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Modeling of Deposition of Nitrogen Compounds In "Grotowice" Intake Zone

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Abstract: This article attempts to determine the size of the deposition of nitrogen compounds (NOx) per the area of the Main Groundwater Reservoir GZWP 333, in particular area of water intake "Grotowice" was analyzed. The analysis was conducted for two selected years: 2003 and 2013. To estimate the size of wet and dry deposition, EMEP MSC-W model version rv4.5 had been used analyses of the 12 designated points allowed to determine the distribution of wet and dry deposition within the intake zone. It was agreed that on the basis of interpolation of deposition of nitrogen pollutants from the air into the intake zone "Grotowice", surface loads of nitrogen pollution can be pre-defined. Whereas, the analysis of land development has allowed for the identification of the major risk factors for water quality. Despite the fact that the analysis of intake water quality shows a positive and lasting trend of reducing the contents of nitrogen pollution, problem with pollution with nitrogen compounds for the analyzed intake is still valid. On the basis of the analyses, proposals for further testing have been formulated. One of the most important is the need to establish a protective zone for each sump of the intake.

Keywords: *groundwater, water intake, nitrogen compounds, modeling*

I. INTRODUCTION

Water is one of the key factors that directly affects the strong socio-economic growth of regions, countries and continents. Thanks to the natural circulation of water in nature and the natural resources of the globe in the water, there is a direct possibility to use this natural raw material for the needs of the population and economy. The following affects the size of water resources, among others [1, 2]:

- hydro-meteorological and geological factors: amount of rainfall, catchment retention capacities, infiltration conditions, sedimentation environment that has conditioned creation of groundwater aquifers horizons,
- anthropogenic factors: areas drainage, regulation of watercourses, land use structure changes, mainly deforestation and afforestation, urbanization and associated with it increase of surfaces with low permeability, volume of water intake, quantity of pollution released into water and soil, water transfers.

The dynamics of changes both in terms of quantity and quality of water depends on a number of factors, i.e.: geological structure, hydrogeological and hydrological conditions, agricultural economy within the areas of feed zone, climatic conditions and a number of other equally important factors. The groundwater has many elements of natural origin. Naturally, trace elements of impurities leak into the groundwater directly from the earth's crust, penetrating into the waters, as free ions. However, they do not constitute any danger and in most cases the amount of pollution of this type is slight. When there is pollution of anthropogenic origin in groundwater, in many cases, groundwater is strongly polluted or contaminated [3].

For a detailed description of the changes in groundwater quality, a number of factors affecting their quality must be considered. However, the susceptibility of groundwater to contamination is also very important apart from the factors themselves. Susceptibility is a natural feature of the aquifer system indicating the risk of migration of harmful substances from the surface to the aquifer [4]. To accurately assess the susceptibility of groundwater to pollution, a number of external factors affecting the sensitivity of the waters should be considered. These factors include: surface runoff from roads, land development (arable land, plants burdensome to the environment, landfills, septic tanks, manure depots and others) and air pollution (i.e. wet and dry deposition) [5].

Air pollution, especially dust and gas pollution from combustion of solid fuels, waste in domestic boilers (low emission) as well as from transport and industrial plants are now a very big problem. They have a direct impact on both the soil and in consequence on the condition of groundwater. This effect is associated with the so-called wet and dry deposition. Gaseous, dust and aerosols pollutants emitted to the atmosphere from a variety of sources, both of natural and anthropogenic origin, undergo there a variety of physical and chemical processes, e.g.: convection, diffusion, chemical and photochemical reactions. These pollutants come back to the earth surface as a result of [6]:

- removal of substances from the atmosphere with precipitation (rain, snow, dew, fog) - wet deposition,
- gravitational sedimentation of large particles on the substrate – dry deposition,
- absorption of gaseous pollutants and aerosols through the substrate.

Taking into account the above factors determining the state of air pollution in the area of the tested facility, using the EMEP MSC-W model, size of wet and dry deposition on the area of the Main Groundwater Reservoir No. 333 as well as on an area covering intake zone Grotowice was calculated.

