International Scholars Journals

African Journal of Geography and Regional Planning ISSN 3627-8945 Vol. 5 (9), pp. 001-009, September, 2018. Available online at www.internationalscholarsjournals.org © International Scholars Journals

Full Length Research Paper

The acidifying gases emission in Cara - Severin county, Romania, in the period of 1997-2006

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Accepted 22 March, 2018

The harmful effects of air pollutants on human, animal and vegetation are the major reason for efforts to control their sources. During the last decades, research on acidic deposition and analysis of observational data were followed by scientific understanding of the relationships between emissions of precursor gases and deposition of acids or acid-forming substances. Cara -Severin County holds many non-renewable resources which have been intensely exploited using old, pollutant technologies. The extractive, iron and steel, metallurgic, energy and construction material industry greatly contributes to the further pollution of the environment with many pollutants, including gases with acid effects on the atmosphere. The analysis done between 1997 and 2006 for measuring the dosage of gases with an acid effect indicates a state of control over the releases and, in the last final of the decade, a constant level of air quality, below the maximum allowed limit; there were no states of alarm and the concentrations of SO_2, NOx and NH_3 were within the maximum allowed concentrations. Still, their polluting effect exists, and this is obvious considering the acid rains that have occurred, which have had detrimental local and distant effects on agriculture, vegetation and living organisms.

Key words: air pollution, acid deposition, acid rain, sulfur dioxide, nitrogen oxides, ammonia.

INTRODUCTION

It has been noticed that the atmosphere is the most sensitive environment receptor regarding the polluting anthropogenic activities which, noticed rapidly on a local level, spread to wider areas relatively fast. Atmospheric pollution affects people's health, disturbs the natural balances within ecosystems and brings considerable economic damage. Acidic precipitation, wet or frozen precipitation with a H^+ concentration less than pH 5.6 is a significant air pollution**.** The acidic precipitation is primarily caused by incorporation of anthropogenic sources such as SOx, NOx. On the other hand, neutralization of acidity in rainwater can be either due to ammonia released from industrial, agricultural and other natural sources (Likens et al., 1972; Likens and Bormann, 1974; Likens et al., 1979).

Resulting mainly from burning fossil fuel, but also from means of transportation, agriculture and zooculture, these gases can persist from hours to days in the atmosphere, and they can be carried hundreds of kilometers from where the pollution was produced. In particular, the provenance of pollutants and mechanisms of pollutant transportation remain poorly constrained (Larssen et al. 2006).

Emissions of SO_2 and NOx from the combustion of fossil fuels are subject to atmospheric transport over large areas and across political boundaries. Conse-quently, large areas of land in Europe, Asia, and North America are affected by acid deposition [Miller and Watmough, 2009]. There is a lack of long-term time series of background concentrations of main atmospheric compounds in Romania.

It is now well understood that air pollution produces significant adverse health effects in the general public and over the past 60 years, there have been on-going efforts to reduce the emitted pollutants and their resulting health effects (Hopke, 2009). In humans and animal, in low dosage, oxides of nitrogen causes severe irritations of the respiratory system, with burns and suffocation, violent cough accompanied by yellow spit, and in high dosages it leads to asphyxiation, convulsions, circulatory blockage,

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and in vegetable cells they cause a diminution of the photosynthesis. Significant amounts of SO_2 near the ground have a direct effect on human health, leading to respiratory symptoms, difficulty in breathing, even premature deaths in extreme cases, and inhibit plant growth. Ammonia emissions having either local or general impact, makes itself noticeable in the respiratory and ocular mucous through intense weeping, pink eye, keratin inflammation, tracheal bronchitis, bronchial pneumonia and reduced pulmonary air exchange (Wu Y et al., 2009).

Hypotheses that relate pollution to foliage-related or soil-related nutritional problems continue to receive considerable emphasis as explanations for recent forest damage. Linkages between acidic deposition and forest damage, however, remain largely coincidental (Lazarus et al., 2006).

The Cara -Severin County is the third largest county in Romania, with a large range of nonrenewable natural resources which were and still are extracted and treated with technological means which lead to the intense pollution of certain areas. The extraction and use of fossil fuels (coal), the mining pits, the iron and steel industries, the energy industry, the construction materials industry and other lead to the substantial pollution of the environmental agents with casual polluters (sulfur dioxide, carbon dioxide, nitrogen oxides and ammonia), with heavy metals, depository dusts, suspensional dusts and other similar pollutants. The major sources of air pollution at the Caras-Severin County are the following companies:

- S.C. U.C.M.R. S.A. Re i a, S.C. T.M.K. Re i a S.A., S.C. Ductil Steel S.A. Buz u, working point O elu Ro u – all in the filed of Plant production of iron and steel;
- C.E.T Energoterm Re i a -powerful combustion installations;
- S.C. Refraceram SA Baru –HD, working point Re i a - Installations for the manufacture of ceramics – bricks;
- S.C. AVIA AGROBANAT S.A. Boc a, S.C. Food 2000 SRL Boc a, S.C. Collini - S.R.L. Boc a, S.C. C.S.A.. Re i a, S.C. Avis Domar S.R.L. Boc a – all in the field of poultry intensive growth.

