

DISPERSION MODELING OF NITROUS OXIDE EMISSIONS FROM A NITRIC ACID PLANT IN DEVNYA REGION, BULGARIA

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Abstract

Within the present research a mathematical modeling is done in order to study the dispersion of nitrous oxide emissions from a single organized source – a nitric acid plant with 363000 tons per year production capacity in the industrial region of Devnya, Bulgaria. Separate simulations are done for the dispersion of N_2O emissions without any emission reduction measures being implemented in the plant and for N_2O emission dispersion with a secondary N_2O decomposing catalyst being installed under different meteorological conditions. Results indicate that a significant decrease of N_2O concentration in the ground atmospheric layer is achieved after the implementation of the secondary decomposing catalyst – over 81 % reduction of the hourly average N_2O concentration and up to 80 % reduction of the annual average N_2O concentration is calculated. Dispersion models also indicate that the territorial dispersion of N_2O emissions is reduced as well – the area with N_2O concentration below $200 \mu\text{g}/\text{m}^3$ is 15 times smaller with a secondary N_2O decomposing catalyst being installed. Research results provide a tool to assess the decomposing catalyst reduction potential and to predict the impact of N_2O emissions upon the ambient air quality in the source region. Research results prove that high temperature catalytic reduction of N_2O emissions from nitric acid production by installing secondary decomposing catalyst is an effective method for N_2O emission reduction and a tool to combat global warming effect.

Keywords: ambient air quality, air dispersion modeling, greenhouse gas, nitrous oxide, catalytic emission reduction

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1. INTRODUCTION

Nitrous oxide N_2O is a greenhouse gas under the Kyoto Protocol [1] and one of the main reasons for global warming effect [2-4]. N_2O emissions from industrial installations for nitric acid production have adverse effect upon the ambient air quality in the surrounding area. The effect level depends on the specific topographic and climate conditions of the source region which also affect the dispersion of the pollutant in the ground atmospheric layer and the processes of photo dissociation, chemical destruction and diffusion [5, 6]. Different measures and techniques for N_2O emission reduction are developed and applied in nitric acid production plants around the world [7-9]. Installing a non-platinum secondary catalyst that is decomposing N_2O to nitrogen and oxygen right after its formation in the ammonia burner is a secondary measure that provides 73 % reduction of N_2O emissions [10]. The achieved N_2O reduction level has a positive effect upon the ambient air quality in the industrial source surrounding area and is a tool to prevent adverse changes of the global climate system.

The present research aim is to study the dispersion of N_2O emissions from a nitric acid plant with and without a secondary decomposing catalyst being installed and to assess their impact upon the ambient air quality in the surrounding area having in mind the specific topographic and meteorological conditions of the region.

2. MATERIAL AND METHODS

Within the present research a mathematical modeling is done along with a software simulation of the dispersion of N_2O emissions from a single fixed source – a nitric acid plant with 363000 tons per year production capacity in the industrial area of Devnya, Bulgaria. A secondary decomposing catalyst for N_2O emission reduction has been installed in the plant in September 2005 [10]. According to the European Environment Agency currently there is no specific software product developed for mathematical modeling of N_2O emission dispersion due to the fact that N_2O is inert in the troposphere [11-17] and thus all dispersion models for emissions from area, transport or point sources in urban regions can not be applied [18, 19]. Within this research a practically approved software product BREEZE AERMOD is used for emission

dispersion modeling taking into account the topography of the region. In order to ensure maximum reliability of the meteorological conditions of the region validated data is used in the form of hourly meteorological file containing information on 6 parameters – wind speed and direction, ambient air temperature, relative humidity, atmospheric pressure, sun radiation intensity. Research period starts in 2005, due to the fact that before that year there aren't N₂O emission reduction measures applied in the nitric acid plant, and ends in 2012.

In order to avoid obtaining of wrong results due to variation of the meteorological conditions N₂O emission dispersion modeling is done over two main scenarios. The first scenario presents N₂O emission dispersion with no N₂O reduction measures being applied in the nitric acid plant. The other scenario presents N₂O emission dispersion with a secondary N₂O decomposing catalyst being installed in the plant. Emission dispersion with no N₂O reduction measures being applied is simulated using data from a single N₂O emission measurement in 2005 before the implementation of the secondary catalyst and meteorological data for 2005 and 2012. Emission dispersion with a secondary N₂O decomposing catalyst being installed is simulated using emission data in the form of hourly N₂O concentration file for 2012 and meteorological data for 2005 and 2012. For every of the four simulations hourly average and annual average N₂O

concentration in the ground atmospheric layer are calculated referring to European and national standards for determination of hourly average and annual average limit values for the content of oxides of nitrogen in the ambient air [20, 21].

3. RESULTS AND DISCUSSION

3.1. Topographic Characteristic of the Region

The nitric acid plant is located in the east industrial area of Devnya, Bulgaria. The terrain is mostly lowland with some hilly areas and the elevation varies between 0 and 300 m. The highest point in the 5 km radius area is to the north-northwest from the source. To the south, where Beloslav Lake is situated, the terrain is flat. The nearest settlement is Poveljanovo, a suburb of Devnya (to the north). Other settlements in the area are Razdelna, Beloslav and Strashimirovo with elevation almost equal to the elevation of the source site. Settlements to the north from the source such as Slanchevo (elev. 145 m), Kipra (elev. 135 m) and Banovo (elev. 340 m) can be affected by the emission dispersion. These settlements are situated in hilly areas where displacement is higher or almost equal to the geometric height of the source and for that reason certain meteorological conditions may cause increased pollutant concentrations in the ambient air. Fig-1 presents a topographic map of the source region.



