TECHNICAL ENGINEERING IN INDUSTRIAL IPPC AS A KEY TOOL FOR AMBIENT AIR QUALITY IMPROVEMENT

Rozalina Chuturkova[1], Maya Stefanova[2], Silviya Radeva[3], Dimitrichka Marinova[4]

[1]*Associate Professor, Department of Ecology and Environmental Protection, Technical University, Varna, Bulgaria*
[2]*PhD Student, Department of Ecology and Environmental Protection, Technical University, Varna, Bulgaria*
[3]*PhD Student, Department of Ecology and Environmental Protection, Technical University, Varna, Bulgaria*
[4]*Research Associate, Department of Ecology and Environmental Protection, Technical University, Varna, Bulgaria*

Abstract

Ambient air pollution of an industrial region in Bulgaria for the period 2003-2013 has been researched before and after the implementation of the Integrated Pollution Prevention and Control IPPC Directive. The aim of the research is to estimate the effect of applying measures and techniques required by the IPPC permits in order to improve ambient air quality. In the industrial area of Devnya there are plants for production of synthetic soda ash (Solvay Sodi), cement (Devnya Cement), mineral fertilizers (Agropolychim) and thermal power (Deven). Monitoring results indicate that concentrations of NO_2, SO_2, CO, O_3, NH_3 and C_6H_6 in the ambient air have decreased significantly ($P < 0.001$) after the enforcement of the IPPC permits. It is also indicated that harmful emissions from separate industrial sources in the area have been reduced due to applying best available techniques BAT and environment friendly industrial practices. Pursuant to IPPC requirements major investments have been made for modernisation of the existing installations and for building new ones: a new circulating fluidized-bed steam generator with low NOx, SOx and DUST emission potential, a new line for the production of soda ash dense, an emission free distillation column, a new installation for the production of ammonium nitrate solution, a carbonizing column and a limestone blast furnace along with highly efficient tail gas treatment facilities etc. The present study proves that the implementation of the IPPC Directive by technical engineering at industrial and combustion plants is a key tool for the improvement of ambient air quality.

Keywords: *ambient air quality, IPPC permits, industrial plants, combustion plants, BAT*

---***---

1. INTRODUCTION

Integrated pollution prevention and control IPPC permits are required by Directive 2008/1/EO of the European Parliament and of the Council [1] for most industrial and combustion plants that affect ambient air quality. Transposition of the Directive in Bulgaria refers to Regulation on terms and methods for IPPC permits issue [7]. The Regulation establishes a general framework for issuing IPPC permits that determine rules for building and operation of new industrial plants or operation of existing plants in the scope of Annex 4 to the Environmental Protection Law [4].
IPPC permits require the implementation of best available techniques BAT in order to guarantee minimization of negative effect upon the environment in particular upon ambient air quality. Each plant operator determines BAT for the installation based on the conclusions for BAT, adopted by a decision of the European Commission or described in the reference documents on BAT. Guidance documents of the European Commission on the implementation of IPPC Directive provide instructions for applying adequate measures at industrial and combustion plants that affect ambient air quality, such as:

- Modernization of technological processes and implementation of tail gas utilization;
- Introduction of clean technologies (best available industrial practices);
- Substitution of raw materials in order to minimize emissions;
- Implementation of new tail gas treatment facilities or modernization of existing ones;
- Application of appropriate tail gas treatment technologies and reduction of harmful emissions into the atmosphere;
- Enhancement of energy and safety efficiency.

In case planned reconstructions apply BAT pursuant to IPPC permit and referent legislation then plant emissions will be reduced to a level that doesn't have significant adverse effect upon local ambient air quality and will provide air quality that corresponds to emission limit values as stated in the Clean Air Law [2, 3, 5].

Pollution of atmospheric air regarding main harmful substances SO_2, NO_2, CO, CO_2, O_3, NH_3, C_6H_6, PM_{10}, $PM_{2.5}$ and metal aerosols has been studied at various industrial regions along with their influence upon exposed population and different ways of industrial impact on the environment. Attention has been paid to air pollution due to emissions of CO_2, NO_2, SO_2 and their contribution to global warming effect, adverse changes of climate system and ozone depletion [29]. Various sources of air polluting emissions of O_3 and PM_{10} have been researched and major industrial impact has been observed [28]. Ozone precursors have also been studied along with O_3 pollution trends, its influence upon climate changes and ozone population exposure [20]. Some authors have studied atmospheric air pollution due to particulate matter emissions at industrial regions [17, 18, 23, 25, 30] and regression modelling has been applied for PM_{10} day level prognosis taking into consideration various meteorological conditions and their effect [22]. Long term epidemiological research has proved that running levels of PM_{10}, CO, NO_2, SO_2 and O_3 are related to short and long term negative health effects on respiratory and cardio-vascular systems including increased mortality rate [15, 16, 24, 27]. In order to reduce C_6H_6 emissions at industrial and urban areas a strategy has been developed based on continuous monitoring of C_6H_6 concentrations in ambient air along with appropriate technical engineering for emission reduction and management improvement [21, 32]. Dispersion of HF, SO_2, SO_3, NH_3 and PM_{10} emissions from mineral fertilizer production at industrial regions have also been researched and a method for ammonia detection in atmospheric air from small emission sources has been developed [14, 19, 33]. Some authors report that IPPC Directive is a key tool of European environmental legislation for integrated pollution prevention and control at large industrial and combustion plants [26, 31].

The aim of this research is to study atmospheric air pollution at an industrial region before and after the enforcement of IPPC permits in order to estimate the effect of applying measures and techniques required by legal and administrative documents referring to ambient air quality improvement.

2. MATERIAL AND METHODS

The present research has been made at the industrial area of Devnya, in the south-east part of Bulgaria. The town Devnya is situated on a total area of 121.052 km^2 and is about 30 km away from the district city Varna. The town is located in a valley surrounded by low limestone hills that are mountainsides of Stara planina and Dobrudjansko plato sloping down to Beloslav lake to the east and through there to the Black sea. The abundance of groundwater and limestone fields as well as salt deposits advantages development of a large-scale chemical industry in the region. There are two industrial areas in the region:

- North industrial area where an industrial plant for production of cement (Devnya Cement) and a limestone career (Martziana) are located;
- South industrial area where industrial plants for production of synthetic soda ash (Solvay Sodi), mineral fertilizers (Agropolychim), chlorine and polymer materials (Polimeri), a thermal power station (Deven), Varna Zapad port and a phosphogypsum landfill are located.

Atmospheric air pollution has been studied at a monitoring station of the National system for ambient air quality control, part of the Bulgarian Executive Environmental Agency. Automatic monitoring station Izvorite is an industrial / urban background monitoring station with a range 10 - 100 m / 100 m – 2 km. The station is handled by Regional laboratory Varna, which is a department of the Executive Environmental Agency at the Ministry of Environment and Water. The station has been operating as an automatic station for continuous monitoring since 1990 (Eoi code BG0013A-Dv1, geographic coordinates +043.13.12.00/+027.33.40.00). Monitoring data is indicated in real time at the regional control station (Regional inspection of environment and water Varna) and at the central control station (Executive Environmental Agency Sofia, National database on ambient air quality). At the monitoring station Izvorite concentrations of the following pollutants are measured: ozone O_3, nitrogen dioxide NO_2, carbon monoxide CO, sulfur dioxide SO_2, particulate matter 10 µm in diameter PM_{10}, ammonia NH_3 and benzene C_6H_6.

