal dose of arsenic for man as 5 to 50 mg per kg body weight, while the National Research Council (1977) estimated a fatal dose of arsenic trioxide at 125 mg or 1.4 mg per kg body weight.

Recent reports of arsenic in groundwater and domestic water wells near Fairbanks, Alaska cite concentrations as high as 10 ppm (Hawkins et al., 1980). Arsenic enters groundwater from geochemical deposits, probably from arsenites or arsenopyrites, and is drawn into well water supplies. In Alaska, placer gold deposits were also implicated in arsenic occurrence in surface waters and sediments. Arsenicism has been reported in Taiwan (Tseng et al, 1968), Chile (Borgono and Greiber, 1971), and Alaska (Hawkins et al., 1980) where local populations have acquired physiologically significant, if not toxic concentrations from drinking water.

Marine organisms also accumulate arsenic from the sea and shellfish have rather high concentrations, up to 170 mg per kg. Unless a diet contains an unusual amount of an accumulator organism, however, exposure will be negligible. Organically bound arsenic has a low toxicity and rats fed large amounts of organic arsenic did not exhibit the usual toxicity symptoms (Coulson et al., 1935).

The major pathway for arsenic toxicity appears to be drinking water. The estimated daily intake of arsenic is 900 μg from water and food that generally contains 0.4 to 0.5 ppm of arsenic (Schroeder and Balassa, 1966). Arsenicals are still used in agriculture as defoliants (dimethyl arsenate and cacodylic acid) and some pesticides. Orchard soils may still contain concentrations of arsenic inhibiting to plant growth from previous applications of arsenical pesticides. The arsenic baseline in many agricultural areas may thus be elevated above natural geochemical levels from the use of arsenicals (Koranda et al., 1979). Schroeder and Balassa (1966) provide a review of the behavior of arsenic in man and the pathways by which it reaches him.

The remaining two essential elements, chromium and nickel, are of relatively low systemic toxicity. Their usual mode of toxic exposure to man is by inhalation from industrial uses. Some dermatological effects are observed from wearing nickel and chromium ornaments and jewelry that touch the skin. Both metals have a relatively high crustal abundance and may be found in food organisms in moderately high concentrations. Apparently, mammals have adapted to relatively high dietary intake of these metals because their gastrointestinal sensitivity is low. Chromium is accumulated by aquatic organisms and is also present in high concentrations (5000 ppm) in the suite of elements occurring in serpentinite and the derived soils. Vegetation endemic to serpentinite areas is often unique because of its taxonomy and the high metal concentrations it contains. The typical oxidation state of the element occurring in surficial mineral materials (Cr^{+3}) is not significantly toxic.

Nickel may be taken up from the soil in relatively high concentrations by plants (to 4 ppm) and in general occurs at higher concentrations in food materials than does chromium. The two metals therefore have contrasting ecological behavior, nickel being easily assimilated into the terrestrial food chain and chromium being accumulated by aquatic organisms. Nickel is also one of the more prominent contaminants in phosphatic fertilizers (104 ppm) but, because of its low gastrointestinal tract absorption, may not present serious problems in agricultural use.

The remaining four elements, which are toxic, nonessential elements, may be considered as two element pairs because of their usual occurrence: lead and cadmium, and vanadium and uranium. Lead, cadmium, and zinc are often found together in polymetallic sulfide deposits. Ore bodies of lead may elevate local levels in soils and to a limited extent, in surface water and groundwater. It can enter food chains at levels that may be toxic to mammals.

The soil-plant absorption pathway for lead is not particularly effective in the transfer of the element to mammals (Sharma and Shupe, 1977). Therefore lead is seldom transferred in large amounts from soil or substratum sources, although some such examples are present (Lag and Bolviken, 1974).

The deposition of lead particulates from industrial and automotive sources bypasses the soil-root pathway (Hirao and Patterson, 1974), and plants and animals acquire lead burdens from atmospheric sources rather than from the substratum. Needles of conifers growing in the San Bernardino Forest in Southern California show an increase from 1 to

3 ppm lead in the first-year needles to 38 ppm in third-year needles, presumably from the same atmospheric sources that deliver oxidants to the forest from the Los Angeles Basin (Coyne and Bingham, 1977). Lead is often bound or chelated in the humus layer of soils by organic colloids and usually exhibits maximum concentration a few centimeters from the soil surface.