Fig-1: Topographic map of the source region

3.2 Climate and Meteorological Conditions of the Region

The climate of the source region is typical for its long and dry summer with high coefficient of windless periods and small rainfall quantity. Winter period is short and relatively soft with greater percentage and quantity of rainfall than summer period. There are breeze currents with east – west direction circulating along Varna Lake and Beloslav Lake. At day time breeze currents come from east while at night they come from west. Moderate winds are typical for the region. The terrain

advantages the formation of inversion fog and considerable pollution of the ambient air. Statistical data indicates that about 60 % of calendar days are foggy.

Fig-2 and Fig-3 present wind roses built for the source region for 2005 and 2012. Both figures indicate that most winds come from southeast with speed varying from 1.54 to 3.09 m/s. Winds with speed over 5.14 m/s are very unusual and mostly come from north-northeast. The percentage of windless periods is very low.

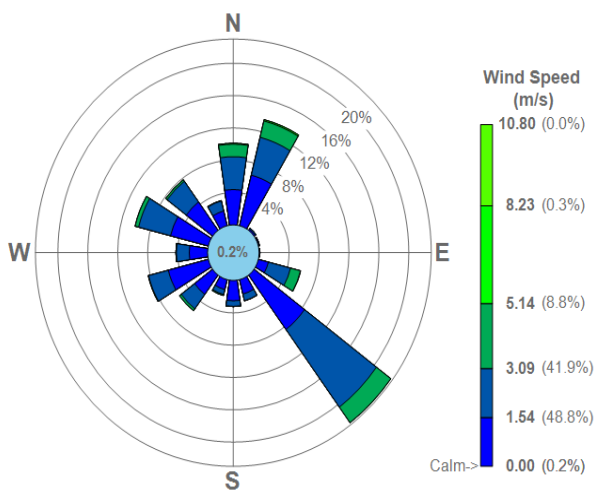


Fig-2: Wind rose for 2005

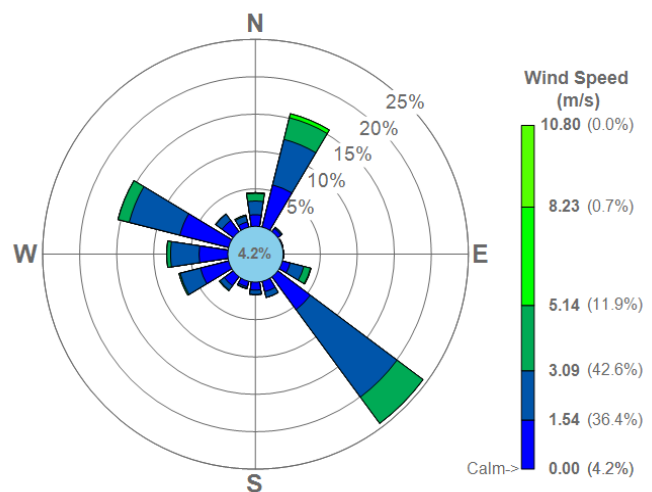


Fig-3: Wind rose for 2012

3.3 Results

Within the present research a single organized source of N₂O emissions is studied – P1 stack at the nitric acid plant. The height of the stack is 130 m and the diameter is 1.44 m. Due to the fact that N₂O is inert in the troposphere and emissions are expected to expand on long distance from the source the study area is determined with the following proportions – 20000 m on west – east direction and 10000 m on south – north direction. The density of the recipients with a certain N₂O concentration is 41 recipients on x (east) and 21 recipients on y (north) with 500 m step or the total amount of the recipients is 861.

Using BREEZE AERMOD software a simulation of N₂O emission dispersion is done. Hourly average and annual average N₂O concentration in the ground atmospheric layer are calculated.

Table-1 indicates calculation results for peak values of hourly average N₂O concentration, recipients’ coordinates and elevation and date/time when peak values are obtained.

Table-1: Peak values of hourly average N₂O concentration (µg/m³)

Avg . Per.	High	Type	Val	Date	UTM		Elev.	Hil l Ht.	Flag Ht.	Rec. Typ e	Grid ID
				YYMMDD HH	East (m)	North (m)	(m)	(m)	(m)		
Simulation without secondary catalyst being installed and meteorological data for 2005											

1HR	1ST	Avg. Conc.	301.96247	5/09/17/18	553291.95	4783610.56	0	0	2	GC	R0G02000
Simulation without secondary catalyst being installed and meteorological data for 2012											
1HR	1ST	Avg. Conc.	16705.48516	12/10/28/01	553785.9	4784607.48	155.1	209	2	GC	MN101000
Simulation with secondary catalyst being installed and meteorological data for 2005											
1HR	1ST	Avg. Conc.	117.69145	5/01/19/10	554791.95	4783610.56	0	0	2	GC	R0G02000
Simulation with secondary catalyst being installed and meteorological data for 2012											
1HR	1ST	Avg. Conc.	3126.84989	12/01/25/05	553785.9	4784607.48	155.1	209	2	GC	MN101000

