Reports

Release of Particles Containing Metals from Vegetation into the Atmosphere

Abstract. *Studies with radioisotopes indicate that in the laboratory pea plants and pine tree seedlings release zinc and lead into the atmosphere. Field studies carried out on radiolabeled plots vegetated with a variety of grasses and small herbaceous plants also show that these elements are released into the atmosphere. The metals, associated with particles of various sizes, are released from the plant surfaces, and the loss mechanism is influenced by growth conditions, the concentrations of the elements in the leaves, and meteorological factors. For plants whose leaves have about equal concentrations of zinc and lead, the amount of zinc released is usually two orders of magnitude greater than the amount of lead. The significance of the process is discussed in terms of the overall trace metal composition of atmospheric particulates.*

In recent years considerable interest has been directed toward monitoring the trace metal content of the atmosphere. Atmospheric analyses have detected localized zones where the trace metal concentration is high as well as a background level of trace metals that extends even to remote regions. The enrichment of these trace elements in atmospheric particulates collected from remote regions of the globe, relative to their concentrations in soil and sea, and their uniform chemical composition cannot be satisfactorily explained in terms of exclusively anthropogenic processes (*1*). We present here evidence that plants give off metal-rich airborne particulates and suggest that this process could play a significant role in overall global atmospheric chemistry.

Even before recent concern about atmospheric pollution, Went reported that large quantities of "volatile" plant products were released into the atmosphere from vegetation (*2*). He and his co-workers (*3*) established a strong correlation between the number of Aitken condensation nuclei (ACN) in the atmosphere and the density of the underlying vegetation. Schell and Vali (*4*) have established that vegetation, especially in a decomposing state, is capable of releasing large numbers of ACN directly into the atmosphere. They suggested that this process plays an important part in the formation of atmospheric ice nuclei and in the initiation of precipitation. Others have presented evidence that plants can act directly as a natural source of atmospheric particles (*5*, *6*). Recently we reported that plants are capable of releasing trace metals, particularly Zn, into the atmosphere (*7*). We outline here more extensive studies of this phenomenon.

The results in Table 1 were obtained by experimental methods described elsewhere (*7*). Pea plants (*Pisum sativum*) were grown in liquid culture containing ^{65}Zn or ^{210}Pb. Fully labeled plants were installed in chambers with the foliage separated from the roots by an airtight seal around the base of the stems. Clean, dry air was passed through the foliage compartment, and the outgoing air was monitored for radioactivity. The air was passed through Millipore filters (pore size, 0.22 μm) and a cold finger trap (solid CO_2 and methyl alcohol). In these experiments most of the radioactivity was found to be in the cold finger condensates. No radioactivity was detected in control experiments in which the foliage had been decapitated and removed from the foliage compartment. The amount of Zn and Pb released was essentially a function of the concentration of these metals in the external solution, as were the concentrations of these elements in the plant parts. Although the Pb and Zn concentrations in the leaves were similar for a particular concentration in the external culture solution, the amount of Pb released was usually two orders of magnitude less than the amount of Zn. Similar results were obtained with pine tree seedlings (*Pinus sylvestris*). The actual amounts of Zn and Pb released were similar for the replicate determinations in any particular experimental set. There was, however, greater variation for similar experiments conducted on different days and with different plant species. The amount of a particular metal released was always a function of the metal concentration in the leaves, but factors such as illumination, humidity, and the general health of the plants also had a controlling effect for a particular concentration.

