

PHOTOCHEMICAL MECHANISM OF AEROSOL  
FORMATION FROM GASEOUS METAL-CONTAINING  
COMPOUNDS GENERATED BY BIO-PLANTS

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### **Introduction**

One of the natural sources of metals in the atmosphere is their emission by plants in the form of volatile metal-containing organic compounds. For some heavy metals, this process is an essential stage in their biogeochemical cycles [1]. In view of high toxicity of heavy metals, and increasing industry-related environmental pollution, the chemical mechanisms of the processes leading to the conversion of metals from gaseous compounds with organic ligands to the atmospheric aerosol particles of submicron size were studied. Cadmium, one of the most toxic heavy metals, and its chemical analogue, zinc, were chosen for this investigation. Preliminarily, the mechanisms of complex formation by cadmium and zinc with organic ligands in plant tissues were studied [2]. Also, the procedures of chromatographic analysis and identification of cadmium and zinc complexes in biological samples and atmospheric aerosol were developed [3].

### **Experimental Studies**

Herbaceous plants representing the ecosystem of forest-steppe zone of West Siberia (cereals, legumes, crucifers, violas), and some coniferous tree species (spruce, pine) were the objects of the study. The herbaceous plants were grown in the soil in which definite amounts of cadmium and

zinc salts were preliminarily added, either together or separately (up to a factor of 4 greater than the maximum permissible concentrations, which was below the phytotoxic level for the plant species under investigation). The plants were placed in the cylindrical quartz reactors through which a mixture of nitrogen and oxygen (4:1 vol.) was passed at a low flow rate. Before admitting the gas into the reactor, solid particles were removed from the gas using aerosol filters. The plants were irradiated with luminescent lamps, and with mercury middle-pressure lamps to investigate the dependence of the oxidation rate on the light wavelength; the necessary spectral regions were singled out using optical glass filters.

Experiments with the trees were carried out under the field conditions near the deposits of complex ores in the Altay district, where elevated amounts of cadmium and zinc were present in the soil; the data obtained in the rural regions of the Novosibirsk District were used for comparison.

To examine the composition of the substances released by the plants in the gas phase, and to estimate the amounts of metals, three sampling procedures were used for measuring three parameters. The first procedure involved sampling in the bubblers filled with appropriate organic solvents. This procedure was applied to measure the total metal content  $Me_{\text{gas}} + Me_{\text{aerosol}}$  in the reactor. The second procedure involved sampling on aerosol AFA-KhA filters for measuring the amounts of cadmium and zinc passed into the aerosol phase ( $Me_{\text{aerosol}}$ ). After passing through the aerosol filter, the gas mixture under analysis entered the bubbler for the measurement of the concentration of metal-containing compounds in the gas phase ( $Me_{\text{gas}}$ ); this was the third sampling procedure.

The amounts of metals in the samples (solutions and aerosol filters) were determined using mass spectrometry with inductively coupled plasma (ICP-MS). Analysis was performed with ELEMENT FINNIGAN MAT (Germany), a high-resolution mass spectrometer [2]. Before starting the measurements, the instrumental parameters were optimized to achieve the maximal analytical signal and the best reproducibility with a low background level. Concentrations of Cd and Zn in the samples under investigation were calculated semi-quantitatively on the basis of linear calibration of the instrument with a standard multielement solution. The detectivity limit for Cd was 0.03 ng/g.

The chemical composition of the samples was studied by means of High-Performance Liquid Chromatography (HPLC) with reverse-phase sorbent LiChrosorb. The volume of a sample introduced into the chromatograph was 10–30  $\mu\text{l}$ . For elution, a mixture of acetonitrile and water (3:1) was used. Detection was carried out at the wavelength of 290 nm. In some runs, the detector wavelength was scanned from 290 to 360 nm to record the absorption spectra of the compounds present in the sample.

The compounds were identified using the specially synthesized witness compounds which were added to the sample before the analysis [3].

Using the semi-microanalysis procedures, the presence of double C=C bonds, hydroxyl, and thiol groups was identified. To detect the presence of carbonyl groups, the samples were subjected to interaction with 2,4-dinitrophenylhydrazine; hydrazones formed after binding with C=O were detected chromatographically at the wavelength of 355 nm.

## Results and Discussion

In the case of joint presence of zinc and cadmium in elevated amounts in the soil, some herbaceous plants, especially violets and saxifrage, were found to release the volatile organic substances with unsaturated bonds containing zinc; no cadmium compounds were detected at this background. For the soil with elevated amount of cadmium alone, many plants, including cereals release cadmium compounds with organic ligands which can be readily detected by means of HPLC. The fractions containing cadmium-organic compounds were isolated; the presence of cadmium in them was additionally confirmed by means of mass spectrometry.

