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TRACE ELEMENTS IN THE ATMOSPHERE OVER SOUTH AFRICA

BY

DR R.B. WELLS AND D. VAN AS

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TRACE ELEMENTS IN THE ATMOSPHERE OVER
SOUTH AFRICA

by

R.B. WELLS

Ph.D. (Natal)

Research Officer

Air Pollution Research Group

Council for Scientific and Industrial Research, Pretoria.

and

D. VAN AS

Ph.D. (Stellenbosch)

Chief Scientist

Isotopes and Radiation Division

Atomic Energy Board, Pelindaba, Pretoria

SYNOPSIS

Natural sources of trace elements in the atmosphere are suspended soil particles, the evaporation of sea spray and smoke from veld fires. In urban and industrialised areas the main sources are fossil-fueled power plants, metallurgical smelters, blast furnaces, incinerators, automobiles, fossil-fueled locomotives and open fires in the Black townships. Often a source can be recognised by the relative concentrations of particular trace elements.

A monitoring programme was established in 1974 by the Air Pollution Research Group of the CSIR and the Isotopes and Radiation Division of the Atomic Energy Board in order to study the levels of trace elements in urban areas such as Johannesburg, Cape Town, and Durban, to measure the effects of industrialisation on trace elements levels in developing

areas such as Richards Bay and Saldanha Bay and also to determine baseline values in rural areas. Extremely sensitive analytical techniques, e.g. neutron activation and atomic absorption were used for the analyses of filter samples. Methods of sampling and analysis are discussed and preliminary results of this programme are presented.

OPSOMMING

Natuurlike bronne van spoorelemente in die atmosfeer is swewende grondstofdeeltjies in die lug, die verdamping van seesproei en rook van veldbrande afkomstig. In woon- en nywerheidsgebiede is die hoofbronne kragstasies wat fossielbrandstof verbruik, metallurgiese smelterye, hoogoonverbranders, motorvoertuie, lokomotiewe wat deur fossielbrandstof aangedryf word en oop vure in Swartwoongebiede. Dikwels kan 'n bron d.m.v. die relatiewe konsentrasies van bepaalde spoorelemente uitgeken word.

In 1974 is 'n moniteerprogram deur die Lugbesoedeling-Navorsingsgroep van die WNNR in medewerking met die Afdeling Isotope en Straling van die Raad op Atoomkrag van stapel gestuur met die doel om spoorelementkonsentrasies in stedelike gebiede van Johannesburg, Kaapstad, en Durban te bestudeer; om die uitwerking van nywerheidsontwikkeling op spoorelementkonsentrasies in ontwikkelende gebiede, bv. Richardsbaai en Saldanhabaai te meet, asook om die agtergrondwaardes in plattelandse gebiede vas te stel. Uiteraars gewoelike analitiese tegnieke bv. neutronaktivering en atoomabsorpsie word vir die analise van filtermonsters gebruik. Die metodes van monsterverzameling en analise word bespreek en voorlopige resultate van hierdie program aangebied.

INTRODUCTION - TRACE ELEMENTS AS AIR POLLUTANTS

In biological terms a trace element is any element which is present in amounts less than 0,01 % of the organisms weight. From the beginning of time life has been exposed to trace elements in the environment and has learnt to live with them. Some trace elements perform vital functions in biological processes, mostly through their action as activators or inhibitors of enzymatic reactions. Twenty trace elements are consistently present in human tissue but only seven of these viz. Fe, Cu, Zn, Co, Cr, Mo and Mn are known to be essential for human life. Others such as Be, Cd, As, Se, Pb, Sb, Hg, Tl and V are highly toxic due to their interference with the function of other elements. Almost any element, even those essential to life, can be toxic if present in large enough amounts; every organism has a limit beyond which its protective mechanisms cannot cope. A further complication is that certain trace elements although not toxic in themselves can be extremely detrimental in combination with other elements or compounds. This is known as the synergistic effect.