THEORETICAL ASPECTS

The problem of acid rain, from emission of pollutants, SOx, NOx and NH_3 through atmospheric transport and transformation, to deposition and biological impacts may be considerably more complex than has been the case with other pollutants (Evans LS et al., 1981). Rainwater chemistry is an intricate result of a complex interaction between cloud dynamics and the microphysical processes as well as series of rainout and washout atmospheric chemical reactions. The study of chemical elements in wet and dry precipitation has increased in the last two decades because of their adverse environmental and human health effect. The composition of rainwater actually reflects the composition of the atmosphere through which it falls (Likens and Bormann, 1974).

There are many instances of water in the atmosphere, from liquid to solid: rain, snow, fog and other precipitations, all containing chemical combinations resulted from both natural and anthropogenic processes. Of these substances, the most influential in creating the acid effect of precipitations are substances deriving from nitrogen and sulfur oxide. An excess of these may lead to a drop in the precipitations' pH to below the value 4. Carbon dioxide dissolves in the atmosphere water determines a pH $\cong$ 5,7 in an unpolluted atmosphere. Depending on the geochemical conditions of the area, on the urban/ rural character, on the industrial/agricultural character the pH of the precipitations varies between large limits, from under 4.7 but also larger than 8.

Nitrogen oxides, NO_x exist in the troposphere as a result of combustion from polluting processes, such as cars'exhaust pipes, or from uncontrolled burning of waste material. Only a small fraction of NO_x in the troposphere pass on to the stratosphere, because these two oxides last for a very short time (Table I), because after approximately 4 days they are transformed in nitric acid and are washed off by acid rains (Spiro, 2003).

The main mechanism (Martin, 1984) through with nitrogen oxides are transformed consists on burning the dioxide through involving the hydroxyl radical:

$$NO_2 + \cdot OH + M \rightarrow HNO_3 + M \quad \text{(M- partner, energy transferer)} \qquad (1)$$

At the same time, in a daily cycle, the following reaction may take place:

$$NO_2 + O_3 \cdot NO_3 + O_2 \qquad (2)$$

through which the nitrate radical $\cdot NO_3$ is formed, but this only builds up during night time because photosynthesis destroys it. Through a rapid, two-step reaction:

$$NO_3 + \cdot NO_2 \rightleftharpoons N_2O_5 \qquad (3)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (4)$$

The nitric acid is removed from the atmosphere by depositing, either in a dry or wet way, mostly during acid rains.

SO_2 oxidizes in the troposphere to form sulfuric acid (H_2SO_4) which is mostly deposited as acid rain, being responsible for the contamination of soil and for the degradation of marble monuments. Moreover, SO_2 plays an important role in cloud formation physics, leading to clouds of high reflectivity (Hopke, 2009).

Most of the existing sulfur dioxide in the atmosphere comes directly from the processes of „frying" the metalic sulfide from the ore used as raw material in the chemical and iron and steel industry, through burning fossil fuel and biomass:

$$Me_2S_{x\,(s)} + x\,O_{2(g)} \rightarrow x\,SO_{2\,(g)} + Me_2O_{x\,(s)} \qquad (5)$$

Table 1. The persistence of nitrogen and sulfur oxides in the atmosphere.

Gases	Atmospheric mixture ratio (ppbv)	Approximate persistence time (days)
Nitrogen oxides, NO_x	1 ÷ 10 (urban)	0.2 (urban, summer)
	0.1 ÷ 1 (isolated)	10 (isolated, winter)
Sulfur dioxide, SO_2,	0.01 ÷ 0.3	2 ÷ 70

$$C(S)_{(s)} + 2\,O_{2(g)} \quad CO_{2\,(g)} + SO_{2\,(g)} \qquad (6)$$

Producing sulfuric acid in the atmosphere starting from sulfur dioxide may be done in two separate ways: oxidation through homogenous reactions and oxidation through heterogenous reactions (Martin, 1984).

The steps of the oxidation process may be seen in the following chemical equations:

$$SO_2 + \cdot OH + M \quad HO^{\bullet}SO_2 + M \qquad (7)$$

$$HO^{\bullet}SO_2 + O_2 + M \quad HOO^{\bullet} + SO_3 + M \qquad (8)$$

$$SO_3 + H_2O \quad H_2SO_4 \qquad (9)$$

When the involved reactants are available in the rain drop in the atmosphere, the sulfuric acid is obtained through a heterogenous oxidation process. Starting with the sulfur dioxide from the atmosphere obtained from the above-mentioned sources, the following reactions take place:

$$SO_{2(g)} \rightleftharpoons SO_{2(aq)} \qquad (10)$$

$$SO_{2(aq)} + 2H_2O \rightleftharpoons HSO_{3(aq)}^{-} + H_3O^{+} \qquad (11)$$

$$HSO_{3(aq)}^{-} + H_2O \rightleftharpoons SO_{3(aq)}^{2-} + H_3O^{+}_{(aq)} \qquad (12)$$