Cadmium is found at low geochemical levels and typical sources in most human ecological situations are from water (pipes), food, tobacco, and airborne particulates. Cadmium is known to occur in elevated concentrations in some areas from endemic geochemical sources, as in the Salinas Valley of California (Burau et al., 1980). Cadmium also occurs as a contaminant in phosphate fertilizers at 92 ppm (Table 6) and was found in phosphate ore at 81 ppm. Cadmium has been identified as the causal agent in the contamination of a human food chain in Japan where the "itai-itai" disease was produced in a local population of fisherman from the outfall of cadmium and other metals from a mine and factory (Kobayashi, 1971).

Uranium and vanadium typically do not exert toxic effects on man from geochemical sources and ecological pathways. Vanadium and uranium often occur together in several rock types and as shown in Table 6 are present in rather high concentrations in phosphatic fertilizers derived from phosphorite ores. Suspended sediments in the Colorado River at Cibola, below Blythe, contain 800 ppm of vanadium, but showed only geochemical levels of uranium. The review of vanadium in biology and physiology by Schroeder et al. (1963) summarized the data on this relatively common element in the Earth's crust. Vanadium reaches man in modest amounts that are, however, larger than several required elements. Vanadium has a low gastrointestinal toxicity. It is present in plant oils, coal, and petroleum products, all of which have common origins. It plays a small role in human physiology in lipid metabolism and seems to undergo some level of homeostatic regulation. Its role in human metabolism has not been clearly defined although several functions of the metal have been demonstrated. Apparently vanadium does not fullfill all of the previously discussed criteria for essentiality and therefore generally is not considered to be an essential trace element; although in a recent discussion by Mertz (1981), vanadium was considered an essential element. Its role in marine invertebrate physiology (ascidian) in the body fluid pigment, hemovanadin, is unique and academically interesting. The high levels in the marine animal are apparently derived from the marine sediments in which it lives and consumes.

Uranium is generally widely dispersed in rock and soil types and is found at 1 to 9 ppm in most surface soil materials. In the Imperial Valley, 37 surface soil samples were analyzed by neutron activation analysis and the mean soil uranium content was 2.9 ± 0.3 ppm. Plant uptake is not particularly effective for uranium but may increase under alkaline conditions.

Both uranium and vanadium occur in treble phosphate fertilizers (Table 6). This anthropic source of uranium is probably the most common pathway to man, except for drinking water. Uranium shows low gastrointestinal tract absorption (1%) (Hursh et al., 1969) and the gut pathway may not be particularly significant in the daily intake.

Actinides that are bound to organic matter may show larger uptake coefficients than the inorganic species of uranium in fresh water, and this pathway may be more efficacious than previously believed (Watters et al., 1980).

Table 12 contains the elemental concentrations of the eight toxic elements in mammalian organs. These data indicate the general location of physiological pools of the elements and thus, conform to the concept of a target organ for the element.

We have reviewed thus far the basic characteristics of the eight geotoxic elements, described their geochemical disposition, and discussed some aspects of their biological and ecological interactions. The presence of natural deposits of these elements in the surface environment constitutes a source of persistent and often readily mobilized hazardous materials to man. Unweathered geological materials may be much more available for transport and dissolution than weathered surface minerals that are often in nontoxic valence states. The fact that only three of these eight elements (arsenic, selenium, and lead) under natural conditions have caused observable toxic reactions in animals and man can be related to the geochemical occurrence, chemical state, and to inefficient pathways to man for the remaining elements. All of the elements have exhibited toxicity in industrial or laboratory conditions, and exposure to six of the elements has caused carcinogenic effects in occupational groups.

DEVELOPMENT OF THE TOXICITY MATRIX

The basic characteristics of toxicity are related to the effects of the element at the cellular and biochemical level. These effects are complex and may vary considerably with dosage, physiological state of the affected organism, and the presence of other elements and compounds (Vallee and Ulmer, 1972; Eichhorn, 1978). Synergism and antagonism occur between such element pairs as cadmium and zinc, arsenic and selenium,

TABLE 12. Elemental concentrations of eight elements in mammalian organs (Bowen, 1966).

