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Geochemistry and pollution

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During the past 7 years, the National Science Foundation–Research Applied to National Needs (R.A.N.N.) programme has supported extensive interdisciplinary research concerned with Pb, Cd and other hazardous trace metals. Various aspects of geochemistry and pollution research at the universities of Missouri, Illinois, Colorado State and Purdue are presented and summarized. The transport, pathways and distribution of Pb, Cd and other trace metals are discussed and the utilization of research findings by government and state agencies for the development of standards and by industries for pollution control are presented.

Introduction

Naturally occurring or man-induced pollutants in the geochemical environment have long been a major concern to mankind. Because of improved detection methods and better knowledge of potential beneficial or detrimental impacts, increased emphasis has been placed on trace metal concentrations during the past 20 years. Following the mercury poisoning episodes of the early 1950s, scientific attention was focused on Pb, Cd and other metals known to have widespread distribution or utilization patterns potentially hazardous to human health. In the United States of America, extensive research programmes were implemented to study Pb, Cd and other toxic heavy metals being released to the environment in ever increasing amounts by mining, industries, transportation and in other ways. Knowledge was lacking on these elements as to their natural occurrence and regionalized concentration in the Earth's surface, potential sources of pollution, methods of transport, ecological pathways, possibilities of biomagnification and impacts on human health.

In response to these needs the U.S. National Science Foundation (N.S.F.) sponsored trace contaminant research programmes to answer national questions presented by certain metals. One such metal was Pb which was under indictment by the U.S. Environmental Protection Agency (E.P.A.) for its use in automotive petrol and its suspected health implications. Further investigations were directed at lead mining, milling and smelting operations. Similar concern existed for Cd and associated compounds being added to the environment by industrial or utilization processes.

During the past 7 years, geochemical and pollution research on Pb, Cd and other hazardous trace metals have been performed at the universities of Missouri, Illinois, Colorado State University (C.S.U.), Purdue University and Oak Ridge National Laboratories (presently named Holifield National Laboratory, H.N.L.). Through these studies, research findings have been applied to the development of new or improved regulatory standards along with pollution control technology. Furthermore, the exchange of data and knowledge has become international through the participation and visits of scientists and engineers from the United Kingdom, Australia, Spain, Japan, U.S.S.R., Brazil and other interested countries of the world.

Pollution and metals

Pollution may contribute directly or indirectly to the distribution or concentration of trace elements in the environment. Gaseous emissions, dust and decayed plant particles are returned to the Earth's surface by rain, snow and wind. Additional contaminants may be added to or subtracted from the environment by storm runoff, leaching, sorption or desorption, depending upon the physical characteristics of the soil or rock. Plants and animals also contribute to further metal cycling through nutrient uptake, biomagnification or waste excretion.

A major geochemical consideration is how best to determine what elements are present, their form, ratio concentration and availability. Workshops conducted by the U.S. National Academy of Sciences (N.A.S.) subcommittee on the Geochemical Environment in Relation to Health and Disease have studied the geographic distribution of elements and disease patterns as reported in volumes 1 (N.A.S. 1974) and 2 (N.A.S. 1975) entitled *Geochemistry and the environment*. This work examined individually selected metals and pointed out the need for more detailed studies on combinations of natural and man-induced metals in the environment.

Unfortunately, it is difficult to determine what effects trace amounts of such heterogeneous mixtures will have upon a wide range of polution tolerant or sensitive biological systems (including man) under varied physical and chemical conditions. The synergistic effects of Pb, Cu, Zn, Cd and other metals vary significantly with certain physical, chemical or biological changes. Organics and organic-rich rocks, soil, sediments and leaf litter collect and concentrate most heavy metals thereby acting as a filtering system which poses a special problem under acidic conditions and the release of toxic metals. Nevertheless, such information is necessary and vital for the establishment of regulatory standards or pollution control methodology.

Further controversy on metal pollution was raised by the N.A.S. Lead Panel in its examination of the biological significance of airborne Pb (N.A.S. 1972) and its conclusion that no definite health effects could be attributed to atmospheric Pb. This was in conflict with the E.P.A.'s position (U.S. E.P.A. 1973) and recommendations were made for more detailed studies.

