Journal of International Scientific Publications: Ecology and Safety
Volume 8, ISSN 1314-7234 (Online), Published at: http://www.scientific-publications.net

RISK ASSESSMENT OF WATER ACIDIFICATION BASED ON LONGTERM HYDROCHEMICAL RESEARCH AT FORESTED CATCHMENTS

Nadka Ignatova, Maria Mladenova
University of Forestry, Department of Plant Pathology and Chemistry,
10 Kliment Ohridski str, Sofia 1156, Bulgaria

Abstract

Longterm hydrochemical research in forested catchment in Petrohan area has been carried out for risk assessment of water acidification. The time series are 27 years long. Deposition shows declining sulfate and nitrogen. The concentration of base cations has been decreased in both bulk precipitation and surface water showing the decrease of the neutralizing capacity of stream water. The mean value of pH for spring water have been averaged as 5.99 pH units and for stream water at the same catchment area 6,68 pH units respectively. It has been found that the ratio between the sum of base cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) and the sum of acidifying pollutants, like nitrogen sulfate and chloride, has been decreased for the period 1986- 2013. Critical loads of acidity, sulfur and nitrogen have been calculated in order to determine the sensitivity of water bodies to the acidifying pollutants and the results obtained showed different sensitivity. The time series analyzing has been shown that all critical loads of acidity, sulfur and nitrogen have been decreased showing the decreasing of the tolerance of the water ecosystems to the acidifying pollutants. The exceedances of critical loads were used to evaluate the risk for acidification.

Key words: *acidification, bulk precipitation, critical loads, exceedances, risk assessment, source and stream water chemistry.*

1. INTRODUCTION

There is an agreement that the acidity of some stream waters originated from the catchments situated closely to the acid ones, remains neutral. It means that the stream water acidification depends not only on acid depositions but also on the background substrate, the buffering capacity of the soils in the catchment area, the vegetation cover, the climate etc (Davies et al. 1992; Probst et al. 1992; Moldan et al. 2001; Ignatova 2005, 2007). For this purpose, we have applied the Steady-state mass balance method for sustainable development of water ecosystems using monitoring data collected at the LTER site “Petrohan” in Bulgaria. Taking into account that the relationship between the risk of water acidification and the environmental conditions could be given by the critical loads of acidifying pollutants, steady state mass balance approach has been selected for determining critical loads of acidity, sulfur and nitrogen, in order to avoid the stream water acidification and pollution (Hettelingh et al. 2004; Ignatova 2007).

The critical loads concept is a reliable solution for the assessment of multicomponent ecosystems. It has been successfully applied to solve problems with acidification and eutrophication in forested catchments. Nowdays it is in potential use in negotiations on the reduction of acidifying pollutants emission in Europe. The critical load is the highest total input of pollutants that prevents ‘significant harmful effects on specified sensitive elements of the environment’ (Nilsson and Grennfelt, 1988). The relationships between the effects of air pollution and the response of ecosystems on a European scale are expressed by comparing deposition to critical loads mostly for forest ecosystems (De Vries et al. 1995; Hettelingh et al. 2004) but the number of effect studies in the aquatic environment is limited.

Since forest ecosystems have many functions, related to biodiversity, forest products, water protection and carbon sequestration, it is crucial to know the amount of deposition of acidifying pollutnts protecting them from damage and decline. Critical loads have been defined as quantitative estimates of an exposure to one or more acidifying pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge (Nilsson and Grennfelt 1988). Bulgarian focal center has been contributed to this calculating and mapping procedure too, determining critical loads of acidifying pollutants and heavy metals mostly for forest and aquatic ecosystems (Ignatova 2005, 2007; Ignatova et al. 1998, 2003, 2007, 2008; Slootweg et al. 2007).

In the beginning of each risk assessment procedure, a selection and specification of relevant indicators must take place for the quantification. The list of potential indicators has been derived from most recent literature. Critical loads for different receptors can be used for determining the sensitivity of a given receptor (water bodies in our case). When the value of critical load is high the receptor is more tolerant and less sensitive to the pollutant of concern. In this case the receptor can accept high amount of pollutant deposition without harmful effects. On the other hand the risk of damage can be assessed by means of exceedances of critical loads by current deposition of a pollutant of interest (De Vries et al. 1995, UBA 2004). This approach is very effective because the investments in reduction of the deposition of acidifying pollutants can be addressed only to the regions with critical load exceedances (De Vries et al. 1995; Hettelingh et al. 1995, 2004; Slootweg et al. 2007).

