

TRACE ELEMENTS AND CONTAMINANTS

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Summary

Contamination of the environment refers to the anthropogenic tertiary dispersion of chemical substances from localized sources into worldwide distribution in the environment. The exponential trend in growth of production or consumption of many trace elements in the early twentieth century has, over the period from 1980 to 2000, slowed to moderate growth or a stagnant trend. However, the natural cycles of some elements have been significantly disturbed by the anthropogenic impacts of recent

years. Other new substances have entered the environment and their cycles have just begun.

Some of the chemicals entering the environment are not considered dangerous for ecosystems. Other substances have direct and/or indirect influences on life forms and can cause serious damage. Toxic metals such as mercury, cadmium, arsenic, and lead, as well as many other organic substances, tend to accumulate in certain reservoirs (soil, sediments, etc.) from which they may be released by various processes of remobilization. They may also change form or speciation and become available to the biological food chain, thereby affecting life, including human life, by causing chronic and acute disorders. Trace metals are not usually eliminated from the ecosystems by natural processes, in contrast to most organic pollutants.

Although the most dangerous organic substances are those that have the potential to bioaccumulate and biomagnify, toxicity and other related parameters of the substances such as mutagenity, teratogenity, etc., also determine the potential threat.

1. Trace Elements

Only 10 (oxygen, silicon, iron, aluminum, calcium, potassium, sodium, magnesium, titanium, and hydrogen) of the naturally occurring 89 elements account for over 99% of Earth's crust by mass. The other 79 elements (including the inert gases), that together form less than 0.5% by mass, are known as the trace elements. They do not play a fundamental role in the makeup of Earth's crust but their significance in economy, ecology, agriculture, medicine, toxicology, and many other areas is completely disproportional to their low crustal abundances. The term "trace element" has no precise definition in the earth sciences, because the concentration of an element in a given phase can be so low that it is considered a trace element, whereas the same element can constitute a main part of another phase. For example, Al is a main element in most common rocks and soils, but is a trace element in vegetation and water. In contrast, Fe is a trace element in quartz, and is a main element in mafic minerals.

In geochemistry, the most frequently used definition is: trace elements (also known as microelements) are chemical elements whose concentration in Earth's crust is less than 0.1% by mass. (See *Trace Elements, Contaminants*.)

1.1. Primary Dispersion

In order to understand the role played by trace elements in the environment, we must investigate the main mechanisms of dispersion to find out how trace elements achieved their present distribution on Earth. In the course of primary dispersion, trace elements become concentrated along with major elements in certain types of geological formations. During the crystallization of rocks from the cooling and solidifying melt, the major constituents form a sequence of minerals dependent on the prevailing temperature and pressure. The microelements usually occupy spaces in the lattices of these minerals according to the rules of diadochic substitution.

These processes are largely controlled by the elements' valence, ionic radius, and electronegativity. In the case of the first row transition elements, crystal-field stabilization energies are also important. On this basis it is possible to explain why individual trace elements may or may not be incorporated into particular coordination sites in the common rock-forming minerals, thereby effectively substituting the major elements that normally occupy these sites.

Unlike the major elements, where concentrations rarely vary by more than a factor of two over a wide range of geological formations, the concentration of trace elements varies very considerably from material to material.

1.2. Secondary Dispersion

Secondary dispersion of elements from the bedrock into the surface environment occurs as a result of physical and chemical weathering, which transforms fresh rock, which is frequently nonporous, into soft and porous soil. Physical weathering breaks the rock into smaller particles, thereby increasing the surface area of the material that is exposed to air and water. Atmospheric oxygen and water are the main agents of chemical weathering. During chemical weathering, primary minerals, which have been formed at high temperatures and pressures mostly in the absence of air and water, are changed into phases that are stable under surface conditions. Surface conditions are characterized by low temperatures and pressures and also by the presence of air and water. The order of rock-forming minerals' relative stability is in general the reverse of that in Bowen's reaction series during the crystallization of igneous rocks.

The redistribution of chemical elements involves interactions between bedrock and water from atmospheric precipitations containing dissolved gases.

