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Trace elements in the atmosphere

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The distribution and behaviour of particulate trace elements in the atmosphere have been studied by continuous measurements for 5 years at seven non-urban sites in the United Kingdom. Samples have been taken regularly of airborne dust, rainwater and dry deposition: these have been analysed for up to 36 elements.

Concentrations of trace elements vary considerably between sites but the relative concentrations are more uniform: this suggests similarity of origin or good atmospheric mixing. By comparing the relative concentrations with those in soil it is possible to differentiate between trace elements that are derived from soil and those that may be attributed to industrial activity. This classification is supported by estimates of the particle sizes in air.

The deposition of trace elements can be related to the concentrations present in soil and to the annual removal by crops. Retrospective analyses of stored samples from one site describe the history of trace element concentrations in air since 1957. The sea surface is considered as a possible source of atmospheric trace elements.

INTRODUCTION

Trace elements in airborne dust can be considered in three roles: (*a*) as nutrients, (*b*) as potentially toxic pollutants and (*c*) as tracers of transfer mechanisms. In order to explain the behaviour of atmospheric trace elements it is necessary to determine the background or baseline levels and the natural and unnatural variations about these levels. Knowledge is required of the mechanism of transfer between air, rain, soil and vegetation, and of the corresponding deposition inventories.

Trace elements in airborne dust arise from the Earth's surface and also descend from sources beyond the atmosphere (Perkin & Tilles 1968). The terrestrial aerosols are raised from the surface of land and ocean by winds, by the eruption of volcanoes and by industrial activities. Particles larger than 10 μm will promptly return to the surface by sedimentation, but smaller particles may be raised by updraughts and turbulence to higher altitudes, so that disposal is more widespread: those particles capable of reaching the stratosphere would eventually be distributed on a world-wide scale. Those that remain in the troposphere will be transported in the zonal circulation before returning to the Earth's surface. Aerosols are transferred to the Earth's surface by wet deposition through precipitation and by dry deposition through sedimentation, impaction and diffusion.

MEASUREMENTS OF TRACE ELEMENTS

The characteristics and behaviour of trace elements in the atmosphere may be reviewed by drawing upon the published results of a continuous programme of sampling and analysis that has been carried out since 1971 at seven non-urban sites in the United Kingdom (Cawse 1974, 1975, 1976, 1977; Peirson *et al.* 1974).

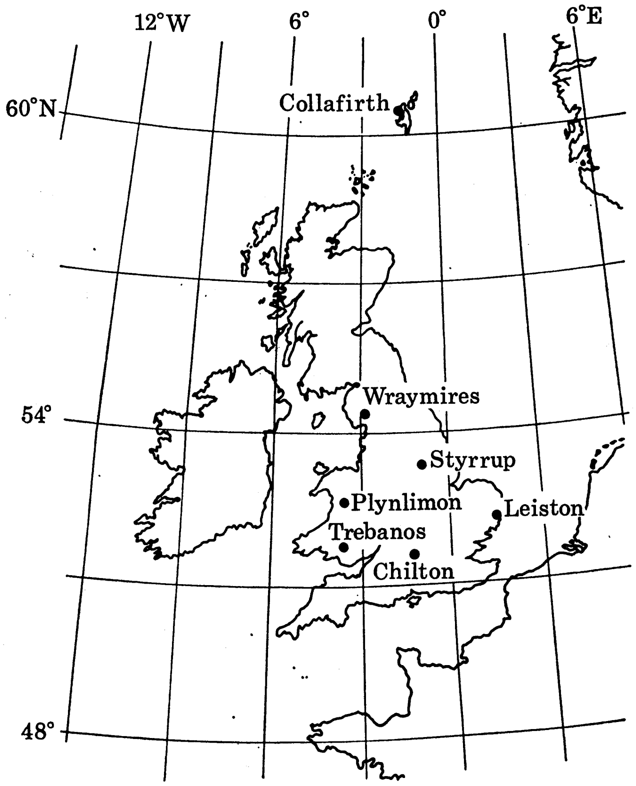

Figure 1. Location of sampling stations.

