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FATE OF AIR POLLUTANTS FROM KONIN INDUSTRIAL COMPLEX IN PINE FOREST ECOSYSTEMS

MIGRACJA ZANIECZYSZCZEŃ POWIETRZA EMITOWANYCH Z KOMPLEKSU PRZEMYSŁOWEGO KONINA W DRZEWOSTANACH SOSNOWYCH

Abstract: In agricultural area of Konin where previously no industrial activity was performed the complex of power stations combusting brown coal was built in the end of the fifties followed by the aluminium smelter which was put into operation in 1965.

Both these industrial works emit considerable amounts of phytotoxic gases (F_2, SO_2, NO_2). Aluminium smelter emits vast amount of fluorine as aluminum is produced by thermoelectrolysis of aluminum oxide in electrolyte consisting of cryolite and aluminum fluoride as well as it is a major emitter of PAHs due to carbon electrode "combustion".

Because these plants did not meet technology parameters and production was poorly controlled in first period of activity harmful effects of their emission in the natural environment were observed.

Beginning from the nineties intensive proecological efforts were made and intensive modernization of the plants was performed. All these activities resulted in a significant reduction of air pollutants emission.

The paper presents the results of investigation carried out in the monitoring net established in Konin area. The fate of air pollutants currently emitted and deposited to the soil within a long period of the plants activity was determined. The vacuum ceramic cup lysimeters were used to assess the concentration and hazard of inorganic and organic chemicals for water – soil environment. On the basis of differences in concentration of cations and anions the rate of nitrification and acidification processes in the soil was also analysed.

Keywords: aluminium smelter, power plant, fluorine, benzo[a]pirene, acid deposition, pine forest, pine forests integrated monitoring

In the period of 1960–1990 Poland – due to intensive development of heavy industry at simultaneous lack of emission control – was one of the main emitters of air pollutants into the air. Big industrial plants apart from their long range effect caused a vast environmental damage in a local scale.

Since the middle sixties the activity of the aluminium smelter in Konin together with PAK (Pątnów, Adamów, Konin) power complex have adversely affected the surrounding

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agricultural and forest area. It resulted in excluding a big area from the agricultural activity and displacement of local people from the areas threatened by industrial emissions.

Implementation of the principles of the State Environmental Policy established in 1991 (eg reduction of pollutants at source and "polluter pays" principles extorted modernization of production technology.

Aluminium smelter emits vast amounts of fluorine as aluminium is produced by thermoelectrolysis of aluminium oxide in electrolyte consisting of cryolite and aluminium fluoride. Fluorine is regarded to be the most hazardous gas which may injure plants at much lower concentrations than other pollutants [1].

After 1993 modernization of the electrolysis process has started. "Wet" anode mass was replaced with "dry" one consisting of a less amount of aromatic hydrocarbons. The use of dry anode mass leads to stabilization of production process which results in the decrease in dust and fluorine compounds emission into the environment (Fig. 1).

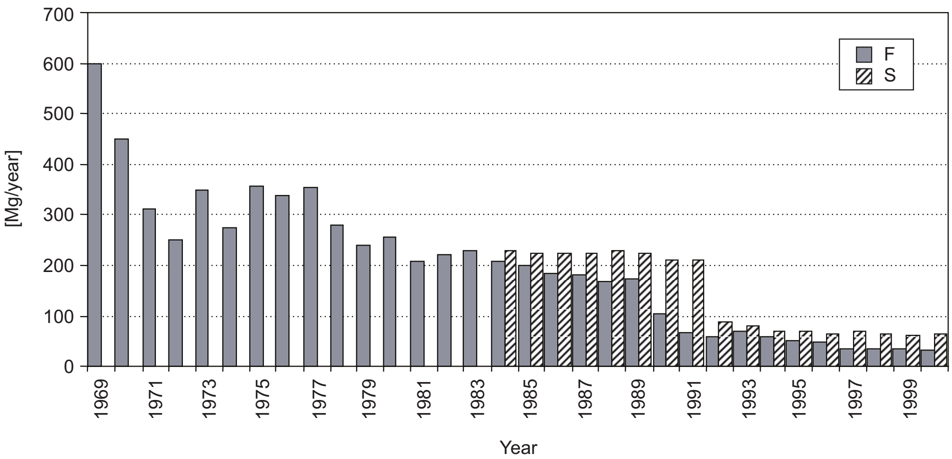

Fig. 1. Fluorine and sulphur emissions from "Konin" Aluminium Smelter

In power stations new boilers fitted with low-emission burners and new electrofilters were mounted as well as installation of wet desulfurization was put into operation. This contributed to the reduction of concentrations of eg phytotoxic gases around the threatened region (Table 1).