The newly formed phases contain particulate and colloidal material, water and fragments of minerals that are resistant to weathering. The fate of a trace element in solution then depends on the behavior of its aqueous species. This behavior can be related to such parameters as ionic potential and effective hydrated ionic diameter. The trace element may be either leached from weathered material into surface and subsurface water or precipitated from solution as hydroxide, oxyhydroxide, carbonate, sulfate, phosphate, etc. It can also be incorporated into a newly formed phase. Less frequently, it may be adsorbed onto the charged surfaces of clay particles or organic matter.

The secondary dispersion of trace elements is strongly affected by the redox potential (Eh), the partial pressure of CO₂ (pCO₂), the pH, and the stability of host minerals that are subject to decomposition in particular weathering environments.

Both primary and secondary dispersions take place spontaneously, independently of human activities. However, some exceptions do exist. For example, acidic atmospheric precipitation accelerates rock weathering by the addition of H⁺ (hydrogen) ions. Hydrogen ions then release some cations from the structure of primary phases. In

addition, nutrients are leached away out of the soils formed on the bedrock, while toxic metals become more mobile and more readily available. (See *Weathering*.)

1.3. Tertiary Dispersion

Industrial development over the twentieth century has caused substantial enrichment in basic environmental media such as soil, vegetation, water, and air, resulting in geochemical neoanomalies that may contain up to 1000 times the normal crustal trace-element content. The normal crustal trace-element concentration is usually described as the “background concentration.” The trace elements concentrated in neoanomalies are often metals, especially heavy metals (density $> 6 \text{ g cm}^{-3}$). Some of them are essential in trace quantities for life processes but in higher concentrations all are toxic to organisms. Metals and nonmetals enter the environment whenever they or their compounds are pulverized, heated, and dissolved during industrial usage. The extent of their emission will depend on the nature and efficiency of the particular industrial process. Considerable neoanomalies of many trace elements are found around mines, smelters, and industrial complexes, along roads, and in most urban areas. Humankind is creating new pathways for the dispersion of many chemical elements in a manner that could be termed tertiary dispersion or pollution. At present, the natural geochemical cycles of some trace elements are considerably disrupted by human activities.

1.4. The Main Sources of Trace-Element Contamination

The main sources and some pathways of trace element movement in the environment are shown in Figure 1 and in the text as follows.