The aim of this study is to carry out long term investigations on the sensitivity of the catchment area of spring and stream water ecosystems and deposition of acidifying pollutants in order to assess the risk of acidification of water resources used for drinking water supply.

From this point of view the following tasks have been taken into account:

1. Long term study on acidity and deposition chemistry of bulk precipitation and throughfall at the LTER Petrohan site;
2. Comparative study on acidity and water chemistry of the spring and surface water bodies at the Petrohan site without local sources of pollution;
3. Determination of the sensitivity of the water ecosystems to the acidifying pollutants at the Petrohan site by means of critical loads of Acidity, Sulfur and Nitrogen;
4. Risk assessment of acidification of water resources using the exceedances of critical loads by the current deposition of acidifying pollutants.

2. MATERIALS AND METHODS

2.1. Site description

The Petrohan site has been established in 1986 with 2 plots in Beech and Spruce forest in the Northwestern Bulgarian part of the Balkan mountain on Granite as a base rock and Brown soils (Dystric Cambisols). Te main water bodies are the Petrohan dam and Barzia river (Fig. 1). The climat is Moderate Continental, Mountaineous, with an annual precipitation amount of 1060 mm (Koleva, Peneva, 1990). The distribution of the mounthly amount of precititation, air temperature and humidity could be seen in fig. 2. The vegetation cover of the catchment area consists of Assosiation Asperulo- Fagetum Sylvaticea (about 95 %) and Picea Abies, Variant Salvia Glutinosa (5 %), Habitat 9130.