Many of the studies not related to health recommended by the N.A.S. study on *Airborne lead in perspective* were conducted through N.S.F. sponsored research at Missouri, Illinois at Urbana–Champaign and Colorado State University concerned with the occurrence, transport, distribution and possible environmental effects of Pb. Investigators from the three universities collaborated to publish important research findings in *Lead in the environment* published by the N.S.F. (Boggess & Wixson 1977). The book contains 14 chapters dealing with the characteristics, monitoring, analysis, transport, distribution and effects of Pb, along with control strategies, economic aspects of control, summary and conclusions. Also included are some 985 pertinent references from both the classic and current literature concerning Pb and associated trace metals. More recent research findings related to each of the three universities may be found in the final reports submitted to N.S.F. by C.S.U. (Edwards 1976), Illinois (Rolfe 1975) and Missouri (Wixson 1977).

Cd was the hazardous metal studied at Purdue University and the Holifield National Laboratory. Early investigations were reported in *Cadmium, the dissipated element* (Fulkerson & Goeller 1972) and, more recently, findings on the *Environmental flow of cadmium and other trace metals* by Purdue University (Yost 1976).

Historically, most investigators have published specific research findings in the proceedings of Missouri's Annual Conference on Trace Substances in Environmental Health, series 1–11

(Hemphill 1977). This conference has become the major meeting place for research on trace substances in environmental health.

Sampling and analysis

Research conducted by the N.S.F. lead and cadmium groups has indicated the need for well planned and well executed sampling programmes, coupled with good analytical methodology involving careful quality assurance programmes. Analytical chemists have worked closely with field personnel in the development of sample collection, storage, preparation and analytical techniques (Boggess & Wixson 1977).

Geochemical characteristics

A knowledge of the physical and chemical characteristics of Pb and Cd is basic to understanding their occurrence, transport, distribution and biological activity under a wide range of environmental conditions. Research, especially at C.S.U. and Illinois, has added appreciably to an understanding of the role of particle-size distribution of Pb containing species, both in automotive emissions and during transport.

Transport and distribution

The presence of Pb alkyls near heavily travelled highways remains an unsolved problem. Researchers at C.S.U. found Pb tetramethyl to be the only Pb alkyl present in measurable amounts within 30 m of a heavily travelled highway. It has been suggested that tetramethyl Pb may originate from evaporation of leaded fuels, rather than from exhaust emissions. Dust particles are thought to act as a scavenging mechanism and serve as a substrate for the conversion of the sorbed Pb species into solid inorganic Pb compounds.

A major effort at C.S.U. involved the development of mathematical and physical models to provide a better understanding of atmospheric transport mechanisms along highways and within cities. Field research near Fort Collins, Colorado suggests that approximately 45% of the consumed Pb remained airborne at the suburban edge of the city (based on consumption of 13 miles per gallon (4.6 km/l) and an emission factor of 45%). Improved methods of aerometric measurements and analyses were then developed which allowed for a more precise evaluation of short-term changes correlated with the time scale of actual meteorological phenomena.

In the Missouri Pb study, fugitive dusts and finely ground materials from tailings, dams and concentrate piles provided the main source of contamination within 4.8 km of the smelter. Stack emissions were more important beyond this distance. Pb-bearing materials were found to enter the environment as dusts while other solids washed by storm runoff into stream.

Storm runoff was the major transport mechanism in moving Pb from terrestrial to aquatic systems. Pb was associated with particles of soil and organic matter and movement was thus associated with suspended sediments rather than water. Sediments acted as a major sink for Pb and other heavy metals in aquatic ecosystems. However, considerable amounts of sediment

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were scoured from the aquatic systems during heavy storms, preventing the possibility of toxic accumulations.

Transport and distribution studies in Illinois were conducted within the context of a 259 ha agriculture watershed ecosystem with a small urban compartment. Combustion of gasoline provided the major Pb input to the watershed estimated at 79 kg/day or 29 t on a yearly basis. Airborne Pb returned to the ground in precipitation accounted for 800 kg, while 9500 kg were returned by dustfall each year.

Drainage water represented the major exit route of Pb from the ecosystem. About 80 % of the Pb was associated with suspended solids, and the remainder was in a dissolved form. The amount of suspended Pb was greatest from the urban compartment with large impervious areas and high Pb-rich particulate material.

Soils became a major sink for Pb and Cd in terrestrial ecosystems with the highest concentrations occurring near sources of contamination. In the Purdue study the annual quantities of Cd, Zn, Pb and Cu entering an ecosystem were not sufficient to account for the total pool of metals impacted by the steel industry. It was thought that the elimination of open-hearth furnaces since 1968 may be responsible for this reduction in metal pollution.