II. CHARACTERISTICS OF THE TESTED FACILITY

„Grotowice" intake is one of the biggest intakes of Main Groundwater Reservoir No. 333 (GZWP). The area of the reservoir is covered with Groundwater Body (JCWPd) No. 116. Presence of Triassic on the area of whole body is a special feature of JCWPd [22]. „Grotowice" intake is one of the biggest intakes of Main Groundwater Reservoir No. 333 (GZWP). GZWP 333 is a reservoir in the forms of The Muschelkalk, gathering water in karstic limestones acquifier. The Muschelkalk aquifer is treated together with the Röt-Formation, due to local contacts resulting from tectonic and lack of insulating layers. GZWP-333 stretches from Opole on the West to Kielcza on the East and from Gogolin, Strzelce Opolskie on the South to Kolonowskie, Ozimek and Opole on the North. The area of the reservoir is 1835 km^2 and disposable resources are estimated at 200 000 – 225 000 m^3/d [2]. The reservoir has a low natural resistance to contamination due to lack of cover deposits especially in the southern part. The reservoir is of fundamental importance in the supply of water to population living in the area between the Odra River and Mała Panew River, in the following communities: Opole, Prószków, Tarnów Opolski, Izbicko, Chrząstowice, Strzelce Opolskie, Jemielnica, Zawadzkie, Ozimek, Gogoli, Krapkowice and Strzelecki [5,7]. The reservoir consists of 4 wells 1A, 1B, 3B and 6B with technical parameters as given in Tab. 1 below. Well 1A is an emergency well. Wells 1B and 6B have been used from 1995, whereas well 3B from 2008. „Grotowice" intake, next to „Zawada" intake, is the basic source of water supply to the residents of Opole. Operational capacity of intake is 16934 m^3/d [8].

Tab. 1. Technical characteristics of the wells of „Grotowice" intake.

Parameters of well	1B	6B	1A	3B
Area level [m amsl]	162,20	160,89	161,50	165,80
Depth [m]	182,00	160,00	170,00	200,40
Operational capacity Q_e [m^3/d]	5448,00	4536,00	2880,00	4070,40
Depression s_e [m]	13,00	1,42	51,05	35,20
Location	forest	farmland	forest	forest

The intake is located east from the Grotowice housing estate in Opole (Fig.1). This area is part of the Opole Plains located on this area on the height of 155 -170 m AMSL and located directly within the catchment area of the Odra River. There are no surface water reservoirs in the vicinity of the intake [9]. The geological structure of the area consists of rocks of the Carboniferous, Permian, Triassic, Cretaceous, Tertiary and Quaternary. Groundwater reservoirs form forms of Upper Buntsandstein, Röt-Formation and The Muschelkalk. Water is supplied on the outcrops of forms from which they are built. Drainage of these reservoirs takes place through watercourses. These reservoirs are separated with a poorly permeable shales, clay marl and marly limestone. However, the essential role in insulation of reservoirs is played by the Keuper loams. In the region of Opole under the Keuper cover, their permeability is less than 400 m^2/d [10]. The analyzed intake area is characterized by a wide range of drainage ditches network, oxbows and meanders, as well as field depressions. Temporary and little accumulation of surface water in natural depressions can be seen in this area. These factors affect area humidity conditions, and the development of specific biotypes in this region. Biocenosis growing in the valleys and oxbows is a specific flora and fauna of areas within the intake. The climate in this part of the south-western part of Poland is characteristic for the temperate zone. This zone is distinguished by a small variety of temperatures, short and rather mild winters, with an average annual air temperature of 8,2°C and normal precipitation 650 mm [9,10]. Distribution of precipitation in each month of the studied period is shown on fig. 2.