The methods of sampling and analysis have been published previously (Cawse 1974) and will be restated only briefly. Samples of airborne dust have been collected by drawing air through a filter paper: rainwater is collected in a polythene funnel and bottle. Because the funnel is exposed continuously, both wet and dry depositions are collected. Dry deposition is collected separately upon a horizontal sheet of filter paper sheltered from rain. The samplers are mounted at 1.5 m above ground, are run continuously and are usually changed each month. The locations of the sampling sites are shown in figure 1. Samples are analysed mainly by neutron activation followed by gamma-ray spectrometry, but also by X-ray fluorescence, atomic absorption and chemical methods (Cawse 1974). The sampling system was designed simply, for trouble-free operation at remote sites: each sample is analysed for up to 36 elements as listed in table 1.

Table 1. List of elements analysed

Na	Cr	Br	La
Mg	Mn	Rb	Ce
Al	Fe	Mo	Sm
Cl	Co	Ag	Eu
K	Ni	Cd	W
Ca	Cu	In	Au
Sc	Zn	Sb	Hg
Ti	As	I	Pb
V	Se	Cs	Th

TRACE ELEMENTS IN AIR

Four of the trace elements have been selected to illustrate the general behaviour. The average concentrations for periods of 3 months are shown in figure 2 for the site at Wraymires during 1971–6. The chosen elements are representative of some 36 that have been measured during this period. The increase in the concentrations during the winter compared with summer is attributed to the seasonal reduction in the vertical diffusion in the atmosphere: it is associated with the increased frequency of temperature inversions in the winter. Additionally there may be an effect due to the increased use of fuel for heating during the winter.

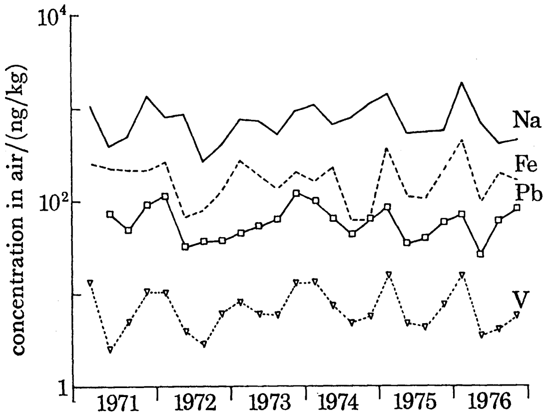

FIGURE 2. Quarterly elemental concentration in air near ground level at Wraymires (1971–6).

The trace elements measured in this survey constitute typically about 15% of the tota particulate material suspended in air near ground level. The bulk of the material is made up of ammonium sulphate and nitrate (*ca.* 45%); carbon, organic material and (other) oxygen (*ca.* 35%); and silicon (*ca.* 5%) (Salmon *et al.* 1978).

The concentrations of some of the trace elements in air at three of the sampling sites are shown in table 2, averaged over the years 1972–6. The concentration of an element can vary between Collafirth, the cleanest site, and Styrrup, the most polluted, by an order of magnitude or more.

TABLE 2. CONCENTRATIONS (nanograms per kilogram) OF TRACE ELEMENTS IN AIR, 1972–6

element	Collafirth,† Shetland Is	Wraymires, Cumbria	Styrrup, Notts.
Na	2000	810	890
Sc	0.012	0.037	0.13
V	2.2	7.4	15
Mn	3.5	10	43
Fe	54	190	700
Zn	14	53	250
As	< 0.5	2.5	16
Se	0.37	0.97	3.0
Pb	21	63	250

† 1973–6.

(*a*) *Enrichment relative to soil*

If the concentrations such as in table 2 are referred to a single element, say Sc, then the ratios so obtained show much less variation from place to place (except for the maritime elements such as Na, Cl and Br). If in addition the concentration ratio in air of an element relative to Sc is normalized to the same ratio in average soil (Bowen 1966), then these 'enrichment factors' given in table 3 for a selection of trace elements demonstrate the reduction in variation from place to place. The elements are seen to separate into two classes, those that are 'soil-derived' like Sc, having factors about unity, and those of 'industrial' origin that are enriched relative to soil by a few to many times. Enrichment factors derived from observation at more distant sites in the northern temperate zone are available from Japan (Mamuro *et al.* 1972) and Norway and Switzerland (Rahn 1972). These have values similar to those in table 3. On the other hand, the enrichment factors also presented in table 3 for Nigeria and South Africa show patterns that are significantly different, presumably because of the smaller degrees of industrialization.