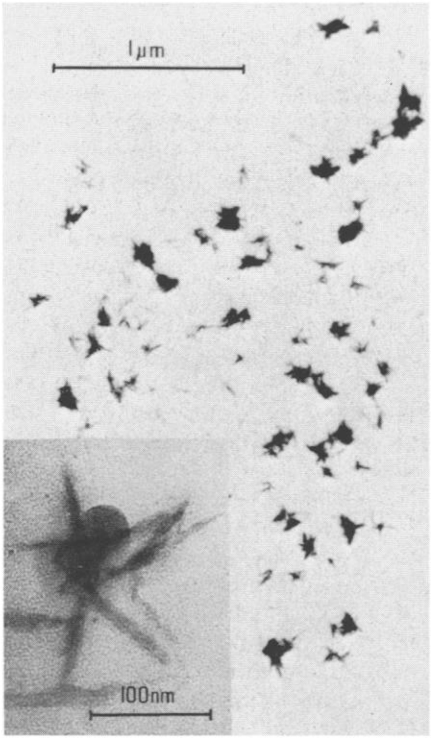

Fig. 1. The deposition of particles collected from pea plants (*Pisum sativum*) with a thermal precipitator. Air was passed over plants in foliage chambers and into a thermal precipitator. Material was precipitated onto copper grids (400-mesh size) covered with Formvar film and coated with carbon. Grids were examined by transmission electron microscopy. Magnification: × 25,000; inset, × 152,000.

The mechanism of metal release could involve either a vapor phase or submicrometer-sized particles. Experiments in which a thermal precipitator with a reciprocating head was used on the outlet side of the foliage chamber indicated that the release mechanism involves particles. Particulates were deposited onto small copper grids by a thermal gradient created by the heating of the platinum wire in the precipitator (current of 1.3 amperes drawn from a 12-volt battery). Examination of the precipitator's collection grid by electron microscopy indicated that needle-like particles up to 200 nm long and 30 nm wide are given off by *P. sativum* plants (Fig. 1). It is not clear whether the particle clustering seen in the electron micrographs is due to natural agglomeration or is induced by the thermal gradient maintained in the precipitator. Nevertheless, it seems likely that these particles are associated with the metal release process.

It can be easily demonstrated that both Zn and Pb are present on or near the surfaces of leaves if one carries out either mild extractions of surface waxes or leaching experiments with water. The amounts of Zn and Pb released by water leaching were usually greater than the amounts obtained after wax extraction, especially in the case of Pb (Table 2). In general, more Zn than Pb was removed by either treatment. For example, when the external concentrations (in the culture medium) were 1 part per million (ppm), the amount of Zn leached represented 1.5 percent of the total Zn content in the leaves whereas for Pb the corresponding value was 0.07 percent.

These results suggest two possible ways in which these metals may be lost from leaves. It is possible that epicuticular waxes are the metal carriers and that fragmentation and loss of wax rodlets occur during rapid leaf expansion. The loss of small wax particles from plants has been reported by several workers (*5*). Another mechanism may involve the production of airborne salt crystals generated by diffusiophoresis associated with water loss during rapid transpiration (*8*), as suggested by Nemeryuk (*6*).

Table 1. Distribution and rate of release of Zn and Pb from pea plants (*Pisum sativum*) grown in liquid culture containing ^{65}Zn and ^{210}Pb (*7*). The rates of Zn and Pb released are expressed in terms of leaf surface area, computed for 4-hour sampling periods, and represent the mean of four replicate determinations.

External concentration (ppm)	Element	Concentration (ppm, wet weight)		Metal released (pg hour^{-1} cm^{-2})	Water released (mg hour^{-1} cm^{-2})
		In roots	In leaves		
0.001	Zn	2.1×10^{-3}	7.0×10^{-4}	8.0×10^{-2}	10.0
0.010	Zn	6.0×10^{-2}	5.2×10^{-2}	0.7	11.6
0.100	Zn	0.5	0.1	4.5	7.0
1.000	Zn	3.6	0.9	21.0	10.6
0.001	Pb	1.1×10^{-3}	5.0×10^{-3}	7.4×10^{-5}	4.0
0.010	Pb	1.3×10^{-2}	3.8×10^{-2}	1.5×10^{-4}	4.0
0.050	Pb	6.0×10^{-2}	5.8×10^{-2}	1.6×10^{-3}	4.4
0.100	Pb	8.8×10^{-2}	0.6	3.6×10^{-3}	7.6
0.250	Pb	0.3	1.7	1.3×10^{-2}	6.0
1.000	Pb	1.0	5.6	1.0×10^{-2}	3.5

Table 2. Fractions of trace metals removable by water and chloroform extraction from the leaves of pea plants (*Pisum sativum*) grown in liquid culture medium containing ^{65}Zn or ^{210}Pb. Fully labeled leaves were leached in distilled water containing 0.1 percent Tween 20 (wetting agent) at *p*H 6.0. Leaves were subjected to an organic leach by short immersions (10 seconds) in chloroform. The amounts of metal leached are expressed in terms of leaf surface area and represent the mean ± the standard deviation of ten samples.