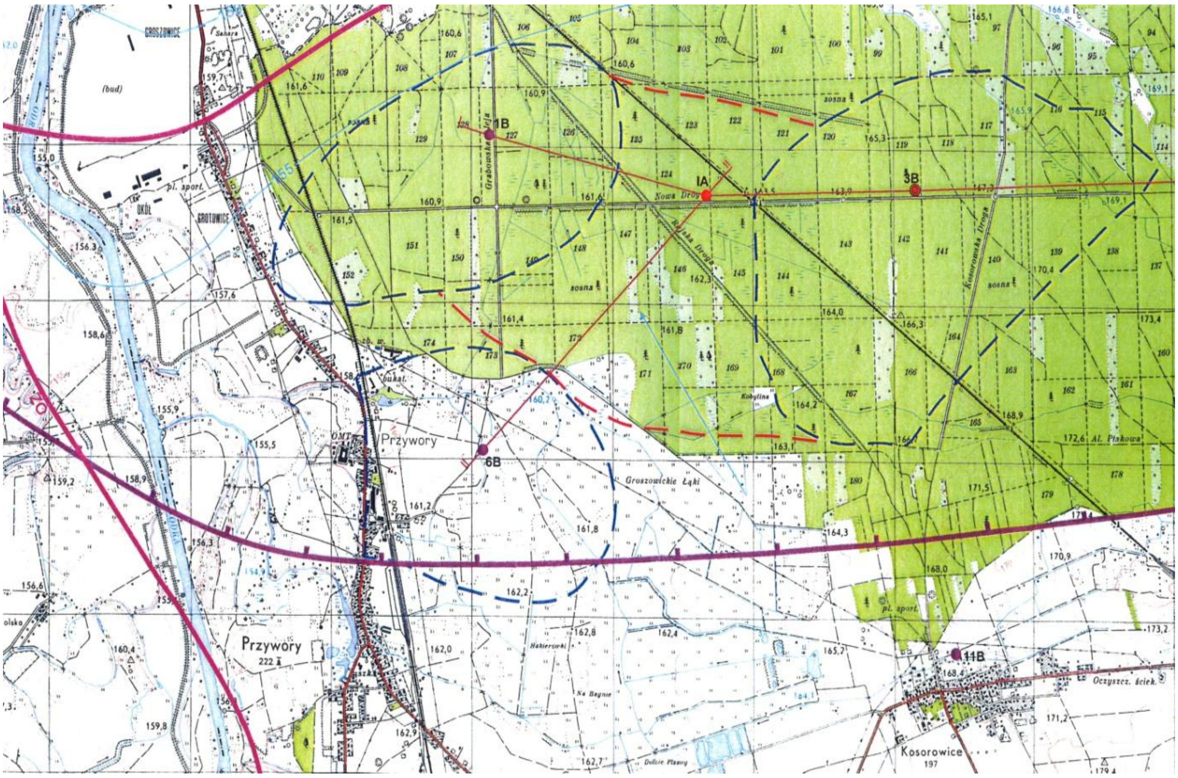

Fig. 1. Wells location 1A, 1B, 3B, 6B "Grotowice" water intake.