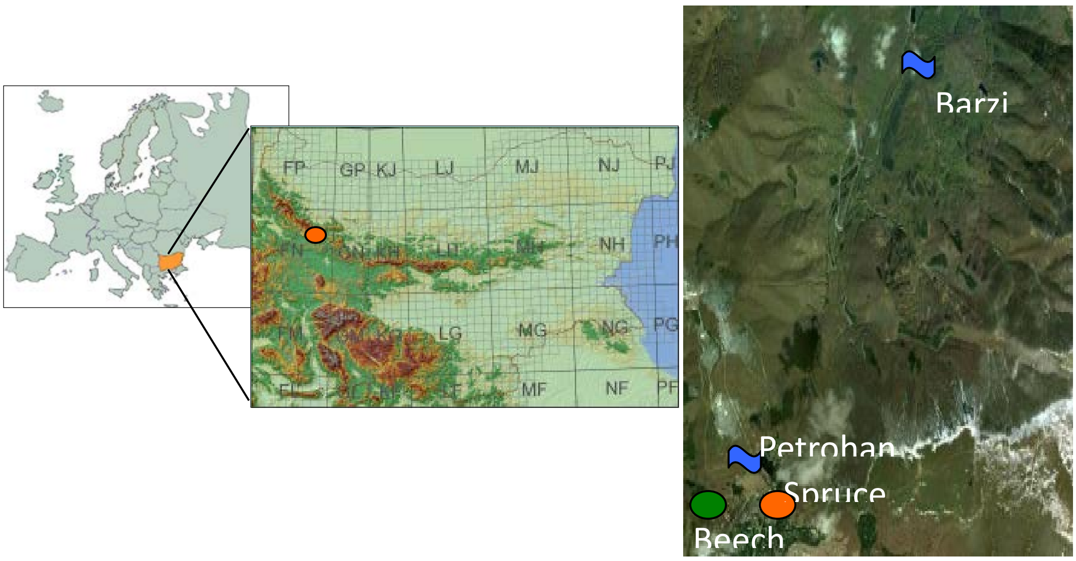

Fig. 1. Location map of LTER "Petrohan" site

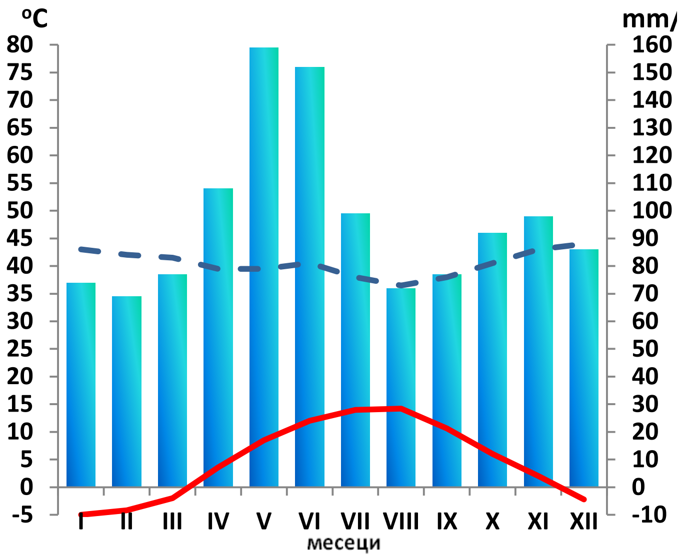

Fig. 2. Destribution of the mounthly precipitation amount (Blue hystograms), temperature (red line) and air humidity (blue line) at the "Petrohan" site

2.2. Sampling, analysis and data base collection

The bulk precipitation and throughfall has been collected with 6 (for bulk precipitation) and 12 (for throughfall) continuously open plastic funnels (1 m above the ground) per plot with an individual collecting surface of 314 cm^2 in polyethylene bottles stored in the upper soil layer. Individual water samples of bulk precipitation, throughfall, spring and surface water have been collected fortnightly after measuring the water volume and the pH on separate aliquots of the unfiltered sample the same day of sampling in the field by ionmeter "Combo" of the "Hanna Instruments". All samples have been filtrated trough 0.45 µm cellulose filter using membrane filtrating system in order to remove any solid materials and to stabilize them for the subsequent analyses, and stored in the refrigerator at 1-4 ^oC until analyses. The chemical composition of the water samples has been determined as follow: NH_4^+ and NO_3^- -using Kyeldal automatic distillation and titration by Tekator (Sweden), SO_4^{2-} - by UV/VIS Spectrometry "Lambda 5, Perkin Elmer"; Cl^- by means of precipitation with $AgNO_3$; Base cations K^+, Na^+, Ca^{2+} and Mg^{2+}– by Atomic Absorption Spectrometry "M 5000, Perkin Elmer". Annual wet throughfall deposition of Base cations, S and N has been defined by multiplying the throughfall amount with the elements concentration in the throughfall. Base cations (K^+, Na^+, $Ca^{2+}$and Mg^{2+}), N and S uptake by the biomass has been derived by multiplying their content in the forest stem and branches, measured by inductively coupled plasma emission spectrometry (ICP-OES Vista MPX, Varian Inc, Australia), with the annual growth Yveg ($kg.ha^{-1}yr^{-1}$) determined after cutting 10 representative trees in the buffering area as follow:

$$Yveg = Va\ \rho / a,$$

Where: Va – the mean volume of all trees at the catchment area in $m^3\ ha^{-1}\ yr^{-1}$; ρ – the wood density in $kg\ m^{-3}$; measured by means of the Tsonmis method (1991); a – the age of trees in years.

The runoff of water under root zone has been measured and mapped as mean annual values for a period of 20 years in grid cells 10 x 10 km for the entire country (Kehayov 1986). The method is based on a splitting of river hydrograghs, hydrogeological parameters of the underground water bodies, measurement of the mineral runoff between neighbouring hydrometric sites, infiltration etc.

In addition ratio between the sum of base cations and the sum of acidifying pollutants as well as between Ca^{2+} and Cl^- concentration in all water compounds has been calculated.

2.3. Method of calculation of critical loads and their exceedances

The effect based Steady state mass balance model in which the input of all chemical elements to the chatchment area of the water body of interest must be equal to their output for keeping the sustainable development of the water ecosystem was used to calculate the critical loads of acidifying pollutants (Fig. 5).

