ORGANIC AND INORGANIC PARTICULATE MATTER IN URBAN AEROSOLS BY SEM AND MICROPROBE ANALYSIS

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Abstract
Industrial filter cakes and PM of atmosphere aerosols have been studied by combination SEM and microprobe analysis. Salt water drops, micro-crystals, metallic spherules, pollen and spores, small-sized insects were observed. Pollen, spores and industrial micro-particles were the main objects of the investigation. Seasonal pollination calendars for pollen and spores have been compiled. Pollen with morphological disturbances and mud on the pollen surface, pollen infected by fungus spores, small-sized insects with mould colonies were observed. These objects may be the indicators of the ecological deviation. Industrial PM and filter cake matter of ferrous and non-ferrous metallurgy and glass industry of Belarus has been studied.

Introduction
A large variety of micro particles of organic and inorganic origin is observed in the atmospheric aerosols. Some of them are the dangerous matters for the human health and the others affect on the plants. Airborne metal transfer problem is of great importance for the heavy metal ecological study of urbanized territories. Minsk-city area showed the increased metal concentration in soil [1], but metal transfer mechanisms are not elucidated in full yet. Invaluable fine particles in the industrial smoke show negative health effects. Airborne tiny particles also known as particulate matter (PM) vary in a range of the different sizes and chemical compositions, such as oxides, organic matter, acids and metals. Particulate matter differentiates usually by fine PM or PM2.5 (less than 2.5 micrometers) and coarse PM (between 2.5 and 10 micrometers). Airborne PM2.5 are the most dangerous particles, which can penetrate deeply into the lungs. The main objective of this study is the investigation of pollen, mould and industrial PM by SEM and microprobe analysis.

Materials and Methods
Two methodological approaches were used: A) trap sampling and single particle study; B) common analysis of massive samples (mould colonies, pollen of the blossoming plants and industrial filter cakes). Trap sampling: The traps with the sticky surface were installed at two levels (1.5 m and 15 m) toward the wind flow at the angle of 45^0. The exposition lasted 24 hours. The regular daily observations in years 2000-2002 were held from April till October The rest of the year the observations were fulfilled from time to time. Scanning electron microscopes JEOL JSM-35C and REM 100 U with microprobe spectrometer have been used for the PM size, shape and chemical analysis.

Filter cakes of the cement industry, foundry, glass industry, and thermoelectric power station were studied in this research. Industrial emissions of Dnepropetrovsky chemical-recovery plant (Ukraine), Zaporozhsky open-hearth shop (Ukraine), Zhlobin metallurgical works (Belarus), Mogilev melting shop (Belarus), melting workshops of Gomel railway-carriage repair works (Belarus), GOMSELMASH (Gomel) metallurgical shop have been studied. Cement industry emissions were investigated at KRASNOSELKCEMENT plant (Belarus)

and KRICHEVCEMENTSHIFER plant (Belarus). Dolomite industry emission was studied at Ruba dolomite plant (Belarus). Glass industry emissions have been collected at Grodno glass-works (Belarus), STEKLOVOLOKNO chemical plant (Belarus) and Borisov crystal-works (Belarus). Emissions of thermoelectric 50 Mw power stations have been studied at Sluck (Belarus) and Ushachi (Belarus) power stations.

Results

Great variety of the solid industrial PM, organic and liquid micro-objects were observed. Salt water drops, micro-crystals, metallic spherules, pollen and spores, small-sized insects with mould colonies present in the samples. The diatoms were observed on traps in the rainy and windy days. Pollen, spores and industrial PM were the main objects of this study.

Table 1.

Pollination calendar for 2002 (altitude 15 m)

Month	February			March			April			May			June			July			August			September		
Ten-day	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
NAME																								
Pollen & Spores																								
Trees & Shrubs																								
Herbs																								
Spores																								
Trees & Shrubs																								
Alnus																								
Corylus																								
Juniperus																								
Betula																								
Salix																								
Populus																								
Picea																								
Pinus																								
Quercus																								
Crataegus																								
Acer																								
Herbs																								
Poaceae																								
Cyperaceae																								
Plantago																								
Urtica																								
Chenopodiaceae																								
Rumex																								
Artemisia																								
Asteraceae																								
Caryophyllaceae																								
Solidago																								
Spores																								
Cladosporium																								
Alternaria																								
Botrytis																								
Ascobolus																								
Aspergillus/Penicillium																								
Saccaromycetales																								
Aeciospore																								
Ustilospore																								
Urediniospore																								
Spinulate spores																								
Rainy days (number)				2		1	1		2	1	2	3	2	2	2		2					1	1	1
Fuzz (number day)										5	10	11	10	3										

Number/ cm/ 24 hour — low 1-10 — middle 11-100 — high 101-1000 — very high >1000

Pollination calendars

Seasonal pollination calendars for pollen and spores were compiled (Table 1).

