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MINERALOGICAL AND CHEMICAL IMPACT OF ANTHROPOGENIC EMISSIONS ON SOILS AND ROCKS OF THE OJCÓW NATIONAL PARK (POLAND)

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Abstract: Air pollution and its influence on soil contamination and the rate of weathering of Jurassic limestone in the Ojców National Park (ONP) in Poland were studied. Phase and chemical analyses were carried out for the soils and rocks. It has been found that the components of anthropogenic origin make up over 90 vol. % of dust particles. The major phases include sulphates, spherical glass particles, unburned coal fragments and grains of metal oxides. The analyses of soils have shown elevated amounts of Cd, Pb and Zn, while the total level of hydrocarbons exceeded the permitted content in soil (samples collected along the road). The limestones are covered with black or white crusts depending on their degree of shelter from rain water. The components of crusts include aluminosilicate glass spherules, iron oxides, unburned coal particles and gypsum crystals. The outer layers of limestone are also enriched with heavy metals. The heavy metals and glass spherules found in the dust fall and in the external parts of Jurassic limestones and soil, and also the higher level of hydrocarbons in soil samples lead to the conclusion that the anthropogenic pollutants generated within and outside the ONP play a significant role in contamination of the analysed components of the environment.

Key words: Poland, Ojców National Park, air pollution, soil contamination, limestone deterioration.

Introduction

The Ojców National Park (ONP) is situated in the southern part of the Cracow-Częstochowa Upland, some 30 km north of Cracow. Its landscape, composed of naturally exposed elements of the geological structure, mainly Jurassic limestones, is rich in rivers and picturesque monadnocks with caves, rock-needles and rock-gates. The climate of the park displays the mountainous features. Soils are developed on Jurassic and Quaternary rocks. The ruins of Ojców and Pieskowa Skała castles stand on preserved flat hill-tops.

The ONP is affected by over 200 industrial, air-polluting emitters (ca. 30 of them situated within the Cracow administrative province — steel mills, heat-power stations, cement plants), and their above-norm emissions are degrading the valuable natural environment of the ONP area. Besides massive industrial emissions, a significant source of air pollution is represented by emissions from local boiler-houses as well as from motor vehicles, the latter associated with dense traffic, mainly of seasonal character (Raport 1996).

Methods

Research on air pollution and its influence on selected components of the environment within the ONP area was conducted in 1996/97. Samples of atmospheric precipitation along with a dust fall were collected by sedimentation at one-month intervals. Dusts collected together with precipitation represent a multiphase system, therefore their preparation for phase and chemical analyses included separation of samples into fractions easily and hardly soluble in water. The hardly soluble fraction is composed of dust particles, while the easily soluble fraction represents a residue after evaporation of rain water, which also contains very fine (< 1 μm) suspended dust particles. The pH of precipitation was measured, total dust fall calculated, and phase and chemical compositions analysed. Soil samples were collected from the immediate vicinity of sites where dust fall was measured, and also in the proximity of the major road clossing the ONP area. In addition to phase and chemical analyses of the soil samples measurements of hydrocarbons were carried out. Samples of Jurassic limestones were also taken, from both natural exposures and historic buildings situated within the ONP area (the Ojców and Pieskowa Skała castles). These samples underwent chemical and phase analyses.

The analyses were carried out by means of a Jenapol (Carl-Zeiss, Jena) optical microscope in transmitting light, a TUR M-61 X-ray diffractometer, and a JEOL JMS 5200 scanning microscope with an EDS EXL attachment for chemical analyses in microareas. Hydrocarbon contents were measured by the infrared method using a UR-10 spectrometer. Chemical components, mainly heavy metals, were analysed by the AAS (Philips PU 9100X) method.