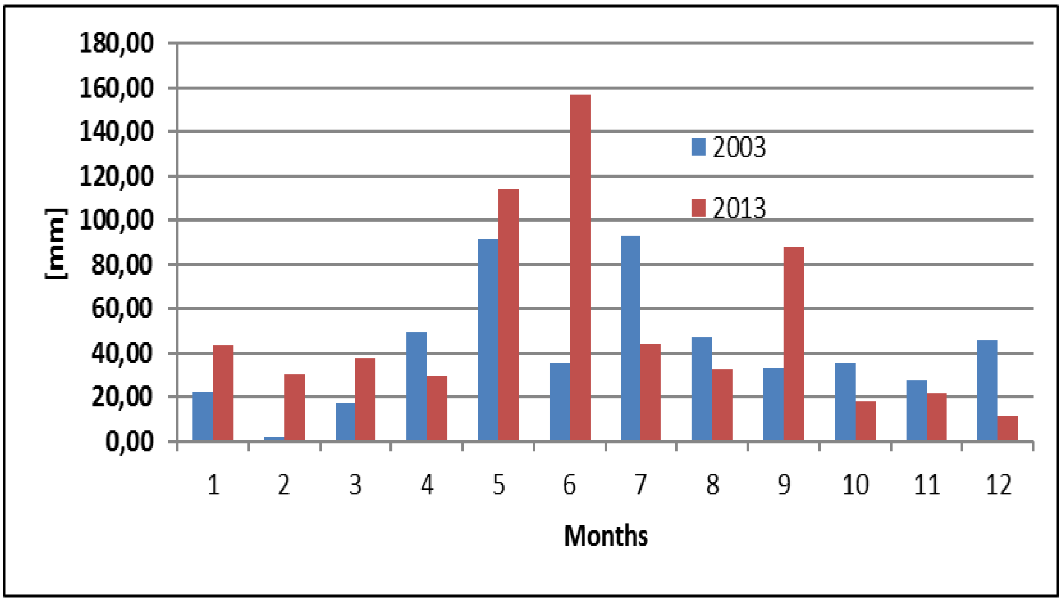

Fig. 2. Average monthly volume of precipitation in the studied years.

Due to the geological structure, both climatic conditions and other environmental values have a significant impact on the penetration of nitrogen compounds pollutants to Grotowice reservoir.

In Grotowice water intake, besides exceeding content of nitrogen compounds, rarely there are slight transgression of individual elements. Therefore, the most current issue of the analyzed intake is the content of nitrogen compounds caused by location of each well. Three of the analyzed wells (1B, 1A and 3B) are located in forest. In contrast, well 6B is located on agricultural land (Fig. 1) [5]. Test results [5] of nitrate content in the study period indicate that the highest values are recorded in water from well 6B as illustrated in fig. 3.

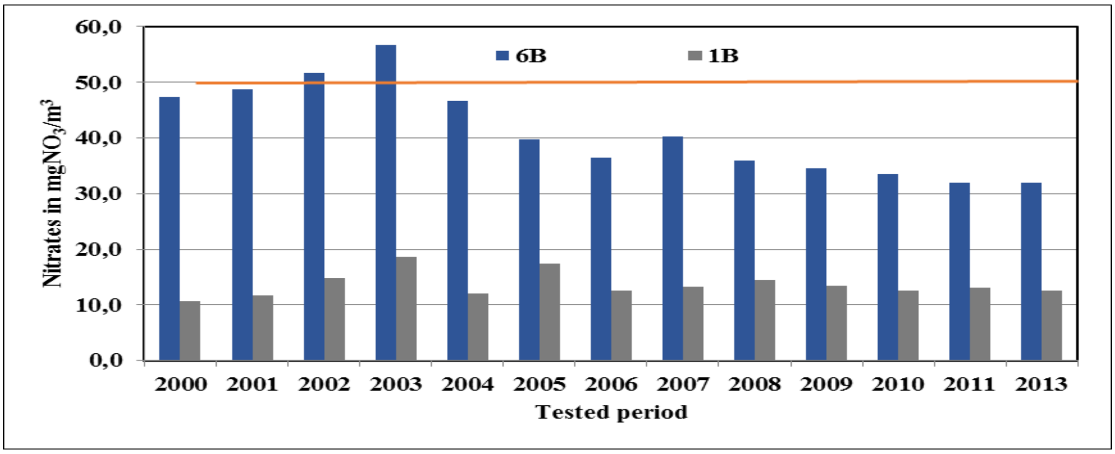

Fig. 3. The maximum nitrate content of the studied period [5]

The content of nitrogen compounds to year 2000 was subject to fluctuations reaching in February of this year value of 66,5 $mgNO_3/dm^3$. It should also be pointed out that until year 2000 the nitrate content increased. This could be due to the effects of flooding the area of intake supply with flood water of the Odra River in 1997 [5,11,12]. Significantly lower nitrate content was observed in the well 1B. Throughout the study period, the nitrate content is less than 27,5 $mgNO_3/dm^3$. However, it should be noted that until 2003 there was a rise in the levels of nitrates, and stabilization followed since 2006. In the years 2006-2011, the maximum content of nitrates in the wells was at the level of $mgNO_3/dm^3$. The standard deviation of the results for this period ranges from 0,613 to 1,144 [5].

On the basis of analysis [5], it can be stated that since year 2005, there have been positive changes in the content of nitrates both in the well 6B and 1B. Particularly significant changes were recorded in improving the quality of water in the well 6B. It should be noted that the supply zone of this well is located on the farmland and near developed areas. Visible improvement of water quality is associated with the activities of local governments in this area after year 1997.

