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AIR POLLUTION WITH SULFUR OXIDES FROM INDUSTRY IN SOUTH-WESTERN AND SOUTH-EASTERN REGIONS OF BULGARIA

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Abstract: *Restructuring of industrial production and the concrete environmental measures such as fuel switching facilities and replacement of process equipment in the energy-intensive industries, the installation of new or increased efficiency of existing treatment facilities have caused emissions into the atmosphere to decrease significantly. However, the concentration of sulfur oxides in air showed no significant improvement, despite reduced emissions.*

Key words: *sulfur oxides, emission, industry, energy.*

Introduction

Bulgarian government and local authorities made efforts in the last years to improve the quality of the air we breathe. There has been a significant improvement but it is insufficient for attaining and ensuring good quality of the air in the city regions. A considerable part of Bulgarian population still lives in cities where the appointed limits of air quality in the EU (imposed in order to preserve human health) are surpassed.

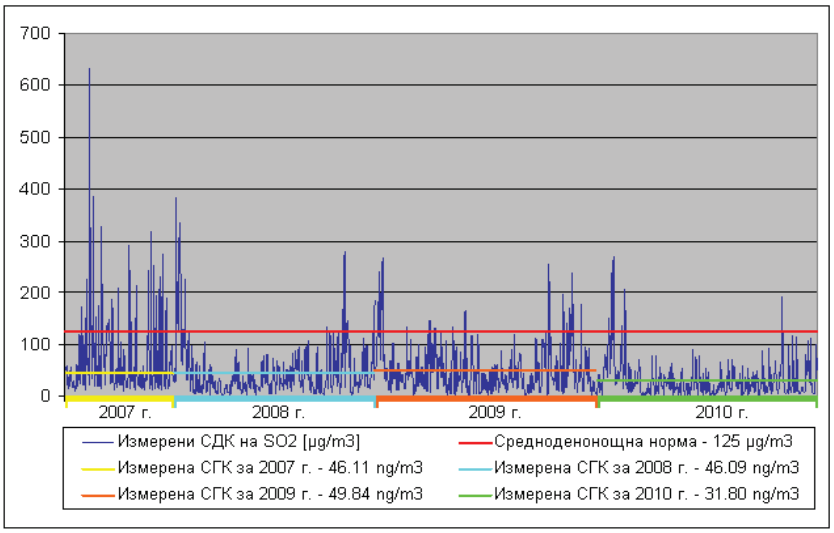

Fig. 1. Average daily concentration of SO_2 in 2007 – 2010 [3]

As a result of restructuring industrial production and the concrete ecological measures applied, such as change of combustible bases and replacement of technological equipment in companies with high energy consumption, fitting new or improving the efficiency of existing purifying stations, toxic emissions in the air are considerably less but the concentration of sulfur oxides in the air did not show any improvement despite the reduced emissions [5].

Exposition

The whole country still has a problem with pollution. Its levels in most cities are about or above the set standards and occasionally surpass the appointed levels of human health protection. The frame directives for managing air quality and better air in Europe appear as a key point in EU strategy for improving air quality as a whole. The corresponding norms in Bulgarian legislature, N 7 from 3 May 1999 for air quality evaluation and management and N 12 from 15 July 2010 for sulphur dioxide limits in the air, arrange both limits of pollution and conditions, order and ways of improving air quality in the regions where the permitted levels are surpassed [4].

In the years of the investigated period 2007-2013 specialists registered excess of the average norms per hour and/ or the average daily norms of sulfur dioxide in two regions for air quality evaluation and management (RAQEM) (South-eastern region – Galabovo and Sliven and South-western region – Kardzhali and Pernik). Excess above the alarm limit is registered in Galabovo and Pernik. The main sources of sulfur dioxide in the South-eastern region are the thermal-electric power stations of Maritsa Iztok energy complex and *Sliven* thermal-electric power station. In the South-western region the main sources are Lead-zinc Company LTD in Kardzhali and Central Heating Supply Station LTD in Pernik.