	Parts per million in organs				
Element	Brain	Heart	Kidney	Liver	Muscle
Arsenic	0.08	0.01	0.34	0.5	0.16
Cadmium	3	0.05	130	6.7	0.06
Chromium	0.12	0.02	0.05	0.02	0.04
Nickel	0.3	0.2	0.2	0.2	0.008
Lead	0.24	0.2	4.5	4.8	0.2
Selenium	2.1	0.7	2.1	2.1	2.5
Uranium	--	0.03	0.03	0.04	0.03
Vanadium	0.03	0.04	0.05	0.04	0.04

nickel and iron, and vanadium and phosphorus. The level of calcium may affect all of the elements being discussed. These effects are too detailed and variable for this discussion and only those toxicity effects operating at the organism level will be utilized here.

A series of toxicity parameters have been compiled from the literature concerned with the eight toxic trace elements. Table 13 lists these parameters with the values for each element of interest. The data on average crustal abundance and soil concentrations of the eight elements indicate their basic geochemical and ecological importance and are not weighted heavily in the toxicity evaluation. It is interesting, however, to note that for many elements, natural soil concentrations can be in the toxic range, and it is obvious that other factors besides the geochemical and ecological occurrence determine the hazard of toxic elements. Drinking water and continuous irrigation water standards are indices of the toxic potential of the element as perceived by regulatory agencies (Environmental Protection Agency, 1976), and are usually based on the lower threshold of toxic responses. The average daily intake and the related body burden of the element are essentially the background physiological levels of the element above which toxicity occurs (Table 14). For some elements, the difference between average daily intake, essentiality, and the lower threshold toxic response is rather small. For example, selenium has a 0.2 mg/d average intake, an essentiality level of 0.04 to 0.1 ppm, and a lower threshold toxic response of 0.7 to 7 mg/d.

TABLE 13. Toxicity parameters for eight toxic metals.

Element	ACA[a] (ppm)	Soil[b] (ppm)	DWS[c] (μg/liter)	IRR HHO[d] (μg/liter)	Daily intake[e] (μg)	Aquatic toxicity (mg/liter)	Plant toxicity (ppm)	Mammalian toxicity	Human toxicity	FISH BIOACCUM[f]
Arsenic	1.8	6	0.05	0.1	900	0.02	0.5-2	11.2 ppm 1-25 mg/kg	125 mg 0.06-1.18 mg/kg	333
Cadmium	0.2	0.06	0.01	0.01	72	0.01-10	0.1-3	72 mg/kg	3 mg/d	200
Chromium	100	100	0.05	0.1	284	0.03-64	0.5-24	1870 mg/kg	4000 ppm	4000
Nickel	75	40	0.05	0.2	500	0.03	25-100	1-3 g/kg	--[g]	100
Lead	13	10	0.05	0.1	300	0.01-50	25-30	0.5-0.8 ppm	1.7 mg/kg	300
Selenium	0.05	0.2	0.01	0.02	200	2	5-20	6 mg/kg	0.7-7 mg/d	167
Uranium	1.8	1	0.1	0.5	1.3	2.8	50+	400 mg/kg	1-4% diet	10
Vanadium	135	100	0.1	0.1	1160	4.8	10-40	50 mg/kg	not known	10

[a] Average crustal abundance.

[b] Average soil concentration.

[c] Drinking water standard.

[d] Continuous irrigation water standard.

[e] Daily intake from food, air, and water.

[f] Bioaccumulation factor for fishes.

[g] Toxic only as the carbonyl ; some cutaneous sensitivity.

TABLE 14. Estimated daily intake of elements from foods (Mahaffey et al., 1975).

Food type	Lead (µg/d)	Cadmium (µg/d)	Arsenic (µg/d)	Selenium (µg/d)
Dairy products	--	3.94	2.34	--
Meat, fish, poultry	4	2.49	5.64	56.3
Grain, cereal	4.16	11.66	1.35	92.5
Potatoes	0.7	9.11	0.64	0.65
Leafy vegetables	3.03	3.18	--	--
Legumes	18.08	0.42	--	--
Root vegetables	3.83	0.76	--	0.25
Fruits, garden	11.36	1.71	--	--
Fruits, orchard	9.49	9.38	--	--
Oil and fats	0.67	1.36	0.17	--
Sugar	0.55	0.68	--	--
Beverages	3.81	6.49	--	--
TOTAL	60.4	51.2	10.1	149.7
Major contributors	Legumes Fruits Grain	Grain Potatoes Fruits	Meat Dairy Grain	Meat Grain

Aquatic animal, plant, and mammalian toxicities are those determined in laboratory or test plot experiments. In some cases a relatively broad range of toxic response is reported because of differences in organism response, elemental form, and mode of exposure. Strong differences are seen between oral, intramuscular, intraperitoneal, and intravenous methods of exposure. The data in Table 13 are confined to oral exposures that would simulate intake by typical ecological pathways. The ecological sources and common exposure modes are the usual routes by which organisms, including man, acquire their daily intake and body burdens (Shacklette et al., 1978).