The location of the monitoring station Izvorite is indicated on Fig-1

.

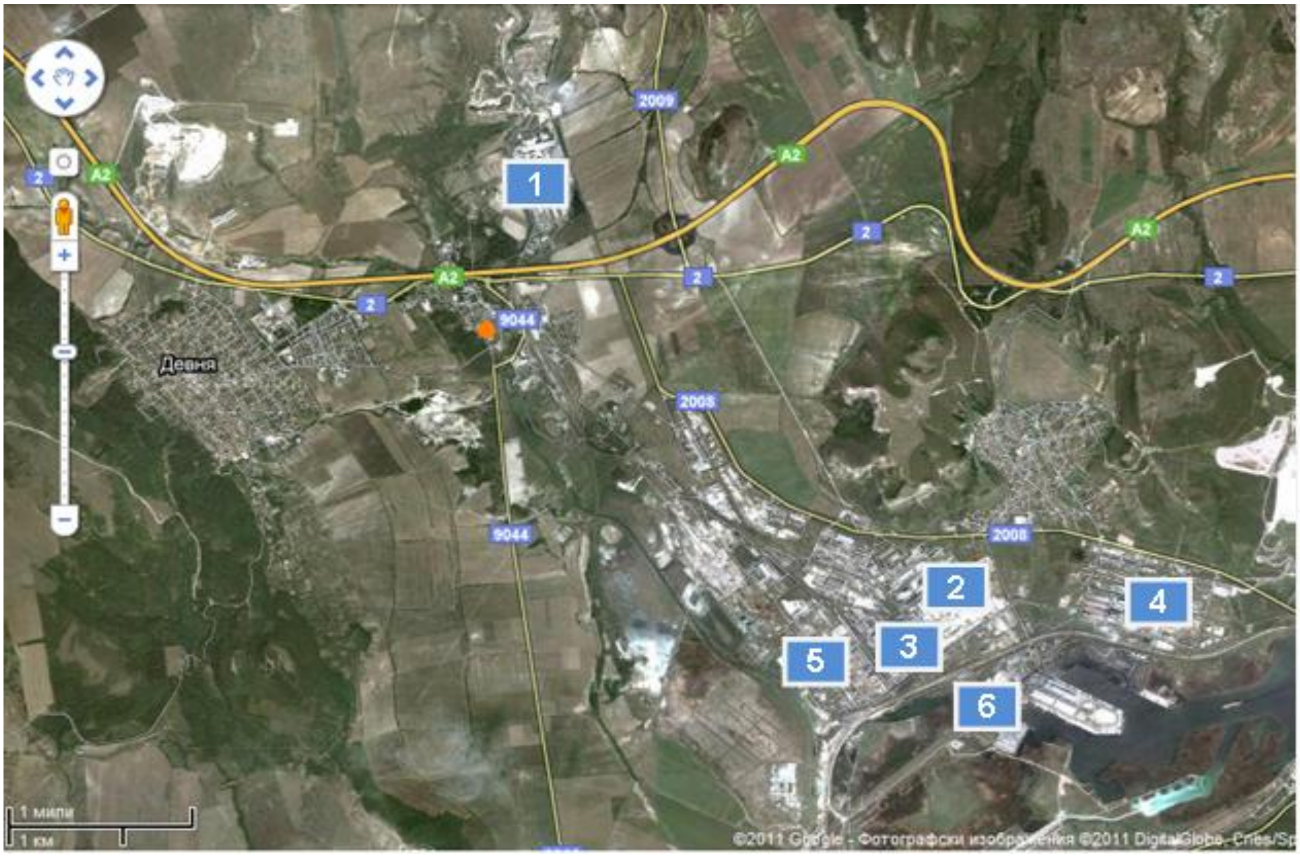

Fig-1: Location of the automatic monitoring station Izvorite and some major industrial emission sources at Devnya industrial region

Legend: ● Automatic monitoring station Izvorite BG0013A-Dv1, +043.13.12.00/+0.27.33.40.00

1. Devnya Cement	4. Agropolychim
2. Solvay Sodi	5. Polimeri
3. Deven	6. Varna Zapad Port

Atmospheric air pollution has been monitored for the period 2003-2013. The monitoring period is chosen with regards to the enforcement of IPPC permits of large industrial installations. The purpose of the research is to estimate the effect of applying measures required by these documents in order to keep emissions of harmful substances from different point sources in the industrial region under the determined limit values. Annual reports for the implementation of the activities required by the IPPC permit of each plant in the region are used as a data source [9-12]. Data from continuous and periodic monitoring of pollutants' concentrations in tail gases (mg/Nm^3) for the entire monitoring period have also been used. Data from annual environmental reports of the Regional inspection of environment and water Varna have been used for studying the trends of atmospheric air pollution at the automatic monitoring station Izvorite for the period 2003-2013 [13]. Results from monitoring of separate air pollutants have been manipulated statistically by the means of variation analysis as differences have been estimated with Student-Fisher's t-criteria.

3. RESULTS AND DISCUSSION

Industrial installations at Devnya industrial region have the following characteristics:

Solvay Sodi is a producer of synthetic soda ash (dense and light) and sodium bicarbonate as a by-product for industrial and food processing consumers. Plant's capacity is 1.5 million tons soda ash light, 1.3 million tons soda ash dense and 30 000 tons sodium bicarbonate per year. The IPPC permit No 74/2005 of Solvay Sodi enforces in January 2006. The main air pollutants are CO, CO_2, NH_3, oxides of nitrogen NO_x/NO_2 and oxides of sulfur SO_x/SO_2.

Deven is a co-generating power station based on separate combustion of imported coal, petroleum coke, natural gas and mazut. Produced thermal and electrical power is transferred to the other industrial plants in the region and part of the electrical energy is transferred to the national energy system. The power plant is equipped with 5 steam generators (4 of them for combustion of coal and one for natural gas combustion) with total capacity 860 MW (1160 tons per hour steam 10 MPa, 540°C), 7 turbo generators with total electrical capacity 121 MW and water preparation system with capacity 1000 m^3 per hour. The IPPC permit No 93/2006 of Deven enforces in May 2006. The main air pollutants are CO, CO_2, oxides of nitrogen NO_x/NO_2, oxides of sulfur SO_x/SO_2 and dust/particulate matter PM_{10}.

Agroplychim is a leading producer of mineral fertilizers in the Balkans. There are two production lines at the plant – one for the production of nitrogen fertilizers (ammonia, nitric acid, ammonium nitrate and urea ammonium nitrate solution) and another one for the production of phosphate fertilizers (phosphoric acid, sodium tripolyphosphate, triple superphosphate and compound fertilizers monoammonium phosphate and diammonium phosphate). The main air pollutants from mineral fertilizer production are HF, SO_2, NH_3, oxides of nitrogen NO_x/NO_2, CO and dust/particulate matter PM_{10}. The IPPC permit No 68/2005 of Agropolychim enforces in January 2006.