As indicated in Table-1 results show a significant decrease of hourly average N₂O concentration in the ambient air after the implementation of the secondary decomposing catalyst. Simulation without secondary catalyst being installed and meteorological data for 2005 indicates that the peak value of hourly average N₂O concentration is 302 µg/m³ while simulation with secondary catalyst being installed and meteorological data for the same year indicates hourly average N₂O concentration of 117.7 µg/m³ which is 2.5 times lower. Simulation without secondary catalyst being installed and meteorological data for 2012 indicates that the peak value of hourly average N₂O concentration is 16705.5 µg/m³ while simulation with secondary catalyst being installed and meteorological data for the same year indicates hourly average N₂O concentration of 3126.8 µg/m³ which means 81 % reduction of N₂O level in the ambient air. Specific

meteorological conditions in 2012 (e.g. ambient air temperature, atmospheric stability class determined by the mixing height, sun radiation, etc.) need to be emphasized leading to higher N₂O concentrations in the ground atmospheric layer. Simulation with secondary catalyst being installed and meteorological data for 2012 indicates that the peak value of hourly average N₂O concentration in the ground atmospheric layer is 10 times higher than the peak value of the simulation without secondary catalyst being installed and meteorological data for 2005. This proves the necessity of modeling 4 simulations for every combination of meteorological data and process conditions.

Figures 4 – 7 present contours of hourly average N₂O concentration (µg/m³) in the ground atmospheric layer for every simulation.

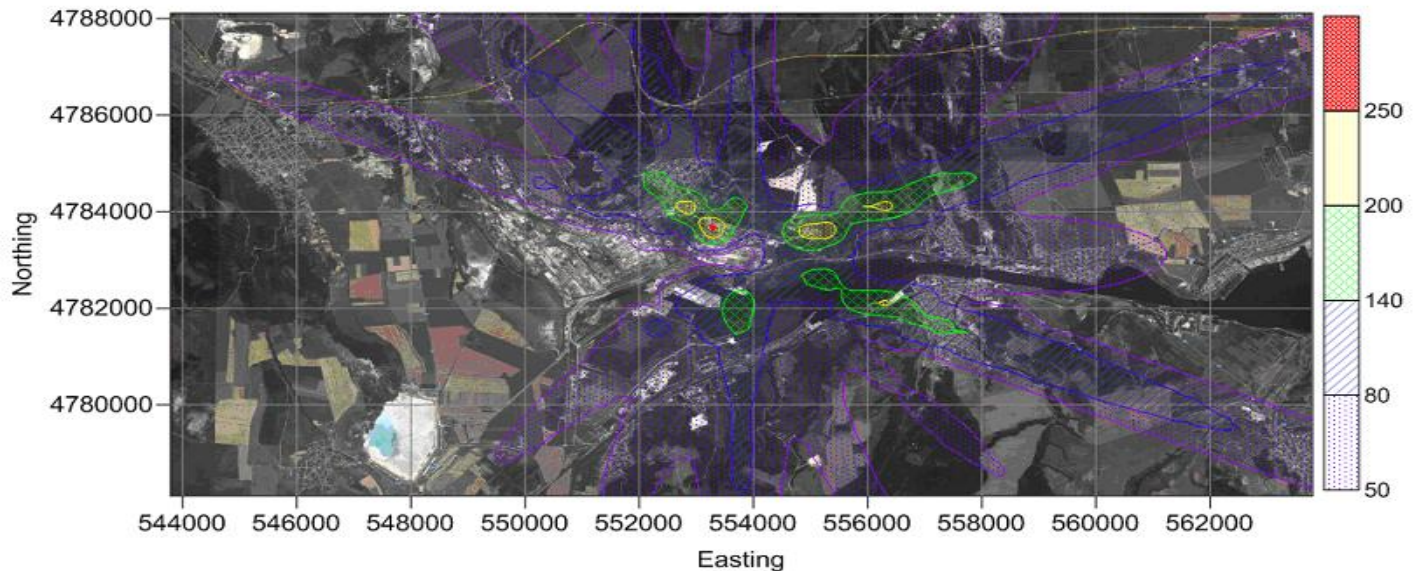


Fig -4: Hourly average N₂O concentration (µg/m³) without secondary catalyst being installed and meteorological data for 2005