The bioaccumulation factor for fish was obtained from the report on environmental, health, and control aspects of coal conversion (Braunstein et al., 1977). Other data on the subject may be obtained from Environmental Protection Agency (1977), where values for minimum acute toxicity concentrations and estimated permissible concentrations for various ecological media are given.

In Table 15, the eight elements are ranked according to their inherent toxicity on the basis of the eight toxicity parameters, with weight given to the peripheral parameters of crustal abundance, soil concentrations, and exposure modes. Only the elements occurring in the upper two ranks were given a toxicity value or point. Uranium did not occur in the upper two ranks in any parameter and, along with vanadium, occurred generally in the lower portion of the matrix.

The ranking of the elements from high to low toxicity on the basis of ten parameters is as follows.

(1) Arsenic
(2) Cadmium
(3) Lead
(4) Selenium
(5) Nickel
(6) Vanadium
(7) Chromium
(8) Uranium

Vanadium and chromium occurred in the upper two ranks only once. Vanadium did so because of its high crustal abundance, which is not as significant as the parameter for which chromium was scored (soil concentration). Nickel is ranked above chromium because greater weight is given to the plant toxicity and uptake of nickel than the bioaccumulation toxicity for fish of chromium. This was done because more plant foods than fish occur in the average diet (International Commission on Radiological Protection, 1975; Rupp et al., 1980). The differences between elements in the lower categories of the toxicity matrix are probably small.

The primary routes by which nickel, chromium, and vanadium exposures to man occur are industrial and occupational. It is unlikely that, as the result of typical ecological transport phenomena, there would be toxic exposures of these three elements to man. Nickel and chromium may occur in high concentration in serpentinite-derived soils, but usually the presence of the metals is self-limiting because the resulting phytotoxicity of the soil reduces or eliminates the trophic transfer of the endemically high metal concentrations characteristic of the serpentinite soil and rock.

Assessment of the geochemical, ecological, and toxicity parameters of eight potentially toxic elements has resulted in a toxicity ranking of the elements. The validity of the ranking is demonstrated by the occurrence of toxic episodes and studies of subtoxic effects of the elements. The occurrence of four cases of arsenicism from high exposures from groundwater or other potable water supplies demonstrates the element's toxic potential.

TABLE 15. Toxicity matrix.

	Toxicity parameters									
	ACA[a]	Soil[b]	DWS[c]	IRR HHO[d]	Daily intake	Aquatic toxicity	Plant toxicity	Mammalian toxicity	Human toxicity	FISH BIOACCUM[e]
HIGH	Vanadium	Chromium	Cadmium	Cadmium	Vanadium	Cadmium	Cadmium	Lead	Arsenic	Chromium
	Chromium	Vanadium	Selenium	Selenium	Arsenic	Lead	Arsenic	Arsenic	Lead	Arsenic
	Nickel	Nickel	Arsenic	Lead	Nickel	Arsenic	Chromium	Selenium	Selenium	Lead
	Lead	Lead	Lead	Arsenic	Lead	Nickel	Selenium	Cadmium	Cadmium	Cadmium
	Arsenic	Arsenic	Chromium	Chromium	Chromium	Chromium	Vanadium	Vanadium	Chromium	Selenium
	Uranium	Uranium	Nickel	Vanadium	Selenium	Selenium	Lead	Uranium	Uranium	Nickel
	Cadmium	Cadmium	Uranium	Nickel	Cadmium	Uranium	Nickel	Chromium	Vanadium	Uranium
LOW	Selenium	Selenium	Vanadium	Uranium	Uranium	Vanadium	Uranium	Nickel	Nickel	Vanadium

Toxicity Ranking

(1) Arsenic : High daily intake ; high plant, mammalian, and human toxicity ; and bioaccumulation toxicity for fish
(2) Cadmium : High drinking water, irrigation water, aquatic, and plant toxicity
(3) Lead : High aquatic, mammalian, and human toxicity
(4) Selenium : High drinking water and irrigation water toxicity
(5) Nickel : No high toxicity or concentrations
(6) Vanadium : High daily intake
(7) Chromium : High bioaccumulation toxicity in fish
(8) Uranium : No high toxicity or concentrations

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[a] Average crustal abundance.

