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ASSESMENT OF NOx EMISSIONS FROM NITRIC ACID PRODUCTION AND THEIR EFFECT UPON AMBIENT AIR QUALITY IN DEVNYA REGION

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Abstract: *Within this research data from monitoring of ambient air quality in Devnya region for the period 2006 – 2012 regarding the concentration of oxides of nitrogen NOx has been analyzed along with data from monitoring of NOx and nitrous oxide N_2O emissions from a nitric acid plant situated in the industrial zone of Devnya for the same period. Results indicate that NOx and N_2O emissions have significant effect upon the quality of the atmospheric air in the region but monitoring data is not a sufficient source to assess the contribution of these pollutants to ambient air quality. A necessity of mathematical modeling the diffusion of N_2O emissions is concluded having in mind the processes of photo dissociation, chemical destruction and dispersion of this air pollutant that occur in the ground atmospheric layer and estimating the effect of the secondary pollutants proceeded from these reactions upon ambient air quality.*

Key words: *ambient air quality, greenhouse gas, mathematical modeling, nitrous oxide emissions, oxides of nitrogen*

I. Introduction

Nitric acid production is a major industrial source emitting oxides of nitrogen NOx that contain mainly nitric oxide NO, nitrogen dioxide NO_2 and nitrous oxide N_2O. Nitrous oxide is a greenhouse gas under the Kyoto Protocol [1] and one of the main reasons for global warming effect [2]. Besides causing adverse changes of the climate system this greenhouse gas emissions have significant effect upon ambient air quality in the regions where industrial sources of N_2O are available. In order to protect human health and the environment as a whole it is extremely important to combat harmful emissions at source. Contributions from natural sources can be assessed but can not be controlled that's why it is a matter of great importance to apply most effective emission abatement techniques at emission source especially when it comes to industrial sources [3-5]. Various techniques for N_2O emission reduction at nitric acid production are developed worldwide [6-8]. Regionally reducing N_2O emissions from an industrial source is proved to have positive effect upon ambient air quality [11-12] while globally it is a tool for global warming prevention.

The present research aims to assess the effect of NOx emissions from an industrial source situated in the industrial zone of Devnya upon ambient air quality in the region.

II. Material and methods

The research is done in the industrial zone of Devnya, Bulgaria where an industrial emission source is situated – emission source P1 at a nitric acid plant. Within this research data from an automatic system for continuous monitoring of NOx and N_2O concentration in the tail gas from emission source P1 for the period 2006 – 2012 has been analyzed, data being expressed as average monthly concentrations and average annual concentrations in mg/m^3. Regarding the assessment of ambient air quality in Devnya region monitoring data about the average monthly concentrations and average annual concentrations of NOx in µg/m^3 for the same period has been used – monitoring data is collected by the automatic monitoring system “Izvorite” which is a part of the National monitoring system for ambient air quality at the Ministry of Environment and Water. The monitoring system “Izvorite” is not equipped to measure the concentration of N_2O in the ambient air and for that reason it is possible to observe only the tendency for NOx pollution. The monitoring period is coordinated with the initial implementation of N_2O emission abatement technique at the nitric aid plant [11] by installing a secondary decomposing catalyst and an automatic system for continuous monitoring of NOx and N_2O concentrations in the tail gas in 2006.

Concentration of NOx in the ambient air is the summary concentration of NO and NO_2 added as parts per billion (ppb) and expressed as concentration of NO_2 in µg/m^3 [9]. Emission limit values ELV for NOx concentrations refer to summary emissions of NO and NO_2 expressed as NO_2 in mg/m^3 [10]. All ELV and air pollutant concentrations in µg/m^3 or mg/m^3 refer to temperature 273 K and pressure 1013 hPa including after humidity correction [10].

III. Results and discussion

III.1. Quantitative assessment of NOx emissions from nitric acid plant

Monitoring data regarding average monthly NOx concentrations (mg/m^3) in the tail gas from emission source P1 at a nitric acid plant situated in the industrial zone of Devnya for the period 2006 – 2012 is indicated in Table 1. Data analysis indicates that for the entire monitoring period average monthly NOx concentrations in the tail gas from emission source P1 do not exceed ELV. Despite that some differences are observed. At the beginning of the research 2006 – 2008 NOx concentrations are quite higher and vary between 300 and 450 mg/m^3. The highest value for this period is registered in August 2006 – 455.93 mg/m^3. Quite high concentrations are registered through the entire 2007 – from 373.63 mg/m^3 to 440.01 mg/m^3.