To determine whether an element is essential or toxic there must be;

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

To illustrate the difficulties of this type of study, the seed of a plant may contain enough of an element to supply the entire needs of the full grown plant. In man the symptoms of a disease such as cancer, which is induced by a toxic element, may take ten or twenty years to manifest itself. For example, the carcinogenic effects of vinyl chloride might have gone undetected for many years if the form of cancer, hepatic angiosarcoma, had not been unusual. Because of these difficulties there may be elements whose necessity for life has not been recognised, or whose toxic properties are unknown. In addition to these difficulties each species has different needs and sensitivities, also the chemical form of an element, and the presence or absence of other elements, may modify its

effectiveness for good or bad.

The natural sources of trace elements in air are wind-blown soil dust, sea spray, volcanic and geothermal activity, and fires. It also appears that the leaves of plants may shed small metal-rich particles¹. Any legal limits which we may place on man-made emissions of trace elements must be viewed in perspective against the natural levels to which man has been exposed during his evolution and to which he has presumably adapted.

Trace elements are released into the air by man through coal combustion, ore smelting, petroleum combustion, and general industrial activity. Potentially toxic elements which are volatile compounds are As, Hg, Cd, Sn, Sb, Pb, Zn, Tl, Ag, Bi, Se, Be, F and Ni. It has also been noted by Natusch et al² that twelve elements are concentrated in the smallest particles of coal fly ash which readily pass collection devices and stay airborne for long periods. Sub-micron particulates also pass the protective barriers of the human nasal system and penetrate into the depths of the lung where they either accumulate or are absorbed. The uptake from the air depends on both the concentration as well as the chemical and physical characteristics, e.g. particle-size distribution. Particles < 1 μm are deposited in the alveolar regions of the lung, where high absorption efficiencies exist. Large particles are deposited in the nasal pharyngeal and bronchial regions of the respiratory system and are removed by ciliary action to the stomach where the absorption efficiency is much lower. For many trace elements the alveolar absorptive efficiency is 50 - 80 % whereas the efficiency in the digestive system is 5 - 10 %.

Trace elements are relevant to air pollution in two ways. Firstly by inhalation they may be directly toxic and secondly the air is a means of transport allowing widespread dispersion of trace elements. Absorption by inhalation is the most obvious threat to man, because although this is difficult, it is the easier threat to quantify. Thus most legislation and measurement is in terms of airborne concentrations of pollutants.

It should be emphasised that there is a major qualitative difference between trace elements and other pollutants such as sulphur dioxide or organic compounds. Harmful though the immediate effects of these latter

compounds may be, their lifetime in nature is short. If pollution could be halted, these compounds would soon be absorbed and degraded. In contrast to transient pollutants, trace elements released by man from relatively immobile states in concentrated ores do not disappear by biodegradation. Instead they remain with us until in the course of their geological cycles they are again deposited in inert ore bodies.

The transport and dispersion of trace elements poses scientific and philosophical problems more severe than the immediate threat through inhalation. Even if airborne levels of a trace element are below presently dangerous levels it can be argued that dispersion and accumulation of the element in our environment constitutes a threat to the future. Controversy over this point can hardly be resolved without detailed knowledge of the geological and biological cycles of the toxic elements. If preventive action is made to wait on full knowledge we may act too late, while if drastic and perhaps unnecessary action is taken against trace element emissions, industry could be seriously disrupted .

Excluding unusual smelting operations which may cause unusual local pollution, six elements namely cadmium, lead, nickel, berillium, antimony and mercury are considered to be potential hazards to large numbers of people. It has been claimed that trace element pollution from coal combustion has not been clearly related to any disease³. Similarly reports prepared for the U.S. Environmental Protection Agency^{4, 5} in 1971 concluded that there was no evidence of ill effects on public health from concentrations of lead normally found in ambient air over large urban areas. These conclusions do not exonerate the toxic trace elements and lead in particular from suspicion, rather they reflect the difficulty of diagnosing non specific effects in populations exposed to low doses of many toxic chemicals. The recent trend in studies of toxic trace elements is to examine subtle effects such as neurological damage, behavioural changes, resistance to disease, and drug detoxification mechanisms⁶.