Tree pollination peaks were observed:

a) Trees and Shrubs in the sequence: *Populus-Alnus-Corylus-Betula-Picea-Pinus-Quercus-Tilia* (*Alnus – Corylus -Populus*-… in season 2002),
b) *Poaceae*,
c) Motley herbs: *Plantaginaceae*, *Rumex*, *Asteraseae* (mainly *Artemisia*), *Urtica*, *Chenopodiaceae* and *Solidago.*

Spores

The fungal conidies, spores and fragments are observed from surface of traps in second of ten-day of May. Their quantity is comparable to the quantity of pollen of herbs. In summer there is observed a significant quantity conidies *Fungi imperfecti* class, the many of which are allergens. The aeciospores [2,3] of a rust fungus in April May, June and September have been captured. The urediniospores on traps since July till September (max) were observed. The ustilospores of smut fungus in May, June, July September was observed [2,3,4]. On some days spinulate spores of *Calvatia* sp. genus are defined. These spores have sizes of 2,5-4 μm. Plenty of spores with spinulate surface are observed in aerosol, especially in August - September. Some of them belong to rust or smuts and part of them relates to slime moulds (*Myxomycota*). Spores of *Didymiaceae*, *Stemonitaceae*, *Trichiaceae* and *Dianemaceae* (*Calomyxa* sp.) family are among them [5].

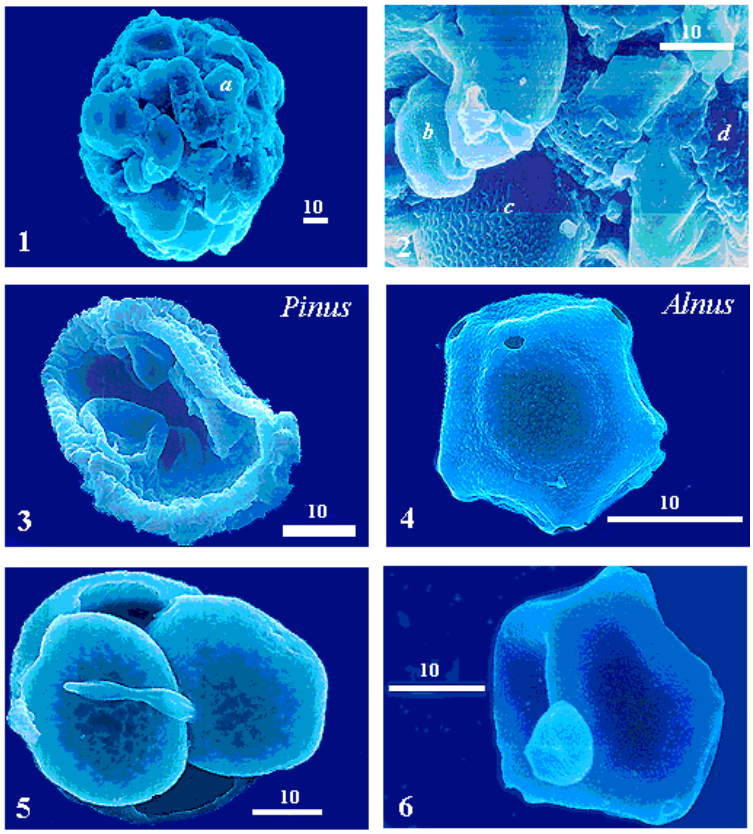

Fig.A : 1-2 Pollen spherule and fragment their construction: pollen a) *Chenopodiaceae* sp., b) *Betula* sp.,c) *Tilia* sp., d) *Pinus* sp., 3-4 pollen grains with morphological deviations, 5-6 pollen grains infected by mould: 5 *Pinus* sp., 6 *Alnus* sp. The bar-scales are in μm.

Deformed and contaminated pollen

Some percent of *Pinus* and *Picea* pollen with morphological deviations have been observed at the pollination peak (Fig. A, 3-4). After mass pollination is finished disrupted pollen grains with the stuck fragments of mud began to be observed (Fig. A, 1-2). Probably, the pollen,

which has been accumulated on the surface of various objects, gets into the atmosphere a second time. Sometimes the fungal spores are fixed on the pollen surfaces (Fig. .A, 5-6).

Industrial filter cake matters

Open-hearth filter cake (Zaporozhstal, Ukraine) is a dark-brown dust containing mostly two iron oxides: hematite (Fe_2O_3) with admixture of maghemite (gamma - Fe_2O_3). Admixtures of MnO (0.15%), SiO_2 (0.4%), Zn (0.8%) and Cr (0.1%) have been observed in this cake. Particle size distribution shows two size maximums at 1 micron and 100 - 250 microns. These particles are spherical. Filter cake dissolubility in water shows 9.46%.