The most important oxidation partner is hydrogen peroxide; in the atmosphere, this is to be found at 1-2 ppbv concentrations, easily soluble in water, reacting according to the equation:

$$HSO_{3(aq)}^{-} + H_2O_{2\,(aq)} \rightleftharpoons HOOSO_{2(aq)}^{-} + H_2O \qquad (13)$$

The peroxymonosulfite rapidly transforms in hydrogensulfate, which, through protonation forms sulfuric acid.

$$HOOSO_{2(aq)}^{-} HSO_{4(aq)}^{-} \qquad (14)$$

$$HSO_{4(aq)}^{-} + H_3O^{+}_{(aq)} H_2SO_{4(aq)} + H_2O \qquad (15)$$

The second way to heterogenously oxidate SO_2 in the atmosphere means that ozone is the oxidation partner, in which case both $HSO_{3(aq)}^{-}$ and SO_3^{2-} are may go through oxidation (29-30):

$$HSO_{3(aq)}^{-} + O_3 \quad SO_{4(aq)}^{2-} + H_3O^{+}_{(aq)} + O_2 \qquad (16)$$

$$SO_{3(aq)}^{2-} + O_3 \quad SO_{4(aq)}^{2-} + O_2 \qquad (17)$$

The exchange of ammonia (NH_3) between the atmos-phere and biosphere influences atmospheric chemistry as well as the nitrogen status of terrestrial and aquatic ecosystems.

NH_3 is a major contributor to secondary aerosol formation in the atmosphere as it reacts rapidly with sulfuric (H_2SO_4), nitric (HNO_3) acids to form ammonium (NH_4^+) aerosol. Ammonium aerosol affects Earth's radiative balance, lead to soil acidification, decreased resistance to climatic stressors, a significant shift in the nutrient economy and shifts in species composition.

Additionally, nutrient over enrichment of aquatic ecosystems may exacerbate eutrophication (Wu et al., 2009).

MATERIALS AND METHODS

Air quality and wet deposition monitoring network

In Cara -Severin County, in the analysis period of 1997 - 2006 there was no automatic network to monitor air quality, but there were more control points. In the County seat, Re ita, there were more data assay points, as seen in Table 2 and Figure 1.

The air quality monitoring network in Re i a, Cara -Severin County: 1 -The Environment Protection Agency Station; 2- Industrial-iron metallurgy company (S.C.T.M.K), 3- Industrial-engineering company (U.C.M.R.) and 4 - Station at the blood center.

In Cara -Severin County, the precipitations are supervised through a network of precipitation quality control consisting of 9 centers of assay placed in representative areas of the county: Re i a, Caransebe , Oravi a, Anina, Bozovici, B. Herculane, Moldova Nou , Semenic, Berzasca.

Acidifying gases content determination

Nitrogen dioxide content determination: The capture of the air samples to be analyzed is made using an installation that contains a capture funnel, glass pipe with inner diameter of 8 mm, vessel acquisition, device measuring air flow, a device for regulating the flow of air to 0.3 L/min, and exhauster.

Dosage method is based on the property of nitrogen dioxide to react in weak acid medium with sulfanilic acid, giving a diazonium compound; this compound is coupling with N-1-naphthyl-etilendiamine and forms an azoic compound of red color, whose intensity is proportional to the amount of nitrogen dioxide and is determinate with spectrophotometer device, to wavelength of 550 nm. It was established a calibration curve (extinction versus concentration) based on sodium nitrite (1 cm^3 of this solution contains 0.005 mg NO_2) by extinctions representation for solutions containing 0, 0.2, 0.4, 0.6, 0.8 and 1.0 g NO_2/cm^3.

Preparation of the absorption solution: dissolve 5 g sulfanilic acid in 600 cm^3 water, after cooling add 50 cm^3 glacial acetic acid, 10 cm^3 acetone, 0.05 g N-1- naftiletilendiamine hydrochloride and fill with water up to 1000 cm^3. The sample shall be absorbed in a flask

Table 2 . The air quality monitoring network in Re i a, Cara -Severin County.