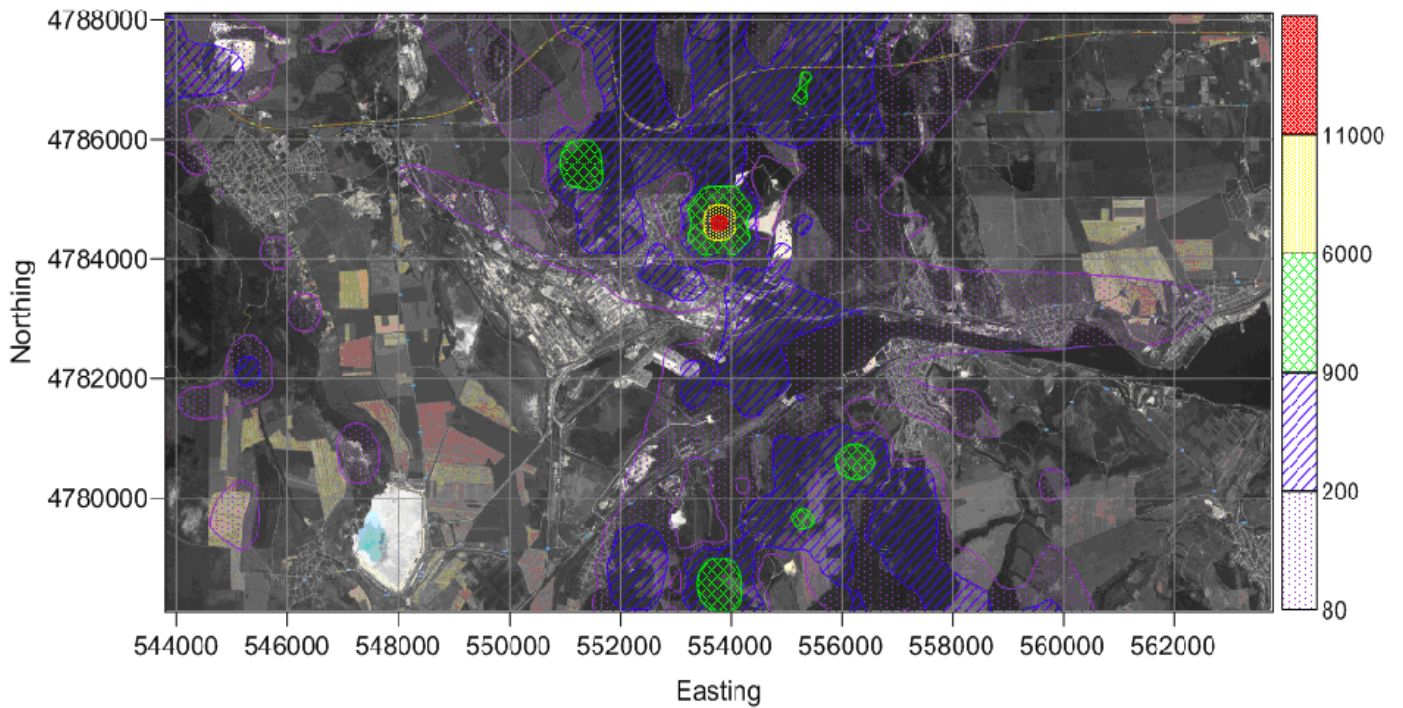


Fig -5: Hourly average N₂O concentration (µg/m³) without secondary catalyst being installed and meteorological data for 2012

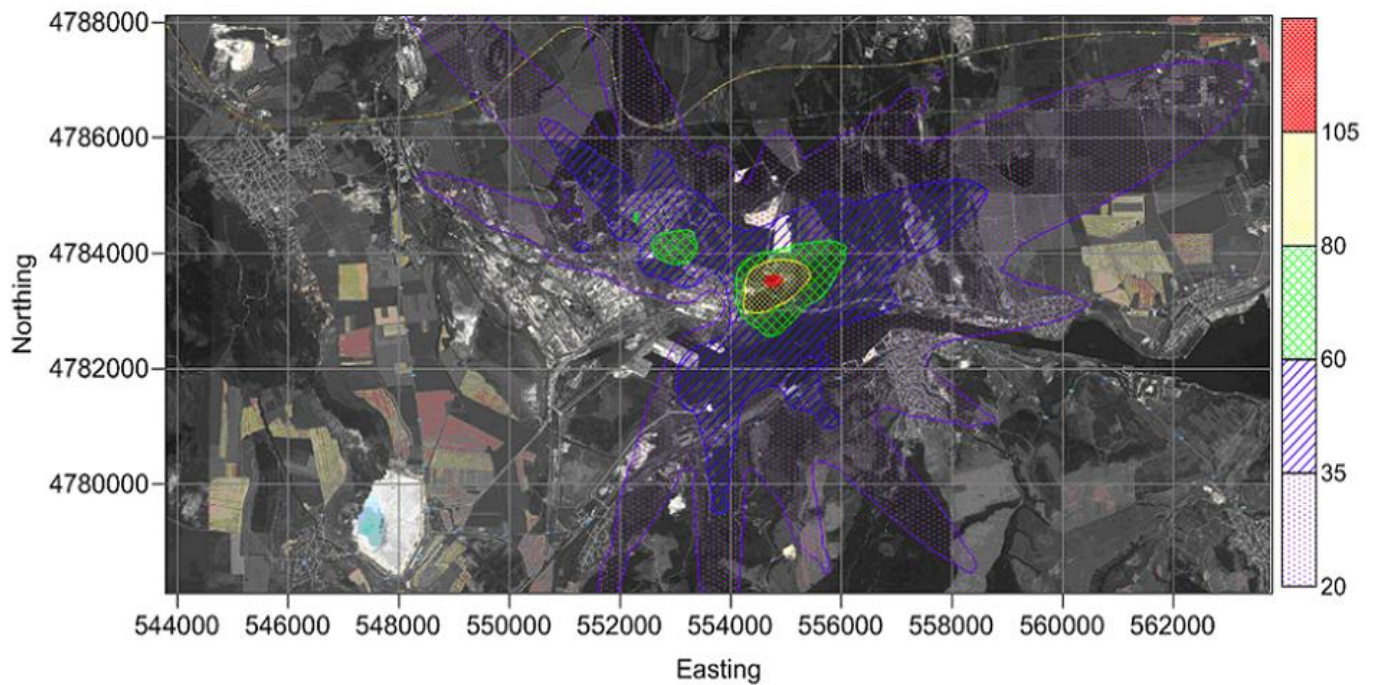


Fig-6: Hourly average N₂O concentration (µg/m³) with secondary catalyst being installed and meteorological data for 2005