Devnya Cement operates installation for wet production of cement and clinker. Limestone, sand and marl are the main raw materials for cement production. Plant capacity is 1.91 million tons clinker per year. The installation is equipped with 6 furnaces, each with capacity 24-70 tons per hour. The IPPC permit No 63-H1/2007 of Devnya Cement enforces in March 2008. The main air pollutants are CO, dust, oxides of nitrogen NO_x/NO_2 and oxides of sulfur SO_x/SO_2.

Polimeri includes installations for chloralkali electrolysis and production of liquid chlorine, hydrochloric acid, ferric chloride and dichloroethane. The IPPC permit No 72/2005 of Polimeri enforces in January 2006. The company is adjudged bankrupt since 1 June 2010 therefore it is not a subject of the present research.

Results from ambient air quality monitoring indicate that NO_2 concentration at the beginning of the monitoring period is 44.48 μg/m^3 and exceeds the annual average limit value for human health protection (40 μg/m^3 [8]) 1.11 times (Fig-2). During the next year NO_2 concentration decreases significantly to 20.93 μg/m^3 as the difference is of strong statistical significance ($P < 0.01$). During the period 2008-2011 annual average NO_2 concentrations vary from 19.76 to 24.40 μg/m^3 and statistically proven are lower than NO_2 concentration in 2006 ($P < 0.01$). In 2012 and 2013 NO_2 concentrations in atmospheric air vary from 11.19 to 12.69 μg/m^3 and are even lower compared to those in 2006 before the enforcement of IPPC permits and to those measured for the period 2008-2011 as the decrease are of strong statistical significance ($P < 0.001$). Major differences between atmospheric NO_2 concentrations before and after the enforcement of IPPC permits indicate that effective technical measures have been applied at the industrial plants in Devnya region for NO_x/NO_2 emission reduction.

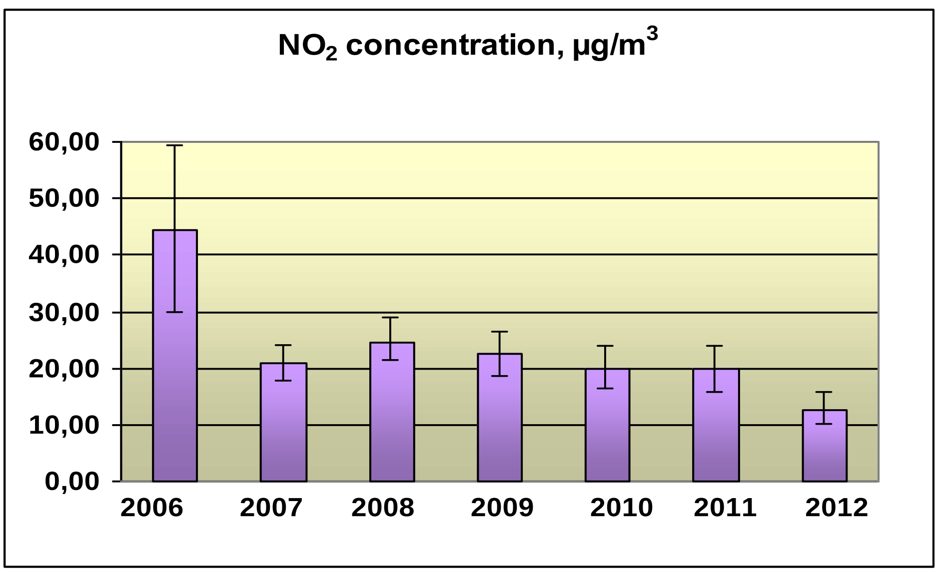

Fig-2: NO_2 pollution of atmospheric air

Monitoring results for sulfur dioxide indicate that annual average SO_2 concentration in 2005 before the enforcement of IPPC permits is 13.45 μg/m^3, decreases gradually in 2006 to 11.11 μg/m^3 ($P > 0.05$) and remains steady till 2010 (Fig-3). In 2011 a significant decrease to 7.55 μg/m^3 is registered ($P < 0.01$) and even lower concentrations are measured in 2013 – 5.36 μg/m^3 as the decrease is of strong statistical significance ($P < 0.001$). It is indicated that SO_2 concentrations are quite below daily average limit value for human health protection 125 μg/m^3 during the entire monitoring period (Bulgarian legislation does not provide annual average limit value for this pollutant).

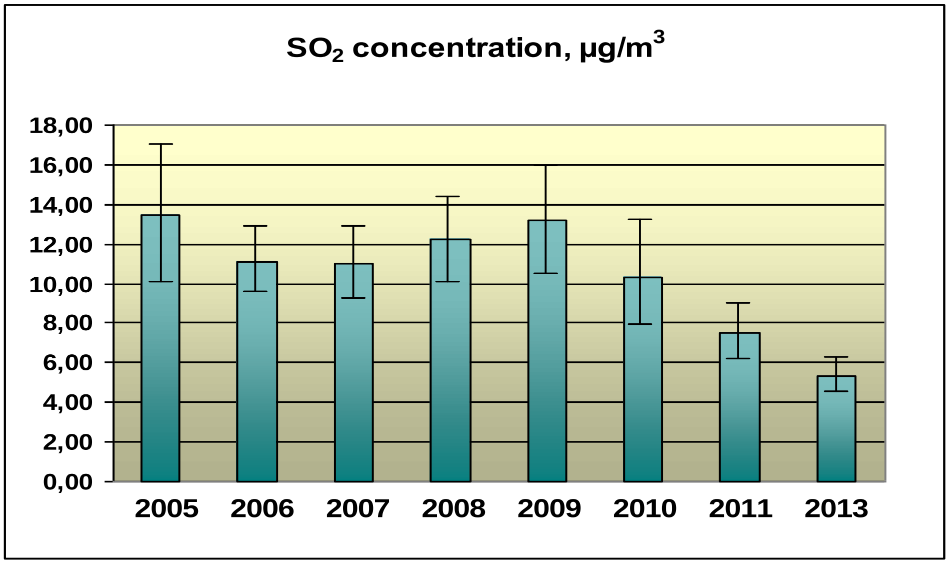

Fig-3: SO_2 pollution of atmospheric air

Fig-4 indicates that at the beginning of the monitoring period (2004-2007) before the enforcement of IPPC permits and implementation of emission reduction techniques CO concentrations in atmospheric air vary from 0.872 to 1.657 μg/m^3. From 2007 onwards CO concentration gradually decreases to 0.512 μg/m^3 in 2010 and 0.470 μg/m^3 in 2013 as the decrease is of strong statistical significance ($0.001 \leq P \leq 0.01$). None of the measured CO concentrations exceeds the limit value for human health protection – daily maximum 8-hour average value 10 μg/m^3.