Table 1

Emission of pollutants from the PAK power complex in the period of 1980–2005 (Mg/year) (http://www.zepak.com.pl/pl/ekologia)

Pollutant	Year				
	1980	1990	1995	2000	2005
SO_2	198 000	125 000	135 000	110 000	115 000
NO_x	n.a.	n.a.	30 000	21 500	20 000
Dust	160 000	55 000	25 000	5 000	4 000

In the paper the present burden of pine stand ecosystems with compounds characteristic for aluminium smelting industry (fluorides, benzo[a]pirene) and other plants of Konin industrial complex (sulphur and nitrogen compounds) was analyzed.

Materials and methods

Site description

Three sites represent Scots pine forests located in the vicinity of the Konin Aluminium Smelter (Fig. 2). Site 1 (Sulanki) is situated 0.4 km from the smelter and represents 35 year-old Scots pine trees planted in the abandoned agricultural area after emission controls had been incorporated. Sites 2 and 3 (Anielew and Rudzica, respectively) are composed of mature Scots pine trees (80 year-old) located 2.5–3.0 km from the smelter.

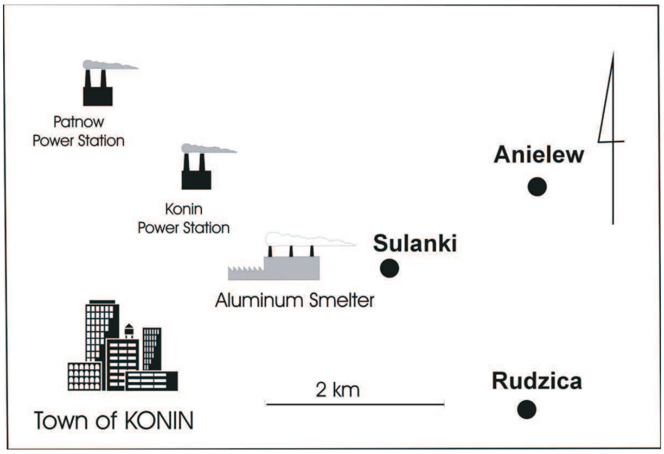

Fig. 2. Location sites

The soils are: dystric cambisols at Sulanki, eutric cambisols at Anielew and haplic podzols at Rudzica [2, 3].

In 2005 each plot was equipped with 15 randomly distributed throughfall collectors and six vacuum ceramic cup lysimeters for soil solution sampling [4]. Lysimeters were distributed regularly at 25 cm depth. Bulk deposition was sampled in an open area, close to the permanent plots. Polyethylene (PE) collectors were used for bulk deposition and throughfall sampling. Six nets 1 m in diameter were mounted to collect litterfall.

The water samples were collected monthly. The concentrations of cations were determined by the AAS method (SpectraAA 300 Varian). Ion chromatograhic method was used for determination of Cl^{-1}, SO_4^{2-} and NO_3^{-1} concentrations (Dionex DX100, column AS4A). Concentration of NH_4^+ in water samples was determined using the Nessler method; pH of water samples was measured using a glass electrode.

Organic compounds were extracted from water and plant material using dichloromethane. Benzo[a]pyrene was separated on florosil and analysed by HPLC (BECKMAN liquid chromatograph) using a UV detector. Identification of the separated compound was carried out by comparison of its retention times with the values obtained from a mixture of the Supelco PAH – Mixture 610-M [5].

Results and discussion

Mean annual pH of precipitation in the investigated area was about 5.0 which testifies to its acidic character (Fig. 3); pH value of throughfalls in all pine stands was higher when compared with bulk deposition and ranged from 4.22 to 4.44. The increase in pH of soil solutions when compared with throughfall pH was observed in all three sites; it was most pronounced for Sulanki where soil solution shows alkaline character (Fig. 3).