External concentration (ppm)	Element	Concentration in leaves (ppm, wet weight)	Water leachate (pg cm^{-2})	Organic leachate (pg cm^{-2})
0.001	Zn	$3.0 \pm 1.0 \times 10^{-3}$	0.4 ± 0.1	0.1 ± 0.1
0.01	Zn	$4.0 \pm 1.5 \times 10^{-2}$	1.9 ± 0.5	0.6 ± 0.2
0.1	Zn	0.4 ± 0.1	52.0 ± 24.0	1.0 ± 0.3
1.0	Zn	1.7 ± 0.6	153.0 ± 30.0	4.0 ± 1.0
0.001	Pb	$3.4 \pm 0.9 \times 10^{-3}$	0.1 ± 0.07	$1.1 \pm 0.3 \times 10^{-3}$
0.01	Pb	$5.6 \pm 2.0 \times 10^{-2}$	0.4 ± 0.1	$6.0 \pm 1.8 \times 10^{-3}$
0.1	Pb	0.7 ± 0.4	9.0 ± 1.5	$5.0 \pm 1.5 \times 10^{-2}$
0.5	Pb	3.2 ± 1.0	23.0 ± 6.0	0.2 ± 0.1
1.0	Pb	5.8 ± 1.9	25.0 ± 5.0	0.9 ± 0.3

Table 3. Concentrations of trace metals in plants and plant particulates. Well-rooted pine trees (*Pinus sylvestris*) were grown in liquid culture containing either ^{65}Zn, ^{115}Cd, or ^{210}Pb. The external concentration of each element was 5 ppm. Particulates were collected from plants by means of a minicyclone. Each result represents the mean of ten samples.

Element	Concentration in plant needles (ppm, dry weight)	Concentration in plant particulates (ppm)	Enrichment/depletion	
			Plant to particulates	Substrate to particulates
Pb	4.20	2.73	0.65	0.55
Zn	16.21	26.49	1.64	5.30
Cd	14.58	24.68	1.69	4.93

We found that in the natural environment, the leaf surface is exposed to a great deal of mechanical agitation due to metereological factors, in contrast to the rather static conditions that prevailed in the laboratory experiments. We therefore investigated the effect of subjecting the plant surfaces to mild mechanical stress. Small intact pine trees (*Pinus sylvestris*) fully labeled with ^{65}Zn, ^{115}Cd, or ^{210}Pb were gently shaken in a polyethylene chamber attached to a minicyclone (*9*). The gentle agitation released considerable amounts of particles of a wide size range which were deposited in collection tubes by the centrifugal action of the cyclone. Electron microscopy indicated that most of the mass collected was composed of particles larger than 1 μm. The metal concentrations of these particles were determined by radioactivity analyses (Table 3). The concentrations of Zn and Cd in the particles tend to be slightly enriched with respect to the concentrations in the external medium and in the leaves; the opposite is true for Pb.

These results indicate that, although submicrometer-sized particles are involved in metal release under static experimental conditions, larger particles can be released if gentle leaf and stem abrasions occur. It would therefore be expected that in the natural environment coarse-sized particles would also be involved in the transport of trace metals into the atmosphere. We carried out the following fieldwork to test this prediction.