It should be noted that, due to the geological structure of the reservoir, different kinds of water exchange take place. The reservoir contains young water, which infiltrated the rock massif several years ago. Precisely, these zones are the most exposed to nitrogen pollution created several years ago, when fertilizing economy and municipal management services were not yet regulated. There are zones where water infiltrated from a few hundred to several hundred thousand years. These zones are completely safe for maintaining clean groundwater [10, 13, 14].

Due to the characteristic feature of the reservoir connected with low resistance to penetration of surface contamination to waters, it can be concluded that the weather conditions especially precipitation have an important role in the migration of nitrogen compounds. An important reason for still persistently high level of contaminants in the well 6B, however, is the infiltration of water of the Lutnia brook, flowing relatively close to the well, formed mainly by the discharge of water from " Tarnów Opolski" mine. Infiltration occurs within the cone of depression of well No. 6B of "Grotowice" intake. The result of this infiltration is a constant increase in the concentration of nitrogen compounds in intake water [13,14].

III. RESEARCH METHODOLOGY

In order to estimate the size of wet and dry deposition, data from the database emissions EMEP (European Monitoring and Evaluation Programme) MSC-W model version rv4.5 were used, broken down into SNAP (Selected Nomenclature for sources of Air Pollution) categories. SNAP categories is a system covering 11 main categories of emission sources, divided into more than 400 subcategories. SNAP classification is used when reporting emissions from individual countries to the needs of the Secretariat of the United Nations Economic Commission for Europe (UN-ECE) and the EMEP [18]. The program measuring background monitoring of air pollution in Poland is the fulfillment of the obligations imposed on Poland with Convention on transboundary air pollution over long distances and the Protocol to the Convention on the financing of EMEP (Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe, working name - European Monitoring and Evaluation Programme), the aim of which is to provide information on concentrations and streams of selected pollutants reaching the ground. Research results of air pollution collected under this program are communicated and supply the data of programs GAW/WMO (Global Atmosphere Watch / World Meteorological Organization) and HELCOM of the Helsinki Commission and are used by the Regional Inspectorates of Environment to support assessment of air quality [9]. EMEP is based on three main elements:

- collecting emissions data,
- measurements of air and precipitation quality,
- modeling of atmospheric transport and deposition of air pollutants.

By combining these three elements, EMEP allows for regular monitoring related to the size of emissions, concentrations and deposition of air pollutants, the amount and significance of transboundary flows and air pollution exceedances to critical loads and threshold levels. The combination of these elements also provides a good basis for the evaluation and qualification of the EMEP estimates. EMEP model is an extremely valuable tool for illustrating size of the pollutants emissions on a European scale, used simultaneously for monitoring changes in emissions and estimating the concentration and deposition of atmospheric pollutants. The spatial resolution which is characteristics of the EMEP model is a mesh of 50x50 km. Based on the data converted from the EMEP model, interpolation was made in tools designed for ArcGIS spatial data analysis. Interpolation was made using the Kriging method. [15, 16, 17]. Interpolation methods use a number of different algorithms to determine the size of interpolated parameters in the nodes. Usually, measurement data lying closest to the node have the greatest impact on this node. The magnitude of this impact can be changed using so called weight parameter. Each method uses a different algorithm to calculate the value of nodes, and what goes with it, it creates a different picture of plotted surface [19]. The Kriging method consists of two stages. First stage is to determine the spatial correlation of the described phenomenon. Variogram and the covariance are usually used to describe the correlation. In the second stage, based on measurement data and the variogram, interpolation is performed. The accuracy of the variogram strongly determines the accuracy of interpolation. Determination of the variogram value for certain distances (1 km, 2 km etc.) is not possible because of the irregular distribution of measurement points. For this purpose, distance tolerance is defined, which is usually taken as half step between successive distances. The course of experimental variogram is determined by the points calculated for different distances. Due to the heterogeneity of the variation of environmental processes in respect of the cardinal directions, the empirical variogram, in addition to the distance, is also a function of direction. Designation of points of the experimental variogram allows to find a mathematical equation describing its course. A theoretical variogram is created to the description of which the following parameters are used [20, 21]:

- catchment area - the distance over which the value of variogram is a quasi-constant,
- threshold value (threshold) - variogram value corresponding to the scope of influence,
- base - variogram value for the distance approaching zero, also called ‘nuggets effect’.

