THE DYNAMICS OF METAL-CONTAINING AEROSOL FORMED THROUGH OXIDATION OF PLANT-GENERATED GASEOUS ORGANOMETALLIC COMPOUNDS

Yu.Yu. DUBININA, G.G. DULTSEVA and G.I. SKUBNEVSKAYA

Institute of Chemical Kinetics and Combustion, SB RAS, Novosibirsk, 630090, Russia

Keywords: SECONDARY ORGANIC AEROSOLS, PARTICLE FORMATION AND GROWTH, GAS-TO-PARTICLE CONVERSION.

INTRODUCTION

Plants are known to be able of accumulating metals from soil and releasing them into the environment in the form of gaseous compounds. This process is an important link in biogeochemical cycles of elements (Panichev, 1997). It involves the formation of volatile metal-containing compounds, either organometallic ones or complexes with organic ligands, terpenes being an example. The organic constituent originates from plants, while the metallic component gets into plant tissues from the contaminated soil. Keeping in mind extreme toxicity of heavy metals for humans, we investigated the possibility of these metals to be transformed into the breathable fraction of submicron aerosol which can penetrate deep into lungs thus causing severe biological damage. We investigated cadmium- and zinc-containing compounds released by some herbaceous species, and followed the light-induced oxidation of these compounds into metal-containing aerosol.

METHODS

To detect metal-containing compounds released by the plants, we placed small plants of the *Violaceae* family (violets), growing on the soil with zinc and cadmium added in the form of nitrates, in a cylindrical quartz tube and sampled the gas phase and aerosol particles varying the distance from plants to sampling sites. Another tube with a similar flowerpot but without any plants in it was used as a reference. The soil in the free pot was identical with that in the first tube. Air was purified from atmospheric aerosol with the help of filters and blown through the tubes at a rate of 0.25 l/min. The total content of metals (a sum of metal concentration in the gas phase and in aerosol) was measured by sampling the air without any filters; to detect metals separately in gas an in aerosol, sampling through the aerosol filters into organic solvents was applied. The amounts of metals in gas and in aerosol phase were determined by means of mass spectrometry with inductively coupled plasma (ICP MS). The metal-containing compounds were identified with the help of high performance liquid chromatography using Milichrom-1 instrument with micro column filled with LiChrosorb. The UV absorption detector at 290 nm was used.

RESULTS

We detected cadmium- and zinc-containing compounds in the gas phase in the vicinity of plants. No metals were present in the gas phase in the reference tube. We studied the dynamics of the oxidation of metal-containing gaseous compounds by the oxygen of the air. It should be stressed that the formation of aerosol occurred only under irradiation; no particulate matter was detected in dark. For zinc-containing organics, the oxidation by air in light was found to be a very slow process; in order to detect a 1 % transformation degree, we had to decrease the air flow rate to 0.1 l/min. Under these conditions, zinc-containing aerosol particles were detected at the outlet of the tube. However, their amount was near the detection limit of the instrument, so no quantitative characteristics of the oxidation process were obtained. For cadmium, the oxidation proceeded more readily. Aerosol particles were among the products of this process. Cadmium was bound to organic compounds with double C=C bonds, and with hydroxyl groups.

The relative amounts of cadmium in samples depending on the distance front plants are listed in Table 1. Since air flow rate was kept constant, the distance here means (is proportional to) the time of oxidation.

Table 1. The amount of Cd in gas and in aerosol phase (expressed in relative units of the intensities of Cd peaks in mass spectra) *versus* the distance from plants.

Distance	1 cm	40 cm	80 cm	120 cm	160 cm
Cd in gas	$3.8\ 10^7$	$1.1\ 10^6$	$7.4\ 10^5$	$2.6\ 10^5$	$2.3\ 10^5$
Cd in aerosol	$1.8\ 10^5$	$5.2\ 10^5$	$8.3\ 10^5$	$1.7\ 10^6$	$2.4\ 10^6$

One can see that the concentration of cadmium in the gas phase decreases with increasing distance from plants, while [Cd] in aerosol increases. We assume this is a result of photooxidation of organic cadmium-containing compounds leading to their transformation into aerosol phase. This mechanism can be actual under natural atmospheric conditions also for other heavy metals. It can be one of the sources of fine atmospheric metal-containing organic aerosol, especially for territories with severe anthropogenic contamination of soil by heavy metals.

CONCLUSIONS

Cadmium- and zinc-containing organic compounds were detected in the gas phase near plants growing on metal-enriched soil. These compounds were prone to photooxidation and transformation into the aerosol phase. This mechanism can contribute into the formation of fine organic metal-containing aerosol in natural atmosphere and requires thorough investigation because of severe health-damaging properties of such a kind of aerosol.

ACKNOWLEDGEMENTS

Financial support from the Russian Foundation for Basic Research (Grant No. 02-05-64816 and Grant No. 02-03-32109) is gratefully acknowledged.

REFERENCE

Panichev, N.A. Sources, forms of existence and methods fort he determination of metals in the atmosphere. *in: Problems of the Physics of Atmosphere,* issue 20. Physics and Chemistry of Atmospheric Aerosol. Ed. Ivlev L.S. St. Petersburg, Russia: The University of St. Petersburg Publishers, 1997.