Plots (1 m^2) were completely cleared of vegetation before the spring of 1975 [see (*10*)]. Each plot was treated with 2 mc of ^{65}Zn or 1 mc of ^{210}Pb. The total concentrations of Zn and Pb in the soil were 55 and 57 ppm, respectively, and were unaltered by the addition of radiotracer. The plots were left to regain their vegetation (a variety of grasses and small herbaceous plants) during the spring and early summer months. Analyses of the new foliage indicated Zn and Pb concentrations of about 1 to 10 ppm (wet weight basis). We collected particles being released from the sites by passing the air immediately above the radiolabeled vegetation through a four-stage cascade impactor (Casella). The amounts of radioactive material collected depended on the meteorological conditions, being enhanced by wind and direct sunlight. Although the data obtained were not related to the mass of material deposited because of background particle contamination, the overall amounts of Zn released were greater than the amounts of Pb. Moreover, most of the radioactivity measured was associated with particles larger than 5 μm. Since no foliage chambers were used in these experiments, the amounts collected could not be related to surface area. However, when chambers were used and the water transpired from the vegetation was collected, the rates of metal loss during rapid transpiration under sunny conditions were comparable to those found in the laboratory for plants having similar concentrations of metals in their leaves.

Our results show that metal-containing particles of various sizes can be generated from the surfaces of plants. Submicrometer-sized particles are probably released under all conditions, particularly when plants are undergoing rapid growth or have high transpiration rates. Larger particles are almost certainly generated by mechanical disturbances at the plant surfaces. Surface abrasion and leaf bending induced by wind action or thermal plumes could dislodge salt particles, wax rodlets, and cuticular and other surface fragments. Microbiological activity could also disrupt the plant surfaces and so produce potential fragments (*11*). All these effects probably play a part in the process of metal release to the environment. There is every reason to believe that a whole range of elements are available for release within the plant, although the amount released will vary with the element, as shown by Zn and Pb above. In principle, biologically important elements such as K, Na, Ca, and Mg should occur at much higher concentrations in plant-derived particulates as compared with trace elements such as Zn, and indeed there is evidence for this (*12*).

It is unlikely that large metal-containing particles from plants play any significant role in the global atmospheric distribution of elements since their residence times would be relatively short. On the other hand, submicrometer-sized particles released from plants could disperse over large areas and give rise to the unexplained metal-enriched particles collected in remote regions of the globe (*1*). At present, we are unable to quantify this effect since the rate of movement of metals into the atmosphere from plants depends on the element in question, its concentration and availability in the soil, seasonal and meteorological conditions, and the sizes of the particles involved. Our experiments, based on leaf area and a background concentration of 1 ppm for both elements in the soil water, indicate that the loss of Zn could be about 20 pg hour^{-1} cm^{-2} and of Pb about 10^{-2} pg hour^{-1} cm^{-2}. Since the leaf area index is about 5, these rates correspond to approximately 9 kg of Zn and 5 g of Pb released from 1 km^2 of vegetation per year. Clearly, since a great deal of the earth's landmass is covered by vegetation, it is conceivable that a proportion of the trace metal composition of the atmosphere is derived from metal-containing particles released by plants. Moreover, it would be expected that, in regions where vegetation grows in highly mineralized soil, plant-derived particles would be rich in metals; this idea has recently been applied in the development of techniques for geochemical exploration from the air (*12*).

W. BEAUFORD
J. BARBER
Department of Botany,
Imperial College,
London SW7 2BB, England
A. R. BARRINGER
Barringer Research Ltd.,
Rexdale, Ontario, Canada