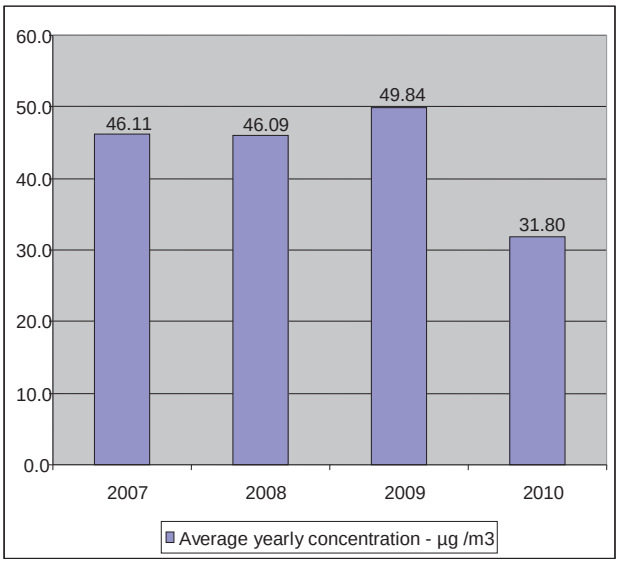

Fig. 2. Average yearly concentration of SO_2 in Kardzhali from 2007 till 2010

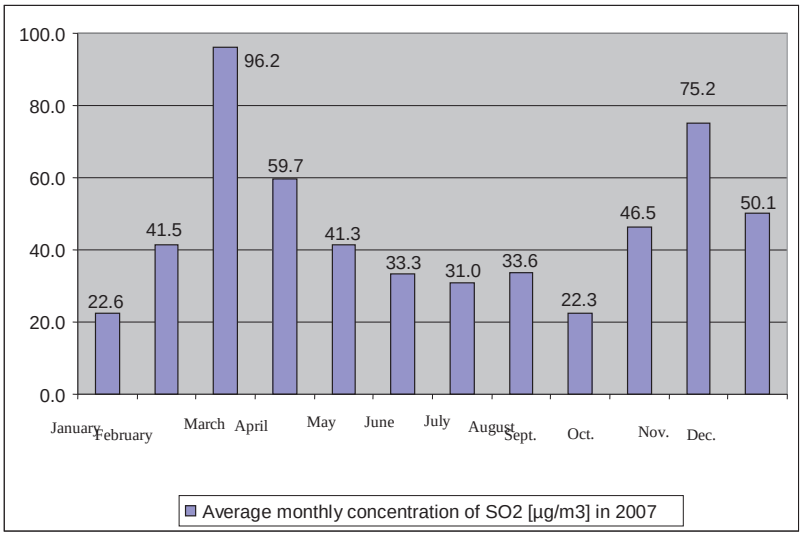

Fig.3 Average monthly concentration of SO_2 in Kardzhali in 2007

On the basis of the investigated emission sources influencing the pollution levels in the region of Kardzhali district the aim of the actual data at the present moment is to suggest new, effective, short-term measures, which should ensure compliance of Air Control with the law requirements about standards of human health protection; to encourage good European practices which increased the emission reduction of particular air pollutants; updating and improving the process of Air Control management via an observation system, increased control and number measurements; to provide the population with more information and better knowledge about the problems of air pollution; to ensure timely and reliable information about air conditions and pollution sources [1] .

Fig. 1 shows the average daily concentration of SO_2, measured in the period from 2007 till 2010. The measurements are made by ”KOS” in the period from 1 January 2007 till 31 July 2008 and by Studen kladenets Automatic Measurement Station in the region of Kardzhali in the period from 1 August 2008 till 31 December 2010.

The number of days with measurements for the corresponding years is as follows:

- 179 days with measurements in 2007 (49.0%);
- 329 days with measurements in 2008 (89.9%);
- 363 days with measurements in 2009 (99.5%);
- 364 days with measurements in 2010 (99.7%).