In a flow reactor, the reaction time can be considered to be directly proportional to the distance from the plant to the sampling site. Therefore, it becomes possible to obtain the temporal distribution of the products of transformation of the metal-containing substances released. The concentrations of metals in the aerosol particles collected on the filters, and in the gas (passed through the filter to the absorbing solution) were examined. Two other reactors under the same conditions (flow rate, irradiation) were used as a background; one of them contained a pot with soil enriched with cadmium but without any plant

in it; the other reactor contained a plant growing in the soil to which cadmium was not added. It was discovered that cadmium-containing compounds are present in the gas phase only in the reactor with the plant growing in the cadmium-enriched soil.

The formation of a complex gaseous compound containing cadmium occurs in the reactor with the plant both under irradiation and in the dark. However, the transition of the metal from the gas phase into the aerosol phase occurs only under irradiation. As the distance from the plant to the sampling site increases, the amount of cadmium in the aerosol phase increases while its concentration in the gas phase decreases correspondingly. In the dark, the amounts of cadmium and zinc on the filters remain very small, almost negligible; concentrations of metals in the gas phase remain almost constant along the reactor. So, light is found necessary for aerosol formation. With the optical glass filters, it was confirmed that the threshold wavelength was about 450 nm. Irradiation with light of a longer wavelength causes the formation of an insignificant amount of aerosol, accounting for 3%–5% of the amount observed under irradiation with light of a shorter wavelength.

Table 1 shows the amount of cadmium in the samples depending on the distance from the plant. One can see that gaseous compounds are oxidized and transformed into aerosol particles.

With zinc, the oxidation is slower than with cadmium; the transformation degree does not exceed 12%–14% along the reactor. In this case, aerosol metal-containing particles form. It was shown by means of liquid chromatography that in the aerosol particles, zinc is bound with organic compounds through their carbonyl groups, double C=C bonds, and hydroxyl groups.

With cadmium, the oxidation rate of gaseous compounds was 7–8 times higher than with zinc. However, due to a smaller total amount of cadmium than zinc (about two orders of magnitude), the sampling time was longer for cadmium.

**Table 1** The amount of Cd in gas and aerosol (in relative units of the intensity of signals in the mass spectra) vs. the distance  $L$  from the plant

$L$ , cm	$Cd_{gas}$	$Cd_{aerosol}$
1	$3.8 \cdot 10^7$	$1.8 \cdot 10^5$
40	$1.1 \cdot 10^6$	$5.2 \cdot 10^5$
80	$7.4 \cdot 10^5$	$8.3 \cdot 10^5$
120	$2.6 \cdot 10^5$	$1.7 \cdot 10^6$
160	$2.3 \cdot 10^5$	$2.4 \cdot 10^6$

The chemical analysis of the gaseous compounds released by the plants was carried out after their chromatographic separation (HPLC). Individual peaks of the chromatograms were identified using the witness compounds. Cadmium was detected to be present in volatile complexes with alkylated analogues of *L*-cysteine, *L*-glutamic acid, glycine, and also in the form of malates and citrates. The ratio of  $\text{Cd}^{2+}$  to ligand in volatile complexes was 1:2, which was the evidence of chelate formation, since the coordination number characteristic of  $\text{Cd}^{2+}$  ion was 4. To study the oxidation mechanism, the identified ligands were synthesized. Under their ultraviolet irradiation in the air, the formation of aerosol was observed; it was collected on aerosol filters. Chemical analysis of the samples indicated that partial oxidation of ligands took place. For example, instead of phenol hydroxyl, a fragment of benzoic acid coordinated with the metal was formed. The ratio of  $\text{Cd}^{2+}$  to the oxidized ligand became equal to 1. So, aerosol formation occurs during the oxidation of hydroxyl groups of the ligand.

When investigating the evolution of cadmium and zinc by trees, it was discovered that the metals were released in the form of complex compounds with terpenes. Their oxidation in the air under irradiation led to formation of aerosol particles. However, correlation was found between the metal content in the soil and metal concentration in the gas phase around the trees. A multiaspect investigation of atmospheric aerosols, tree tissues, and soils in different geochemical provinces is required.

## Concluding Remarks

It is shown that under the elevated cadmium and zinc contents in the soil, the herbaceous plants growing in it release these metals in the form of volatile chelates; they are oxidized by oxygen under sunlight to form submicron aerosol. This process contributes to the formation of atmospheric aerosols.

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## References

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