TRACE ELEMENTS AS AIR POLLUTANTS

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WHAT IS A "TRACE ELEMENT"

When people speak of "trace elements" they mean different things depending on what part of the universe interests them. An astronomer regards almost all elements except hydrogen and helium as trace elements because hydrogen and helium are the building blocks of the cosmos. A geochemist sees that the earth's crust is composed of eight abundant elements, oxygen, silicon, aluminium, iron, calcium, sodium, potassium and magnesium; therefore to him all other elements are trace elements. For a doctor or a biologist, a trace element is usually rather arbitrarily defined as any element present in an amount less than 0,01% of an organisms weight. In the field of air pollution there are two categories of trace elements which are of importance. Firstly, there are those elements which are known to be or are even suspected of being hazardous to man or to the biosphere in which we live. Secondly, there are many elements which present little or no hazard but which can act as tracers allowing us to follow the dispersion of pollution from its sources to its ultimate sinks, in the oceans or the soil.

TRACE ELEMENTS - NECESSARY AND TOXIC

From the beginning of time life has been exposed to trace elements and has learnt to co-exist with them. Indeed, life would probably be impossible without certain essential trace elements. These are vital to biological processes, usually through their action as activators or inhibitors of enzymes. Twenty trace elements are consistently present in human tissue but only nine of these, iron, copper, zinc, cobalt, chromium, molybdenum, manganese, selenium and fluorine, are at present known to be essential for human life. Other elements such as arsenic, beryllium, cadmium, lead and mercury are highly toxic, usually through their interference with essential elements. An interfering element may be similar enough to an essential element to displace it from its position in an enzyme molecule, but be unable to perform all the functions of the essential element in the reaction carried out by the enzyme.

Almost any element, even those essential to life, can be toxic if present in large enough amounts. The response of the growth of an organism to changes in the concentration of an essential element is shown in idealized form in Figure 1[1].

THRESHOLD LIMITS AND CONTROL POLICY

If an element is not essential the portion of Figure 1 showing deficiency does not exist. The situations represented in Figures 2 and 3 can then result. Figure 2 shows the case of an element which is tolerable up to some threshold value beyond which it becomes toxic. Figure 3 shows the case of an element which is toxic at all concentrations and has no threshold limit.

It is debatable whether threshold values which are tolerable to an organism and have no harmful effects at all really exist or whether the action of all toxic elements can be represented by some form of Figure 3[2]. If threshold values exist then a control policy which aims at achieving exposures related to these threshold values has a theoretically sound basis. If threshold values do not exist the way is open for demands for extremely stringent control over emissions. If no threshold values exist then we must ask ourselves what degree of damage is acceptable. The truth of the matter may be that threshold limits exist for some elements but not for others. For example Swenson and Boyer[3] showed that up to 10 sulphydryl groups per mole of the enzyme aldolase could be blocked by p - mercuribenzoate without loss of enzymic activity. This type of finding supports the idea that a threshold limit may exist for at least some elements. In contrast cancer can be initiated by a single molecule of a carcinogen acting on a specific site in one cell. This type of substance may well have a threshold limit indistinguishable from zero. It may be noted in passing that an amenity such as good visibility has a threshold limit of zero.

The symptoms of acute poisoning by large amounts of elements such as arsenic, lead or mercury, have long been well documented. By extrapolation we may fear that they are still harmful at concentrations below the threshold limit for the appearance of acute symptoms, but this is hard to prove or disprove.

For the effective study of toxicity at low levels three conditions must be met -

(a)   a delicate and reliable method of analysis for the element

(b)   a means to control the amounts of the element in the diet and in all alternative sources, including the air breathed

(c)   a clear means of diagnosing the effects of deprivation and of toxicity.