Station	Station type	Polluting type	Analysis method
A.P.M.[1]	Urban /background	NO_2, SO_2, NH_3	see bellow, 3.2.1÷3.2.4
S.C.T.M.K[2]	Industrial-iron metallurgy	NO_2, SO_2, NH_3	see bellow 3.2.1÷3.2.4
U.C.M.R.[2]	Industrial-engineering	NO_2, SO_2, NH_3	see bellow, 3.2.1÷3.2.4
C.R.[3]	Traffic	NO_2, SO_2, NH_3	see bellow, 3.2.1÷3.2.4

[1]The Environment Protection Agency Station; [2] Industrial companies stations; [3] Station at The Blood Center

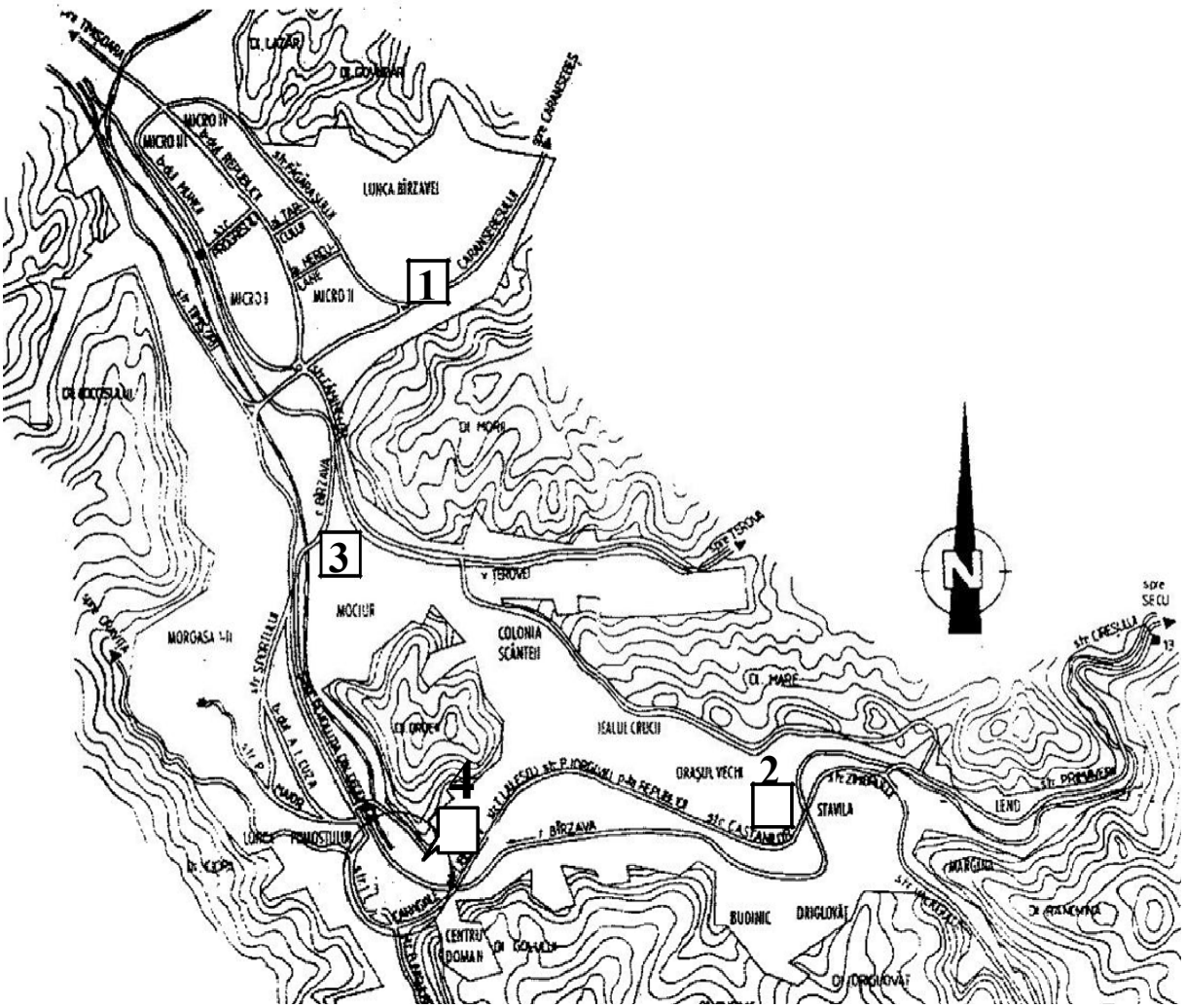

Figure 1. The air quality monitoring network in Re i a. 2 – S.C.T.M.K., 3 – U.C.M.R., 4 – C.R.

of 50 cm^3 and completed to the mark with distilled water. This sample are well mixed and is measured the extinction of colored solution to spectrophotometer in vats of 1cm thick, at wavelength of 550 nm, compared to a reference sample. The value obtained for extinction, read on the calibration curve, gives the concentration of NO_2 in this sample, expressed as g NO_2/cm^3. The content of nitrogen dioxide in air is done with the formula:

Nitrogen dioxid [mg/m^3] = $50 \cdot c/V$

Where; c = concentration of spectrometric analyzed solution in g NO_2/cm^3, V = volume of air collected in dm^3 and 50 = volume of sample flask, in cm^3.

