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## DYNAMICS OF AIR POLLUTION EMISSION FROM NITROGEN PLANTS “PULAWY” AS THE RESULT OF ENVIRONMENTALLY FRIENDLY ACTIONS

### DYNAMIKA EMISJI ZANIECZYSZCZEŃ POWIETRZA Z ZAKŁADÓW AZOTOWYCH „PUŁAWY” JAKO WYNIK DZIAŁAŃ PROEKOLOGICZNYCH

**Abstract:** The paper concerns the dynamics of pollutants emission from Nitrogen Plants in Pulawy and its concentration in the ambient air (immission) in 25 years – since the beginning of the implementation of programs to protect the environment for present with particular reference years 2007–2009, which the research project on the biogeochemistry of nitrogen in ecosystems of the region influenced by Nitrogen Plant “Pulawy” in Pulawy was carried out. Environmentally friendly actions initiated in 1985 resulted in a significant reduction quantity of pollutants emitted by Nitrogen Plants “Pulawy”, average about 65 %, while increasing the output by about 50 %. The greatest reduction was achieved in the case of: ammonia emission by 88 %, fertilizer dust by 85 %, ash particulates by 80 %, nitrogen oxides by 62 %, and sulfur dioxide by 27 %.

**Keywords:** nitrogen plants, air pollutants, emission, immission

Nitrogen Plants “Pulawy” since its inception (1966) have produced nitrogen fertilizers (ammonium nitrate and urea), and since the seventies, the caprolactam and melamine. The products are fabricated on the base of semi-finished products generated in the Works (ammonia, nitric acid, urea and carbon dioxide) and raw materials supplied from the outside (natural gas, benzene and sulfur). The rapid development of the company resulted in the construction successive investments expanding previously offered assortment of chemical products. Sale of chemicals is now 40 % of the total production and gradually increases. Now its production for the year is [1] as follows: total ammonium nitrate (nitrate solution) 1 103 850 Mg, granulated ammonium nitrate 919 875 Mg *urea ammonium nitrate solution* (UAN) 1 000 000 Mg, urea (total) 924 000 Mg, granulated Urea 600 000 Mg, melamine 92 000 Mg, caprolactam 65 000

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Mg, ammonium sulfate 156 000 Mg, hydrogen peroxide 10 000 Mg, liquefied carbon dioxide, 74 250 Mg (AdBlue 100 000 Mg)

Individual production units of Plants produce and emit specific pollutants:

- dusts of ammonium nitrate, urea, melamine and ash;
- gaseous pollutants – SO<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub>, CO, NH<sub>3</sub> organic vapors (toluene, benzene, cyclohexane, hydrogen cyanide).

In addition, the emission components are subject to adsorption processes in the atmosphere, condensation, coagulation, also taking part in photochemical or ion reactions, a result of which may be formed products with properties different to the original issue [2]

In the first period of the action of Nitrogen Plants “Pulawy” in the years 1969–1985 experienced an intense degradation of the surrounding environment [3–9] and in 1990 Plants, were on the Polish “List 80” the biggest polluters of the environment [10], among others due to: excessive emissions of nitrogen oxides, excessive emissions of ammonia, under use of cooling water, excessive emissions of hydrocarbons, especially cyclohexane, groundwater abstraction for production purposes, excessive emission of dust and gas from the power station, excessive load of pollutants discharged to surface waters.

Only since 1985, this situation has changed, when a company involved in the implementation of programs for environmental protection. As a result there has been a significant reduction in emissions and the negative impact of factories on the environment.

The aim of this study was to analyze the dynamics of emission by Nitrogen Plants in Pulawy and immission of pollutants in the ambient air in 25 years – since the beginning of the implementation of programs to protect the environment for present with particular reference years 2007–2009, which the research project on the biogeochemistry of nitrogen in ecosystems of the region influenced by Nitrogen Plant “Pulawy” in Pulawy was carried out.

## Methods

Emission data were determined from the continuous measurements made in the Nitrogen Plant “Pulawy” in Pulawy, in factory power plant and installation of nitric acid, periodic measurements of the main sources of pollutants from technological processes and balances made on the basis of technological indicators for other sources of emissions.

In emission measurements, the following devices were utilized:

- GASMET DX-4000 (measure of gases emissions);
- EMIOTEST-2594 (measure of dust emissions);
- MGA MRU-5 (the measurement of greenhouse gases).