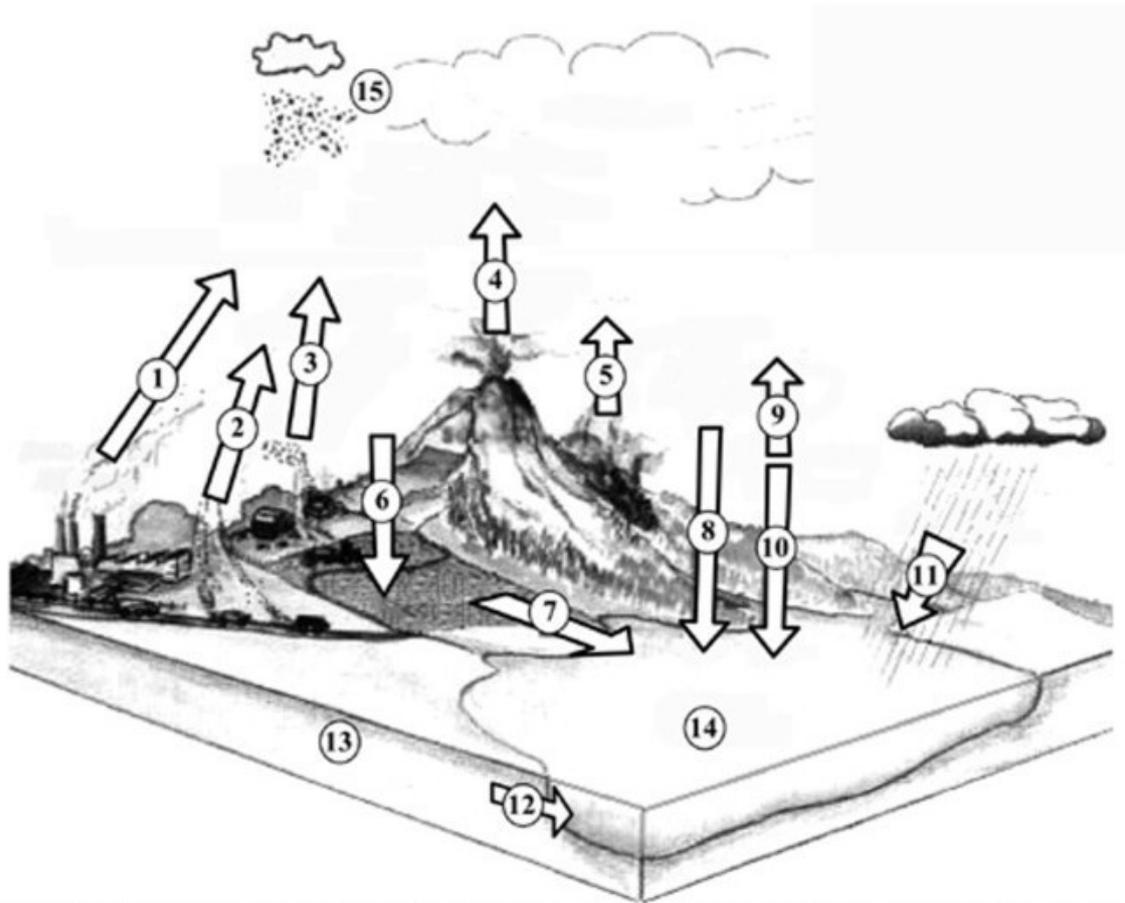


Figure 1. Sources, reservoirs, and pathways of the trace elements and other chemical substances

Manmade sources: Industrial emissions (1), vehicular emissions (2), household emissions (3)

Natural sources: volcanic eruptions (4), forest fires (5)

Pathways: ground deposition (6), surface runoff (7), dry deposition (8), air/water gas exchange (9,10), wet deposition (11), groundwater water flow (12)

Reservoirs: soil and bedrock (13), water (14), atmosphere (gases, particles, etc.) (15)

Mining, Smelting, and Industrial Processing of Ores and Metals. While the world population has doubled in the second half of the twentieth century, the production of five heavy trace metals (copper, lead, nickel, tin, and zinc) has increased more than eightfold. Mining and smelting have been the cause of major pollution problems for as long as they have been practiced. In the year 2000, for example, a large quantity of cyanide escaped into the waters of the Tisa and Danube rivers during gold mining and processing in the ore district of Baia Mare (Romania). This event has initiated a giant ecological catastrophe in southeast Europe whose impact can be compared to that of the Chernobyl accident in 1986.

Presently, particular interest from an environmental point of view is directed towards sulfidic mining waste. The sulfidic ore bodies have remained practically unchanged in the bedrock for very long periods. However, when brought into contact with

atmospheric oxygen and water, traces of metal sulfides in waste material are oxidized to produce an acidic leachate containing heavy metals. The highest priority problems are associated with the enormous masses of mine tailings. Their global quantity of approximately $18 \text{ billion m}^3 \text{ y}^{-1}$ is in the same order of magnitude as the actual sediment discharge to the oceans. A simplified estimation suggests that due to the extraction of lower grade ores in future, the production of mine wastes will double within a period of from 20 y to 30 y. In addition, current rates of mining exceed the natural rates of cycling for a number of trace elements. For heavy metals such as Cu, Pb, Zn, and Cr the rates of mobilization from mining are estimated to exceed the rates of mobilization from natural cycling by a factor of ten. (See *Contamination*.)

On the other hand, the downward trend in use of raw materials in industrialized countries should be borne in mind. Mature economies became increasingly tied to high technology that requires less intensive use of raw materials, thanks to miniaturization and substitution. Future development will depend crucially on the extent and quality of recycling.

Coal Combustion. Coal combustion is the second serious source of trace element contamination of the environment. In particular, the combustion of pulverized coal in modern furnaces for power production results in a variety of products. The organic matter is converted mainly to sulfur oxides, nitrogen oxides, carbon dioxide, carbon monoxide, and water, which are the main constituents of the flue gases. The mineral matter is decomposed to give several mineral phases and aluminosilicate glassy material. Trace elements are distributed between the bottom slag and the fly ash (the incombustible residue, mostly of micron and submicron size, which is carried along with the combustion gases). Most trace elements in coal are usually associated with the fly ash removed from the gases, some are associated with slag, and a small amount reaches the atmosphere in fine fly ash particles. There are two environmental effects: first, the disposal of the slag and retained fly ash, and second, the dispersion of some trace elements in the stack gases. There is some evidence that very fine particles of fly ash escaping with the stack gases to the atmosphere may have a higher trace element content (especially of volatile elements such as As, Sb, Sn, Pb, etc.) than the large particles. In addition, different metals may also show distinct density distributions. It has been noted that metals such as Be, Cd, and Hg tend to be concentrated in light density fractions of fly ash, whereas Co, Cr, Mn, Ni, V, and Zn tend to concentrate in higher density fractions. (See *Coal Combustion*.)