IV. RESULTS OF MODELING DEPOSITION OF NITROGEN COMPOUNDS

On the “Grotowice" intake zone occupying approx. 22,26 km^2, 12 measurement points were designated, located on the outskirts of the supply zone. For each of the measuring points, balance deposition NH_x of pollutants divided into wet and dry deposition was defined. The location of the measurement points is illustrated in fig. 3.

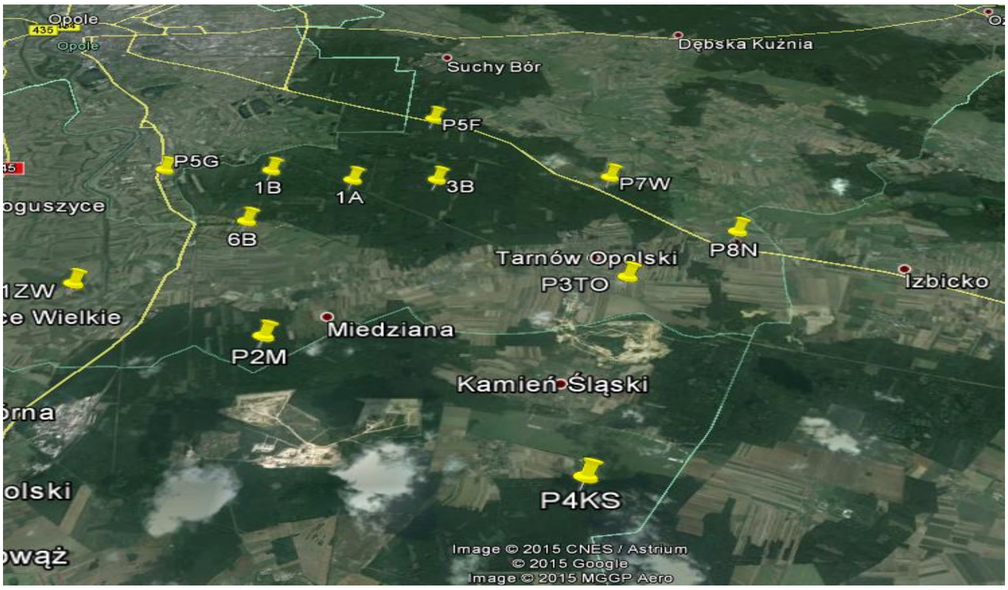

Fig 3. Map location of measurement points.

Two selected annual periods were analyzed. Year 2003, as a year with relatively high NOx pollution in the water and year 2013 as the year of comparison. The chart below presents the maximum results for NO_3 in two years of research.