Sulfur dioxide content determination: The capture of the air samples to be analyzed is made using an installation that contains a capture funnel, glass pipe with inner diameter of 8 mm, a small vessel harvesting device for retaining acid aerosols, device measuring air flow, device regulation flow from 0.5 – 1 L/min., and

exhauster. Dosage method is based on the property of SO_2 to form with mercury (II) tetrachloride ion the dichloride-sulfide-mercury complex (II), which in the presence of formaldehyde react with pararosaniline forming a colored compound (pararosanilin methyl sulfonic acid) whose absorbance are measured at 548 nm, in vats of 1 cm thick. It sets a calibration curve based on anhydrous sodium sulfite (which contains 5 mg SO_2/cm^3) by extinctions representation for solutions prepared from stock solution (5 g SO_2/cm^3) and containing 0, 0.2, 0.4, 0.6, 0.8 and 1.0 g SO_2 $/cm^3$. Introduce in absorption vessel 10 cm^3 absorbent solution and collect the air sample. The obtained solution is moved in a 25 cm^3 flask. Add 1 cm^3 formaldehyde solution, 5 cm^3 pararosaniline solution, bring water to sign and mixed well. Prepare a parallel con-trol test for reagents. The absorbances of sample and reagent control are measured at wavelength of 548 nm, in vats of 1cm thick, comparatively to distillated water. Make the difference of these values. The obtained extinction, read on the calibration curve, gives the concentration of SO_2 in analyzed sample, expressed as g SO_2/cm^3 . The content of sulfur dioxide in air is done with the formula:

Sulfur dioxid [mg/m^3] = $V_1 \cdot c / V_2$

Where; c = content of SO_2 in the spectrometric analyzed sample (g SO_2/cm^3, V_1 = volume of absorbent solution used in taking the sample (cm^3), V_2 = volume of air collected (dm^3).

Determination of ammonia: Device to capture the air sample is similar to 3.3 descriptions. Ammonia in the form of ammonium ion, reacts with reagent Nessler (solution of potassium tetraiodomercurate (II) in potassium hydroxide) forming a water soluble, yellow-brown mixture in variable proportions of amido-oximercury iodide and amido-mercury triiodide. The intensity of color is proportional to the amount of ammonia and is measured using a spectrophotometer at the wavelength of 450 nm, in vats of 1cm thick. By air filtering on glass wool remove the interference substances. Transfer the sample in a flask of 50 cm^3, add absorbent solution to 40, 4 cm^3 Nessler reagent and complete the mark with absorbent solution. After 30 min, measure the extinction of colored solution to spectrophotometer at wavelength of 450 nm, in vats of 1 cm thick, compared to a reference sample consisting of 4 cm^3 Nessler reagent and 46 cm^3 absorbent solution. The value obtained for extinction, read on the calibration curve, gives the concentration of ammonia in this sample, expressed as g NH_3/cm^3. Determine the content of ammonia in the air, using the formula:

Ammonia [mg/m3] = c / V

Where; c = ammonia content in the spectrophotometer analyzed sample (g NH_3/cm^3 mg), V = volume of air collected (dm^3).

RESULTS AND DISCUSSION

Acidifying atmospheric pollutants

This work plans to analyses the acidifying atmospheric pollutants in the Cara -Severin County, Romania, a county which has a powerful extractive and iron and steel industry.

Table 3 presents the sources of pollution with acidifying gases, classified by fields of activity, for two years of the decade taken into consideration, specifically for 2003 and 2004. It can be seen that the burning processes in the field of energy and transformation industries, as well as the industrial unities, are not the main SO_2 and N_2O polluters, this place being taken by the non-industrial burning plants.

The means of transportation are the main source of NO_X pollution, alongside the non-industrial burning plants. Ammonia is a result of waste handling processes but also of agriculture, sylviculture and changes in the timber land.

The average annual evolution of SO_2 si NO_X concentrations in the period of 1997 - 2006 can be seen in Figure 2.

In Re i a town, after a relatively constant degree of the SO_2 concentration in the period of 1997 - 2001, an increase can be noticed in the period of 2002 - 2006. However, between 1997 and 2006, in Cara -Severin County the concentration of SO_2 was constantly within permitted limits (MEC - 0,060 mg/m^3).

The NO_2 emissions in Re i a (Figure 2) were constant in the considered period within 0,011 - 0,015 mg/m^3 (with one exception, in the year 2002, when the emissions got to 0,0185 mg/m^3); in other industrial places in the county, precisely in Caransebe and O elu Ro u, the level of emissions decreased after the year 2002 until they reached inessential values.

What is important is that all the daily concentrations, 24 h for all the acidifying gases, measurements being taken in all the network's air monitoring points in Cara -Severin County, are within the limits allowed by the current legislation (STAS 12574/87 and O 92/2002). The alarm limit (70% of the maximum permitted concentration, Order 756/1997) was never reached, for any acidifying gas.

