Investigation of the dynamics of metal-containing aerosol formation at oxidation of organometallic gaseous compounds emitted by vegetation

Yu.Yu. Dubinina and G.G. Dul'tseva

Institute of Chemical Kinetics and Combustion,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk

Received January 27, 2003

The methods of mass-spectrometry and liquid chromatography were used to study the content of cadmium and zinc in volatile emissions of *Violaceae* grown on soils with different concentration of these metals. The plants were placed in a flow reactor blown with air. Organic components present in plant emissions were determined by the HPLC method. The oxidation dynamics of emitted organometallic compounds in air was studied on light and in the dark. It was shown that at illumination the cadmium concentration in gaseous emissions of a violet decreases as the distance from the plant increases, while the amount of cadmium transformed into the aerosol phase increases.

Biological objects are known to take part in biogeochemical cycles of migration of chemical elements. In particular, plants are capable of accumulating metals from soil into tissue and discharging volatile gaseous compounds including metals into the ambient medium.[1] This is manifested as halos due to dispersal in the atmosphere. For example, it was shown that halos of coniferous trees include the following metals: Na, Li, Mo, Ni, Sn, Cd, Cu, Zn, Bi, etc. Emission of metals is accompanied by emission of terpene substances: isoprene, pinene, and myrcene. It was supposed that the existence of halos can be explained by production of volatile complexes of metals with such terpenes. Keeping in mind the high toxicity of heavy metals, it is necessary to study the possibility of their ingress from plants into the aerosol of submicron fraction – the aerosol with particles of breathable size that constitutes a hazard to human health.

In our investigations of income and accumulation of cadmium and zinc in grass plants it was shown that biomass accumulates rather high concentrations of these metals. In addition, it was found that plants of the violet family growing on soil with high content of cadmium and zinc emit volatile cadmium- and zincorganic compounds into the atmosphere. This study was undertaken to reveal the nature of these compounds and their properties.

Experimental part

Investigations were conducted with ornamental plants of the *Violaceae* family. Plants were grown on soil with different amounts of cadmium (soil 1), zinc (soil 2), and the mixture of cadmium and zinc (soil 3) introduced into the soil in the form of nitrates.

Plants were placed in cylindrical 1.6-m long quartz reactors. The carrier gas was blown through the reactors at the volume rate of 0.1 l/min. As a carrier gas, we used nitrogen/oxygen mixture (70 and 30%, respectively) – artificial air, as well as pure nitrogen from a gas cylinder.

For illumination of plants in the reactor, we used fluorescent lighting and, when studying the wavelength dependence of the oxidation rate, DRSh-250 medium-pressure mercury lamps; the needed spectral ranges were separated out with color glass filters.

To study the composition of substances emitted by plants into the gas phase and to estimate the amount of emitted metals, sampling was performed by three methods for determination of three parameters. The first method was sampling into absorption devices filled with different organic solvents. This method was used for determination of the total amount of metals $\mathrm{Me_{gas}} + \mathrm{Me_{aerosol}}$ in the plant emissions. The second method was sampling onto AFA-KhA aerosol filters for estimation of the amount of cadmium and zinc transformed into the aerosol phase ($\mathrm{Me_{aerosol}}$). Having passed through the aerosol filter, the analyzed gas phase free of aerosol particles came into an absorption device for measurement of the concentration of metal-containing compounds in the gas phase ($\mathrm{Me_{gas}}$) – it was the third method.

The amount of metals in samples (solutions and aerosol filters) was determined by inductively coupled plasma-mass spectrometry (ICP-MS). Analysis was conducted with an Element Finnigan MAT (Germany). It is a high-resolution (300) ICP-MS instrument with a magnetic sector system and double focusing. Before the beginning of measurements, the instrumental parameters were optimized to obtain the maximum analytical signal and best reproducibility at low background level. The Cd content in the samples analyzed was calculated by the semiquantitative method based on linear instrument calibration using a multielement standard solution with the Cd concentration of 1 ng/g. The limit of Cd detection as estimated from the background variation in the check test was 0.03 ng/g (Ref. 2).

0235-6880/03/05–06 380-03 $02.00

The sample composition was studied using high-performance liquid chromatography (HPLC) method on a Milikhrom-1 chromatograph with a LiChrosorb sorbent filled column. The volume of sample introduced into the chromatograph was 10 to 30 μl. Elution was carried out by a 3:1 mixture of acetonitril and water, which prior was blown with helium for 20 min to remove dissolved air in order to avoid formation of air bubbles hindering measurements of the optical density. Detection was performed with an UV detector based on absorption at the wavelength of 290 nm. In some experiments, in recording chromatograms, the detector wavelength was scanned from 290 to 360 nm to obtain more complete information about absorption spectra of compounds present in a sample.

Compounds were identified with the use of "witnesses" – specially synthesized substances added to a sample before chromatographing.

The presence of multiple C=C bonds, hydroxyl and sulfhydryl groups was detected using semi-microanalysis methods. The presence of carbonyl groups was judged from the formation of hydrazones at binding of C=O groups with 2,4-dinitrophenylhydrazine; hydrazones were detected chromatographically at the wavelength of 355 nm (Ref. 3).