SOUTH AFRICAN SAMPLING PROGRAMME

An atmospheric sampling programme for the measurement of radioactive fallout over South Africa was introduced in 1965 by the Atomic Energy Board⁷. Since June 1974 these samples, collected at Pelindaba, the University of Cape Town and the University of Lourenco Marques have also been subjected to trace element analysis. Other air samples have been collected at Pelindaba since 1970 for analyses by the UKAEA, Harwell, as part of a programme for the study of trace elements in rural areas in the United Kingdom⁸.

Through a collaborative effort by the Air Pollution Research Group of the CSIR and the Atomic Energy Board an exploratory sampling programme was established in 1975 with the following objectives (i) to determine the range of trace element concentrations and their possible sources in the densely populated urban areas (ii) to measure the effect of expanding industrialization at Saldanha Bay and Richards Bay and (iii) to measure baseline levels at rural sites.

An ideal sampling site should allow the collection of a representative sample of the area and should be removed and protected from local sources of contamination and human or animal interference. Further requirements are a dependable power supply and easy access for service and maintenance.

For the sampling of urban atmospheres stations were established at the Johannesburg and Cape Town city halls and at the Durban central fire station, where the above requirements are met. Samples are collected 5 m above street level.

At present, Saldanha Bay and Richards Bay, with few industrial sources of atmospheric trace element pollution, are considered to be semi-rural areas. In Saldanha Bay the harbour activities and fish factories are the main sources of pollution. A sampling station was established in the vicinity of the harbour at the laboratories of the Department of Industries. Dust from extensive building operations at the Richards Bay harbour, and the development of townships as well as fires in the sugar cane plantations, form the main pollution sources of this area. A

sampling site was erected at the water purification plant of the Town Board where well established roads and gardens exclude localised dust problems. Pelindaba is a semi-rural site situated 30 km west of central Pretoria and samples are collected at the National Nuclear Research Centre. Possible sources of atmospheric trace elements in this area are smoke from fossil-fueled open fires from a Black township and the ISCOR Works in Pretoria West.

Langebaan, a small sea resort situated 13 km from Saldanha Bay, is presently the closest approximation to a rural site in our programme. Samples are collected 30 m from the shore of the lagoon.

SAMPLING METHODS

Trace element determinations imply low concentrations and thus sensitive measuring techniques. Under these circumstances contamination and/or material losses are of the utmost importance and extreme care are taken to minimize these effects during sampling, handling and analysis. For the quantitative collection of the particulate fraction ambient air was sampled by drawing 100 - 200 m³ through filter paper of high purity and efficiency. The air was moved by a diaphragm pump at constant rate of between 2 and 4 l/min and the total volume was measured with a gasmeter. The filter (5 cm diameter) was fitted, in an all polypropylene duct and the linear velocity was of the order 3 cm/s. Filters were handled with tweezers only and after removal from the duct the exposed filter was covered by a blank filter paper and clamped in a polythene petri-disk for transportation and storage.

No material is entirely free of trace elements and the concentration in blank filters is most important for the accurate measurement of trace elements in air. Numerous studies of trace elements in commercial filter papers^{9, 10} revealed the presence of almost every element in varying concentrations. When a particular element is being investigated, a suitable filter can be chosen. No one filter type is superior, however, when 20 elements are being investigated.

In Table 1 the maximum blank values of certain trace elements found in Sartorius membrane filters (SM 11306, pore size 0,8 μm) are given. The total masses of these elements in average 100 m^3 urban and rural samples are also shown. It is apparent that Cu and Cd in blanks contributes appreciably to the urban samples and that corrections are necessary. In the case of rural samples serious errors will be introduced by inconsistencies in blank values and sample volumes must be increased to a minimum of 500 to 1 000 m^3 in order to obtain reliable values for Cr, Sb, Zn, Cd and Cu.

Positive evidence was found of material losses from the surfaces of collecting membrane filters under conditions of high filter loading. For quantitative collection it is essential the filter be exposed in an up-facing position with a suitable shield to prevent the direct deposition of particulate material.