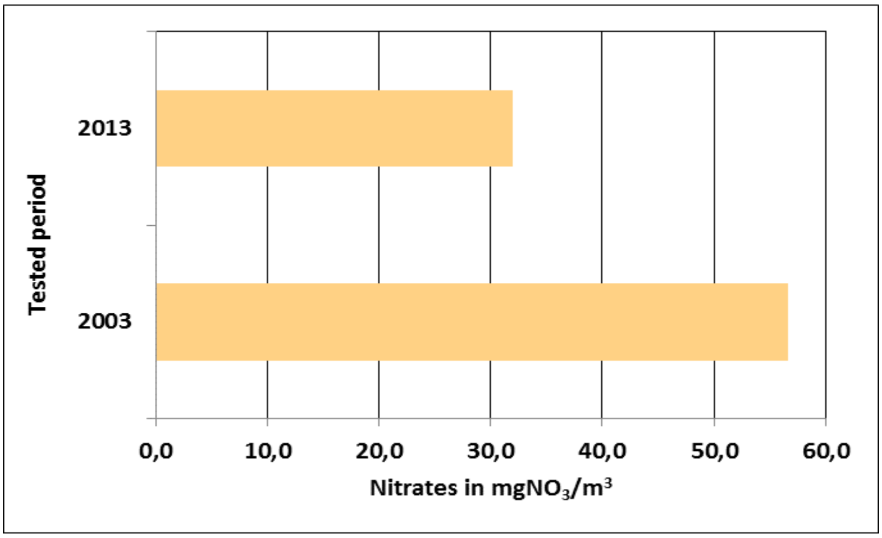

Fig 4. Maximum concentrations of NO_3 in waters intake of two model years.

Using the Kriging method, interpolation of results with EMEP to the individual points in intake zone was performed. Modeling results of wet are dry deposition are presented on the below figures.

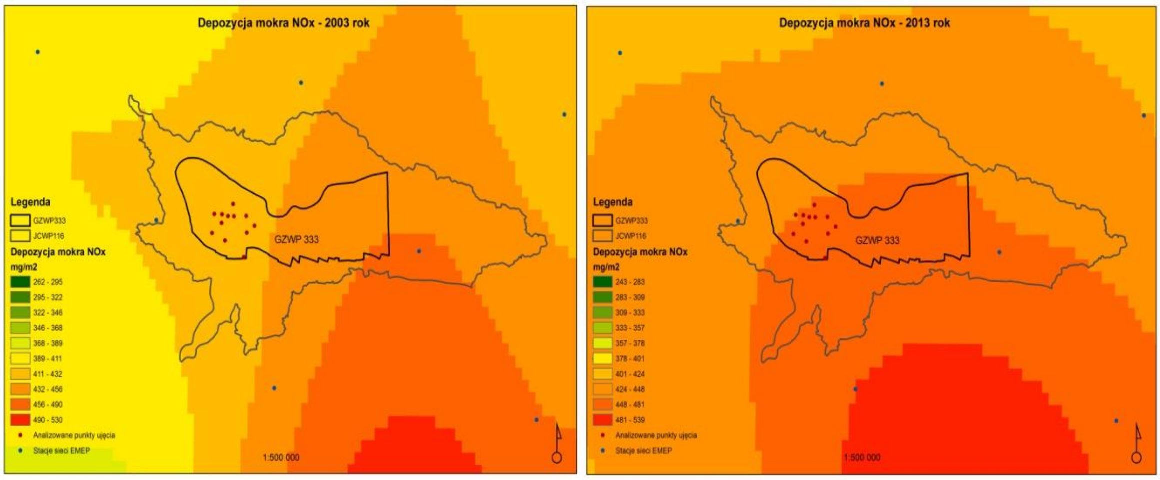

Fig 5. Wet deposition in 2003 and 2013.

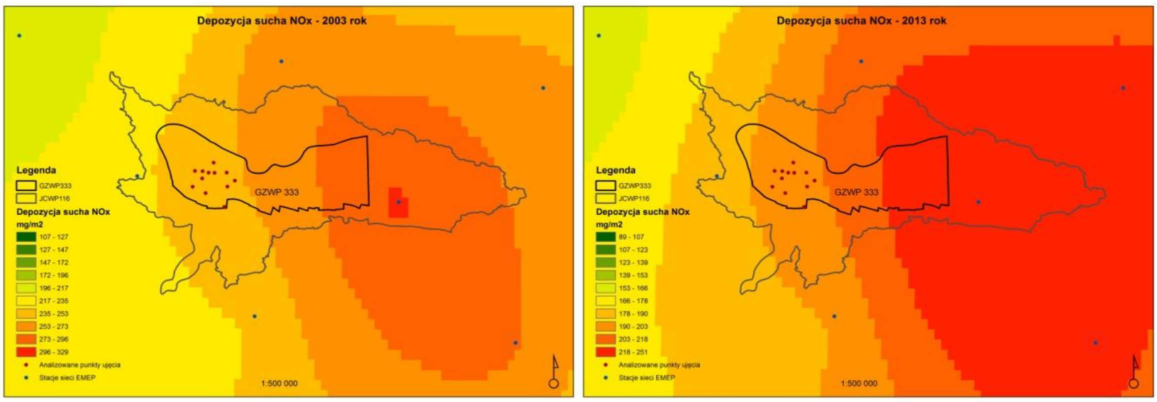

Fig 6. Dry deposition in 2003 and 2013.