References and Notes

1. D. H. Pierson, P. A. Cawse, R. S. Cambray, *Nature (London)* **251**, 675 (1974); R. A. Duce, G. L. Hoffman, W. H. Zoller, *Science* **187**, 59 (1975); W. H. Zoller, E. S. Gladney, R. A. Duce, *ibid.* **183**, 198 (1974).
2. F. W. Went, *Proc. Natl. Acad. Sci. U.S.A.* **46**, 212 (1960).
3. ———, D. B. Slemmons, H. N. Mozingo, *ibid.* **58**, 69 (1967).
4. R. C. Schell and G. Vali, *Nature (London)* **236**, 164 (1972); *ibid.* **246**, 212 (1973).
5. J. Moorby and H. M. Squire, *Radiat. Bot.* **3**, 163 (1963); P. Arpino, A. Van Dorsselaer, K. D. Sevier, G. Ourisson, *C. R. Acad. Sci.* **275**, 2837 (1972); B. R. Fish, *Science* **175**, 1239 (1972).
6. G. E. Nemeryuk, *Fiziol. Rast.* **17**, 673 (1970).
7. W. Beauford, J. Barber, A. R. Barringer, *Nature (London)* **256**, 35 (1975).
8. P. Goldsmith and F. G. May, *Diffusiophoresis and Thermophoresis in Water Vapour Systems in Aerosol Science*, C. N. Davies, Ed. (Academic Press, London, 1966), p. 163.
9. British Coal Utilisation Research Association minicyclone (Airflow Developments Ltd. model 7033701).
10. Sites were located at the Imperial College field station, Silwood Park, Ascot, Berks; soil, Bagshot green sand.
11. T. F. Preece and C. M. Dickinson, Eds., *Ecology of Leaf Surface Microorganisms* (Academic Press, London, 1971), p. 3.
12. A. R. Barringer, "Applications of remote sensing mineral and mineral fuel exploration," paper presented at the First William T. Pecora Memorial Symposium, Sioux Falls, S.D., 1975; *U.S. Geol. Surv. Prof. Pap.*, in press.
13. We thank H. M. White for assistance with the Pb experiments and M. Martin for help with the electron microscopy. We acknowledge the technical assistance of M. J. Barber, R. Dawes, and J. Whittick.

15 June 1976; revised 13 September 1976

Excitation of the Venus Night Airglow

Abstract. *The strongest spectral features in the Venus night airglow between 3000 and 8000 angstroms are identified as the Herzberg II* ($c^1\Sigma_u^- - X^3\Sigma_g^-$) *bands of molecular oxygen. These bands have been produced in a laboratory afterglow by the recombination of oxygen atoms in the presence of carbon dioxide molecules. It is hypothesized that the same mechanism produces this emission in the upper atmosphere of Venus.*

During orbital operations of the Venera 9 and Venera 10 spacecraft, observations were made of nighttime emissions from the upper atmosphere of Venus (*1*). From an analysis of spectra obtained in November 1975 Krasnopolsky concluded that the 11 spectral emissions arose from one molecular band system, but the identities of the band system and of the molecule were not determined (*2*). In this report we identify the emission spectrum of the Venus night airglow to be the Herzberg II ($c^1\Sigma_u^- - X^3\Sigma_g^-$) system of molecular oxygen (*3*). In addition, in an effort to understand the excitation mechanism in the Venus airglow, we have produced the oxygen Herzberg II bands in a laboratory afterglow under conditions that simulate the upper atmosphere of Venus.

In the laboratory experiment, we produced oxygen atoms by pumping a 0.3 percent oxygen-helium mixture through a microwave discharge at a total pressure of 22 torr. Downstream of the discharge, carbon dioxide at a partial pressure of 10 torr was added to the stream of oxygen atoms. This glowing gas was pumped through an observation tube 7 cm in diameter and 1.8 m long. The spectral emissions from this afterglow tube were measured with a scanning spectrometer having a spectral resolution of 27 Å and a relative spectral sensitivity determined by the response of a tri-alkali photomultiplier and a grating blazed at 3000 Å. The principal emissions from the oxygen–helium–carbon dioxide afterglow were a progression of bands from the lowest vibrational level ($v' = 0$) of the $c^1\Sigma_u^-$ state of molecular oxygen. In 1968, Degen (*4*) had observed and analyzed the 0,7 and 0,8 bands of this progression in an oxygen-argon afterglow. Using the wavelengths of these bands and of the absorption bands measured by Herzberg (*3*), Degen calculated a table of wavelengths for the entire band system (*4*). The wavelengths of the bands observed in the laboratory afterglow corre-