Condtions (a) and (b) are not always easy to achieve while condition (c) is difficult to meet even with laboratory animals kept under controlled conditions. For a complex, long-lived species such as man meeting these conditions is a severe problem. Analysis is usually only possible on a dead patient whose previous existance may only be roughly documented and whose reactions as a living organism can no longer be tested. Below the level at which acute symptoms become manifest we must look for subtle effects such as changes in the nervous system[4], increased risk of genetic damage, or reduced resistance to the challenge of disease[5]. Even when effects such as these are demonstrated they may be of so general a nature that it is hard to prove a cause and effect relation in a population exposed to many potential hazards.

An additional problem is that in man, a disease such as cancer may take ten or twenty years to become noticeable. Because of these difficulties our estimates of threshold limits for trace elements in man are frequently uncertain and must be revised in the light of increased knowledge.

An alternative to the procedure of trying to determine the threshold value at which symptoms of toxicity first appear is to approach the limit from the healthy side of the limit. Here one assumes that threshold values do exist and that they may be estimated by measuring the concentrations of trace elements in healthy people. The determination of trace element concentrations in man entails the analysis of all the major organs and is an important field of study[6]. The major difficulty is the lack of volunteers for analysis. The analysis of individuals who die of extreme age or from disease is interesting in itself but cannot be expected to show the trace element content of a healthy person. A way round this problem is to analyse accident victims. This assumes that accidental death is entirely random and cannot be attributed to effects such as slower reaction times or poor co-ordination which in turn could be blamed on low level poisoning. This approach appears to evade the difficulty of diagnosing the effects of low level toxicity, but in trying to define a normal healthy population sample for analysis one finally meets the same problem of clear diagnosis.

It would be useful to know how trace element concentrations would vary with age and sex in the major ethnic groups of the world if each could live a simple life close to the earth. In fact civilization has affected almost everyone and we may never know by direct means what range of trace element concentrations is natural to man.

A WORLD UNDEFENDED

I have written so far mainly of man and how trace elements can be either essential or toxic to man, this outlook takes no account of the needs and sensitivities of all other life forms. It is possible that in the process of nobly cleaning up our own ecological niche we may contaminate someone elses. However praiseworthy an altruistic concern for other species may be, the self interest of man is probably the best way to get results. If we come to see our respect for life as an essential element in our existance then outright conflict of interest disappears.

THE ROUTES BY WHICH TRACE ELEMENTS REACH MAN

Our interest in this article is in trace elements as air pollutants. However, the amounts of an element absorbed by people via the air they breathe must be compared with other sources such as the food they eat and the water they drink. When comparing trace element intakes via each of these routes it must be remembered that the efficiency with which the body absorbs an element will be different for each route. For most trace elements, the air we breathe contributes only a small fraction of the total intake of an element[7,8] but the absorption efficiency in the lung is usually higher than in the gastro-intestinal system (see 'How trace elements penetrate the lungs').

In addition to allowing trace elements to reach us directly via our lungs, air acts as a medium of transport which can allow trace elements to reach the water we drink, the food we eat, and even the dust which filters into our homes.

THE CHEMICAL AND PHYSICAL FORMS OF TRACE ELEMENTS

I have so far referred to trace elements as if they each occurred in one form only or at least as if their properties were independent of their chemical and physical form. This is not true. The toxicity of many elements depends strongly on the oxidation state of their ions while others have organic forms whose properties differ vastly from those of the free element. Two contrasting examples of this are mercury and arsenic. The methylated forms of mercury are more dangerous than the inorganic forms, whereas for arsenic methylated compounds are less toxic than the inorganic species.

THE NATURAL AND MAN-MADE SOURCES OF TRACE ELEMENTS IN AIR

The amounts of trace elements released into the air by man's activities and any limits we may seek to place on these emissions must both be seen in perspective by comparing them to natural emissions. The natural sources of trace elements in air are wind-blown soil dust, sea spray, volcanic and geothermal activity, and fires. Two more exotic sources which have been suggested are the slight volatility of rocks and the shedding of metal-rich particles by plants. Man has been exposed to these sources throughout his evolution and has presumably adapted to the normal range of their fluctuations.