The red line shows the average daily norm (ADN) of 125 µg/m^3. The maximum number of excesses of ADN of sulfur dioxide (SO_2) per year is 3. The number of excesses of ADN for the corresponding years is [1] :

- 33 days with excesses above the ADN out of 303 days with measurements in 2007 (10.9%);

- 23 days with excesses above the ADN out of 326 days with measurements in 2008 (7.10%);

-23 days with excesses above the ADN out of 363 days with measurements in 2009 (6.3%);

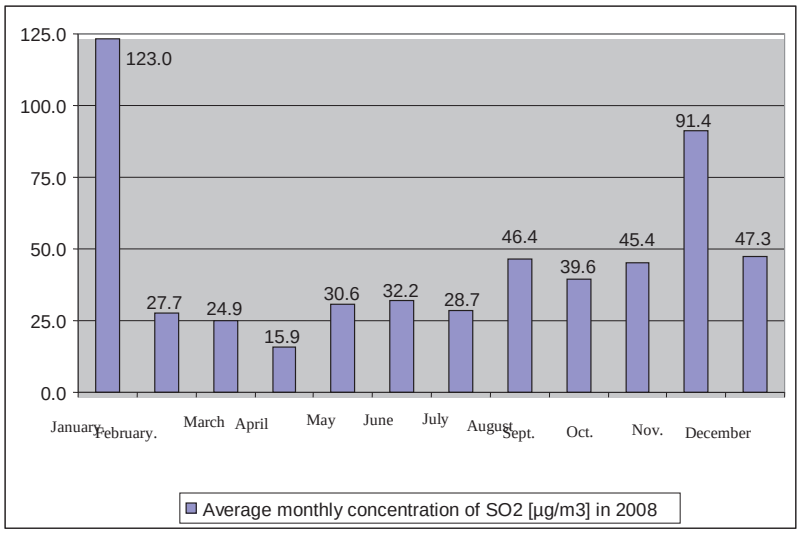

Fig. 4. Average monthly concentration of SO_2 in Kardzhali in 2008

-9 days with excesses above the ADN out of 362 days with measurements in 2010 (2.5%).

There is an average norm per hour (ANH) for the sulfur dioxide of 350 $\mu g/m^3$. The maximum number of excesses of ANH for the sulfur dioxide (SO_2) per year is 24 [2] .

The number of excesses of ANH for the corresponding years is as follows:

-28 excesses of ANH out of 902 hours with measurements in 2007 (3.1%);

-171 excesses of ANH out of 5734 hours with measurements in 2008 (3.0%);

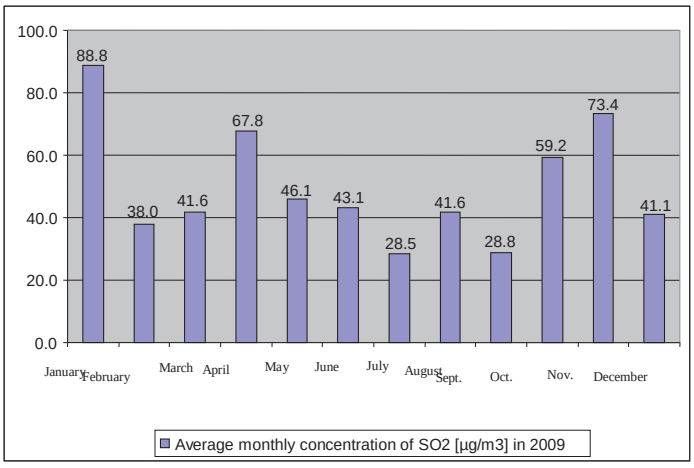

Fig. 5. Average monthly concentration of SO_2 in Kardzhali in 2009

-203 excesses of ANH out of 8301 hours with measurements in 2009 (2.4%);

-88 excesses of ANH out of 8316 hours with measurements in 2010 (1.1%).

The number of days with excesses of ANH in the corresponding years is as follows:

-28 excesses of ANH in 25 out of 303 дни с days with measurements in 2007 (55.6%)

-171 excesses of ANH in 169 out of 326 days with measurements in 2008 (51.8%)