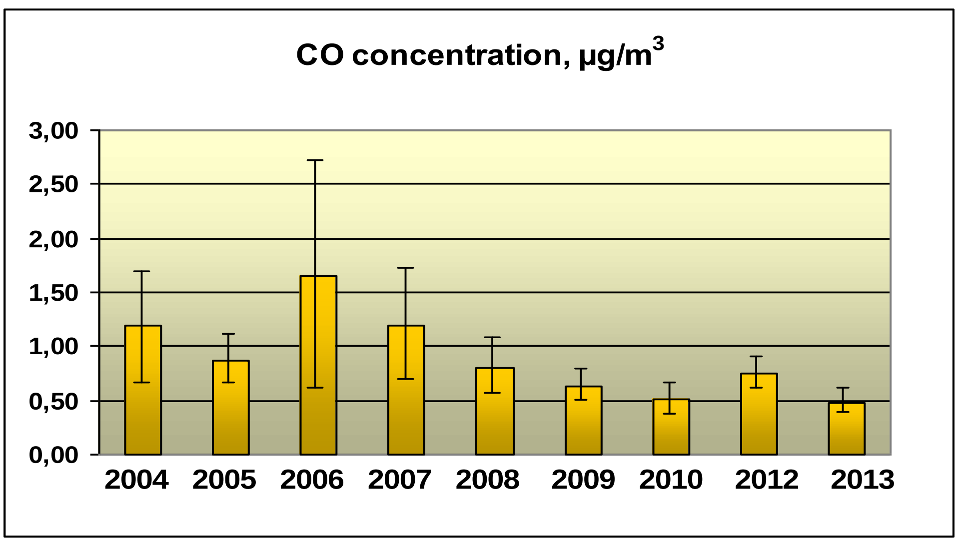

Fig-4: CO pollution of atmospheric air

Monitoring results indicate that in 2006 before the enforcement of IPPC permits and implementation of emission reduction techniques at the industrial plants ammonia concentration in atmospheric air is 30.359 μg/m^3 (Fig-5). During the next year the average annual concentration of NH_3 decreases significantly to 8.734 μg/m^3 ($P < 0.001$). During the period 2008-2010 concentrations of NH_3 are even lower and vary from 2.270 μg/m^3 to 5.593 μg/m^3 ($P < 0.001$). In 2011 another considerable concentration drop is registered – 0.540 μg/m^3 as the decrease is of strong statistical significance ($P < 0.001$). Such low levels are registered till the end of the monitoring period – from 0.618 μg/m^3 to 0.733 μg/m^3. None of the measured NH_3 concentrations exceeds the limit value 100 μg/m^3 [6].

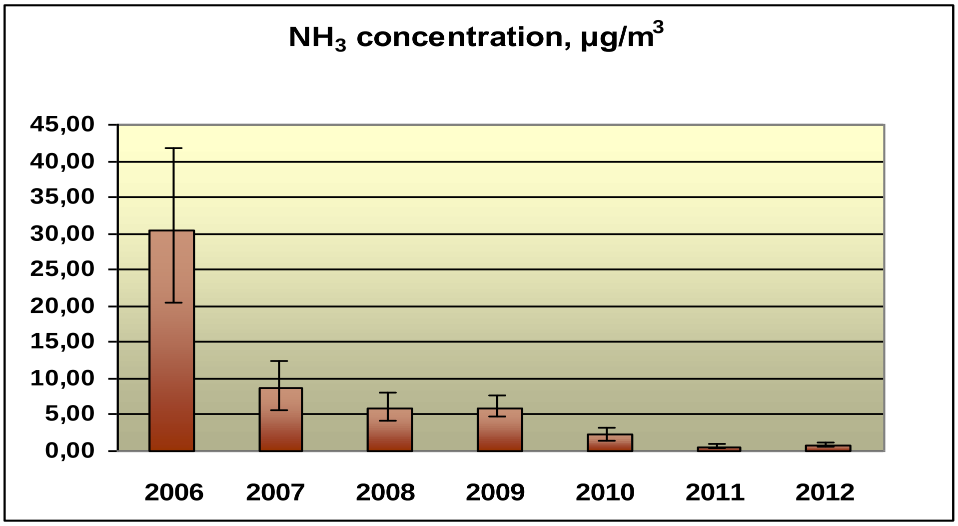

Fig-5: NH_3 pollution of atmospheric air

Ozone is a secondary atmospheric pollutant that occurs in the atmosphere due to photochemical reactions of volatile organic compounds VOC, oxides of nitrogen NO_x and CO at high temperature and ultra violet sun radiation. Ozone is not emitted directly in the atmosphere from industrial sources. There is sufficient data on ozone concentration for assessment of ambient air quality for the period 2003-2013. Monitoring results indicate that in 2003 before the enforcement of IPPC permits ozone concentration is 63.56 μg/m^3 and decreases to 48.93 μg/m^3 in 2004 ($P < 0.05$) (Fig-6). During the period 2005-2010 ozone concentrations vary from 41.61μg/m^3 to 50.68 μg/m^3. From 2010 onwards a significant drop is registered as ozone concentrations vary from 31.82 μg/m^3 to 33.31 μg/m^3 ($0.001 \leq P \leq 0.01$). The enforcement of IPPC permits requires implementation of emission reduction measures regarding ozone precursors such as NO_2, VOC and CO thus achieving reduction of ozone as well. For the entire monitoring period there are no ozone concentrations exceeding the long term limit value for human health protection 120 μg/m^3 [8].

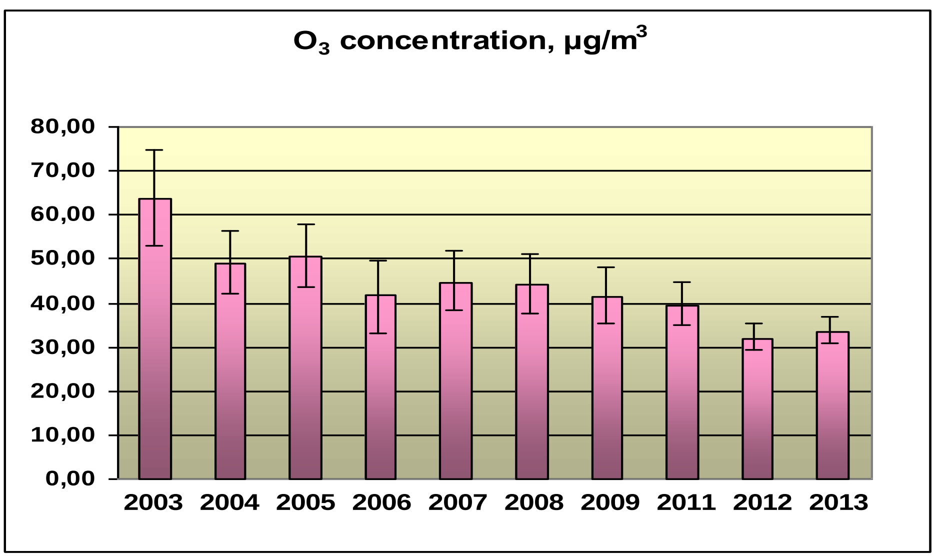

Fig-6: O_3 pollution of atmospheric air

Monitoring results indicate that a solid decrease trend regarding PM_{10} concentrations in atmospheric air is not registered. During the period 2005-2008 PM_{10} concentrations vary from 28.26 μg/m^3 to 32.72 μg/m^3 (Fig-7). From 2008 onwards concentrations decrease to 22.95 μg/m^3 ($P < 0.05$) but stay within the interval 25.48 μg/m^3 – 27.23 μg/m^3. A relevantly constant PM_{10} pollution of atmospheric air is observed but the average annual limit value for human health protection 40 μg/m^3 is not exceeded for the entire monitoring period [8]. Possibly PM_{10} concentrations stay rather constant due to emissions from various unorganized sources in the industrial region – Martziana limestone career, Agropolychim's phosphogypsum landfill, Padina slurry pond, municipal landfills for communal solid wastes and construction wastes, open areas for bulk materials storage, construction plots, concrete plants, etc.