The total emissions of polluting acidifying gases, measured in tons/year (Figure 3), indicate a small decrease in the concentration of SO_2 and NOx for 1997-2006. The total emissions concentration of ammonia in Cara -Severin have been increasing until 2004, but the tendency in the next years is to decrease (Table 4).

The evolution of medium annual concentrations of ammonia, between 1997 and 2006 is presented in Table 5. It can be seen that the emissions of ammonia have disappeared in two of the main towns in the county, and the concentration in Re i a town has remained relatively constant.

Acid rains

Rainwater chemistry is strongly influenced by local anthropogenic sources rather than natural sources. The pollutants in rainwater samples are mainly derived from long distance transport, local industry and traffic sources. For Caras-Severin county, table below shows the number of acid rains in 2003 and 2004 in the 9 points of wet deposition monitoring network.

The Figure 4 reflects the evolution of pH average rainfall in Caras-Severin at the 9 monitoring stations between 2001 and 2004.

Though the emissions of SO_2 and NO_2 are much below the maximum permitted concentration, there were a high number of acid rains in Cara -Severin: out of 258 rains

Table 3. The contribution of different industrial activities (percentages of total emissions) to the pollution with acidifying gasses in 2003 and 2005 in Cara -Severin County, Romania [data obtained from Environmental Protection Agency Caras-Severin County, annual reports, www. apmcs. ro].

Year	2003				2005			
Activity	**SO_2 %**	**NO_2 %**	**N_2O %**	**NH_3 %**	**SO_2 %**	**NO_2 %**	**N_2O %**	**NH_3 %**
Burnings in the energy field and in the transformation industries	0.37	6.14	2.16	-	0.18	4.93	1.57	-
Non-industrial burning plants	98.15	3.39	62.32	0.67	98.21	25.04	63.05	0.60
Burning in the refinement industry	0.05	0.78	0.85	0.002	0.29	2.21	0.80	0.002
Production processes	0.07	1.52	0.25	-	0.30	6.90	1.07	-
The extraction and distribution of fossil fuels and of geothermal energy	-	-	-	-	-	0.04	-	-
Means of transportation	1.19	64.64	6.08	0.004	0.85	56.96	3.19	0.004
Other mobile sources and devices	0.15	3.51	1.80	0	0.16	3.4	1.88	0
Treatment and storage of waste materials	0	0.003	0	46.35	0	0	1.19	41.82
Agriculture, sylviculture and the altering of timber land.	-	-	26.56	52.96	-	-	27.24	57.56

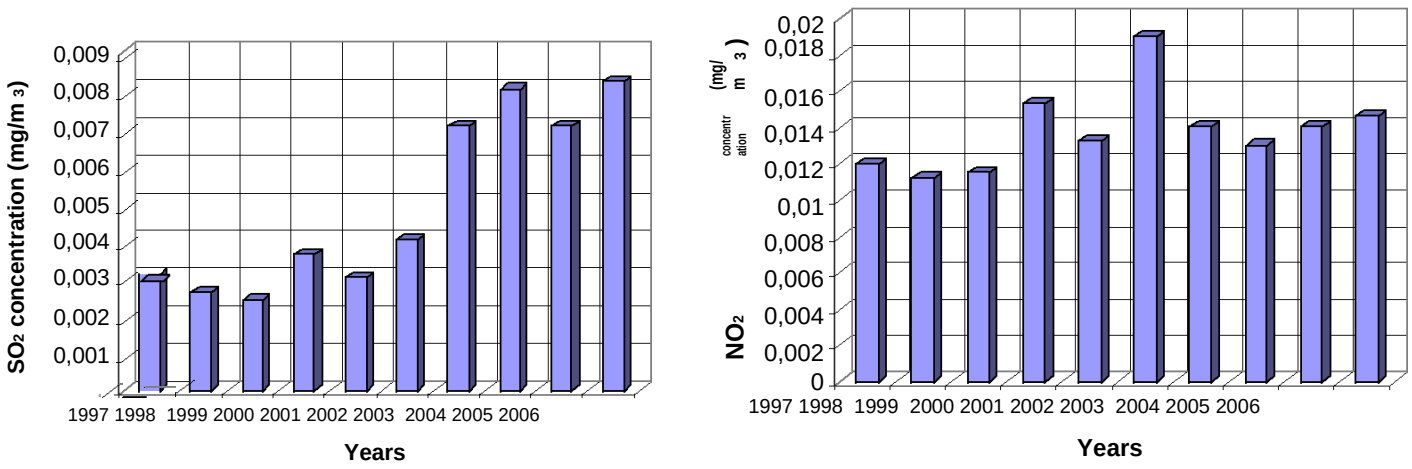

Figure 2. Evolution of medium annual concentration of sulfur dioxide (mg/m^3) and NO_2 , between 1997 - 2006, in Re i a city, Cara Severin County (MEC-maximum emission concentration SO_2– 0.060 mg/m^3, NO_2-0.040 mg/m^3).