Parallel samples were collected over several months on both Whatman 41 and Sartorius (0,8 μm pore size) membrane filters to compare efficiency etc. The samples obtained were comparable with no bias in collection of any of the elements. This result was confirmed by comparison between UKAEA samples collected on Whatman 41 filters at Pelindaba and the results of our own samples collected on membrane filters. The choice between these two filter media is thus purely one of convenience.

SAMPLE ANALYSES

Filter samples were divided into equal halves and submitted for atomic absorption analyses of the elements Cd, Cu, Fe, K, Na, Mg, Mn, Ni, Pb and Zn, while the other half were analysed by means of instrumental neutron activation for the elements Al, Br, Co, Cs, Eu, Fe, Mn, Rb, Se, Sb, Th, V, Zn. In total 21 elements are measured of which Fe, Mn and Zn were analysed by both methods and which served to control the quality of analyses. In Fig. 1 the results for Fe and Mn are compared. The comparison for these elements as well as for Zn were satisfactory and no bias was observed in the methods used.

Ranweiler and Moyers¹¹ have shown that flame atomic absorption analysis of particulate samples representing 2 000 m³ to air is capable of determining up to 22 elements. In their procedure the sample is split into five aliquots each with a different dilution and matrix. In the present study, for our purposes, simplicity of sample preparation was regarded as the prime objective, even at the cost of initially restricting the range of elements analysed. Every dilution or matrix adjustment, besides taking more time, is an opportunity for errors and contamination to occur. In our procedure the samples on the membranes, typically representing about 100 m³ of air, are treated with concentrated nitric acid (5 cm³) and evaporated to near dryness, hydrogen peroxide (5 cm³, 30 %) is added and the solution again evaporated to near dryness. Finally concentrated hydro-chloric acid (5 cm³) is added, the sample is evaporated to near dryness and diluted to 10 cm³. If sodium and potassium are being determined then cesium chloride solution is added to give a cesium concentration of 100 ppm. The solution is then analysed by flame atomic absorption on a Varian Techtron AA6. At the concentrations found, nickel, cadmium, and chromium are often near or below the detection limit. This procedure avoids ashing, which even at low temperatures may cause losses of elements such as cadmium. The use of chelation and organic extraction¹² was investigated initially. This method has little to offer for routine air pollution analysis, it cannot increase the amount of analyte available and after correction for increased nebulisation rates only increases sensitivity by a factor of about 2,5.

Neutron activation analyses were performed without any form of chemical-treatment. Filter samples were placed in individual polythene vials of high purity and a known mass of InCl₃ was added to each vial by automatic pipette. The In served as an internal standard to correct for exposure time and neutron flux variations. The elements Al, Br, Mn and V are determined by the irradiation of individual samples in a pneumatic irradiation facility with a neutron flux of $2,87 \times 10^{13}$ n/s/cm² for 1 min. After allowing 5 min. for certain short-lived impurities to decay samples were counted for 2 minutes on high resolution Ge(Li) gamma spectrometer coupled to a 2 000 channel analyser and a magnetic data storing device to determine the neutron-induced isotopes of Al and V eg ²⁸Al (half-life

= 2,3 min) and ^{52}V (half-life = 3,75 min). After a further decay period of 12h the induced isotopes ^{56}Mn (half-life = 2,8 h) and ^{82}Br (half-life = 36 h) were measured by counting for 10 minutes.

Quantitative results are obtained by comparison to standard filters prepared from standard solutions of the various elements and irradiated and counted under similar conditions.

The elements Co, Cr, Cs, Eu, Fe, Rb, Sb, Se, Sc, Th, Zn all have neutron induced isotopes with half-lives of the order months to years, and are determined by the bulk irradiation of 6 samples, 2 standards and 1 blank for 8 h in the same pneumatic facility. The irradiated samples are allowed to decay for 1 month and are then counted for 2 h. Gamma spectra are analysed by a computerized peak procedure and quantitative results are found by comparison with the standard filters.