Studies at Illinois indicated that heavy concentrations along streets and parkways were reflected in equally large amounts of Pb in dust blown into buildings through open doors and windows or brought inside on the feet.

House dust, especially that collected from rugs, also contained unusually high amounts of Cd. The source was found to be the rubber backing on rugs or the padding used as a base for carpet installations and indicated that this may be sufficient to create a health hazard for small children. Elevated Pb levels were also found in forest-covered soils near mining, milling and smelting operations in Missouri. Pb was concentrated in the organic horizons, with only slight penetration into the underlying mineral soils due to humic acids in leaf litter.

Pb was concentrated in the soil surface horizon, but moved downward with time. Movement was generally considered to be quite slow based on the relative insolubility of Pb compounds and the bindings capacity of surface organic fractions. However, recent studies at Illinois suggest that much more rapid movement is possible. The greater amounts of Pb present at various depths in urban soil profiles than in rural soil profiles also suggest that the depth of penetration bears some relation to the Pb deposited on the surface. Pb added to the surface may also be unavailable to plants by its being complexed and bound with organic fractions.

The total Pb content of a soil is not a good measure of availability to plants. Availability, rather, depends upon the amount of Pb present in relation to the capacity of the soil to sorb Pb and decreases with increases in soil pH, cation exchange capacity, organic matter content, and levels of available phosphorus.

In the Purdue Cd study, preliminary research indicates that Cu was leached into water leaving the impacted ecosystem, while Ca, Zn and Pb were bound in the organic complex of the upper soil horizon. Research is also being conducted to determine the amounts of trace metals present in reservoir silt near industrial and municipal sources in East Chicago, Illinois.

The concentration of Pb associated with vegetation follows that of soil, with greatest amounts found near heavily travelled streets and highways or near other sources of contamination such as mines, mills, smelters and ore-haulage roads.

Sediments constitute the major sink for Pb in aquatic systems. In Illinois, Pb concentrations are several times higher in the top 10 cm of sediments in urban streams than in rural streams

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draining the ecosystem, and most of the Pb was associated with silt-sized particles. Aquatic biota from urban streams also have body Pb concentrations several times higher than those from water-courses in the rural area.

Effects

On the basis of available data, it is difficult to evaluate Pb or Cd toxicity since the effect of any given metal concentration is influenced by many other environmental and physiological factors. Studies at C.S.U. found that Pb emissions from vehicle exhausts apparently have no effect on inadvertent weather modification.

The greatest probability of deleterious effects from Pb emissions is generally in areas near the source. In rural areas, the major impact is on a narrow corridor along highways. In cities, large areas may be affected because of the volume and density of traffic. Relatively small amounts of Pb can be detected at great distances; however, no serious environmental effects have been established for these lower levels of contamination. Control strategies therefore generally attempt to reduce the release of Pb or Cd into the environment.

Pb does not appear to be a threat to aquatic ecosystems in southeastern Missouri streams. The possibility of damage is minimized by the alkaline reaction of streamwaters, which retards solubilization of the predominant Pb sulphide ores.

Controls

Control of industrial emissions requires preplanning in site selection and the use of good housekeeping procedures. Fugitive dusts should be contained and transport vehicles should be covered or dampened. The control of smelter stack emissions requires the use of advanced technologies to remove particulates and noxious gases. Waste waters require treatment dependent upon the kind and concentration of pollutants involved.

The atmospheric exposure of people in the urban environment to Pb and other pollutants can be reduced by using mass transit to move people from congested city canyons to peripheral areas. Pollutant transport may be further reduced by proper spacing of individual tall structures in urban areas.

Further studies are needed on control technology and the establishment of realistic emission standards for Cd entering the geochemical environment near industrial operations.

Cooperative efforts

The continued involvement of industry and regulatory agencies in research activities has played a major role in data utilization. Federal and state agencies have been able to obtain specific data at a much lower cost to the taxpayer. Metal industries have committed considerable resources toward implementing necessary environmental controls (Wixson 1974). It is hoped that these efforts will serve as a model for metal pollution control throughout the world.

The assistance of N.S.F. in supporting this research and making possible travel to the meeting is gratefully acknowledged. Thanks are also extended to the various universities, agencies, and industries that have cooperated in our work on this problem.

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