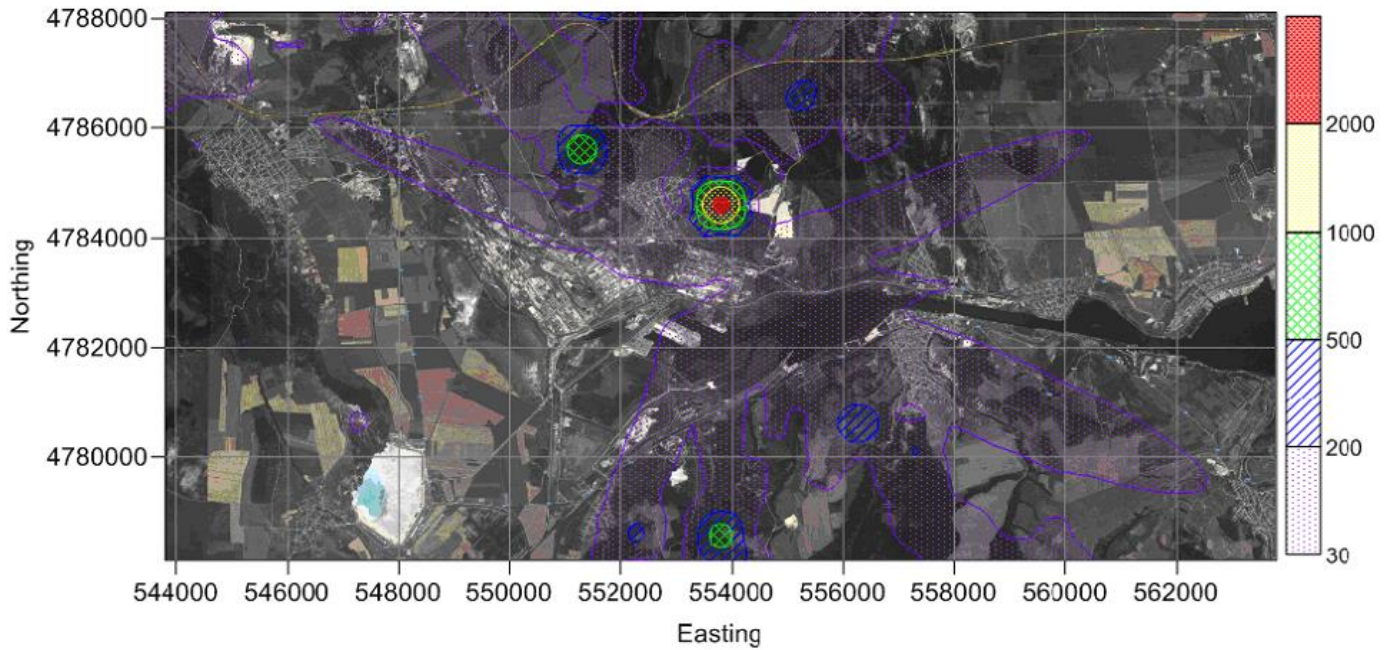


Fig-7: Hourly average N₂O concentration (µg/m³) with secondary catalyst being installed and meteorological data for 2012

The peak value of hourly average N₂O concentration for simulation without secondary catalyst being installed and meteorological data for 2005 is obtained at 18.00 h on 17 September 2005 with southeast wind blowing with speed 2.53 m/s (Table-1 and Fig-4) while the peak value for simulation with secondary catalyst being installed and meteorological data for the same year is obtained in January with west-northwest wind blowing with speed 0.5 m/s (Table-1 and Fig-6). Logically the implementation of the secondary decomposing catalyst leads to 61 % decrease of the hourly average N₂O concentration due to significant N₂O emission reduction at the nitric acid plant.

Peak values of hourly average N₂O concentration in the ground atmospheric layer for both simulations with meteorological data for 2012 are obtained with south wind blowing with speed 2 m/s – in October for simulation without secondary catalyst being installed (Table-1 and Fig-5) and in

January for simulation with secondary catalyst being installed (Table-1 and Fig-7). Both peak values are registered in the same recipient with higher elevation than the source height. Excluding the impact of the adverse meteorological conditions in 2012 a significant decrease of hourly average N₂O concentration is calculated – over 81 % reduction for simulation with secondary catalyst being installed compared to simulation without secondary catalyst being installed. Beside N₂O concentration decrease a significant reduction of N₂O dispersion area in the atmosphere is observed. As indicated on Fig-5 and Fig-7 the area with hourly average N₂O concentration below 200 µg/m³ [20, 21] is 29 km² for simulation without secondary catalyst being installed and less than 2 km² for simulation with secondary catalyst being installed.

Peak values of annual average N₂O concentration and recipients’ coordinates and elevation are presented in Table-2.

Table-2: Peak values of annual average N₂O concentration (µg/m³)

High	Avg. Conc.	UTM		Elev. (m)	Hill Ht. (m)	Flag Ht. (m)	Rec. Type	Grid ID
		East (m)	North (m)					
Simulation without secondary catalyst being installed and meteorological data for 2005								
1ST	8.92915	553291.95	4783610.56	0	0	2	GC	R0G02000

Simulation without secondary catalyst being installed and meteorological data for 2012								
1ST	48.37149	551285.9	4785607.48	157.2	260	2	GC	MN101000
Simulation with secondary catalyst being installed and meteorological data for 2005								
1ST	2.11113	553291.95	4783610.56	0	0	2	GC	R0G02000
Simulation with secondary catalyst being installed and meteorological data for 2012								
1ST	9.57512	551285.9	4785607.48	157.2	260	2	GC	MN101000

Results in Table-2 indicate that annual average N_2O concentration in the ground atmospheric layer is over $8.9 \mu\text{g}/\text{m}^3$ for simulation without secondary catalyst being installed and meteorological data for 2005 and $2.1 \mu\text{g}/\text{m}^3$ for simulation with secondary catalyst being installed and meteorological data for the same year which is over 4 times lower. For simulation with secondary catalyst being installed and meteorological data for 2012 annual average N_2O concentration is $9.6 \mu\text{g}/\text{m}^3$ which is over 5 times lower than the peak value for simulation without secondary catalyst being installed and meteorological data for the same year.