Analyzing the results shown in fig. 5 and 6, it can be indicated that, contaminants from the dry and wet deposition of nitrogen compounds occurring in the intake zone "Grotowice" and within GZWP 333 reservoir Opole Zawadzkie are characterized by a relatively high concentration in both examined years. The average results of analysis of the deposition of nitrogen compounds on the surface of "Grotowice" intake are presented in the Tab. 2.

The calculation results summarized in Tab. 2 indicate that the amount of nitrogen contamination from wet deposition in both model years is greater than the nitrogen pollution from the dry deposition. The biggest wet deposition in both years was recorded in points P4KS and P8N. However, in the case of dry deposition also two points had the highest load of NOx – there were points P7W and P8N. All of these points are located in the nearby distance from the two main mining areas belonging to the mines: Tarnów Opolski and Górażdże. P4KS point is near Górażdże mine, while P7W and P8N points are located near Tarnów Opolski mine. This may indicate a strong impact of mining areas on air quality, and thus the deposition of NOx.

Due to the geological conditions and deteriorating air quality conditions, as illustrated by increasing nitrogen loads coming especially from wet deposition, there is a serious risk of deterioration of water quality in intake.

Tab. 2. The size of wet and dry deposition for the model years.

Mark	Wet deposition [kgNO_x/ha]		Dry deposition [kgNO_x/ha]	
	2003	2013	2003	2013
1A	422,51	449,87	244,81	196,48
1B	421,43	449,24	243,45	195,28
3B	423,78	450,57	246,16	197,63
6B	421,58	450,65	243,12	195,06
P1ZW	420,55	451,25	241,55	193,70
P2M	422,97	452,80	243,69	195,66
P3TO	426,93	455,10	247,92	199,44
P4KS	**427,43**	**458,26**	246,13	198,15
P5G	420,42	448,61	242,15	194,13
P5F	423,48	448,98	246,52	197,85
P7W	426,28	451,81	**249,20**	**200,34**
P8N	**428,02**	**454,12**	**250,15**	**201,33**
Average value	190,38	202,95	110,24	88,54

V. CONCLUSION

Despite emerging the downward trend of nitrogen compounds over the years, the problem of pollution with nitrogen compounds for the analyzed intake is still current. This is due to its location and hydro-geological structure. The intake is located in the western part of 333 reservoir (GZWP). The reservoir has a low natural resistance to contamination due to lack of cover deposits especially in the southern part. This points to the need to protect groundwater resources, not only in the proposed intake protection zone "Grotowice", but also on the entire uninsulated surface of the reservoir (approx. 750 km^2), planned as an area of best protection (ONO).

Taking into account the above conditions of the researched area and the results of the deposition modeling of nitrogen compounds on intake zone, the following conclusions can be formulated:

1. Any point, linear and surface contamination can affect occurrence of the nitrogen pollution in the waters of "Grotowice" intake. In order to conduct a thorough analysis of their impact, nitrate concentrations from individual pollution centers should be monitored.
2. On the basis of interpolation with Kriging method of nitrogen pollutants deposition supplied from the air into the intake zone "Grotowice", the size of the load of nitrogen pollutants can be specified. Data obtained from EMEP model can be used to generate maps presenting spatial distribution of the concentration of dry and wet deposition of NOx compounds. EMEP model allows for the study of spatial changes in the concentration and deposition of pollutants over time, taking also into account the variability of climatic conditions.
3. To maintain good water quality of the intake, it is necessary to create a protection zone. To establish such a zone, a numerical model should be drawn up taking into account the geological structure, hydrogeological conditions, the planned volume of water consumption and existing land use. Due to the geological conditions and deteriorating air quality conditions as illustrated by increasing nitrogen loads coming especially from wet deposition, the model should also take into account the size of these pollutants.

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