[b] Average soil concentration.

[c] Drinking water standard.

[d] Continuous irrigation water standard.

[e] Bioaccumulation factor for fishes.

Cadmium from ecological exposures has been implicated in essential hypertension and other cardiovascular diseases in the general population. The industrial exposure of a Japanese population to cadmium via their aquatic food chain is well documented (Kobayashi, 1978). The high levels of lead in children in cities and in the urban population in general from air particulates and in the general population from processed (canned) food (Settle and Patterson, 1980) also attest to the widespread exposure to this toxic element.

Selenium is geochemically the least abundant of the elements considered but has a high potential for accumulation in vegetation, especially small grains grown in the Western U.S. Organically complexed selenium is relatively more toxic to mammals in this form, in contrast to arsenic, but this source is apparently effectively diluted in the cosmopolitan origin of the average diet. The only known human toxic exposure to selenium occurred in Mexico and South America where a high rate of ingestion of locally grown foods was related to the intoxication. The toxic and lethal exposures of range cattle to selenium have been frequently described and the specific accumulator plant species identified. If the range animal consumes vegetation with a selenium concentration of 100 to 1000 ppm, the total diet easily reaches the toxic level of 4 to 7 ppm, even though the accumulator plants constitute a fraction of its food intake.

Naturally occurring nickel, chromium, vanadium, and uranium seldom reach man or animals in concentrations that will induce toxic symptoms, primarily because of the low levels of gastrointestinal uptake. Although these elements occur in groundwater and surface water, the elemental form is nontoxic and the concentrations coupled with the low gastrointestinal uptake are generally insufficient to cause systemic effects.

Despite the large deposits of toxic elements present in the surficial environment, especially arsenic, cadmium, lead, and selenium, the occurrence of toxic events has been relatively rare. When they do occur, they are relatively easy to diagnose and rectify. Modern methods of elemental analysis, especially water analysis, have provided the biogeochemist with effective tools in detecting elevated levels of anthropic and naturally occurring elements and compounds.

The behavior of man-deposited toxic substances in the surficial environment may be reasonably predicted from the behavior of naturally occurring toxic elements. When the dominant elements composing the toxic substances are known, elemental behavior may be assumed to be analogous with elements already present in the geological medium chosen for a disposal. Baseline geochemical reconnaissance and analyses can be a useful component of any siting study related to waste and hazardous material disposal.

Natural concentrations of certain elements may provide a significant role in localization of mobile substances in a waste material. Bentonite and other alumino-silicates have high complexation potential for elements released into the deposit. Carbonates, sulfide deposits, and other types of ore bodies should be systematically investigated for their ability to play a useful role in hazardous waste repositories.

SUMMARY

The geologic disposal of radioactive and other hazardous waste does not present a new or unique problem. Toxic materials have been incorporated in the Earth's crust by man or nature during the history of the planet. Useful insights on the biological effects of geotoxic materials can be gained from a study of their natural abundance and transport. For this purpose, the current review of the existing data has been initiated to provide a resource for future study.

This report provides a basis for evaluating the problem and identifying useful areas for continued investigation. Such study can provide information for

- a perspective on the severity of problems resulting from underground burial of hazardous waste,
- improved understanding of transport processes of toxic materials,
- development of an overview on siting radioactive and hazardous waste repositories in areas of high natural geotoxicity, and
- improved understanding of geochemistry in health and disease.

From this preliminary study, it is concluded that the following are the most useful areas for future study.

- Transport of stable element analogs of biologically significant radionuclides in nuclear waste.
- Impacts resulting from naturally occurring geotoxic materials with the most biologically serious consequences. These include arsenic, cadmium, lead, and selenium.

Extensive information exists in the current literature relative to the required study. Future work should be focused on accumulating and systematically organizing the data so that it may be readily applied to problems involving geotoxic materials in the surficial geological environment.

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