Man releases trace elements through coal combustion, ore smelting, petroleum combustion and general industrial activity. Toxic or potentially toxic elements which are themselves volatile or have compounds which are volatile at moderately elevated temperatures include silver, arsenic, beryllium, bismuth, cadmium, fluorine, mercury, nickel, antimony, selenium, tin, thallium and zinc.

HOW TRACE ELEMENTS ESCAPE DESPITE CONTROL MEASURES

Modern air pollution control equipment frequently removes 98% or more of the particulates in a gas stream. How then can trace elements still escape in significant amounts? Firstly control apparatus such as bag filters or electrostatic precipitators often work best at temperatures of a few hundred degrees. At these temperatures some substances such as mercury are in the vapour form and therefore do not even enter into the efficiency calculations for control apparatus. Secondly the vast amounts of material consumed by a power station mean that even with high efficiency control measures significant amounts of fly ash will escape to the air. It has been estimated that with 99% efficient removal of fly ash a 3 000 MW coal-burning power station will discharge about 7 000 tons of fly ash a year. With present technology particle removal efficiencies can be increased above their already impressive levels but this entails rapidly escalating costs for each slight improvement.

The efficiency with which electrostatic precipitators work depends on particle size and passes through a minimum at about 0,4 μm (Fig. 4)[9]. Natush et al[10] have found that twelve trace elements are concentrated on the smallest particles of fly ash which are least efficiently retained by electrostatic precipitators. Subsequent work has shown that trace elements

which are volatile or have volatile compounds under combustion conditions condense on the surface of fly ash particles as they leave the combustion zone and cool down[11].

HOW TRACE ELEMENTS PENETRATE THE LUNGS

Particles larger than about 10 μm are removed from inhaled air before they leave the nasal passage. As the air passes through the branching passages of the respiratory system smaller particles are trapped; these particles are mostly removed to the gastro-intestinal system where absorptive efficiencies for trace elements are typically about 5-15%. Only particles of about 1 μm reach the alveolar sac in the lung where they are in intimate contact with body fluids through thin diffusable membranes which lack selectivity.

It is now seen that the category of particles which escape to the air in spite of controls, are coated on their surfaces by volatile trace elements, and can finally penetrate to the depths of the lung where trace elements are absorbed with efficiencies varying between 50 and 80%.

ARE TRACE ELEMENTS A REAL THREAT?

The harassed industrialist and the man who lives next to a power station both have reason to ask how real a threat to the public is posed by trace elements as air pollutants. To be honest, not nearly enough is known to give a straight answer. It is typical of our scanty knowledge that different authorities each view the threat differently. For example, Schroeder[12] considered atmospheric Cd, Pb, Ni and Hg to be significant health hazards. Woolrich[7] concluded that "those outside the industrial environment are not currently threatened by these trace metals through the air they breathe". Stern[13] pointed out that in some cases (in the USA) the natural background emissions exceed national ambient standards. Mercury in areas of California is a notable example of this. Stern's outlook points the way to using natural trace element concentrations as a yardstick in assessing the impact of man's activities. The problem is to decide which natural concentrations should be used as our guide. The extreme emissions of nature, such as volcanoes, are no better a guide to us than the excesses of man. Until we have accumulated enough really thorough knowledge of threshold values the natural concentrations of trace elements offer us the best comparison by which to judge our industrial emissions.