RESULTS AND DISCUSSION

The results that are available do not yet cover a complete seasonal cycle and the discussion which must be regarded as preliminary is restricted to general trends and comparisons.

The concentrations of those elements measured so far ranged over almost 5 orders of magnitude from $> 1\ 000\ \text{ng}/\text{m}^3$ to $< 1\ \text{ng}/\text{m}^3$ (or more than 1 part in 10^9 to less than 1 part in 10^{12}). The approximate ranges of the elements in urban areas are

Al, Fe	>	1 000 ng/m^3
Zn, Pb, Mg	100 -	1 000 ng/m^3
Cu, Cr, Ni, Mn, V, Eu	10 -	100 ng/m^3
Co, Sb, Se	1 -	10 ng/m^3
Cs, Sc	0,1 -	1 ng/m^3

$$1\ \text{ng} = 10^{-9}\ \text{g}.$$

There is a large scatter in the monthly concentrations of particular elements. Johannesburg, Pelindaba and Durban show a general trend towards increased concentrations in the winter months - at the former two stations this increase is a factor 3-4 above the summer level while at the latter

station the summer levels are double those in winter. Strong temperature inversions during the winter months which cause stagnant conditions, increased fuel-burning and the low rainfall could be responsible for this effect. At all 3 stations this trend is noticeably absent in the case of Zn, Ni and V. for which the levels stay fairly constant.

In Cape Town, Saldanha Bay and Langebaan the trend is reversed and levels decrease by a factor of about 2 in winter months. Again the scavenging effect of winter rains may be responsible. Noticable exceptions are Sb and Pb in Cape Town and V in Saldanha Bay, all of which increased sharply in winter.

A comparison of the average concentration in South African urban, semi-rural and rural areas and the levels in similar areas in the U.K.⁸ are given in Table 2. The elements Al, Cu, Sb and Pb are factors 3 to 4 times higher in London than the highest levels in local cities. While the Mn-levels in Johannesburg are noticeably greater than in London. In semi-rural and rural areas obvious features are the high Al and Fe levels at South African stations which probably reflects high soil-dust loading of the air because of the dry climates. Saldanha Bay exhibits exceptionally high V and Ni levels.

Comparing South African cities, we notice that the level of Pb in Cape Town is 3 times that of Durban and Johannesburg, while the Cr and Zn levels are again 3 times lower. The very low levels of V and Ni in Johannesburg also seems significant.

Little information exists on the upper limits of atmospheric concentrations of trace elements for human beings. Recommendations for so-called threshold limit values (TLV) for occupational exposure in workrooms were published by the American Conference of Government Industrial Hygienists¹³. These values refer to a 40 h work week and does not take into consideration long-term low-level exposures, simultaneous exposure to several elements or the exposure of vulnerable groups such as infants, pregnant women, aged people or individuals with lung ailments. These values are therefore not strictly applicable but has nevertheless been scaled for

continuous exposure (168 h week) and compared with maximum monthly levels measured in South Africa cities. From Table 3 it is evident that the existing levels are far below the TLV's. However, as mentioned before, very little knowledge exists on synergistic etc. effects.

Sampling techniques and analytical methods are now well established and this programme is continuing and will be expanded to include other areas and more elements viz. As, Br and Hg. Specific sampling to identify the sources of certain elements will also be introduced.

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TABLE 1

MAXIMUM TRACE ELEMENT CONCENTRATION OF FILTER BLANKS AND
AVERAGE 100 m³ AIR SAMPLES

Element	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Zn
Filter blank ng/filter (0,08 g)	1 000	30	3	100	250	3 000	20	40	300	10	500
Average mass (ng) ³ collected in 100 m ³ of urban air	20 000	100	100	2 000	2 000	200 000	3 000	1 500	70 000	500	10 000
Average mass (ng) ³ collected in 100 m ³ of rural air	20 000	100	40	200	1 000	50 000	1 000	500	20 000	40	2 000