Results and discussion

The average annual dust fall within the ONP area is 50 t/km^2 (1996/97), exceeds the total suspended particulate standard for protected areas (Table 1, Fig. 1). Precipitation is acid and weakly acid (pH values are 3–4.5). Acidification is caused

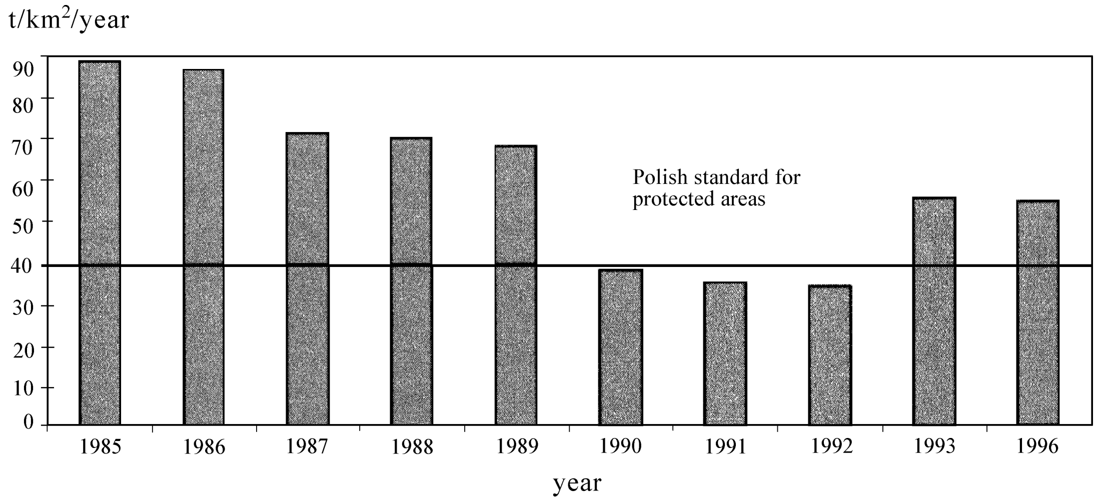

Fig. 1. The annual dust fall in the ONP (t/km^2/year).

Table 1: Mean annual dust fall in the years 1985-93 (Raport 1996) and in 1996/97 (own measurements) in ONP (t/km^2/year).

Year	1985	1986	1987	1988	1989	1990	1991	1992	1993	1996/97
Dust fall	88	86	68	67	61	34	31	30	54	50

mainly by anthropogenic emissions of gases with prevailing SO_2. Sulphur dioxide is one of the most hazardous gases, transported into the area of the ONP (Monitoring 1996). Amounts reaching up to 2,000 μg/m^3 have been recorded, while the Polish norm for the areas under protection limits a temporary concentration to 250 μg/m^3. In 1985, ten field stations were established to monitor concentrations of SO_2 and particulate matter (Łęcki 1995).

Natural and anthropogenic components (Table 2) have been distinguished among the polluting compounds. The natural ones, associated with the secondary deflation of the surface, include quartz, clay and carbonate minerals, feldspars. The major anthropogenic components are sulphates with various degrees of hydration (results of SO_x emissions), silicate glass and unburned coal fragments (high-temperature combustion), grains of metal oxides (emissions from metallurgical plants — Fig. 2).

By means of an optical microscope (Table 3) anthropogenic particles in dust deposited with rain water have been quantified conducted. The anthropogenic particles are the most frequent essential in dust fall. In the case of the ONP area they form over 90 vol. % of the total dust of particles. Aggregates with particles of natural origin occur in subordinate quantities.

The granulometric analysis of the dust particles has revealed that 80–90 vol. % of them are contained in the particularly harmful fraction < 3 μm. Such a high amount of this fraction indicates a significant contribution of grains deposited from a long transport.

The content of heavy metals (Pb, Zn, Cd, Cr, Ti) is particularly high in rain water (Table 4). These elements enter directly the biogeochemical cycle of the ONP environment (Fig. 3).