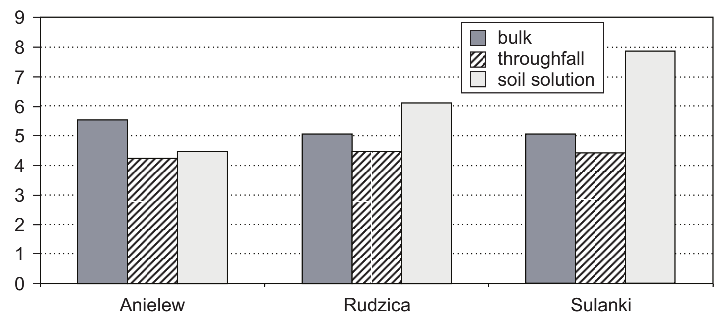

Fig. 3. pH of water

Concentrations of fluorine and sulfur increased in the following order: bulk, throughfall, soil solution (Fig. 4, 5). Increase in the concentrations of ions after passing the crowns points out that dynamic processes occur in the course of the water passing through canopy. Concentrations of individual ions and their quantity ratios differed significantly in both forms of precipitation.

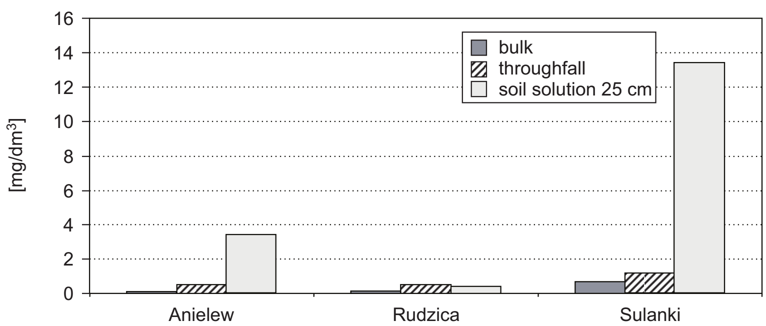

Fig. 4. Concentration of fluorine in compartments of pine ecosystem

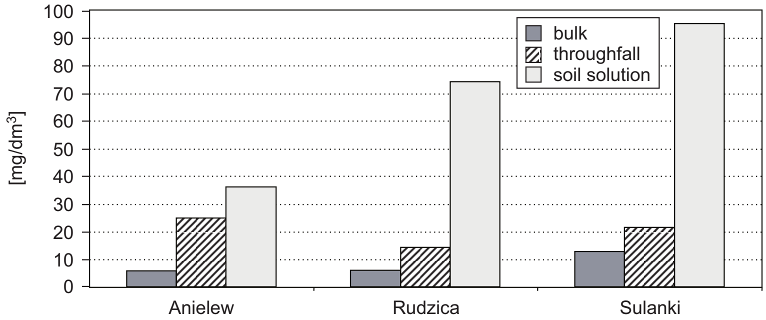

Fig. 5. Concentration of sulfate ions in compartments of pine ecosystem

This trend was the most intensive for Sulanki – site located close to the smelter. Permissible level of fluorides in surface water amounting to 1.5 mg/dm^3 was exceeded in soil solution in Anielew and Sulanki [6] (Fig. 4).

The analysis of loads reaching the forest ecosystem shows that in regard to acidifying substances the annual load of sulfur exceeded the load of total nitrogen (1.5–3 times) (Fig. 6). It is a consequence of the power plants activity. In all throughfalls ammonium form prevailed over nitrate form in the total pool of nitrogen (Fig. 7). The fluorine load