TABEL 3

THRESHOLD LEVEL VALUES (TLV) AND MAXIMUM MONTHLY
CONCENTRATIONS IN SOUTH AFRICAN URBAN AREAS

Element	TLV ng/m ³	Maximum monthly concentration ng/m ³	Station
Al	-	6 000	Johannesburg
Cd	50 000	8	Saldanha Bay
Co	24 000	4	Johannesburg
Cr	24 000	56	Johannesburg
Fe	250 000	6 000	Johannesburg
Mn	1 200 000	250	Johannesburg
Ni	240 000	100	Saldanha Bay
Pb	36 000	4 300	Cape Town
Sb	120 000	8	Cape Town
Se	50 000	4	Johannesburg
V	120 000	80	Saldanha Bay
Zn	1 200 000	480	Johannesburg

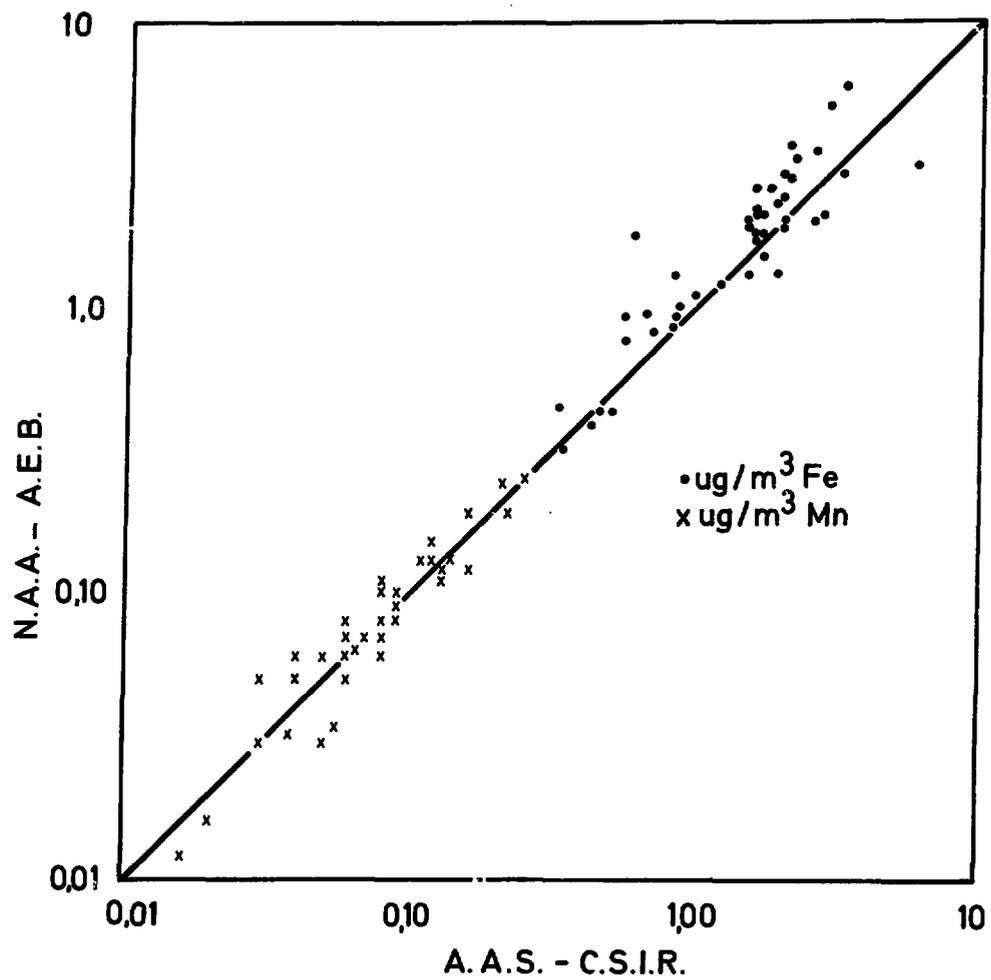


FIGURE 1. Comparison of neutron activation and atomic absorption analysis for the elements Fe and Mn.