Comparison between simulations with and without secondary catalyst being installed and meteorological data for 2005 indicates that 76.4 % reduction of annual average N_2O concentration has been achieved. Comparison between both simulations with meteorological data for 2012 indicates 80.2 % reduction of annual average N_2O concentration.

Figures 8 - 11 present contours of annual average N_2O concentration ($\mu\text{g}/\text{m}^3$) in the ground atmospheric layer for every simulation

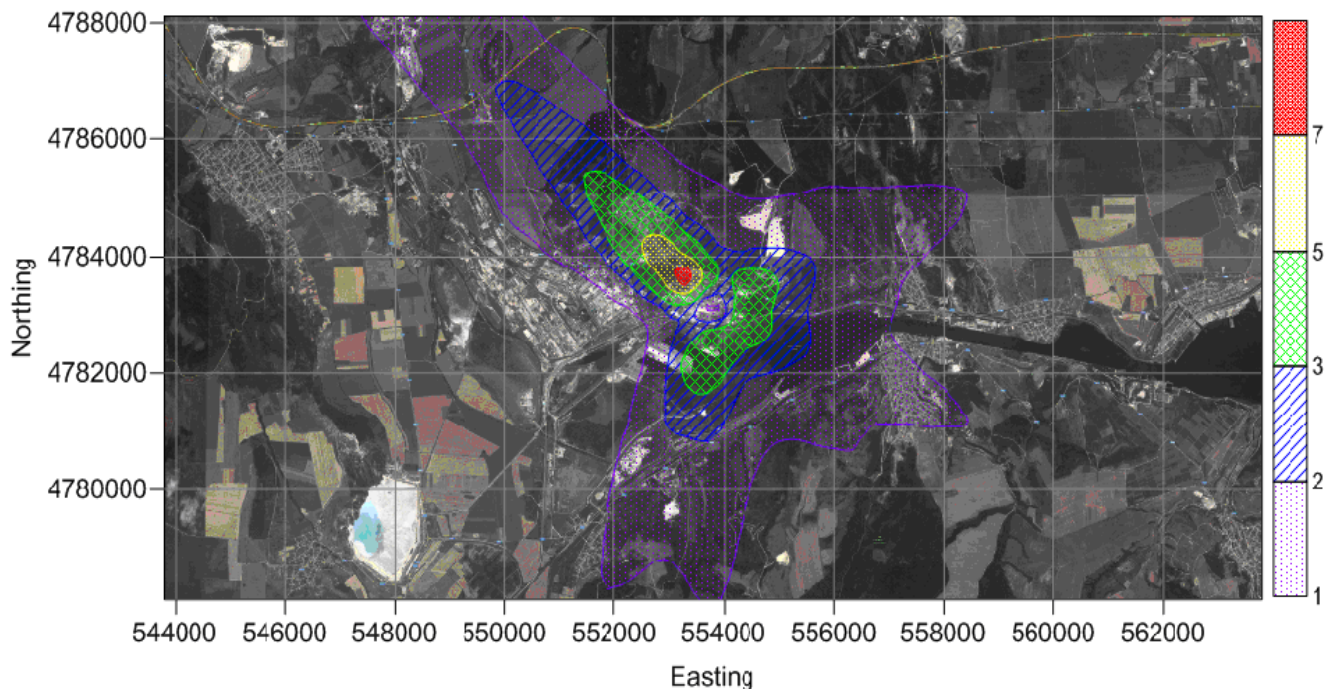


Fig-8: Annual average N_2O concentration ($\mu\text{g}/\text{m}^3$) without secondary catalyst being installed and meteorological data for 2005