53 were acid (20.5%) in 2003 and 59 in 2004. The maximum number of acid rains with the highest degree of acidity (pH 4.7) has been noticed at an altitude of 1422 m, on the Peak of Semenic Mountain (15% of the total of

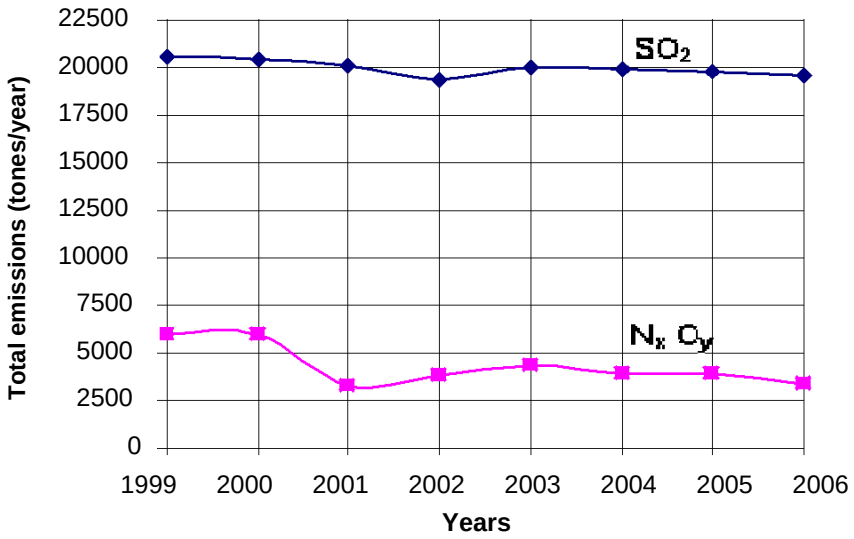

Figure 3. Total emissions of sulfur dioxide and nitrogen oxides in the time 1997-2006, in Caras Severin County (tones/year).

Table 4. Total emissions of ammonia in the in recent years in Cara -Severin County (tons/year).

Caras-Severin	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Annual emissions (tons/year)	3890	3860	3920	3942	3712	3789	5236	5951	5805	5349

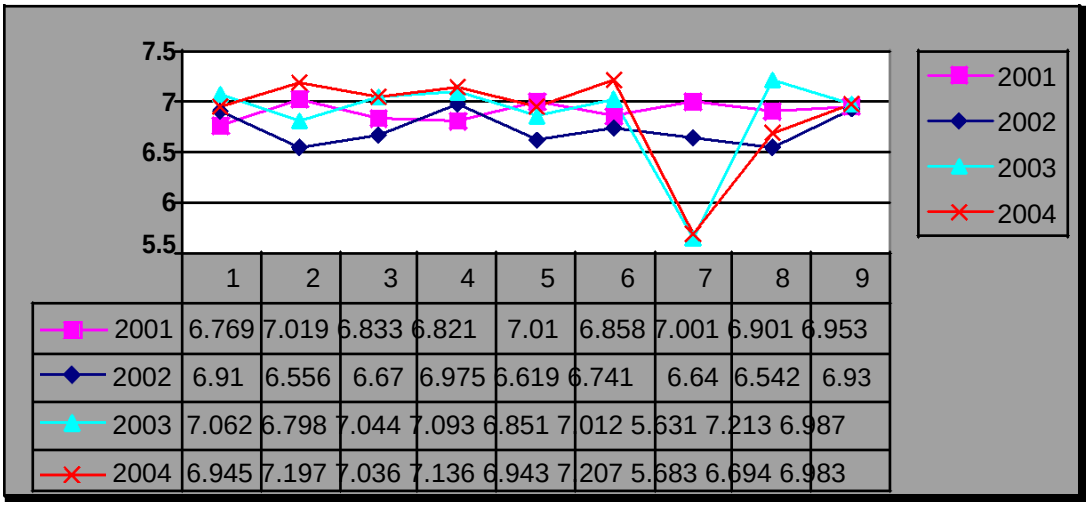

Figure 4. Average rainfall pH in Cara -Severin County. Legend: 1 - Re i a, 2 –Moldova Nou , 3–Oravi a, 4–B ile Herculane, 5–Bozovici, 6–Caransebe , 7–Semenic, 8– Berzasca, 9–Anina.

Table 5. The evolution of medium annual concentrations of ammonia by areas in towns in Cara -Severin County (mg/m^3).

Area	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**
Re i a	0.035	0.034	0.038	0.047	0.033	0.040	0.040	0.035	0.037	0.038
Caransebe	0.044	0.038	0.048	0.051	0.036	-	-	-	-	-
O elu Ro u	0.043	0.037	0.051	0.054	0.041	-	-	-	-	-

Table 6. Statistics regarding the number of acidic rains in Cara -Severin's cities in 2003 and 2004.