Table 1. NOx concentrations in the tail gas from emission source P1 at nitric acid plant for the period 2006 – 2012, mg/m^3

Period	2006	2007	2008	2009	2010	2011	2012
January	316.85	422.57	411.59	322.03	243.03	292.29	291.94
February	317.90	412.47	382.63	344.05	221.83	269.91	295.31
March	322.03	419.33	376.38	358.74	222.10	259.01	295.99
April	343.63	403.37	415.96	372.63	213.16	277.01	*
May	366.20	378.67	348.17	*	218.31	308.32	306.19
June	392.98	440.01	368.99	*	*	346.84	325.89
July	*	*	450.21	*	*	398.62	*
August	455.93	373.63	374.32	382.78	242.94	328.65	344.87
September	379.86	402.70	332.89	380.14	283.77	330.24	263.99
October	339.64	434.70	319.51	333.76	275.35	278.90	253.30
November	329.85	416.42	258.33	311.58	299.74	252.24	313.15
December	388.64	398.26	*	281.27	262.96	273.90	223.39

* Nitric acid plant is not operating

After 2009 lower concentrations are registered as the lowest value is 213.16 mg/m^3 registered in April 2010 which is 2.14 times lower than the highest value registered for the entire monitoring period. The reason for NOx concentration drop during the second half of the monitoring period (after 2009) is the replacement of the secondary decomposing catalyst at the nitric acid plant which took place in November 2009 due to its' reduction potential exhaustion [12].

Figure 1 represents average annual NOx concentrations in the tail gas from emission source P1. It is obvious that neither concentration exceeds ELV. The highest average annual concentration is registered in 2007 – 409.28 mg/m^3 while the lowest concentration is 248.32 mg/m^3 registered in 2010. The average annual NOx concentration drop follows the replacement of the secondary catalyst.

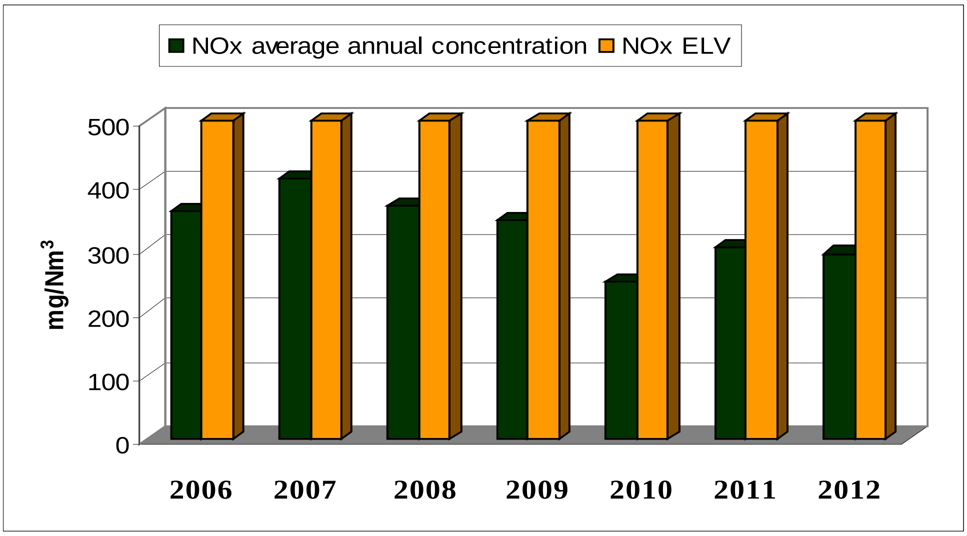

Figure 1. Average annual NOx concentrations in the tail gas from emission source P1 for the period 2006 - 2012

III.2. Quantitative assessment of N_2O emissions from nitric acid plant

Monitoring data regarding average monthly N_2O concentrations (mg/m^3) in the tail gas from emission source P1 at a nitric acid plant situated in the industrial zone of Devnya for the period 2006 – 2012 is indicated in Table 2.