Table 2: Phase composition (XRD, optical microscopy) of rainwater evaporate from the ONP area (salts and anthropogenic particles).

Fraction easily soluble in water		**Fraction hardly soluble in water**	
Gypsum	$CaSO_4 \times 2\ H_2O$	Hematite	Fe_2O_3
Kainite	$KMg\ [Cl/SO_4] \times 3\ H_2O$	Magnetite	Fe_3O_4
Hexahydrite	$MgSO_4 \times 7\ H_2O$	Anhydrite	$CaSO_4$
Syngenite	$K_2Ca[SO_4]_2 \times H_2O$	Mullite	aluminosilicate
Langbeinite	$K_2Mg_2[SO_4]_2$	Unburned coal fragments	
Halite	$NaCl$	Silicate glass	
Mascagnite	$(NH_4)_2SO_4$		
Salmiac	NH_4Cl		
Sylvite	KCl		
Burkeite	$Na_6[CO_3\ (SO_4)_2]$		

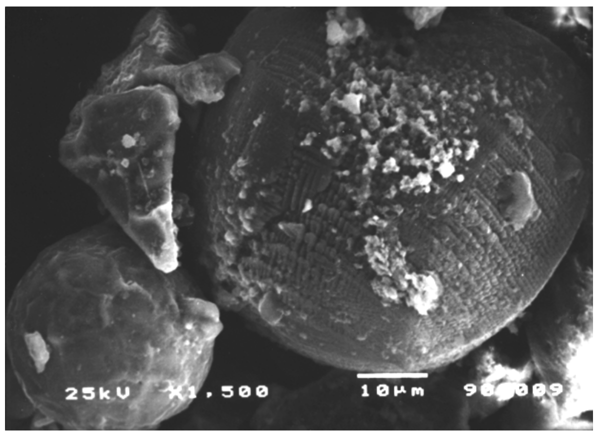

Fig. 2. Iron oxides particles (mostly spherical) (SEM).

Table 3: Contents of grain fractions and of anthropogenic particles in dust fall (wt. %).

Grain fraction	0 – 3 μm	3 – 10 μm	> 10 μm	**Anthropogenic particles**
Summer period (no heating)	34	50	16	84
Winter period (with heating)	86	11	3	98

Table 4: Concentration of trace elements (ppm) in dust fall in the area of ONP.

Fe	Ti	Mn	Zn	Pb	Cu	Cr	Ni	Cd
46477	3533	557	1812	520	213	120	161	31

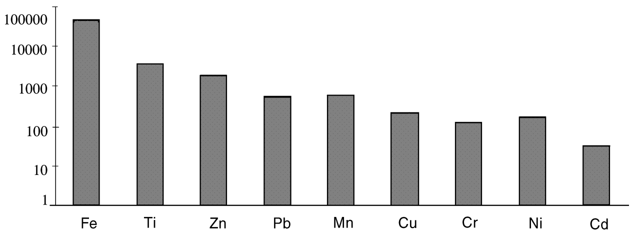

Fig. 3. Concentration of trace elements in dust fall (ppm).

The soil samples collected include brown and calcareous (rendzina) soils, and as such should represent rather a good protection against pollutants (Kabata-Pendias et al. 1993). Those developed on limestones are composed mainly of quartz and carbonates: the latter minerals, if they occur in higher amounts, control the buffer properties of soils. Goethite and clay minerals are present in minor quantities (< 5 wt. %), but they are important elements stabilizing heavy metals in soils. Considering low contents of organic matter (6 wt. % on average) and a small amount of clay fraction (7 wt. % on the average), the soils studied reveal a small capacity of their sorptive complex. An average soil reaction oscillates around pH = 7, being typical of neutral and alkaline soils. This pH stabilizes heavy metals in soils and thus hinders their migration, as the metals are bound to inert compounds.