TABLE 3. ENRICHMENT FACTORS† OF TRACE ELEMENTS IN AIR, 1976

element	Collafirth, Shetland Is	Wraymires, Cumbria	Styrrup, Notts.	Pelindaba, Pretoria, S. Africa	Northern Nigeria
Mn	2.1	2.0	2.0	1.5	0.4
Fe	0.9	0.8	0.9	0.6	0.7
V	9.1	9.3	6.4	0.8	0.5
Zn	140	155	210	24	1.8
Se	1420	1170	990	46	< 11
Pb	940	770	1200	140	7.2

† Defined as $(C_{a,e}/C_{a,Sc})/(\bar{C}_{s,e}/\bar{C}_{s,Sc})$, where $C_{a,e}$ and $C_{a,Sc}$ are the air concentrations of the element and Sc respectively, and $\bar{C}_{s,e}$ and $\bar{C}_{s,Sc}$ are average soil concentrations of the element and Sc respectively.

(*b*) *Particle size*

Although it is unlikely that individual elements are contained in separate particles, it is possible to characterize the elements according to particle size. Occasionally, samples of airborne dust have been taken using a size-selective sampler (Cawse 1974): a more continuous indication of particle size may be derived from the regular measurements of dry deposition velocity that is given by the ratio of rate of dry deposition divided by concentration in air (Chamberlain 1960). The dry deposition velocity has been shown to increase regularly with mass median diameter of the aerosol particle (Cawse 1974). In figure 3 the enrichment factor for various elements is plotted against dry deposition velocity recorded at Chilton during 1972. Parallel measurements with a size-selective sampler show that at this site a deposition velocity of 0.5 cm s^{-1} corresponds to a mass median diameter of about 1 μm (relative density of unity); at the lower end Se and Sb are associated with a diameter of about 0.5 μm and at the upper end Sc with about 4 μm (Cawse 1974). The ordering of the elements in figure 3 applies to all the non-urban sites, although the absolute scale of dry deposition velocity depends upon the degree of exposure of the collector.

It follows from figure 3 that those trace elements that are enriched above the natural levels in soil are associated with small particles, presumably formed by condensation after industrial combustion, whereas natural particles formed by grinding and wind erosion are larger. But it is

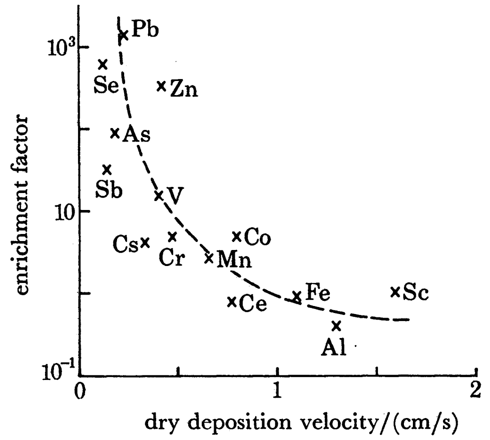

FIGURE 3. Enrichment factor for air particulate (normalized to Sc) and dry deposition velocity at Chilton (Oxon.) in 1972.

not impossible that the combustion of fossil fuels for example can produce both large and small particles.

(*c*) *Possible origins and distribution*

The evidence accumulated in the previous sections may be summarized as follows:

(*a*) Airborne particulate material exhibits a chemical uniformity, apart from the maritime elements, that is characteristic of the United Kingdom (away from sources) and possibly of foreign sites at the same latitudes but not at other latitudes.

(*b*) Within this pattern of uniformity the atmospheric trace elements may be classified, according to the enrichment relative to soil, as either soil derived or industrial.

(*c*) The distribution of particle size is such that the industrial trace elements, having a high enrichment relative to soil, are associated with small particles of mass median diameter less than 1 μm and the soil derived elements with larger particles of over 1 μm.