Table 2. N_2O concentrations in the tail gas from emission source P1 at nitric acid plant for the period 2006 – 2012, mg/m^3

Period	2006	2007	2008	2009	2010	2011	2012
January	404.00	534.20	732.70	558.30	316.30	448.10	474.90
February	395.00	597.50	773.50	783.90	359.20	474.40	514.50
March	502.00	673.70	867.40	908.60	389.30	550.60	588.70
April	497.50	715.50	1023.50	979.50	454.70	613.80	*
May	563.70	695.00	835.50	*	358.80	663.30	553.20
June	548.70	775.10	700.50	*	*	674.90	491.00
July	*	*	978.30	*	*	373.60	*
August	151.10	406.50	110.50	728.80	223.10	250.50	69.40
September	199.40	525.30	219.60	711.00	343.60	344.40	75.40
October	267.60	609.90	440.80	716.60	418.90	414.70	82.80
November	223.90	624.10	496.30	884.50	471.60	388.50	98.30
December	439.50	707.90	*	448.10	434.60	428.80	105.80

* Nitric acid plant is not operating

For the monitoring period high temperature catalytic reduction of N_2O emissions is applied at the nitric acid plant throughout installing a secondary decomposing catalyst which converts N_2O to oxygen and nitrogen [11]. A research upon the behavior of the catalyst along the production campaign proves that the efficiency of the catalytic reduction depends on the duration of the catalyst's operation and the specific technological conditions of the production process [12]. For that reason higher N_2O concentrations are registered at the end of the production campaign (months right before the usual plant shut down for platinum gauze pack replacement once a year) compared to those measured at the start of the campaign (right after the replacement of the platinum gauze pack). A solid trend for higher N_2O concentrations in the tail gas (over 800 – 900 mg/m^3**)** indicates the exhaustion of the secondary catalyst's reduction potential and the necessity of its replacement. The highest average monthly N_2O concentration for the entire monitoring period is 1023.50 mg/m^3 registered in April 2008 due to nitric acid plant operation at increased capacity at the end of the production campaign. The lowest average monthly N_2O concentration is 69.4 mg/m^3 registered in August 2012 due to simultaneous replacement of the secondary decomposing catalyst and the platinum gauze pack.

III.3. Assessment of ambient air quality in Devnya region regarding NOx

Monitoring data from automatic monitoring system “Izvorite” regarding average monthly NOx concentrations (μg/m^3) in the ambient air in Devnya region for the period 2006 – 2012 is indicated in Table 3.

Table 3. NOx concentrations in the ambient air in Devnya region for the period 2006-2012, μg/m^3

Period	2006	2007	2008	2009	2010	2011	2012
January	20.84	22.01	36.06	*	20.51	27.24	13.30
February	19.77	25.65	33.16	*	20.99	28.09	15.63
March	17.59	26.08	22.27	25.44	18.74	28.13	13.61
April	43.00	28.82	17.92	30.84	18.55	12.86	10.78
May	51.27	27.84	18.70	26.42	14.59	18.97	7.29
June	49.07	26.55	19.16	19.95	13.36	12.51	7.75
July	47.07	32.27	21.22	16.40	13.38	13.22	*
August	47.41	12.62	32.89	14.25	16.96	17.32	10.19
September	32.48	14.89	26.13	14.45	16.21	16.73	10.87
October	24.13	17.08	25.35	10.04	15.93	18.16	10.97
November	30.88	10.53	20.90	24.26	31.21	24.09	10.77
December	*	26.37	23.70	22.33	32.67	21.81	22.28

* No data available

Analysis of the monitoring data from the automatic monitoring system “Izvorite” indicates that the average monthly NOx concentrations are higher at the beginning of the research 2006 – 2008 as well and the highest value is registered in May 2006 – 51.27 μg/m^3. In 2008 NOx concentrations scale up to 36.06 μg/m^3. After 2009 NOx concentrations gradually decrease and in 2012 they vary between 7.29 μg/m^3 and 22.28 μg/m^3. The NOx concentrations drop during the second half of the monitoring period is caused by the significant reduction of NOx and N_2O emissions from the nitric acid plant after the replacement of the secondary decomposing catalyst.

Results represented on Figure 2 indicate that neither average annual NOx concentration for the entire monitoring period exceeds the annual average limit value for human health protection 40 μg/m^3 [9]. A comparable trend is observed regarding the NOx pollution of the ambient air - average annual NOx concentrations significantly decrease after the replacement of the secondary catalyst at the nitric acid plant as the lowest value for the entire monitoring period is 12.13 μg/m^3 registered in 2012.