Town area :	Number of rains					
	overall		pH 6 - 6.5		pH < 6.0	
	2003	2004	2003	2004	2003	2004
Re i a	29	29	0	1	0	0
Caransebe	28	28	0	2	2	0
Oravi a	27	27	1	1	0	0
Semenic	39	39	7	7	25	28
Moldova Nou	26	26	5	0	3	1
Bozovici	31	31	3	6	3	1
Berzasca	19	19	1	6	1	4
Anina	29	29	2	0	0	1
B ile Herculane	30	30	0	1	0	0
TOTAL	**258**	**258**	**19**	**24**	**34**	**35**

acid rains noticed in the county and 82% of the rains on Semenic Mountain) . This evidence to make us believe that the acidifying effect is more noticeable in high altitude areas and further away from the pollution areas. In the towns of Re i a, Caransebe , Oravi a, Anina, towns with important pollution sources, there have been no acid rains, which confirm the previous conclusion. In the total 258 rain events in 2003, 19 events were observed in acidic range 6 - 6.5 and 34 in acidic range less than 6.0. In the next year, in the same rain events (258) , 24 events were observed in acidic range 6-6.5 and 35 in acidic range less than 6.0 (Table 6).

As well there have been numerous acid rains in Moldova Nou city: 30.8%, of the total rains in the area in 2003, and 22.6% in the next year. In Bozovici, the acid precipitation has decreased significantly from one year to another, which reflects changes in local industry (from 19.3%of the total rains in the area in 2003 - 3.85% in 2004). It can see that if we relate to the same number of rain in 2003 and 2004, the location occurring acid rain (pH between 6 and 6.5) and strongly acidic (pH less than 6) are the same: Semenic Montain. At the Semenic Montain was recorded strong acid rain with pH around 5.6 in two consecutive years.

Paradoxically, the towns B ile Herculane and Re i a seem to be clean from this point of view since there having been no acid rains there.

Air quality in Caras-Severin county

The overall quality of air and acidifying substances parameter is the general pollution coefficient. Between 1997 and 2006 it varies as shown in Figure 5.

It can be seen that, regarding air quality in the period of 1997 - 2006, the year 2002 has been the most polluted, the year 2001, the least polluted, but lately, due to a more and more professional monitoring system, the air quality

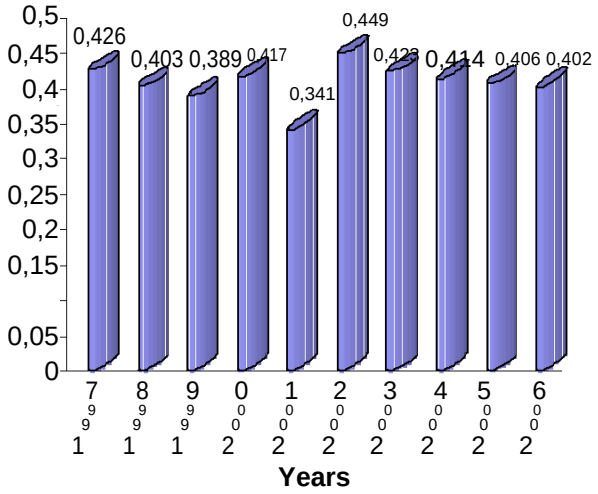

Figure 5. Evolution of air quality, between 1997 - 2006, in Cara Severin County, Romania.

is around the same pollution level, with small variations (coefficient of pollution around 0.4).

Conclusion

Romania is a country with a number of useful energy and mineral resources. The exploitation of these resources, however, has led to high levels of air pollution. The aim of the present paper is to give an overview on acidifying gases emission in the period of 1997 - 2006 of the one of the most industrialized regions, Caras-Severin County.

By analyzing the data presented above the following conclusions can be drawn:

- between 1997 - 2006, in Cara -Severin County, the acidifying gases in the atmosphere are mainly a result of

non-industrial burning devices (heating devices using fuel that is high in sulfur content) and from the means of transportation;

- non-industrial burning devices play a great part in acidifying the atmosphere by providing 98% of the county's emissions of SO_2 and about 63% of the emissions of N_2O, followed by the emissions resulted from the traffic, especially - through the NO_2 nitrogen oxides from the exhaust gases;
- The evolution of the annual medium concentration of de SO_2 and NO_2 between 1997 and 2006 in Cara -Severin County reflect on the one hand the changes caused by industry, on the other hand the activity of the county Environment agency of Cara -Severin County regarding the permanent monitoring of air quality and the actions done to reduce pollution;
- Though the emissions of acidifying gases have remained within non-alert limits, there have been numerous acid rains, representing 20% of the total number of rains in the year taken into consideration (2003);
- The maximum number of acid rains has been registered on Semenic Mountain, which proves the fact that acidifying gases travel at great altitude and length from the polluter;
- Though the general air pollution coefficient has been relatively constant in the last years (0.40), the fact that there have been numerous acid rains indicates a significant pollution with acidifying gases, with effects (that are seen wither immediately or in time) on vegetation and on the health of the people living in Cara -Severin County.

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