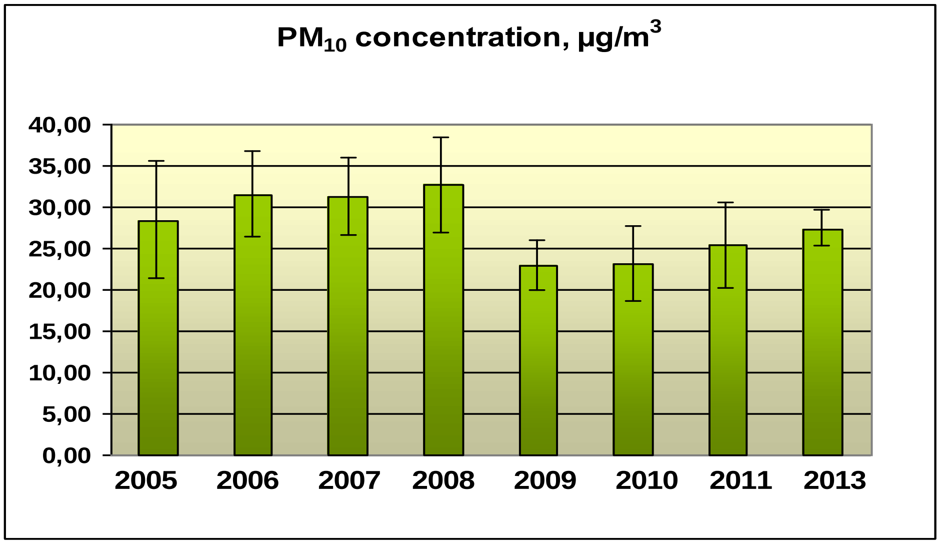

Fig-7: PM_{10} pollution of atmospheric air

Fig-8 indicates that the annual average concentration of benzene in 2007 is 1.185 μg/m^3. There is no sufficient data on C_6H_6 pollution of atmospheric air at the beginning of the monitoring period 2003-2006. During the next years C_6H_6 concentrations gradually decrease and vary from 0.657 μg/m^3 to 0.908 μg/m^3 for the period 2008-2011. At the end of the monitoring period C_6H_6 concentrations decrease even more to 0.585 μg/m^3 in 2012 and 0.603 μg/m^3 in 2013 ($P < 0.05$). None of the registered C_6H_6 concentrations exceeds the annual average limit value for human health protection 5 μg/m^3 [8].

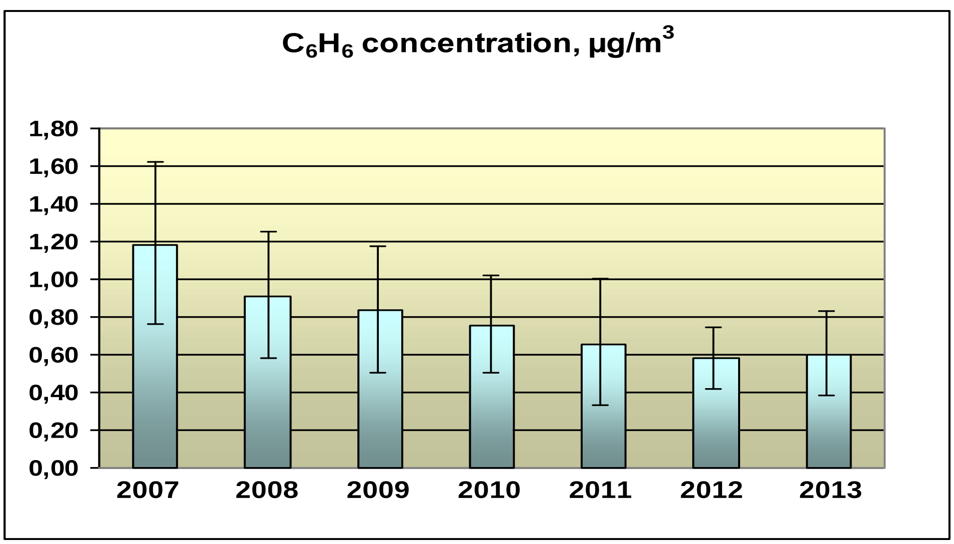

Fig-8: C_6H_6 pollution of atmospheric air

The observed decrease trend regarding the main atmospheric pollutants in Devnya industrial region might be related to harmful emissions from adjacent industrial sources. Monitoring results indicate that annual average NO_x/NO_2 concentration in tail gas emissions from lime production at Solvay Sodi is 148.67 mg/Nm^3 in 2008 (the IPPC permit enforces in January 2006), decreases gradually to 136.42 mg/Nm^3 in 2010 and 98.30 mg/Nm^3 in 2013 (Table-1). The same trend is registered for tail gas emissions from absorption and distillation. In 2008 NO_x/NO_2 concentration is 129.17 mg/Nm^3 and decreases to 90.62 mg/Nm^3 in 2013. None of the registered NO_x/NO_2 concentration in tail gas emissions from both emission sources exceeds the emission limit value ELV for the entire monitoring period. Emissions of SO_x/SO_2 decrease gradually as well. SO_x/SO_2 concentration in tail gas emissions from lime production is 163.42 mg/Nm^3 in 2008 and decreases to 115.17 mg/Nm^3 in 2010 and 66.52 mg/Nm^3 in 2013.