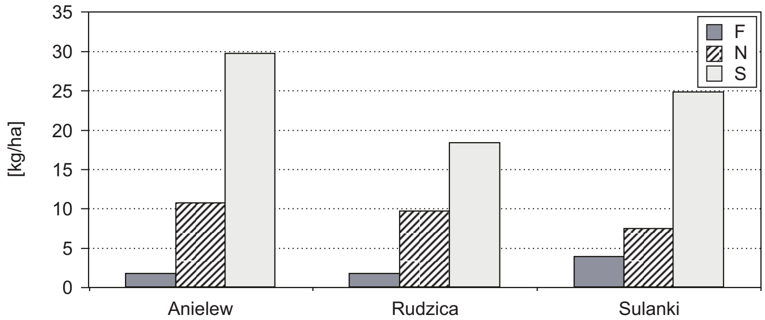

Fig. 6. Annual loads of fluorine, nitrogen and sulfur reaching the forest soil

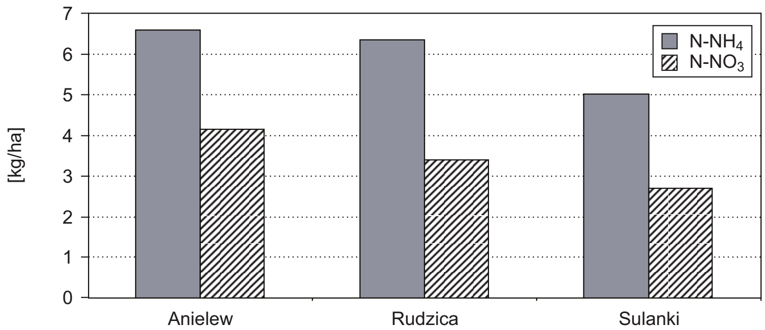

Fig. 7. Annual loads of nitrogen forms reaching the forest soil

Table 2

Annual loads of elements reaching the pine stands in 3 sites [kg/ha]

Site	Type of water	F	NH_4	NO_3	SO_4	$N\text{-}NH_4$	$N\text{-}NO_3$	N_{tot}	S	Al	Na	Mg	K	Ca
Anielew	Bulk	0.47	4.98	18.02	25.03	3.87	4.07	7.94	8.34	0.25	8.29	2.33	2.61	16.94
	Throughfall	1.75	8.47	18.35	89.30	6.59	4.14	10.73	29.77	1.08	12.86	4.98	17.97	25.65
Rudzica	Bulk	0.62	7.04	17.62	30.13	5.48	3.98	9.46	10.04	0.33	9.75	2.14	3.09	13.24
	Throughfall	1.71	8.42	14.70	57.17	6.34	3.28	9.62	18.40	0.74	12.55	3.47	7.01	18.37
Sulanki	Bulk	2.99	6.43	10.50	57.38	5.00	2.37	7.37	19.13	0.47	11.53	1.28	1.82	8.16
	Throughfall	3.94	7.22	8.05	74.54	5.61	1.82	7.43	24.85	1.48	21.69	2.36	5.31	13.16

was found to be the highest in Sulanki, close to the smelter – the main emitter of this element in the region (Fig. 6). It should be noted that in 1994 in Sulanki site the loads of fluorine, nitrogen and sulfur amounted to 6.9, 21.4 and 34.1 kg/ha, respectively [7].

The increase in load of ammonium was observed in both throughfalls when compared with bulk deposition, but it was not such pronounced as for alkalic ions (Table 2). One of the reasons may be the exchange of alkalic cations with ammonium ions in leaves. Laboratory studies showed that at low concentrations of $(NH_4)_2SO_4$ solution the leaching of magnesium and calcium from Austrian pine (*Pinus nigra var. maritima*) needles was over ten times higher than from needles treated with distilled water [8].

In Table 3 the ratio of ammonium to alkalic cation concentrations in successive environment compartments is presented. The level of exchange is differentiated. The highest level of exchange was observed for potassium – cation not firmly bound with structure of leaf cells so easy washable. The level of ammonium ion exchange to calcium was the lowest.

Table 3

The ratios of NH_4^+/alkalic ions and NO_3^-, and the Al/Ca ratio in different parts of ecosystem [meq/meq]

Site	Type of water	NH_4/K	NH_4/Mg	NH_4/Ca	NH_4/NO_3	Al/Ca
Anielew	Bulk	4.14	1.42	0.65	0.95	0.02
	Throughfall	1.04	1.18	0.78	1.66	0.06
	Soil solution	3.28	0.46	0.22	0.15	0.51
Rudzica	Bulk	4.95	2.17	1.18	0.69	0.04
	Throughfall	3.18	1.94	1.19	2.50	0.06
	Soil solution	1.74	0.34	0.18	0.27	0.33
Sulanki	Bulk	7.67	3.31	1.75	2.11	0.09
	Throughfall	3.42	2.25	1.35	3.22	0.17
	Soil solution	0.27	0.01	0.08	0.55	0.14

After passing the canopy the concentration of ammonium form exceeded the nitrogen concentration in the nitrate form. (Table 3). In all soil solutions this proportion is reverse (Table 3). On this basis you can conclude about occurrence of nitrification processes in the upper layer of soil.

In soils with no or relatively low nitrification rates the enhanced ammonium fluxes may lead to accumulation of ammonium in the top layer of the mineral soil and the loss of potassium, magnesium and calcium in the deeper soil layers. This results in the increased ammonium/cation ratios [8].