Contamination of soils with petroleum-derived substances is particularly distinct in the samples collected along the major road intersecting the ONP. The total of aliphatic and aromatic hydrocarbons is above 300 ppm (the permitted content in soil is 100 ppm — Fig. 4). Such a high contamination is caused by very intense traffic of motor vehicles. For comparison purposes, the authors have analysed the amount of hydrocarbons in soil samples collected farther (ca. 300 m) from the main road (Table 5).

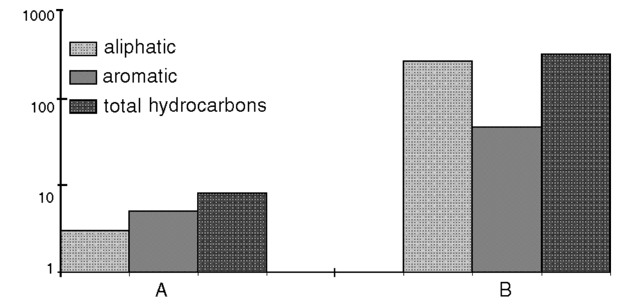

Fig. 4. Contamination of soil with hydrocarbons (ppm). **A** — soil samples distant from the main road, **B** — soil samples close to the major trunk road.

Table 5: Contamination of soils with hydrocarbons (ppm).

Hydrocarbons	1	2
Aliphatic	2.63	263.75
Aromatic	5.56	45.68
Total	8.19	309.43

1 — soil samples distant from the main road,
2 — soil samples along the major road.

Table 6: Concentration of trace elements (ppm) in soil in ONP.

Element	Mn	Zn	Pb	Cu	Cr	Ni	Cd
Fraction > 10 µm	574	500	132	36	35	24	6
Fraction < 10 µm	601	950	208	48	34	37	9
Total	1175	1450	340	84	69	61	15

Chemical analyses of soil (Table 6) have indicated higher amounts of Zn, Pb and Cd (the geochemical backgrounds have been exceeded 5 times for Zn, and 3 times for Pb and Cd — Fig. 5). High amounts of these elements, particularly of Pb and Cd, result not only from dust and gas emissions, but also from motor vehicles, passing a relatively small area of the ONP. The remaining elements: Cu, Ni, Cr and Mn, occur in amounts close to their global geochemical backgrounds, that is their natural content in soils. Mineralogical

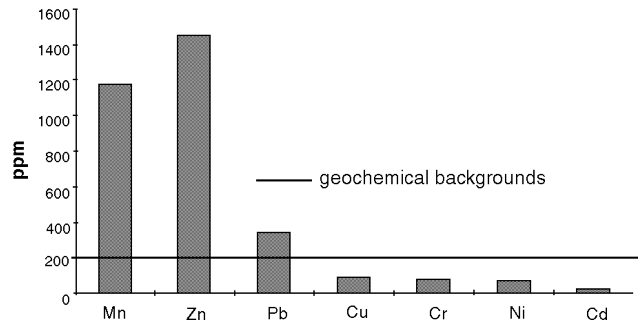

Fig. 5. Concentration of trace elements in soil (ppm).

and chemical investigations have shown that the soils of the ONP actually possess rather weak protective properties and not too high resistance to contaminations.

This resistance is, however, partly enhanced by acid-basic equilibrium of the soils in question (due to the presence of carbonate minerals), and this slightly lowers the mobility and harmful effects of toxic forms of heavy metals.

The outer surfaces of Jurassic limestones are covered most often by strongly coherent, black crusts 0.3 mm thick. Sometimes, mainly where there is shelter from rain water, it is possible to find white crusts (on stone elements exposed to rainfalls) and black dendritic ones (along the borders between the stone areas exposed to and sheltered from running rain water). The components of crusts include aluminosilicate glass spherules, iron oxides (hematite, magnetite), unburned or coked coal particles, and gypsum crystals (Figs. 6, 7). The outer layers are enriched in heavy metals (Table 7), and among others Pb, Cd, Fe, Zn contents exceed the clark values for calcareous rocks (Fig. 8).