Table-1: Tail gas emissions at Solvay Sodi, mg/Nm^3

Year	**2008**				**2010**				**2012**				**2013**			
Pollutant	**ELV**	**Lime prod.**	**ELV**	**Absorption and distillation**	**ELV**	**Lime prod.**	**ELV**	**Absorption and distillation**	**ELV**	**Lime prod.**	**ELV**	**Absorption and distillation**	**ELV**	**Lime prod.**	**ELV**	**Absorption and distillation**
CO	-	**> 2500**			-	**> 2500**			-	**> 749**			-	**> 749**		
NO_x/NO_2	1500	**148.67**	500	**129.17**	1500	**136.42**	500	**124.90**	1500	**98.33**	500	**93.69**	1500	**98.30**	400	**90.62**
SO_x/SO_2	500	**163.42**			500	**115.17**			500	**66.50**			400	**66.52**		
Dust	80	**41.56**			80	**31.18**			20	**32.43**			50	**32.40**		
NH_3			50	**16.10**			50	**17.84**			50	**16.52**			50	**16.53**

Monitoring of dust emissions at Solvay Sodi indicates that a slight decrease trend is registered (Table-2). Dust concentration in tail gas emissions from dust collectors at lime production plant decreases from 11.00 mg/Nm^3 in 2008 to 5.92 mg/Nm^3 in 2013. Dust concentration in tail gas emissions from dust collectors at calcination, soda ash dense and sodium bicarbonate production decreases from 20.38 mg/Nm^3 in 2008 to 7.48 mg/Nm^3 in 2013.

Table-2: Dust emissions at Solvay Sodi, mg/Nm^3

Year	**2008**		**2010**		**2012**		**2013**	
Treatment facilities	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**
Dust collectors at lime production	80	**11.00**	80	**12.90**	20	**7.08**	20	**5.92**
Wet scrubber at calcinations plant	80	**22.70**	80	**19.60**	20	**11.80**	20	**8.72**
Dust collectors at calcination, soda ash dense and sodium bicarbonate production	80	**20.38**	80	**16.10**	20	**9.26**	20	**7.48**
Packaging machine dust collection	80	**9.75**	80	**11.53**	20	**7.31**	20	**8.40**

Table-3 indicates that NO_x/NO_2 concentration in tail gas emissions from a shared outlet of steam generators SG_1-SG_6 at Deven is 1140.77 mg/Nm^3 in 2008 (the IPPC permit enforces in May 2006) and decreases gradually to 923.98 mg/Nm^3 in 2010 and 604.32 mg/Nm^3 in 2013. Emissions of SO_x/SO_2 are reduced significantly as well. SO_x/SO_2 concentrations during the period 2008-2009 vary from 781.63 mg/Nm^3 to 795.90 mg/Nm^3 and exceed the ELV from 1.95 to 2 times. In 2010 SO_x/SO_2 concentration decreases gradually to 531.27 and exceeds the ELV 1.33 times. In 2012 and 2013 SO_x/SO_2 concentrations stay up to 372.63 mg/Nm^3 and do not exceed the ELV.

Similar trend is registered for dust emissions. Dust concentration is 373.81 mg/Nm^3 in 2008 and exceeds the ELV 7.48 times. In 2009 dust concentration decreases to 188.95 mg/Nm^3 and exceeds the ELV 3.78 times. In 2010 dust concentration stays close to the ELV – 52.36 mg/Nm^3 and in

2012 and 2013 it is below the ELV – 45.23 mg/Nm^3 (ELV – 50 mg/Nm^3). A slight decrease trend is registered for CO with no concentrations exceeding the ELV – from 820.92 mg/Nm^3 in 2008 to 659.58 mg/Nm^3 in 2013.

Monitoring data for the new circulating fluidized-bed steam generator (in operation since 2010) indicates that NO_x/NO_2 and SO_x/SO_2 emissions decrease gradually (Table-3). In 2010 NO_x/NO_2 concentration is 242.53 mg/Nm^3 and exceeds the ELV 1.21 times. During the next years NO_x/NO_2 concentration gradually decreases and in 2013 it is 166.53 mg/Nm^3 (ELV – 200 mg/Nm^3). Higher concentrations are registered for SO_x/SO_2 in 2010 – 282.15 mg/Nm^3 and exceed the ELV 1.41 times. At the end of the monitoring period in 2013 SO_x/SO_2 concentration is 137.23 mg/Nm^3 (ELV – 200 mg/Nm^3).

Table-3: Tail gas emissions at Deven, mg/Nm^3

Year	**2008**		**2009**		**2010**		**2012**		**2013**	
Pollutant	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**
Shared outlet of steam generators SG_1-SG_6										
NO_x/NO_2	1200	**1140.77**	1200	**923.98**	1200	**620.81**	1200	**557.61**	1200	**604.32**
CO	1000	**820.92**	1000	**806.23**	1000	**825.99**	1000	**745.51**	1000	**659.58**
SO_x/SO_2	400	**795.90**	400	**781.63**	400	**531.27**	400	**370.50**	400	**372.63**
Dust	50	**373.81**	50	**188.95**	50	**52.36**	50	**46.28**	50	**45.23**
Circulating fluidized-bed steam generator										
NO_x/NO_2					200	**242.53**	200	**174.39**	200	**166.53**
CO					250	**25.39**	250	**29.23**	250	**22.21**
SO_x/SO_2					200	**282.15**	200	**152.19**	200	**137.23**
Dust					30	**9.83**	30	**9.86**	30	**9.13**

Emission monitoring at Devnya Cement indicates that major reduction is registered for dust emissions from blast furnaces (Table-4). In 2008 dust concentration is 50.12 mg/Nm^3 and gradually decreases to 33.32 mg/Nm^3 in 2009 and 18.38 mg/Nm^3 in 2013. None of the measured concentrations of NO_x/NO_2, SO_x/SO_2, CO and dust exceed the ELV.

Table-5 indicates that dust emissions from separate sources at Devnya Cement decrease significantly: coal grinding mill – from 30.21 mg/Nm^3 in 2008 to 10.92 mg/Nm^3 in 2013; blast furnace stave cooler – from 26.10 mg/Nm^3 in 2008 to 10.00 mg/Nm^3 in 2013; cement packaging installation – from 24.80 mg/Nm^3 in 2008 to 10.50 mg/Nm^3 in 2013.

Table-4: Tail gas emissions from blast furnaces at Devnya Cement, mg/Nm^3

Year	**2008**		**2009**		**2012**		**2013**	
Pollutant	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**
NO_x/NO_2	1500	**786.21**	1400	**775.39**	1200	**787.89**	1200	**733.15**
CO	2000	**45.79**	2000	**47.60**	2000	**43.44**	2000	**43.25**
SO_x/SO_2	750	**441.31**	750	**347.02**	750	**366.79**	750	**369.94**
Dust	80	**50.12**	80	**33.32**	50	**19.61**	50	**18.38**

Table-5: Dust emissions at Devnya Cement, mg/Nm^3

Year	**2008**		**2009**		**2012**		**2013**	
Emission source	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**
Coal grinding mill	50	**30.21**	50	**19.75**	50	**16.80**	50	**10.92**
Cement mill – main process	50	**9.88**	50	**8.19**	50	**8.83**	50	**8.44**
Blast furnace stave cooler	50	**26.10**	50	**25.15**	50	**16.50**	50	**10.00**
Cement packaging installation	50	**24.80**	50	**21.60**	50	**11.50**	50	**10.50**

Monitoring of NO_x/NO_2 emissions at Agropolychim indicates a decrease trend (Table-6). NO_x/NO_2 concentration in tail gas emissions from nitric acid production is 367.16 mg/Nm^3 in 2008 (the IPPC permit enforces in January 2006) and decreases to 248.02 mg/Nm^3 in 2012 and 205.44 mg/Nm^3 in 2013. Similar trend is observed for other NO_x/NO_2 emission sources: stack I at ammonia production – from 236.90 mg/Nm^3 in 2008 to 196.50 mg/Nm^3 in 2013; stack II at ammonia production – from 257.50 mg/Nm^3 in 2008 to 206.90 mg/Nm^3 in 2013.