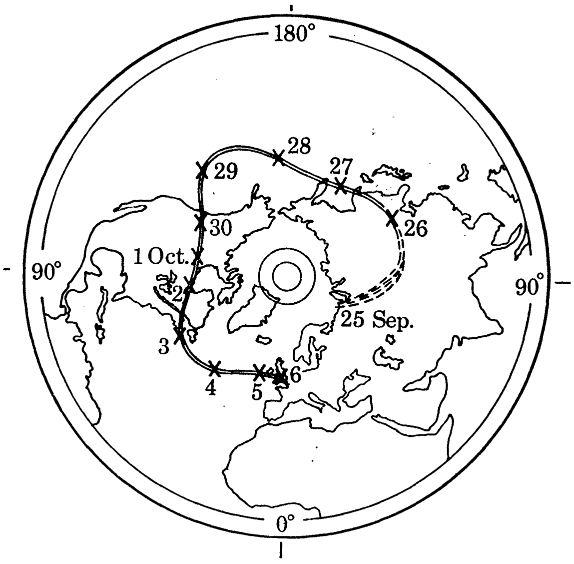

FIGURE 4. Trajectory of nuclear weapon debris at 500 mbar (50 kPa) (5.5 km), September–October 1962.

If the results presented are representative not only of the United Kingdom but also of foreign sites in the same latitudes, then it seems necessary to assume either that a roughly similar degree of industrialization causes, on average, a common pattern of trace elements in the atmosphere, or that there is a general aerosol pervading this zone of latitude having a varying concentration but essentially the same elemental composition – apart from the maritime elements and regions in the vicinity of pollution sources. It is possible for material to be raised from the Earth's surface by wind, causing the suspension of soil and dust or by industrial processes. Enough of this material may diffuse vertically upwards, against competition from sedimentation and washout by rain, to join the westerly airstreams in the middle and upper troposphere. These airstreams have been invoked to explain the passage of radioactive debris from nuclear explosions. For example, in figure 4 is shown the trajectory, at 5.5 km altitude, of radioactivity from a nuclear weapon test in the Russian Arctic to the United Kingdom during 11 days in September and October 1962 (Peirson & Cambray 1965).

TABLE 4. CONCENTRATIONS (nanograms per kilogram) OF TRACE ELEMENTS IN AIR IN URBAN AND NON-URBAN REGIONS

element	non-urban Collafirth, Shetland Is (Jan.–Dec. 1976)	urban Brent, London (Nov. 1975–Oct. 1976)	urban Walsall, West Midlands (Dec. 1975–Nov. 1976)	maximum ratio, urban : rural
V	1.4	32	25	23
Cr	0.39	6.4	28	72
Mn	2.7	28	154	57
Fe	52	1010	1750	34
Co	0.062	0.74	1.1	18
Zn	11	152	2220	202
As	<0.5	12	53	>106
Cd	<0.9	16	37	>41
Sb	0.35	11	13	37
Pb	14	860	1070	76

(d) *Atmospheric concentrations: urban*

Although all of the sampling sites considered in this survey were chosen in non-urban situations, there is a considerable range of the trace element concentrations observed (table 2). This comparison is extended in table 4, where the concentrations of some of the trace elements measured at Collafirth are listed against the corresponding values from sites in two built-up populated areas, in Brent and Walsall. The ratios urban : non-urban are in some cases considerable: the urban excess is probably related to population density and could be magnified by traffic on paved surfaces, which would favour resuspension. The variability of these ratios implies a departure from the enrichment pattern observed at non-urban sites and therefore the presence of specific sources of pollution.

However, it is not possible to estimate the potential health hazard attributable to the elevated values in urban areas, because no standards are available for the quality of outside air. Sometimes a guideline is used equivalent to the threshold limiting value for factory air, divided by a factor of 40. Generally there is no hazard according to this rough guideline, but some elements have concentrations that are a significant fraction of the guideline value.

(*e*) *History of trace element concentrations*

At one site, Chilton, it has been possible to observe the concentrations of a number of trace elements during 1957–74 by the retrospective analysis of air-filter samples, stored after collection of nuclear weapon debris (Salmon *et al.* 1978).