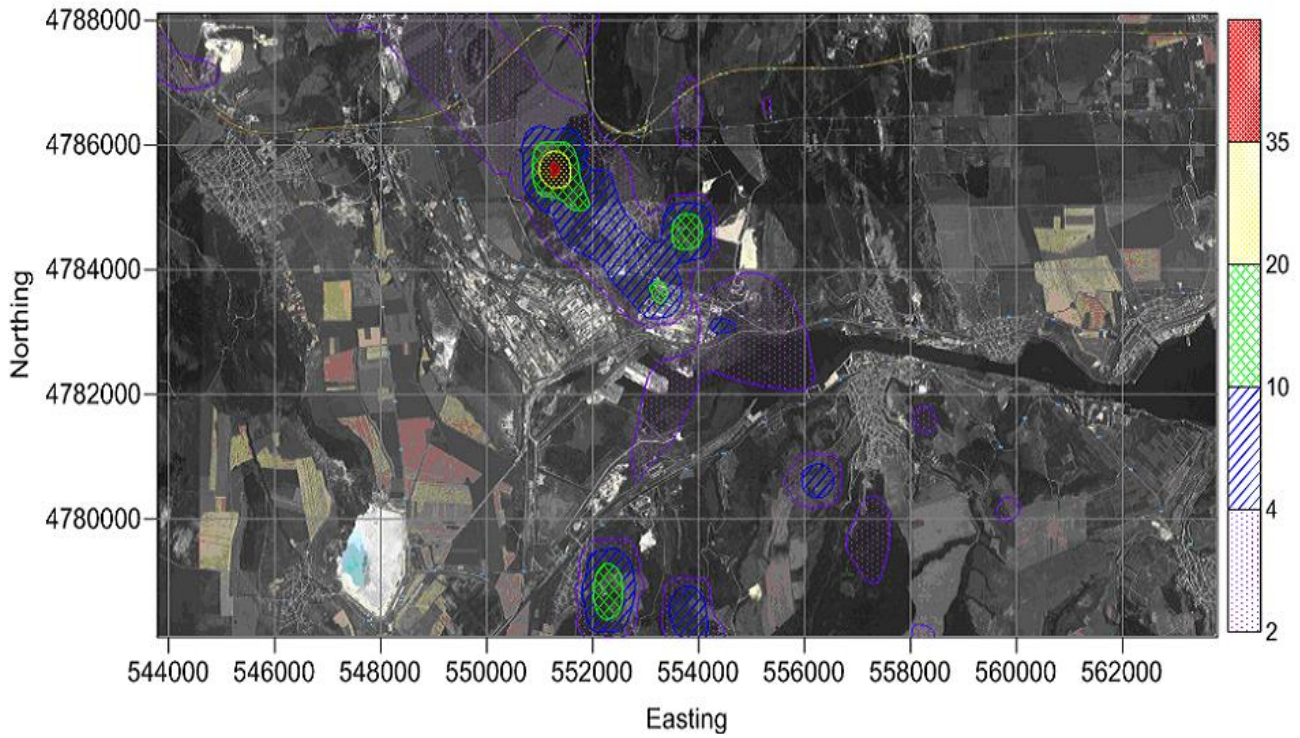


Fig-9: Annual average N₂O concentration ($\mu\text{g}/\text{m}^3$) without secondary catalyst being installed and meteorological data for 2012

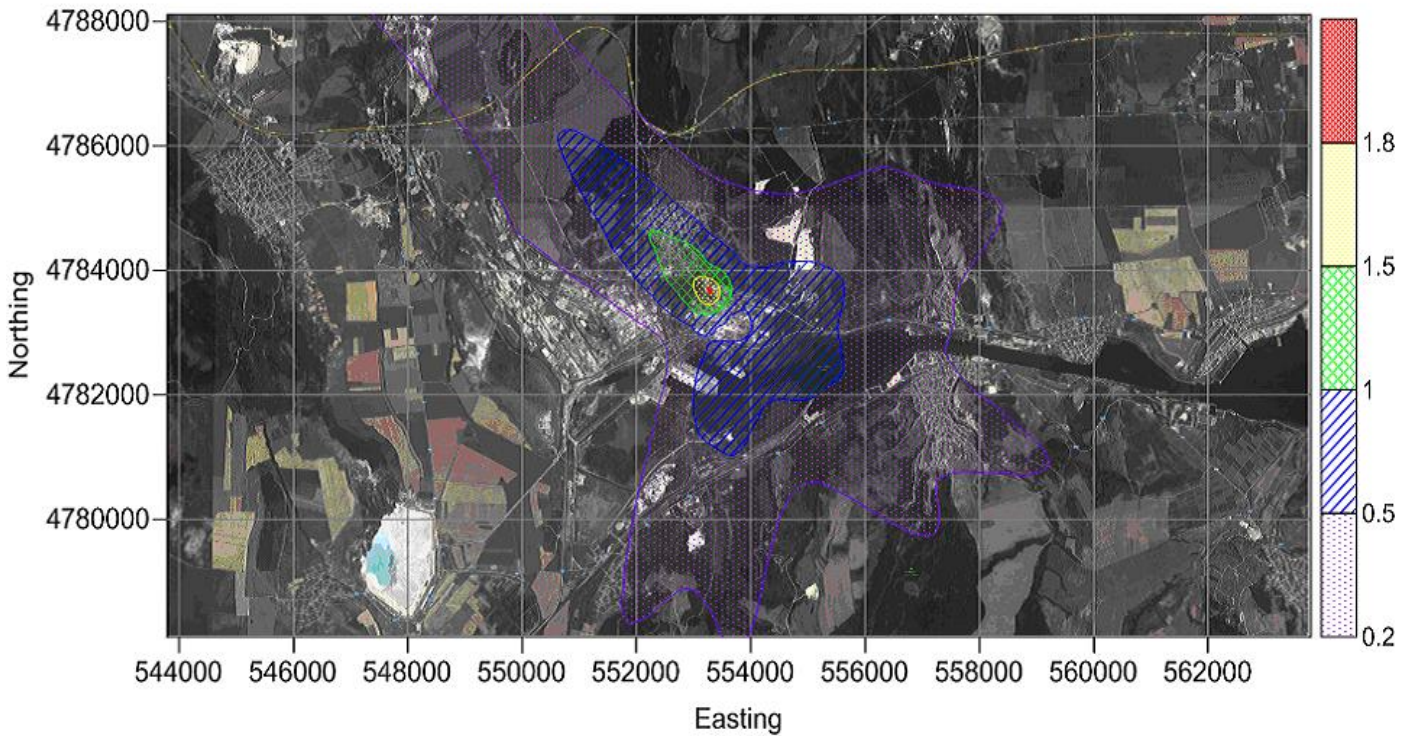


Fig-10: Annual average N₂O concentration ($\mu\text{g}/\text{m}^3$) with secondary catalyst being installed and meteorological data for 2005