Table-7 indicates that NH_3 concentration in tail gas emissions at Agropolychim decreases slightly without exceeding the ELV. NH_3 concentration in tail gas emissions from Prilling towers is 3.79 mg/Nm^3 in 2008 and decreases gradually to 1.74 mg/Nm^3 in 2013.

Table-6: NO_x/NO_2 emissions at Agropolychim, mg/Nm^3

Year	2008		2010		2012		2013	
Emission source	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**
Nitric acid production	500	**367.16**	500	**310.03**	500	**248.02**	400	**205.44**
Thermal power plant at ammonia production	300	**194.10**	300	**197.11**	300	**176.89**	300	**176.50**
Stack I at ammonia production	500	**236.90**	500	**263.22**	500	**196.44**	400	**196.50**
Stack II at ammonia production	500	**257.50**	500	**273.88**	500	**206.78**	400	**206.90**

Table-7: NH_3 emissions at Agropolychim, mg/Nm^3

Year	2008		2010		2012		2013	
Emission source	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**
Air mixers at ammonium nitrate production	30	**4.44**	30	**4.32**	30	**4.05**	30	**3.21**
Prilling towers at ammonium nitrate production	30	**3.79**	30	**2.42**	30	**2.76**	30	**1.74**
Scrubbing section at triple superphosphate production	30	**10.20**	30	**10.80**	30	**11.50**	30	**4.00**

Monitoring data for dust emissions at Agropolychim indicates a slight decrease trend (Table-8). Dust concentration in tail gas emissions from dust collectors at triple superphosphate production is 6.02 mg/Nm^3 in 2008 and decreases to 3.36 mg/Nm^3 in 2013, while dust concentration in tail gas emissions from dust collectors at phosphate grinding installation is 8.48 mg/Nm^3 in 2008 and decreases to 5.68 mg/Nm^3 in 2013.

Table-8: Dust emissions at Agropolychim, mg/Nm^3

Year	2008		2010		2012		2013	
Emission source	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**	**ELV**	**Concen-tration**
Air mixers at ammonium nitrate production	80	**5.51**	80	**5.70**	80	**5.46**	50	**4.27**
Prilling towers at ammonium nitrate production	15	**12.63**	15	**12.83**	15	**11.03**	15	**8.05**
Dust collectors at triple superphosphate production	80	**6.02**	80	**5.62**	80	**4.92**	50	**3.36**
Phosphate grinding mill	80	**3.20**	80	**3.05**	80	**2.54**	50	**1.19**
Dust collectors at phosphate grinding installation	80	**8.48**	80	**8.09**	80	**6.09**	50	**5.68**

In order to accomplish IPPC requirements for ambient air quality improvement Solvay Sodi starts in 2007 investment program on total cost 300 million BGN including a new cogeneration plant. Major part of the program is modernization of soda ash production with capacity increase from 1.2 million tons to 1.5 million tons per year. Investment projects have been developed for building a new line for soda ash dense production, a distillation column with low energy consumption and emission potential, a new carbonizing column and a limestone blast furnace. Another project has been developed for building up the dike of Padina slurry pond. All new and reconstructed installations correspond to BAT and relevant environmental standards.

Deven produces thermal power for soda ash production. The combustion installation is cogeneration for combined heat and power production and completely corresponds to BAT regarding greenhouse gas emission reduction. Cogeneration is the only reasonable solution for industrial power production especially in synthetic soda ash production. A new circulating fluidized–bed steam generator is set into operation at Deven in 2010. A typical feature of that steam generator is continuous circulating of the fuel through the furnace and separators in order to prolong reaction time and ensure low temperature combustion. Such technology is environment friendly with low emission potential regarding oxides of nitrogen (< 200 mg/Nm^3), oxides of sulphur (< 200 mg/Nm^3), dust (< 30 mg/Nm^3). It is simply constructed, highly efficient and reliable and provides options for combustion of various types of solid fuels thus utilizing primary energy resources. Building the new circulating fluidized–bed steam generator complies with Deven's politics for sustainable development, emission reduction, energy efficiency and resource consumption reduction required by European environmental directives.

According to the IPPC permit of Devnya cement biomass might be used as a fuel at cement production. Utilization of renewable resources that are carbon neutral has been promoted as one of the company's main targets is to reduce greenhouse gas emissions. Applying BAT at Devnya Cement refers to:

- implementation of environment management systems considering local characteristics;
- strict control of all substances incoming to the blast furnace so that emission prevention/reduction is assured;
- process and emission monitoring on a regular basis at newly built and reconstructed installations;
- heat consumption reduction;
- reduction of primary energy consumption considering reduced clinker content in cement and cement products;
- minimization of electrical power consumption through application of separate or combined measures/techniques.

Agropolychim introduces an ambitious investment program in order to meet the IPPC permit requirements. Investment projects have been developed for implementation of systems for continuous monitoring of harmful substances emissions in the air, introduction of highly efficient facilities for tail gas emissions treatment and reconstruction of the plant for production of ammonium nitrate. The reconstruction of the plant is based on a pipe reactor technology and ammonium nitrate with a higher content of nitrogen – 34,5 % and a stabilizing supplement – aluminum sulphate $Al_2(SO_4)_3$ is produced. The capacity of the plant is 1250 t/day thus making the production process more effective. The applied technology is non-waste and environment friendly. It complies with all standards of the European Union for implementation of BAT in production of nitrogen fertilizers. The reconstructed plant is equipped with the necessary treatment facilities that provide treatment of particulate matter and ammonia emissions in air so that emissions are being kept under ELV in accordance with the IPPC permit. The investment project applies the technology of GPN (France); the project is designed and developed by Chemoproject (Czech Republic). The entire investment cost is 20 million euro.

Agropolychim started in 2005 a project for greenhouse gas emission reduction at total cost 12 million euro which is the first of its kind in East Europe. The project is conducted under joint implementation between Agropolychim and Danish Environmental Agency DEA and provides for reduction of nitrous oxide emissions from nitric acid production. Due to the secondary decomposing catalyst installed in the ammonia burners nitrous oxide emissions are reduced significantly – from the start of the project till the end of 2013 a total amount of 2.8 million tons CO_2-eq. have been reduced.

4. CONCLUSIONS

Considerable improvement of ambient air quality in Devnya industrial region is registered due to implementation of emission abatement measures and techniques at the industrial installations pursuant to IPPC requirements. After the IPPC permits enforcement a significant decrease is registered regarding concentrations of the main atmospheric pollutants - SO_2, NO_2, CO, O_3, NH_3 and C_6H_6 ($P < 0.001$). Considerable reduction of harmful emissions from separate industrial sources is registered as well due to application of BAT and relevant best practices for environmental protection. A relevantly constant PM_{10} pollution of atmospheric air is observed not exceeding the limit value for the entire monitoring period. Possibly PM_{10} concentrations stay rather constant due to dust emissions from various unorganized sources in the industrial region – Martziana limestone career, Agropolychim's phosphogypsum landfill, Padina slurry pond, municipal landfills for communal solid wastes and construction wastes, open areas for bulk materials storage, construction plots, concrete plants, etc.