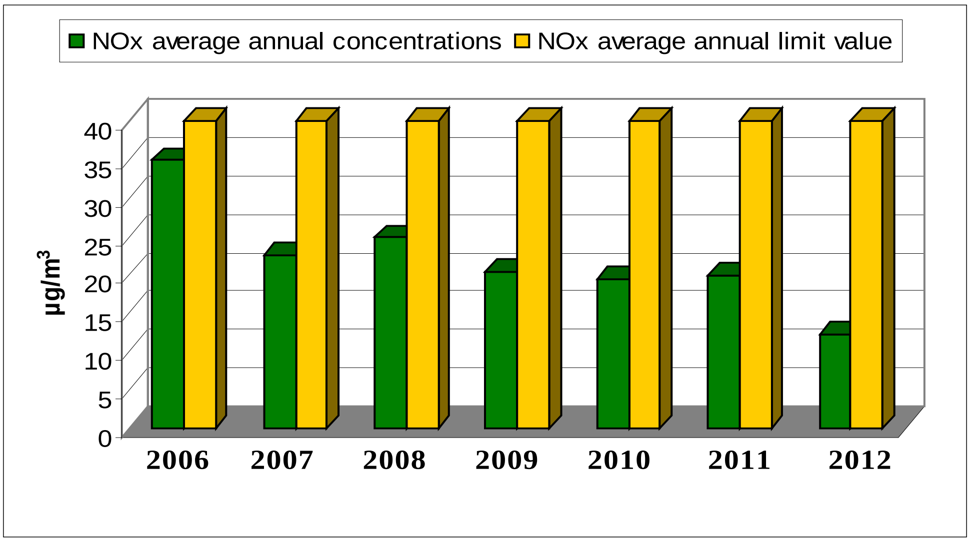

Figure 2. Average annual NOx concentrations in the ambient air in Devnya region for the period 2006 - 2012

III.4. Assessment of NOx emissions upon ambient air quality in Devnya region

NOx emissions mainly contain NO which consequently oxidizes to NO_2 with the participation of ozone and other oxidizers. At oxidizing process unsaturated hydrocarbons and carbon monoxide CO take part as these air pollutants are available in the environment. Spatial distribution of NO_2 depends mainly on chemical reactions of NO transformation to NO_2, photochemical equilibrium with ozone and other oxidizing agents in the atmosphere [13]. Nitrous oxide N_2O is destroyed in the atmosphere by photo dissociation as follows – Equation (1) [14]:

$$\left.\begin{aligned} &N_2O + h\nu \rightarrow N_2 + O(^1D), && \lambda<3370\ \text{Å} \\ &\rightarrow N_2 + O(^1S), && \lambda<2100\ \text{Å} \\ &\rightarrow NO + N(^4S) && \lambda<2500\ \text{Å} \end{aligned}\right\} \qquad (1)$$

Additional destruction occurs chemically as follows - Equation (2):

$$\left.\begin{aligned} &O(^1D) + N_2O \rightarrow NO + NO, \\ &\rightarrow N_2 + O_2 \end{aligned}\right\} \qquad (2)$$

It is indicated that N_2O destruction in the atmosphere leads mainly to formation of NO, nitrogen and oxygen. The content of NO as a product of N_2O destruction affects the ambient air quality in addition to other NOx emission sources.

Monitoring data analysis indicates that certain dependence between NOx emission levels from an industrial source and NOx concentration in the ambient air of the region is observed.

More detailed information about the correlation between NOx emissions and NOx concentrations in the atmosphere can be provided by mathematical modeling the distribution of polluting emissions from emission source P1 in the ground atmospheric layer of Devnya region. Modeling process should take into consideration N_2O diffusion, photo dissociation and chemical destruction in the atmosphere as well as cumulative effect of the formed reaction products upon ambient air quality in the region. Mathematical modeling in order to assess the effect of N_2O emissions upon ambient air quality is a subject of further scientific research.

IV. Conclusions

In regions where NOx and N_2O emission sources are available ambient air quality regarding NOx (NO and NO_2) content depends on the emission levels and the specific climate and topographic conditions in the region as they define the parameters of pollutants' distribution in the ground atmospheric layer along with the processes of photo dissociation, chemical destruction and diffusion. Nitrous oxide N_2O is a greenhouse gas and limiting its' emissions is a significant tool for climate change combat. Monitoring data is not a sufficient source to define the contribution of N_2O emissions to ambient air quality in the region regarding NOx concentrations. That's why mathematical modeling should be done by using appropriate software tool and detailed database containing information about N_2O emission levels, climate and topographic conditions in the region for the entire monitoring period.

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