Results

It was shown that violets grown on soil 2 and 3 emit volatile organic zinc-containing compounds with unsaturated bonds, and cadmium-containing compounds cannot be detected against this background. Plants grown on soil 1 emit cadmium-containing compounds that can be readily detected using liquid chromatography. Fractions containing cadmium-organic compounds were separated, and the presence of cadmium in them was proved using mass-spectrometry.

In the flow reactor, the reaction time increases with the distance from the plant to the sampling point. Therefore, changing the position of the sampling point along the reactor, we can draw the pattern of the process of transformation of metal-containing substances in the reactor. We have studied the concentrations of metals in the aerosol phase (deposited on filters) and in gas (having passed through the filter into the absorption solution). As a background, we used the identical reactor under the same conditions (gas composition, flow rate, illumination), which housed a flowerpot with soil having the same concentration of the metal, but without a plant. It was found that organometallic compounds in the gas phase were present only in the reactor with the plant. In the background reactor, as soil got dry, we observed a small amount of aerosol particles of likely the soil origin, which decreased down to almost the limit of detection as soil got wet. Therefore, during experiments the soil was kept wet.

Production of an organometallic compound in the reactor with a plant occurred both in the dark and on light. However, transformation of metal from the gas phase into aerosol occurred only at illumination: as the sampling point was farther separated from the plant, we observed the increase in the content of metal in the aerosol phase and, correspondingly, the decrease in the concentration of gaseous organometallic compounds. At darkening of plants in the reactor, the content of cadmium and zinc on filters was very low and almost did not change with the distance from the plant; the content of the metal in the gas phase varied insignificantly. Thus, light is needed for formation of aerosol. Using glass filters, we found that the threshold wavelength was about 450 nm. Irradiation by light with the wavelength longer than 450 nm led to production of very small amount of aerosol: about 3–5% of the amount observed at irradiation by light with the shorter wavelength.

It was shown that oxidation in the presence of zinc was rather slow, and the degree of transformation during the travel-through time did not exceed 12–14%. Aerosol particles containing the metal were produced in this process. Using liquid chromatography, it was shown that zinc in the aerosol phase is combined with organic compounds including carbonyl groups, double C=C bonds, and hydroxyl groups.

In the presence of cadmium, formation of the aerosol phase was also observed only in the presence of oxygen and under illumination. The oxidation rate of gaseous Cd compounds was 7 to 8 times higher than that for zinc. However since the total amount of cadmium in soil and plants is roughly two orders of magnitude lower than that of zinc, we had to increase the sampling time for accumulation of a sufficient amount of substance. In spite of this, for cadmium we failed to identify functional groups present in the molecules of its organic companion, because chromatographing was accompanied by formation of associates hindering the analysis. The amount of cadmium in samples as a function of the distance from the plant is shown below in the Table.

Amount of Cd in gas and aerosol (in relative units of intensity of mass-spectrum signals) as a function of the distance to the plant

Cadmium	Distance, cm				
	1	40	80	120	160
In gas	$3.8\cdot10^7$	$1.1\cdot10^6$	$7.4\cdot10^5$	$2.6\cdot10^5$	$2.3\cdot10^5$
In aerosol	$1.8\cdot10^5$	$5.2\cdot10^5$	$8.3\cdot10^5$	$1.7\cdot10^6$	$2.4\cdot10^6$

As can be seen from the Table, the cadmium concentration in gaseous emission of violet decreases as the separation between the plant and the sampling point increases, while the amount of cadmium on the aerosol filter increases. Most probably, the gaseous emission is oxidized by oxygen and transformed into aerosol particles. With the allowance made for adsorption of compounds on the reactor walls, the effective constant of the gas–aerosol transformation process can be estimated as $\sim 10^{-14}$ cm^3/s. For more accurate estimation, further measurements with a modified experimental procedure are needed, and we plan to conduct such measurements in the future.

Conclusions

1. It is shown that under conditions of the enhanced content of metals (cadmium and zinc) in soil the plant (violet) growing on this soil emit these metals in the form of gaseous organometallic compounds.

2. The gaseous organometallic compounds emitted by the violet are oxidized by air oxygen under the action of light with formation of aerosol particles.

3. Without oxygen and in the dark, transformation of gaseous emissions into aerosol does not occur.

References

1. N.A. Panichev, in: *Problems of Atmospheric Physics*. Is. 20. *Physics and Chemistry of Atmospheric Aerosols*, ed. by L.S. Ivlev (St. Petersburg University Publishing House, St. Petersburg, 1997), pp. 81–96.
2. Yu.Yu. Dubinina, S.V. Palesskii, G.G. Dul'tseva, and G.I. Skubnevskaya, Ekol. Khimiya, No. 1 (2003) (in print).
3. G.I. Skubnevskaya and G.G. Dul'tseva, Zh. Ekolog. Khimii, No. 3, 29–34 (1994).