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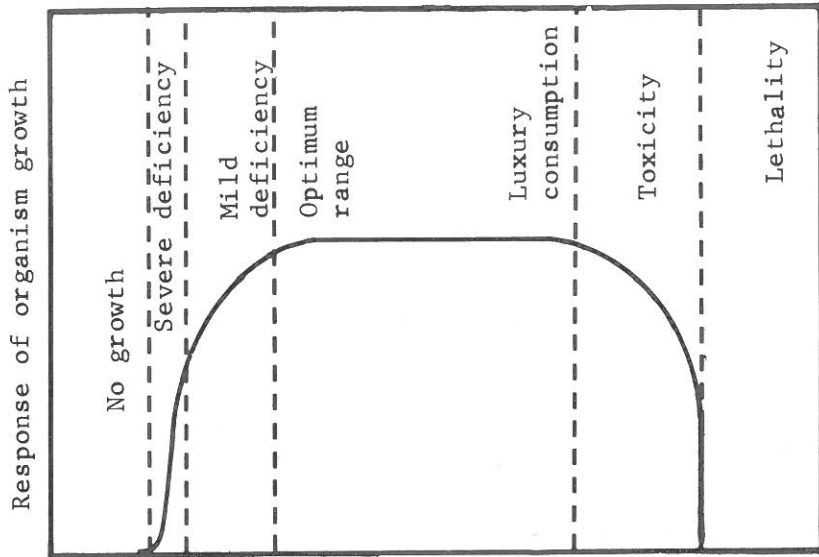
Figure 1.   Nutrient concentration
    Idealized diagram of growth of an organism as a function
    of the concentration of an essential nutrient. After
    P.F. Smith, 1962, Annu. Rev. Plant Physiol., 13, 81.

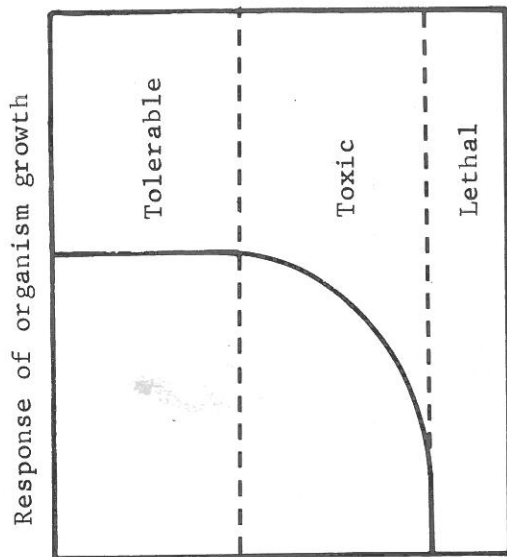

Figure 2.   Trace element
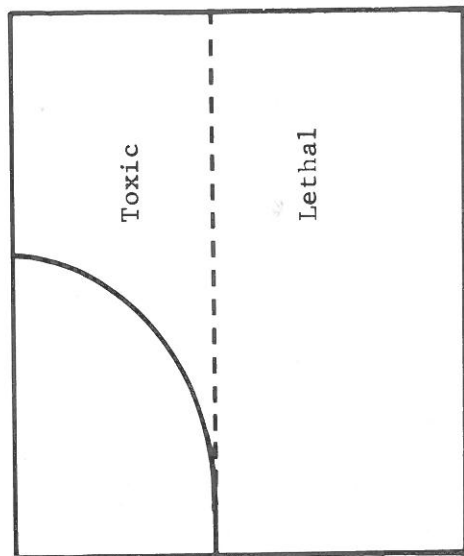   concentration
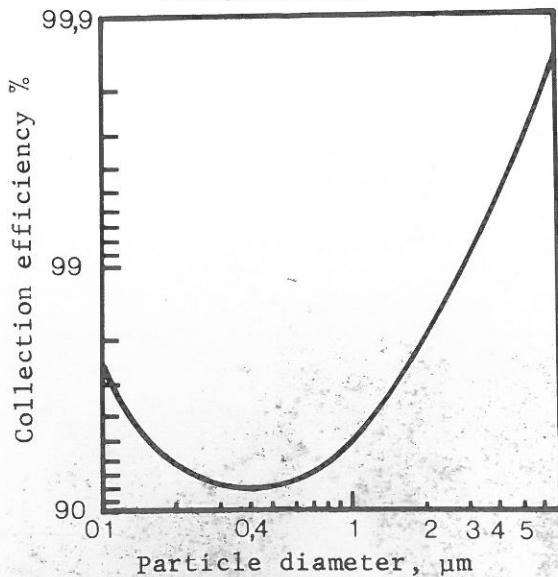

Figure 3.   Trace element
            concentration

Figure 4.   Collection efficiency as a
            function of particle size for fly ash
            precipitator, based on field measure-
            ments on full-scale precipitator .