Traffic. Another potential source of metal pollution of urban areas and soils adjacent to highways is traffic. Innumerable studies indicate that lead concentrations in soils near highways are high and decline exponentially as a function of distance from the highways. Meteorological situation, vegetation, topography, and traffic intensity are the major factors that influence Pb concentrations in roadside soils. Fortunately, emission of lead compounds into the environment has been considerably reduced by the use of unleaded fuel in vehicles since the 1980s. Other modes of transportation such as trains and aircraft also contribute to the contamination of the environment by heavy metals (Cd, Ni, Pb, V, Pt, and Zn). However, the extent of contamination from these sources has not been clearly assessed.

Chemical Industry. A further source of trace element contamination is the chemical industry. Economic growth in the chemical industry has been induced by increases in production. Thus, for example, the global production of sulfuric acid has increased more than sevenfold from 20 million tons recorded before World War II (early 1940s) to 140 million tons in the late 1990s. A sharp increase in the production of fertilizers and pesticides has also been observed. It is estimated that 80 000 different chemicals are produced worldwide. Plastics are by far the most important products of the chemical industry, but production of fine and special chemicals is also rising. This area includes detergents, cleansers, softeners, and catalysts.

The problem with this product group is that it frequently uses of a mixture of chemicals whose ecological and/or toxicological safety cannot be guaranteed. These sources are summarized in Table 1. As can be seen from this table, the same trace elements are contained in many different contamination sites. In addition to the sources of contamination mentioned above, there are municipal wastes, agricultural wastes, sewage sludge, etc., which contains various quantities and species of trace elements.

Material	As	Cd	Cr	Pb	Cu	Hg	Sb	Zn
Paints and coatings	X	X	X	X	X	X	X	X
Crude oil processing	X		X	X				X
Iron and steel production	X	X	X	X	X	X	X	X
Nonferrous metal refinery	X	X	X	X	X	X	X	X
Plastic production		X	X	X				X
Batteries		X	X	X	X	X	X	X
Pesticides, fungicides, herbicides, etc.	X		X	X		X		X

Table 1. Sources of selected chemical compounds

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Biographical Sketches

Tom Navrátil was born in 1976 at Klatovy, western Czech Republic. He started a basic education at Prague in 1981. In 1990 he began secondary school at Prague. His studies were interrupted in 1993 when he joined his family to live in Abingdon, Oxfordshire, United Kingdom. He attended John Mason State School in Abingdon. After 1994 when he returned to Czech Republic, he finished his secondary education and started university studies at Charles University, Prague. After his bachelor course he launched his masters studies in the geochemistry. He finished his M.Sc. course (environmental geochemistry) in 1999 and joined the Institute of Geology, Academy of Sciences of the Czech Republic. His professional interests concentrate on the problems of environmental acidification and related phenomena such as trace elements mobility. Recent papers include:

Skřivan P., Navrátil T., and Burian M. (2000). Ten years of monitoring the atmospheric inputs at the Černokostecko region, Central Bohemia. *Scientia Agriculturae Bohemica* 31(2), 139–154.

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Minařík L. was born in 1931 and has worked for most of his life at the geochemical research center of Institute of Geology ASCR in the field of trace-element distribution and mobility. His original interests were associated with magmatic rocks, especially granites, and their leaching and deposition in hydrothermal environment. He has also been engaged in study of zeolites. During the past 15 years he has been working on the problems of trace element fluxes in small catchments areas where the anthropogenic and natural sources combine to contribute to overall geochemical cycles under different pH conditions.

His major professional interests are trace-element analysis, geochemistry of magmatic rocks, crystallochemistry of rock-forming minerals (especially feldspars and micas) in some plutonic complexes of the Bohemian massif, migration of the minor and trace elements during weathering of crystalline rocks, and environmental geochemistry.

He is the author of five monographs, 60 papers, and numerous environmental reports.

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