Pursuant to IPPC requirements a new circulating fluidized-bed steam generator with low NO_x, SO_x and dust emission potential has been set into operation at Deven; a new line for the production of soda ash dense, an emission free distillation column, a carbonizing column and a limestone blast furnace at Solvay Sodi; a new installation for the production of ammonium nitrate solution along with highly efficient tail gas treatment facilities at Agropolychim; etc. The present study proves that the implementation of the IPPC Directive by technical engineering at industrial and combustion plants is a key tool for the improvement of ambient air quality.

REFERENCES

[1]. Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning Integrated Pollution Prevention and Control. OJ L 24, 29.1.2008

[2]. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. OJ L 152, 11.6.2008

[3]. Clean Air Law. GN 45, 28.5.1996, amendments GN 102, 21.12.2012

[4]. Environmental Protection Law. GN 91, 25.92002, amendments GN 22, 11.3.2014

[5]. Regulation No 7 of 3 May 1999 on ambient air quality assessment and management. GN 45, 14.5.1999

[6]. Regulation No 14 of 23.9.1997 relating to limit values for harmful substances in atmospheric air of urban areas. GN 88, 3.10.1997, amendments GN 42, 29.5.2007

[7]. Regulation on terms and methods for IPPC permits issue. GN 80, 9.10.2009, amendments GN 69, 11.9.2012

[8]. Regulation No 12 of 15 July 2010 relating to limit values for sulfur dioxide, nitrogen dioxide and oxides of nitrogen, particular matter and lead in ambient air. GN 58, 30.7.2010

[9]. Annual reports for implementation of the activities for which the IPPC permit No 68/2005 of Agropolychim is issued, 2006 to 2013

[10]. Annual reports for implementation of the activities for which the IPPC permit No 74/2005 of Solvay Sodi is issued, 2006 to 2013

[11]. Annual reports for implementation of the activities for which the IPPC permit No 93/2006 of Deven is issued, 2007 to 2013

[12]. Annual reports for implementation of the activities for which the IPPC permit No 63-H1/2007 of Devnya Cement is issued, 2008 to 2013

[13]. Annual environmental reports, Regional inspection of environment and water Varna, 2003 to 2013

[14]. Abdel Salam H. A. Prediction of Pollutants Emission Dispersion of Phosphate Fertilizers Production Facility. International Journal of Research in Engineering and Technology, Vol. 02 (11), 306, 2013

[15]. Brown M. J. The health effects of PM_{10} air pollution in Reefton, South Island New Zealand. University of Canterbury, 2009

[16]. Chen T. M., J. Gokhale, S. Shofer, W. G. Kuschner. Outdoor air pollution: nitrogen dioxide, sulfur dioxide and carbon monoxide health effects. American Journal of Medical Sciences, Vol. 333 (4), 249, 2007

[17]. Chuturkova R., P. Todorov. Atmosphere pollution evaluation in Bulgarian industrial region. Proceedings of 2nd International Conference on Environmental Research and Assessment, Bucharest, Romania, October 5-8, 2006, 189-195

[18]. Chuturkova R., A. Simeonova, J. Bekyarova, N. Ruseva, V. Yaneva. Assessment of the environmental status of Devnya industrial region, Bulgaria. Journal of Environmental Protection and Ecology, vol. 12 (3), 805, 2011

[19]. Erisman J. W., A. Bleeker, A. Neftel, V. Aneja et al. Detecting change in atmospheric ammonia following emission changes. In: Atmospheric Ammonia, 383-390. Springer Science and Business Media, 2009

[20]. Health risk of ozone from long-range transboundary air pollution, WHO Regional Office for Europe, 2008

[21]. Houston Regional Benzene Air Pollution Plan for Major Sources. City of Houston, Mayor’s Office of Environmental Programming, Department of Health and Human Services, Bureau of Air Quality Control, 2007

[22]. Hrdlickova Z., J. Michalek, M. Kolar, V. Vesely. Identification of factors affecting air pollution by dust aerosol PM_{10} in Brno City, Czech Republic. Atmospheric Environment, vol. 42, 8661, 2008

[23]. Ielpo P., V. Paolillo, G. de Gennaro, P. R. Dambruoso. PM_{10} and gaseous pollutants trends from air quality monitoring network in Bari province: principal component analysis and absolute principal component scores on a two years and half data set. Chemistry Central Journal, vol. 8 (2), 14, 2014

[24]. Karakatsani A., A. Analits, D. Perifanou, J. G. Ayres et al. Particulate matter air pollution and respiratory symptoms in individuals having either asthma or chronic obstructive pulmonary disease: a European multicentre panel study. Environmental Health, vol. 11, 75, 2012

[25]. Karar K., A. K. Gupta, A. Kumar, A. K. Biswas. Seasonal variations of PM_{10} and DUST in residential and industrial sites in an urban area of Kolkota, India. Environmental Monitoring and Assessment, vol. 118 (1-3), 369, 2006

[26]. Karavanas A., A. Chaloulakou, N. Spyrellis. Evaluation of the implementation of best available technique in IPPC context: an environmental performance indicators approach. Journal of Cleaner Production, vol. 17 (4), 480, 2009

[27]. Katsouyanni K. Ambient air pollution and health. British Medical Bulletin, vol. 68, 143, 2003

[28]. Lopes M., M. L. Figueredo, A. Monteiro, J. Ferreira, J. Martins, C. Borrego. A contribution to air quality management in urban industrialized areas. In: Air Pollution XX, 125-139. WIT Press, 2012

[29]. Narwal M. S., Ajit, R. Bhool. An Analysis of environmental impacts of various environmental aspects for

Indian manufacturing industries. International Journal of Research in Engineering and Technology, vol. 3 (3), 291, 2014
[30]. Salam A., T. Hossain, M. N. A. Siddique, A. M. S. Alam. Characteristics of atmospheric trace gases, particulate matter and heavy metal pollution in Dhaka, Bangladesh. Air Quality, Atmosphere and Health, vol.1 (2), 101, 2008
[31]. Schoenberg H. Integrated pollution prevention and control in large industrial installations on the basis of best available techniques – the Sevilla Process. Journal of Cleaner Production, vol. 17 (16), 1526, 2009
[32]. Singh A. K., N. Tomer, C. L. Jain. Monitoring, assessment and status of benzene, toluene and xylene pollution in the urban atmosphere of Delhi, India. Research Journal of Chemical Sciences, vol. 2 (4), 45, 2012
[33]. Van Damme M., L. Clarisse, C. L. Heald et al. Global distributions and trends of atmospheric ammonia (NH_3) from IASI satellite observation. Atmospheric Chemistry and Physics Discussions, vol. 13, 24301, 2013