This work has been mainly used for measurements of nitrogen emissions, namely: ammonia, nitrogen oxides, sulfur dioxide, fertilizer particulates (dust: ammonium nitrate, urea, ammonium sulfate). In order to determine the size of distributed pollutants in ambient air at designated points were made 60-minute measurements of immission.

Air samples were collected with devices SAG 12V COM connected to a scrubber containing a solution absorbing identified contaminants. Then the samples were determined: NH<sub>3</sub> spectrophotometric indophenol method according to PN-Z-040009-2; NO<sub>2</sub> spectrophotometric method with reagent Saltzmana according to PN-Z-04009-9.

## Results and discussion

Table 1 shows the relative growth of emissions of key gaseous pollutants and particulate pollutants emitted into the atmosphere by Nitrogen Plants “Pulawy”, adopting emissions for 100 when conducting environmental actions in 1985. The greatest reduction was achieved in the case of ammonia emissions by as much as 88 %, nitrogen oxides by 62 %, ash particulates by 80 %, fertilizer particulate by 85 % and sulfur dioxide by 27 %. Generally, the amount of emitted pollutants decreased by about 65 %, while global production increased by 50 %, compared with 1985.

Table 1

The relative changes in emissions from Nitrogen Plants “Pulawy”

Type of emission	1985	1990	1995	2000	2005	2010
Ammonia (NH <sub>3</sub> )	100	152	125	16	11	12
Nitrogen oxides (NO <sub>x</sub> )	100	136	84	52	31	38
Ash dusts	100	73	31	32	34	20
Fertilizer dust	100	54	32	21	14	15
Sulphur dioxide (SO <sub>2</sub> )	100	163	142	94	78	73

Individual production units of Nitrogen Plants “Pulawy” produce and emit specific pollutants:

- Power Plant: ash dust, gaseous pollutants – SO<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub>, CO;
- Urea manufacture: gas ammonia, urea dust;
- Ammonium nitrate manufacture: ammonium nitrate dust;
- Manufacture of nitric acid: nitric oxides;
- Manufacture of caprolactam: SO<sub>2</sub>, sulfuric acid mist, carbon monoxide, organic vapors (toluene, benzene, cyclohexane, hydrogen cyanide);
- Manufacture of melamine: ammonia, melamine dust.

Percentage of major pollutants in the total emission from Nitrogen Plant of “Pulawy” to the atmosphere shown on the chart (Fig. 1) indicates the dominant role of sulfur dioxide (SO<sub>2</sub>) – 56 % and nitric oxide NO – 27 %. These pollutants are a total of over 83 % of emitted gases and dust into the atmosphere. It should be emphasized that these compounds in addition to the environmental impact significantly increase the proton charge and lead to acidification [11–14]. One mole of the SO<sub>2</sub> creates the appearance of 2 moles of protons, while the nitric oxide is the source of one mole of H<sup>+</sup>. Acidifying effect, directly or indirectly as a result of physiological, biochemical and chemical

processes in soil also indicate: of gaseous pollutants – ammonia ( $\text{NH}_3$ ) and nitric oxide (I),  $\text{N}_2\text{O}$  and fertilizer dust – ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), urea ( $\text{CO}(\text{NH}_2)_2$ ) and ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ). This may lead to increased chemical degradation of the environment and biological homeostasis disorders [15].

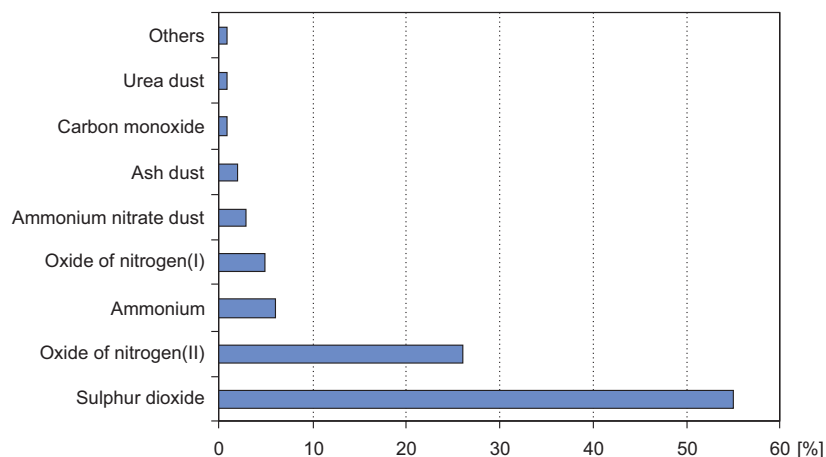


Fig. 1. Share of main pollutants emitted to the atmosphere of Nitrogen Plants "Pulawy" in 2009 [%] (Nitrogen Plant 2010)