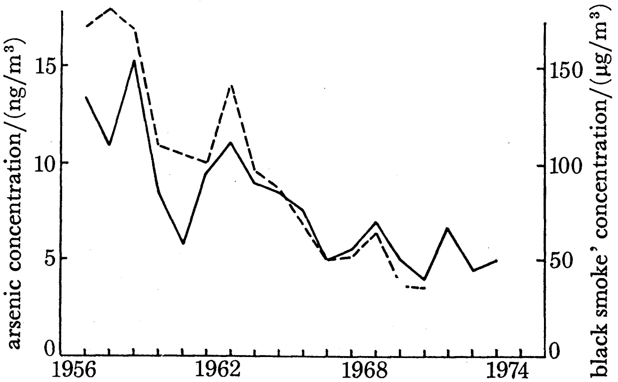

FIGURE 5. Temporal comparison of atmospheric black smoke at Oxford 20 km north of Chilton (– –) and arsenic at Chilton (—) in winter months.

Some constituents have increased during this period. The major constituent, ammonium sulphate, has increased possibly because of oxidants from the increased consumption of automobile fuels, which has also caused the increase in Pb (from 1960) and Br. On the other hand, concentrations of trace elements associated with the burning of coal have decreased. For example, in figure 5, the fall in concentration of As at Chilton is linked with the smoke level at Oxford.

DEPOSITION OF TRACE ELEMENTS

The concentration of a trace element in rain can be related to that in air by the washout factor (Chamberlain 1960), which is given by the ratio of concentrations in equal masses of rain and air. In principle, this relates to the efficiency of removal by rain of particulate material from the atmosphere. In practice, the collection of dry deposition in the open rain collector will exaggerate the apparent washout of the larger soil-derived particles. Also, at coastal sites the presence of sea-spray will enhance the collection of maritime and other elements. An inventory of total deposition, wet plus dry, can be drawn up for each trace element: this does not account for the biological availability of that element.

The measured total deposition of some heavy metals exceeds the amounts removed by normal crops of grass, kale and wheat grain, sometimes by more than two orders of magnitude (Cawse 1974). Even for the essential elements Cu and Zn, removal by harvest is less than 20% of the annual deposition. Deposition of Na, Cr, Co, Zn, As, Br and Pb is significant in relation to the amount analysed in surface soil near the sampling stations. At Chilton, continued deposition of Pb at the present rate would increase the content of the surface soil considerably during the next decade.

TRACE ELEMENTS IN THE OCEAN SURFACE

The sea has been regarded as the most significant source of the major maritime elements. However, it has been recently established that trace elements in the sea are massively enhanced in the surface layer (Duce *et al.* 1972) and are therefore available for resuspension in the form of wind-driven spray. Although it is not yet clear how this enhancement is caused, it has been possible to observe (Peirson *et al.* 1974) elevated levels of a number of trace elements deposited in the rain collectors sited in coastal regions. The effect of these resuspended trace elements is probably restricted, unlike the major maritime elements, to the coastal regions.

SUMMARY

It has been shown that a multi-element survey of trace elements in the atmosphere is feasible, and is capable of discovering the distribution, behaviour and possible origin of the trace elements. Although the atmospheric concentrations can vary considerably between sites, the relative concentrations are more uniform. This leads to a classification of trace elements that differentiates between those that are derived from soil and those that may be attributed to industrial activity, together with the maritime elements. The uniformity of relative concentrations may extend to other sites in the same latitude zone as the U.K. The notable enrichment of the industrial trace elements relative to soil is related inversely to the size of the airborne particles. The deposition of trace elements to the ground is, in some cases, greatly in excess of the amount removed by crops and could be comparable to the content of surface soil. The trends of trace element concentrations measured retrospectively at one site indicate that some have increased and others have decreased during the past 20 years.

Suggestions for further work and study can be conveniently divided into two forms: geo-scientific (dealing with the production, behaviour and subsequent fate of airborne particulate material) and medical (dealing with the health implications). An explanation of the aerosol mixture is required: this could be pursued by a microscopic examination of the physical and chemical characteristics of the particles, together with a closer investigation of the trace elements emitted by large industrial sources, especially power stations. For potential toxicity, what is the acceptable level of human intake for an element overall, and how should this be apportioned to the atmospheric pathways, namely inhalation and ingestion of food that has been exposed to deposition?

The survey of trace elements at the non-urban sites was initially sponsored by the Natural Environment Research Council and subsequently by the Department of the Environment. The results relating to Walsall and Brent are published by courtesy of the respective Borough Councils.

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