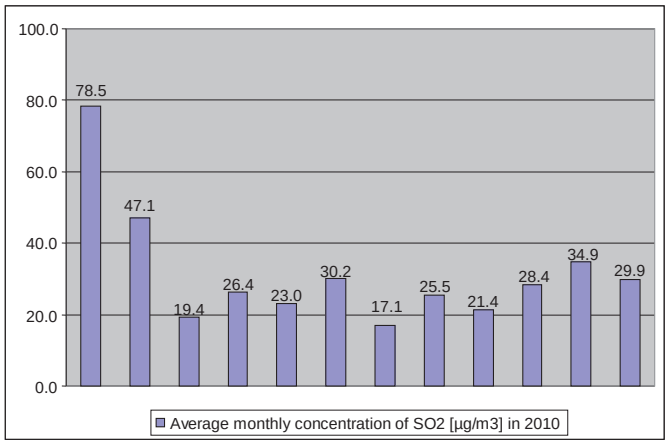

Fig. 6. Average monthly concentration of SO_2 in Kardzhali in 2010

-203 excesses of ANH in 202 out of 363 days with measurements in 2009 (55.6%)

-88 excesses of ANH in 62 out of 362 days with measurements in 2010 (17.1%)

The analysis of Fig. 1 leads to the following conclusions:

1. The number of excesses of the average daily norm (2007 - 33; 2008 - 23; 2008 - 23; 2010 - 9) shows a tendency to decrease.

2. The value of the average concentration per year has considerable decrease in 2010.

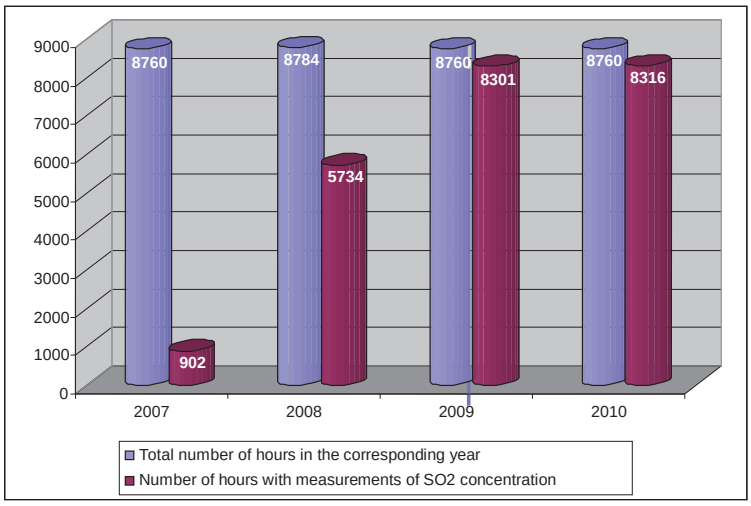

Fig. 7. Comparison of the number of hours with measured concentration of SO_2 from 2007 till 2010 with the total number of days with measurements in the corresponding years

3. There is no tendency for increasing the values of the average concentration per year in the winter months. This shows that pollution is not related to the seasonal emissions of domestic heating but to the production processes of the main source of pollution in the district - Lead-zinc Company LTD.

There is an analysis of the number of excesses of the average norm per hour for human health protection in all the years under investigation. The analysis shows that the norm is not kept during the four years and more than the allowed 24 excesses of ANH are registered (2007 – 28; 2008 - 171; 2008 - 203; 2010 - 88).

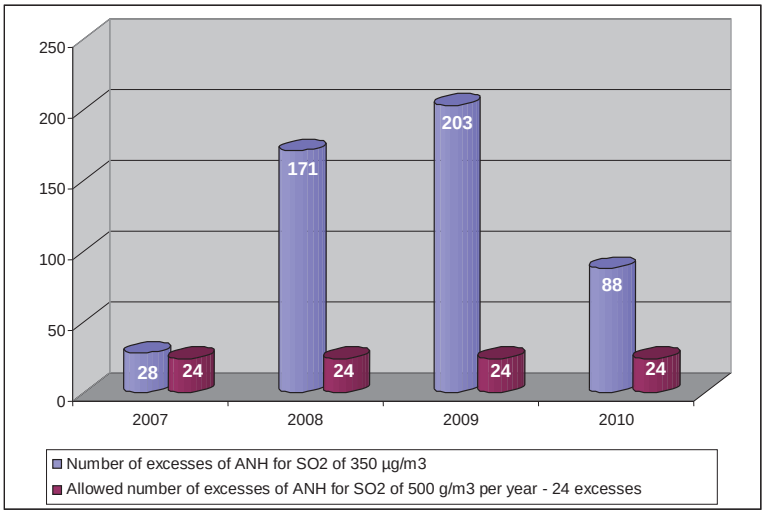

Fig. 8. Number of excesses of ANH of SO_2 in the period 2007 - 2010 of 500 $\mu g/m^3$

In chapter 4 of the program ”Character and evaluation of pollution” [1] there is a detailed analysis of air quality and there are conclusions made about the possible reasons for the values which are measured for this pollutant [2].