Differentiation of air emissions in the years 2007–2009 from Nitrogen Plant "Pulawy" shown in Fig. 2 confirms the downward trend, particularly in relation to sulfur dioxide  $\text{SO}_2$  and  $\text{NO}_x$ . There was lower variation and an increasing trend in the case of fertilizer dusts (Fig. 3) and ammonia  $\text{NH}_3$  emissions into the atmosphere in the last three years.

In addition to gaseous pollutants as nitrogen oxides and ammonia significant role in the eutrophication and disruption of ecosystems around the Nitrogen Plant "Pulawy"

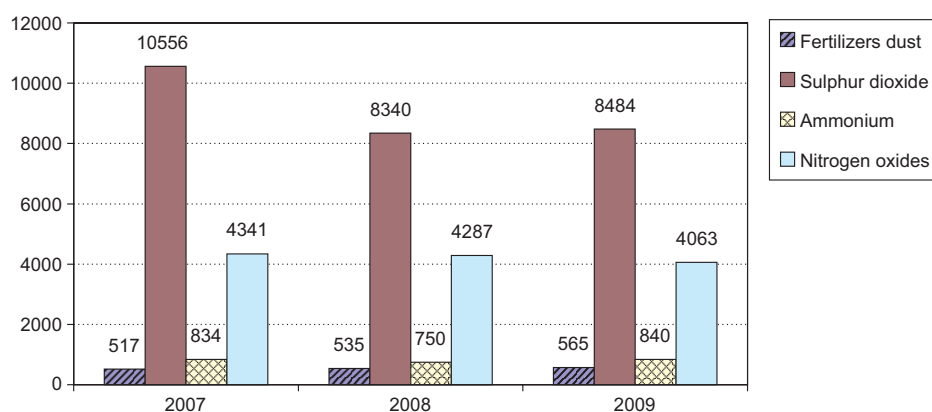


Fig. 2. Emissions of selected contaminants from Nitrogen Plants "Pulawy" in the years 2007–2009 [Mg]

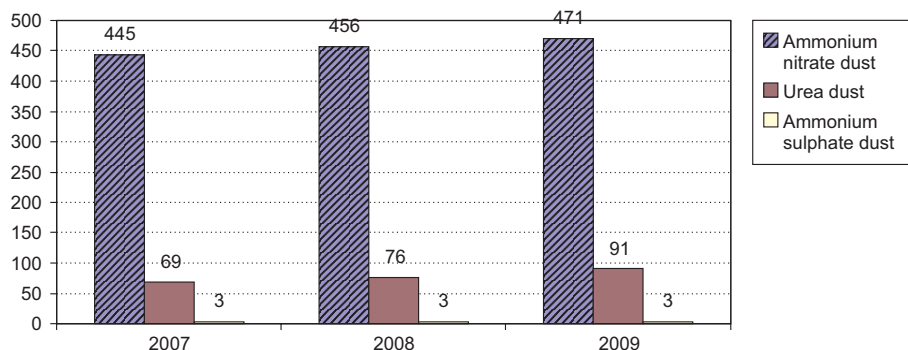


Fig. 3. Fertilizer dust emission by Nitrogen Plants “Pulawy” in 2007–2009 [Mg]

play fertilizer dusts of ammonium nitrate  $\text{NH}_4\text{NO}_3$ , urea ( $\text{CO}(\text{NH}_2)_2$ ) and ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$ . Particulate pollution is usually deposited in a much smaller distances from the emitter than gas.

Immission (Table 2) as the amount of particulate matter or gas in a unit volume of air (the concentration of pollutants or level of substances in the air) [16] in the study area has a significant impact on chemical and biological properties of soils, as well as on health, growth and assimilation organs of experimental plants. Differentiation of the major gaseous pollutant immission emitted into the atmosphere by Nitrogen Plants “Pulawy” is given for example, at several points from the year 2008.