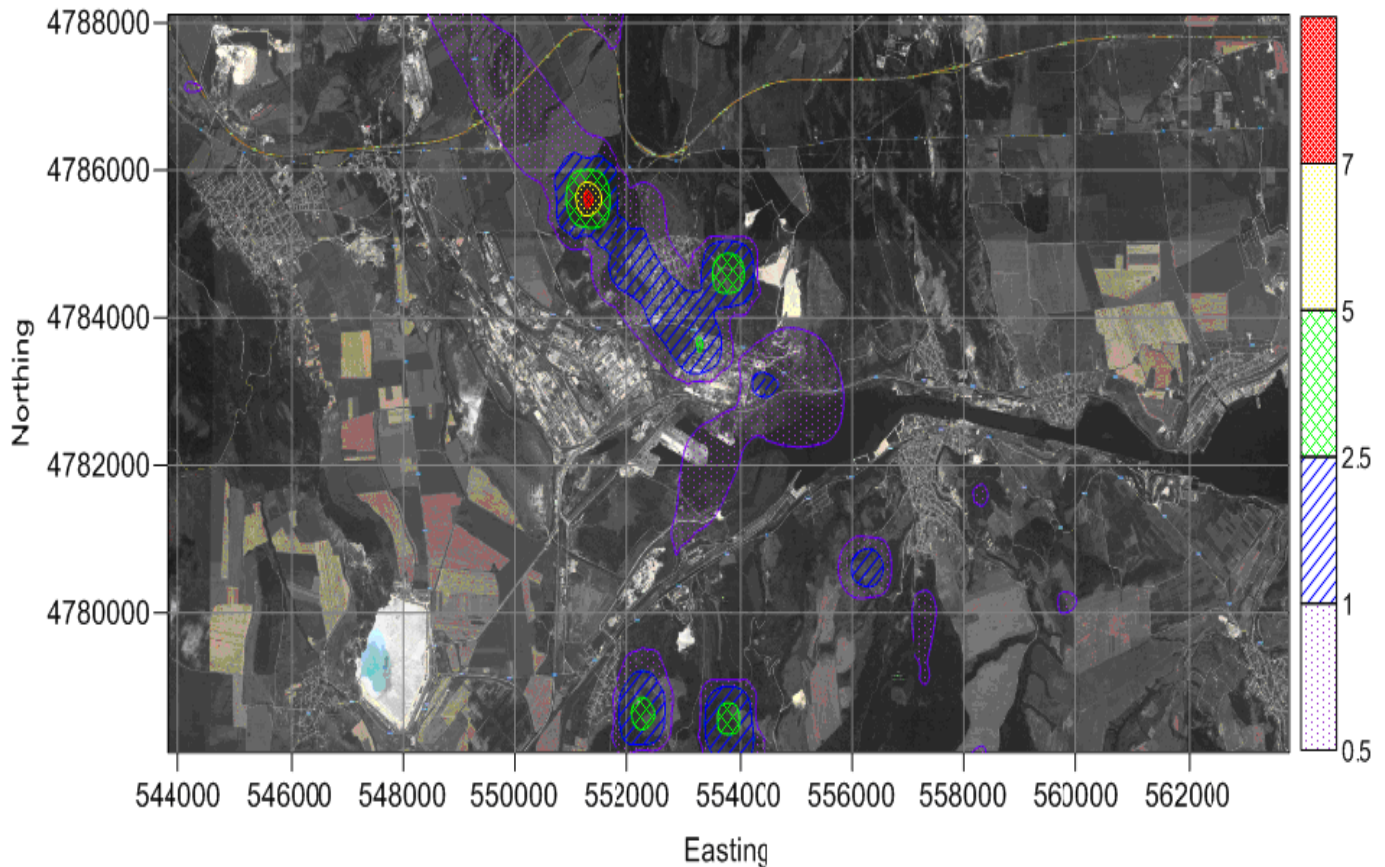


Fig-11: Annual average N_2O concentration ($\mu g/m^3$) with secondary catalyst being installed and meteorological data for 2012

As indicated on Figures 8 – 11 annual average N_2O concentration in the ground atmospheric layer depends strongly on the meteorological conditions of the region. Adverse meteorological conditions in 2012 affect the dispersion of N_2O emissions thus causing 4 times higher annual average N_2O concentrations than peak values calculated for simulations with meteorological data for 2005. Although meteorological conditions have considerable influence upon N_2O emission dispersion a significant decrease of annual average N_2O concentration is registered after the implementation of the secondary decomposing catalyst in the nitric acid plant. By analogy with the results obtained for hourly average N_2O concentration modeling annual average N_2O concentration in the atmosphere proves significant decrease of N_2O emission dispersion area. As presented on Fig-8 and Fig-10 the area with annual average N_2O concentration below $2 \mu g/m^3$ is over 20 km^2 for simulation without secondary catalyst being installed while for simulation with secondary catalyst being installed N_2O concentration below $2 \mu g/m^3$ is registered on a small area directly next to the emission source.

4. CONCLUSIONS

Research results indicate a significant decrease of N_2O concentration in the ground atmospheric layer after the implementation of the secondary decomposing catalyst in the nitric acid plant – 71 % average reduction of hourly average N_2O concentration and 78 % average reduction of annual average N_2O concentration for all the simulations done. Beside the reduction of N_2O concentration a significant decrease of N_2O emission dispersion area in the ground atmospheric layer is observed. Research results prove the reduction potential of the secondary decomposing catalyst and the positive effect of N_2O emission reduction upon ambient air quality in the source region. On that basis a conclusion is made that nitric acid plants with similar parameters can be situated directly next to urban areas without causing adverse effect upon ambient air quality having in mind the topography of the region and possible cumulative effect with other air pollutant sources [22]. High temperature catalytic reduction of N_2O emissions from nitric acid production is proved to be an effective measure for atmospheric N_2O concentration decrease and a tool to combat adverse changes of global climate system.

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