Analysis of the SO_2 concentration measured in the region of Kardzhali in the period 2007 - 2010 with the number of allowed days with excesses - 3 days.

According to the presented data of measured air concentration in the region of Kardzhali in the period 2007 - 2010 the following conclusion about pollution with sulfur dioxide (SO_2) can be made:

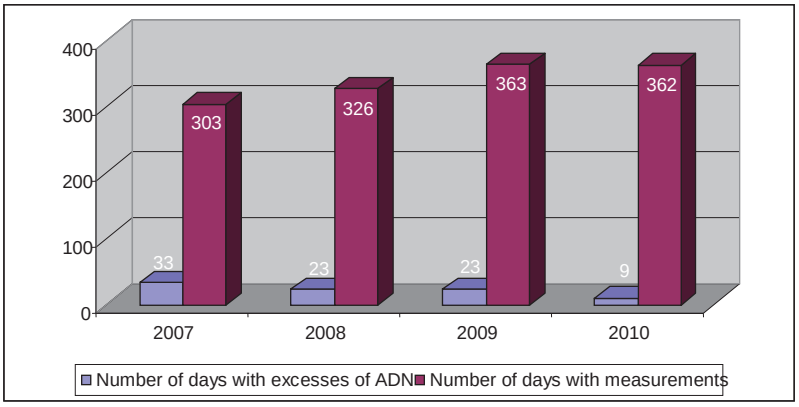

Fig. 9. Comparison of the number of days with excesses of ADN for SO_2 with the number of days with measurements in the period 2007 - 2010

- during the four years of investigation the average norm per hour for human health protection is surpassed more than 24 times, which is the limit allowed (2007 - 28; 2008 - 171; 2009 - 203; 2010 - 88). And despite the 2010 tendency to decrease, the excesses are 3.7 times more than the allowed limit;

- the number of days with excesses of the average daily norm shows a tendency to decrease (33 days in 2007 - 9 days in 2010), nevertheless it surpasses significantly the maximum number of excesses allowed for the ADN of SO_2, which is 3 per year;

- numerous excesses above the alarm limit for sulfur dioxide of 500 $\mu g/m^3$. According to the instruction the population was informed about 3 successive excesses of the average norm per hour for sulfur dioxide above the alarm limit of 500 $\mu g/m^3$;

- the values of the average concentration per year are not a controlled parameter for the atmospheric air but they are an integral indicator, which is actually directly related to the total yearly emissions of SO_2O.

The value measured in 2010 is lower than the values measured in the period 2007-2010. The following tables give evidence for this:

Table 1

Average measurements per hour of sulfur dioxide [3]

Place	Registered data Concentra tion per hour	Number of excesses of ANH [350 μg/m^3]	Maximum average concentration per hour measured [μg/m^3]	Number of excesses above the AL*
Kardzhali – Studen kladenets	8318	85	1516.63	1
Dimitrovgrad - Rakovski	8481	13	965.09	0

*****AL **–** alarm limit for sulfur dioxide (500 μg/m^3, measured in three successive hours)

Table 2

Average measurements per day of sulfur dioxide [3]

Place	Registered data Concentration per day (24 hours)	Number of excesses of ADN [125 μg/m^3]	Number of excesses of *UL [75 μg/m^3]	Maximum average concentration per day measured [μg/m^3]	Average concentra tion per year [μg/m^3]
Kardzhali – Studen kladenets	363	9	29	271.48	31.56
Dimitrovgrad - Rakovski	357	0	16	123.41	25.38