Table 2

Some results of immission measurements made by Nitrogen Plants “Pulawy” in 2008

Months	Point – I			Point – II			Point – VIII		
	$\text{NH}_3$	$\text{NO}_2$	$\text{SO}_2$	$\text{NH}_3$	$\text{NO}_2$	$\text{SO}_2$	$\text{NH}_3$	$\text{NO}_x$	$\text{SO}_2$
	[ $\text{mg} \cdot \text{m}^{-3}$ ]								
January	<b>0.703</b>	0.037	0.008	0.038	0.041	0.005	0.127	0.033	0.002
February	0.279	0.103	0.010	0.040	0.049	0.006	0.108	0.087	0.008
March	0.217	0.031	0.000	0.201	0.065	0.002	0.050	0.040	0.000
April	0.036	0.075	0.008	0.048	0.055	0.010	0.050	0.080	0.020
May	0.024	0.021	0.006	0.040	0.031	0.005	—	—	—
June	0.076	0.040	0.004	<b>0.533</b>	0.038	0.005	0.001	0.043	0.005
July	0.015	0.036	0.000	0.064	0.039	0.001	0.000	0.047	0.000
August	0.620	0.049	0.002	0.397	0.041	0.000	0.083	0.072	0.008
September	0.305	0.028	0.000	0.064	0.030	0.004	0.033	0.047	0.005
October	<b>0.426</b>	0.060	0.012	0.053	0.045	0.010	0.054	0.102	0.000
November	0.062	0.042	0.007	0.181	0.072	0.004	0.010	0.019	0.000
December	0.000	0.026	0.009	0.037	0.025	0.010	0.022	0.028	0.009
Average	0.195	0.046	0.006	0.141	0.044	0.005	0.049	0.054	0.005

The average concentration of pollutants in the individual study points were characterized by great diversity in the year, largely because they are dependent on not only the emission of pollutants but also the direction and strength of winds and weather conditions at the time of the measurement. Exceeding of the allowable concentration have been found only in the case of ammonia at the points nearest emitters.

## Conclusions

Environmentally friendly actions initiated in 1985 resulted in a significant reduction of quantity of pollutants emitted by Nitrogen Plants "Puławy", average about 65 %, while increasing the output by about 50 %.

The greatest reduction was achieved in the case of: ammonia emissions by 88 %, fertilizer dust by 85 %, ash particulates by 80 %, nitrogen oxides by 62 %, and sulfur dioxide by 27 %.

The permissible average concentrations of pollutants in the air were exceeded in some months only in the case of  $\text{NH}_3$  at the points closest to the issue, on the direction of prevailing winds in that area. Despite a marked reduction of emissions from Nitrogen Plants "Puławy", substances accumulated in the environment are still pose a potential threat to the still unstable ecosystems.

A detailed analysis of pollutants emissions from Nitrogen Plants "Puławy" significantly reduced during the last 25 years demonstrated in the years 2007–2009 variation, which locally may have still an adverse impact on the functioning of ecosystems.

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**DYNAMIKA EMISJI ZANIECZYSZCZEŃ POWIETRZA  
Z ZAKŁADÓW AZOTOWYCH „PUŁAWY”  
JAKO WYNIK DZIAŁAŃ PROEKOLOGICZNYCH**

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**Abstrakt:** Praca dotyczy dynamiki emisji zanieczyszczeń powietrza z Zakładów Azotowych „Puławy” i stężenia zanieczyszczeń w otaczającej atmosferze w 25 latach – od początku realizacji programu proekologicznego do teraźniejszości, ze szczególnym uwzględnieniem lat 2007–2009, w których prowadzono projekt badawczy dotyczący biogeochemii azotu w ekosystemach rejonu oddziaływania Zakładów Azotowych „Puławy”. Działania proekologiczne zainicjowane w roku 1985 spowodowały znaczącą redukcję zanieczyszczeń emitowanych przez Zakłady Azotowe „Puławy”, średnio około 65 %, przy jednoczesnym zwiększeniu produkcji o około 50 %. Największą redukcję osiągnięto w przypadku: amoniaku o 88 %, pyłu nawozowego 85 %, cząstek popielnych 80 %, tlenków azotu 62 % i ditlenku siarki 27 %.

**Słowa kluczowe:** zakłady azotowe, zanieczyszczenia powietrza, emisja, imisja