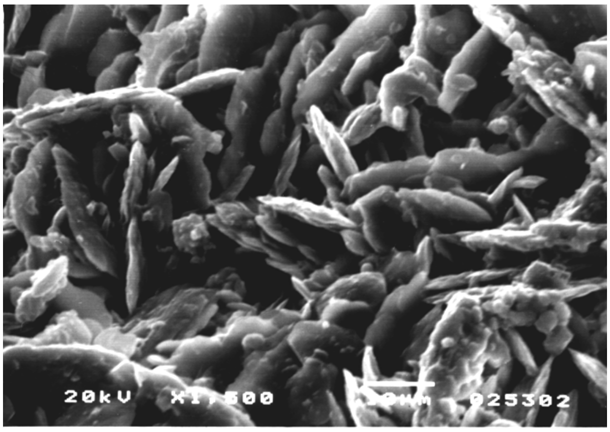

Fig. 6. The surface layer of Jurassic limestone with gypsum crystals (SEM).

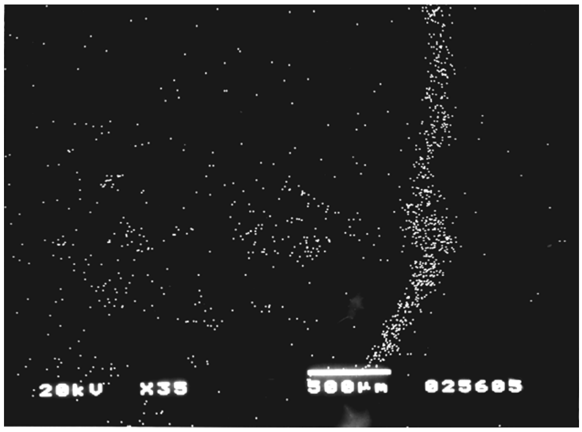

Fig. 7. SEM-EDS analysis of Jurassic limestone — the image shows concentration of S at the rock surface.

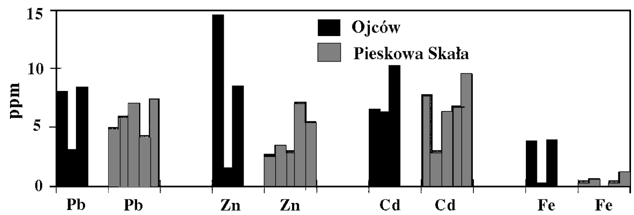

Fig. 8. Concentration of trace elements in Jurassic limestones from ONP (calculated against a „clean Jurassic limestone" unexposed to dust fall).

Table 7: Coefficients of enrichment of trace elements in the Jurassic limestones studied (calculated against a „clean Jurassic limestone", i.e. the limestone unexposed to dust fall).

Sample	Pb	Zn	Cd	Fe
O-2	8.03	14. 60	6.50	3.80
O-4	3.05	1.53	6.25	0.27
O-5	8.38	8.47	10.25	3.91
O-6	3.03	0.90	9.50	0.35
Z-1	4.95	2.69	7.75	0.47
Z-2	5.88	3.42	3.00	0.66
Z-3	6.93	2.99	6.25	–
Z-4	3.78	1.57	7.75	0.61
Z-5	4.33	7.12	6.75	0.45
Z-7	7.38	5.46	9.50	1.14

O — Ojców; Z — Pieskowa Skala

Conclusions

High contents of heavy metals have been found in the dust fall, in soils and in coating crusts on Jurassic limestones (Manecki et al. 1996). Higher levels of hydrocarbons have also been observed in soil samples collected along the major road. These facts point to the significant adverse effects of the urban and industrial agglomerations, bordering the ONP. The biggest emitters in southern Poland are the power and metallurgical industries (iron, steel and of base metals). Another source of pollution is road traffic, which is too intensive for the small area of the ONP.

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