*****UL – upper limit for sulfur dioxide in the atmospheric air

In the last years sulfur cleaning installations caught 824,4 thousands tons of sulfur. A National program for decreasing the total yearly emissions of sulfur dioxide, nitric oxides, volatile organic compounds and ammonia in the air was approved by virtue of the Law for cleaning atmospheric air (LCAA) under article 10 in order to ensure the application of Directive 2001/80/EO and the fulfillment of the obligations of the country in the EU Accession Agreement. The document was approved with Decision N 261 by the council of ministers. Its application leads to considerable reduction of the pollution with sulfur oxides as can be seen in Tables 2 -6 below**.**

Table 3

Average values per hour for sulfur dioxide – 2011 [3]

Place	Registered data Concentration per hour	Number of excesses of ANH [350 μg/m3]	Maximum average concentration per hour measured [μg/m3]	Number of excesses above the AL*
Kardzhali – Studen kladenets	8366	38	960.70	0
Dimitrovgrad - Rakovski	8379	20	710,74	0

*****AL **–** alarm limit for sulfur dioxide (500 μg/m^3, measured in three successive hours)

Table 4

Average values per day for sulfur dioxide – 2011 [3]

Place	Registered data Concentration per day (24 hours)	Number of excesses of ADN [125 μg/m^3]	Number of excesses of UL* [75 μg/m^3]	Maximum average concentration per day measured [μg/m^3]	Average concentration per year [μg/m^3]
Kardzhali – Studen kladenets	365	4	31	172,07	29,91
Dimitrovgrad - Rakovski	361	2	20	133,83	28,32

*UL – upper limit for sulfur dioxide in the atmospheric air

Table 5

Average values per hour for sulfur dioxide – 2012 [3]

Place	Registered data Concentration per hour	Number of excesses of ANH [350 μg/m3]	Maximum average concentration per hour measured [μg/m3]	Number of excesses above the AL*
Kardzhali – Studen kladenets	8331	8	593,62	0
Dimitrovgrad - Rakovski	8302	19	876,10	1

*AL – alarm limit for sulfur dioxide (500 μg/m^3, measured in three successive hours)

Table 6

Average values per day for sulfur dioxide – 2012 [3]

Place	Registered data Concentration per day (24 hours)	Number of excesses of ADN [125 μg/m^3]	Number of excesses of UL* [75 μg/m^3]	Average concentration per year [μg/m^3]
Kardzhali – Studen kladenets	361	1	8	14,17
Dimitrovgrad - Rakovski	361	2	13	22,20

*UL – upper limit for sulfur dioxide in the atmospheric air

There is a program developed which makes provision for measures reducing the emissions. As a result the program aims at the application of Directive 2001/80/EO and achieving the national limits listed below:

Table 7

Average values per day for sulfur dioxide – 2013 [3]

Place	Registered data Concentration per day (24 hours)	Number of excesses of ADN [125 μg/m3]	Number of excesses of UL* [75 μg/m3]	Average concentration per year [μg/m3]
Kardzhali – Studen kladenets	92	0	1	88.88
Pernik - Shahtyor	82	2	17	183.35
Galabovo	92	0	3	117.85

*UL – upper limit for sulfur dioxide in the atmospheric air

Table 8

Emissions of pollutants in the atmospheric air by anthropogenic sources (without nature) compared to other atmospheric pollutants and international agreements of Bulgaria, kt [3]

Atmospheric pollutants	Emissions in 2011	Agreements according to Directive 2001/81/EO	Agreements according to Gotheburg Protocol to the Convention on Long-range Transboundary Air Pollution (LRTAP)		Aims of the National program approved with Decision N 261 by the Council of ministers	
		2010	2010	2010 г.	2015	2020
SO_x (i.e. SO_2)	514	836	856	380	300	250
NO_x (i.e. NO_2)	136	247	266	247	247	247
NMVOC	92	175	185	175	175	175
NH_3	48	108	108	108	108	108

Summary

In the period 2011 – 2013 there is a tendency to decrease the pollution in the atmospheric air and to reach the allowed norms of pollutants in the region of Kardzhali.

This can be seen in the analyses made for sulfur oxides in the period 2007-2013 of the average daily concentration of SO_2, measured in the period from 2007 till 2013. Data is received from ”KOS” for the period from 1 January 2007 till 31 July 2008 and from Studen kladenets Automatic Measurement Station for the period from 01 August 2008 till 31 December 2013.