The NH_4/Mg and NH_4/K ratios in soil solutions of three sites were definitely lower than values regarded as a critical for coniferous trees growth and vitality, amounting to 5 and 10, respectively [8].

The high Al/Ca ratio resulting from the dissolution of aluminum by mineral acids and from leaching of calcium is harmful to the root system. The value of Al/Ca ratio > 5 in soil solution was mentioned as very critical for root system [9], and the Al/Ca ratio = 1 was regarded as inhibiting calcium uptake [10]. Values of this ratio observed on the investigated plots were lower and ranged from 0.14 to 0.51 (Table 3).

Fate of benzo[a]pyrene – carcinogenic compounds emitted mainly from the aluminium smelter through 35 m stacks was also investigated. Short range of B[a]P emission was found. Table 3 shows that the main portion of this compound is accumulated close to the emitter. At the distance of about 3 km from the smelter (Anielew, Rudzica) the amount of B[a]P reaching the forest stands makes only about 25 % deposition of this compound found in Sulanki. A part of B[a]P is kept in tree crowns (difference between bulk and throughfall) which after time reaches also forest soil with litterfall (Table 4).

Table 4

Loads and concentration of B[a]P in pine stands compartments

Site	Bulk	Throughfall	Litterfall	Concentration in soil solution
	g/ha			ng/dm^3
Sulanki	2.25	1.58	0.12	180
Anielew	0.50	0.40	0.03	25
Rudzica	0.35	0.27	0.02	15

A similar distance-dependent pattern of B[a]P concentration changes was observed in soil solutions. Only in Sulanki the amount of B[a]P was found to be at a high level – 180 ng/dm^3, which is close to the permissible value for surface water – 200 ng/dm^3 [6].

Conclusions

The investigation has shown that the consequent activities in metallurgical and energetic sectors, consisting in modernization and proecological activities, result in the decrease of acidic deposition to forest ecosystems. It leads also to improvement of soil water quality. Slight hazard to forest posed by water taken up by the roots can be observed only in the close distance (0.5 km) from the aluminium smelter.

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MIGRACJA ZANIECZYSZCZEŃ POWIETRZA EMITOWANYCH Z KOMPLEKSU PRZEMYSŁOWEGO KONINA W DRZEWOSTANACH SOSNOWYCH

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Abstrakt: W otoczeniu Konina na obszarze typowo rolniczym, gdzie uprzednio nie prowadzono działalności przemysłowej, na początku lat pięćdziesiątych, wykorzystując węgiel brunatny z kopalni odkrywkowych uruchomiono kompleks elektrowni PAK (Pątnów, Adamów, Konin), a w roku 1966 oddano do eksploatacji Hutę Aluminium "Konin". Zakłady te emitowały znaczne ilości gazów fitotoksycznych (F_2, SO_2, NO_2). Huta aluminium emituje duże ilości fluoru, ponieważ aluminium produkowane jest w procesie termoelektrolizy tlenku glinu w elektrolicie zawierającym kriolit i fluorek glinu, jak również jest znaczącym emiterem WWA (PAHs) powstających w wyniku „spalania" elektrod węglowych.

Ze względu na to, że zakłady przemysłowe w początku swej działalności nie spełniały wymaganych parametrów technologicznych, a emisje do atmosfery gazów odlotowych były niewystarczająco kontrolowane w środowisku przyrodniczym występowały wyraźnie szkodliwe efekty. W latach dziewięćdziesiątych podjęto intensywne działania proekologiczne i modernizacyjne zakładów, które doprowadziły do znacznej redukcji emisji zanieczyszczeń powietrza.

W pracy przedstawiono wyniki badań przeprowadzonych w lasach sosnowych znajdujących się w sieci monitoringowej ustanowionej na obszarze Konina. Przedstawiono poziom depozycji zanieczyszczeń do ekosystemów leśnych oraz migrację aktualnie emitowanych zanieczyszczeń i zdeponowanych w glebie w okresie długoletniej działalności zakładów. Do oceny stężeń i zagrożenia środowiska wodno-glebowego związkami organicznymi i nieorganicznymi zastosowane ceramiczne lizymetry próżniowe. Na podstawie różnic w stężeniach kationów i anionów w różnych przedziałach ekosystemu leśnego określono także natężenie procesów nitryfikacyjnych w glebie.

Słowa kluczowe: huta aluminium, elektrownie, fluor, benzo[a]piren, depozycja kwaśna, lasy sosnowe, monitoring zintegrowany