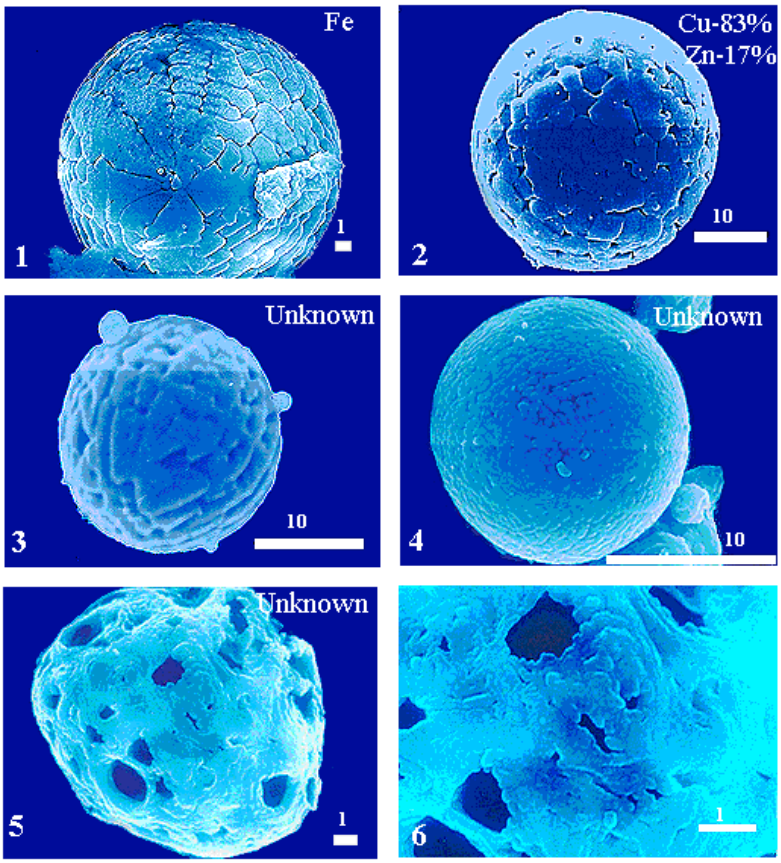

Fig. B: 1-4 Spherules with crystallized surface, 5-6 unknown spherules and their surface.
The bar-scales are in μm.

Electro-smelting (Zhlobin, Belarus) filter cake is a brown dust consisting mostly of ferrous oxide (Fe_3O_4). Dust contains Fe_3O_4 - 73.2%, CaO - 1.8%, K_2O - 1.1%, SiO_2 - 4.2%, Al_2O_3 - 0.6%, MnO - 4.3%, S - 6.2%, Cl - 7.4%, Cr - 0.3%, Cu - 1.8%. Cake dissolubility in water is 6.2%. Filter dust consists of tiny particles 0.2 - 0.4 microns and their aggregates.

Glass industry emissions have been collected at NEMAN glass-works (Belarus) and Borisov crystal-works (Belarus). Plumbum containing matters are widely used for the crystal-works, that is why plumbum oxides and borates ($Pb(BO_2)_2$, $Pb(BO_2)\cdot 2H_2O$) have been oserved in the filter cakes. NEMAN filter cake matter consists of Pb - 66.9%, K - 5.1%, Zn - 0.53%, Fe - 0.06%. This cake dissolubility in water shows 34.7 - 39.0% and solvate is nite (KNO_3). Particle size distribution has two maximums at 1 microns and 0.1 - 0.3 mm. Both fractions have got the same chemical composition.

Some other industrial aerosols of electric power stations, chemical-recovery plants, cement and dolomite plants have been studied. Particle characteristics and dissolubility in water

change greatly, but metal containing are much more smaller and usually show metal concetration less than 1%. Nevertheless, some heavy metals (vanadium) prevail in combustion products and their behavior in environment have to be studied especially.

Single industrial PM study

Industrial aerosols prevail in the trap samples in the winter period because of the reducing of the natural micro-particles. They may be defined by their shape (spherules) and chemical composition (Fig. B). Some spherules (Fig.B,1-4) show the specific texture of crystallization. This texture arises in the melt crystallization processes while front of crystallization moves up lengthways the melt drop. Microprobe analysis shows the variation of PM chemical composition. Ferrous micro-particles prevail, but Cu-Zn alloys and some other matters have been observed.

Discussion

Metal bearing filter cakes and airborne PM have been investigated in this study with emphasize on particle size, shape and chemical content. So far, particulate matter with their sizes up to 10 microns considered being dangerous for human health. Minsk-city area shows metal bearing PM sizes up to 30 microns, which easy transfer by air. These coarse PM have to be taken into consideration and their toxicity have to be studied.

Data on pollination is the base for the allergic and respiratory situation prediction. The other aspect of the pollen and spore investigation is the complex health impact. Deviated pollens and spores growing on the pollen (spore – pollen system) are the objects for the further investigations.

Conclusion

- Pollen -spore - inorganic PM complex is the specific object, which takes place in the urban aerosols.
- Airborne organic and inorganic PM is the important matter for the evaluation of the allergic and respiratory situation, ecological monitoring, climatic reconstruction and geological sediment correlation.
- Combined aeropalynological research may be used for the ecological and climatic influence study on the reproductive sphere of the various plants. It also helps to understand better the processes of the pollen conservation in the geological deposits. SEM and microprobe analysis may be effectively used for PM study.

Acknowledgments

The authors thank Organization Committee of Sixth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe and the Commonwealth of Independent States (Prague 2003) for a fellowship support.

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