These data can be also used when a morphological model is constructed, then the main elements are defined and the risks and criticalities for air pollution with sulfur oxides are determined [5].

We can use a turbulent stream model and the accompanying program PLUME based on it [4].

Scenarios are reproduced which allow the specialists to take decisions about the ecological security of the region.

Air pollution with sulfur oxides in the residential areas and the damages they can cause to the population are evaluated with an improved method of probability. The method uses eight probability criteria for evaluating the risk of pollution. These criteria allow us to analyse and determine the chance character of emissions and immissions that influence the risk and criticalities.

Conclusions

The analysis of the results of the concentration of sulfur dioxide leads to the following conclusions:

1. With regard to the number of excesses of the average norm per hour for human health protection (fig.1-fig.8):

- the diagram shows excesses above the allowed limit for all the years investigated;
- the comparatively small excess above the allowed limit in 2007 can be explained with the fact that the measurements at this place are done with manually taken samples. The analysed data include 902 average values per hour out of all 8760 hours in the year, which is only 10.3%;
- although the data for 2010 (88 excesses) show considerable decrease compared to the values measured in 2008 and 2009, still they are 3.67 times above the allowed 24 excesses of the average norm per hour.

2. With regard to the number of excesses of the average daily norm:

- the diagram shows excesses for all the years investigated;
- although the data for 2010 show considerable decrease (3 days with excesses) compared to the values measured in 2008 and 2009, still they are 3 times above the allowed 3 excesses of the average daily norm.

3. With regard to the average concentration per year (Fig. 1):

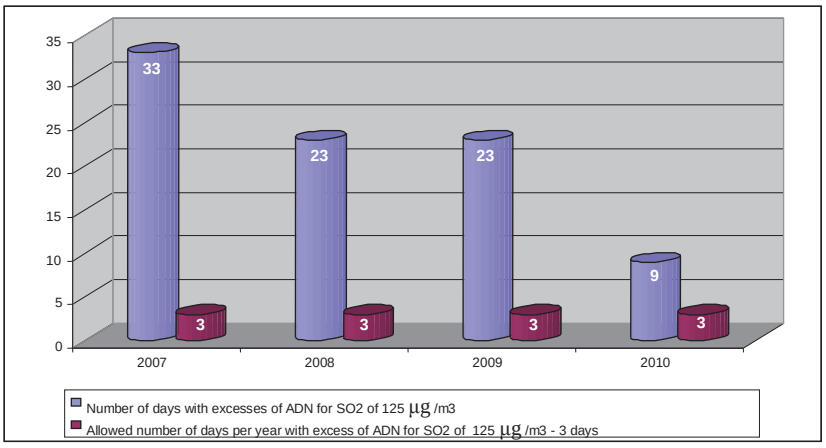

Fig. 10. Comparison of the number of days with excesses of ADN for SO_2

- these values are not a controlled parameter for the atmospheric air but they are an integral indicator, which is actually directly related to the total yearly emissions of SO_2;

- the values for the period 2007 – 2009 are almost equal, while the diagram shows a considerable decrease in 2010.

4. The diagrams for monthly distribution of the average daily concentration (Fig.1 - Fig.6) show no tendency for maximal values of the average daily concentration in the winter months. This means that pollution is not related to the seasonal emissions of domestic heating but to the production processes of Lead-zinc Company LTD.

5. The overall evaluation of the possibilities for preventing the pollution with sulfur dioxide is not favourable. The serious breach of the atmospheric air norm determines the necessity for a series of radical measures not only for decreasing the emissions per year but for protection from exceeding the average norms per hour and per day. There are excesses registered above the alarm limit of sulfur dioxide of 500 $\mu g/m^3$ and according to the instruction the population was informed about 3 successive excesses of the average norm per hour for sulfur dioxide above the alarm limit of 500 $\mu g/m^3$.

6. In the period 2011 – 2013 in the region of Kardzhali there is a tendency to decrease the pollution with sulfur dioxide, to reduce considerably the pollutants in the atmospheric air and to reach the allowed norms of harmful substances. This is shown in tables 1- 8.

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