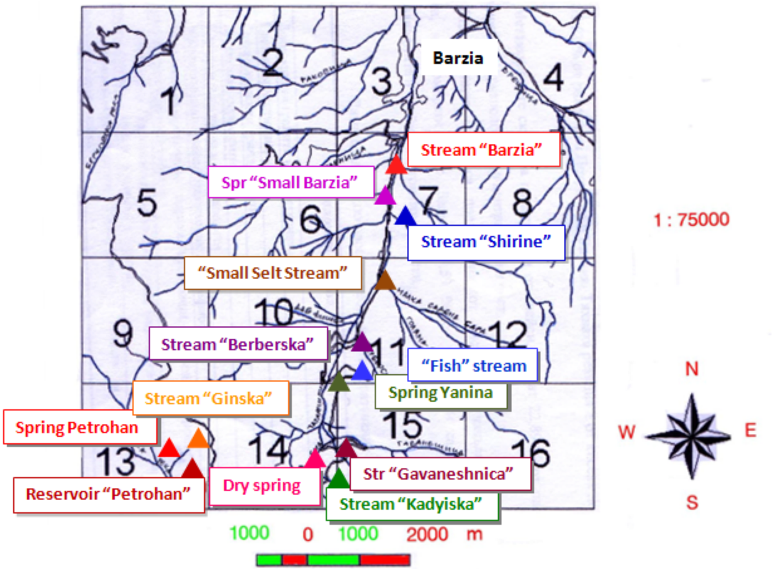

Fig. 3. Sampling points for spring and stream water chemistry at the Petrohan site

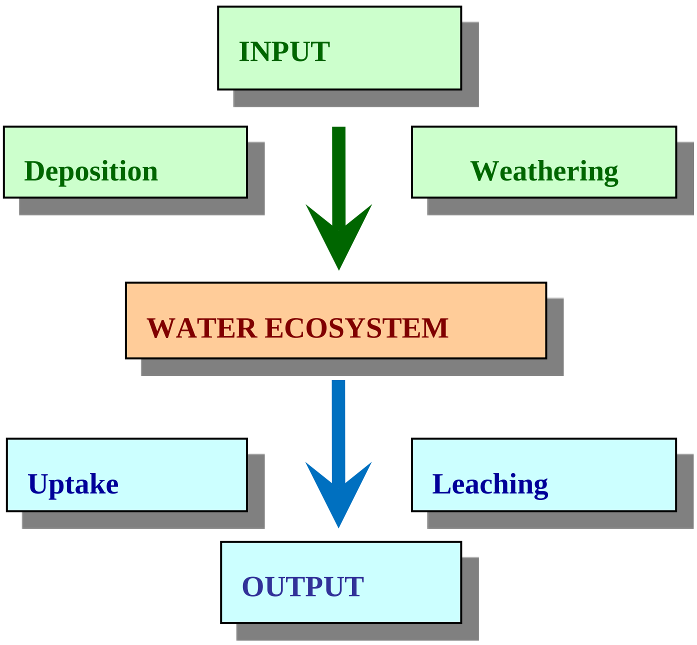

Fig..5. Steady State Mass Balance approach – (The input must be equal to the output)

The effect based Steady-state mass balance model was used to calculate the critical loads of acidity CL (A), sulfur CL max (S) and nitrogen [CL max (N), CLnut (N)], according to the follow equations (UBA 2004):

CL (A) = BC w + Q [H] crit + R Al/Ca (BC dep + BC w - BC u)

= 2.5 BC w + 0.09 Q + 1.5 BC dep - 1.5 BC u

CL max (S) = CL (A) + BC dep - BC u

CL max (N) = CL min (N) + CL max (S)

CL nut (N) = N u + N i + N le (crit)

Exceedances of critical loads of acidity Ex (A), sulfur Ex (S) and nitrogen Ex (N) by present depositions were defined as follow:

Ex (A) = PL (S) + PL (N) - BC dep - BC u - N u - CL (A)

Ex (S) = PL (S) - Sf (BC u - BC dep) - CL (S)

Ex (N) = PL (N) + (1- Sf) (BC u - BC dep) - CL (N)

where:

BC w – input of base cations by weathering;

BC dep- input of base cations by deposition;

BC u and N u- uptake of base cations and nitrogen by the biomass;

N i- nitrogen immubilisation;

N le (crit)- nitrogen leaching ;

where: Sf – relative part of sulfur deposition in the common deposition of acidifying pollutants (Sf = PL (S) / PL (S) + PL (N) - N u - N i)); PL (S) – present deposition of sulfur [PL (S) = PL (S-SO_2) + PL (S-SO_4^{2-})]; PL (N) – present deposition of nitrogen [PL (N) = PL (N-NO_2) + PL (N-NO_3^- + N-NH_4^+)]

In the absence of acid streams in Bulgarian forested areas the results obtained in this study have been compared with the data for acid stream water (pH 4.3) in the "Vosges" mountain, France, produced on quartzitic sandstone and acid soils with acid atmospheric deposition (Dambrine, Nourrisson, 1992; Angeli et al., 2005; Probst et al., 2005; Posch et al., 2005).

3. RESULTS AND DISCUSSION

3.1. Longterm monitoring study on the deposition of acidifying pollutants by bulk precipitation and throughfall at the Petrohan site.

The trend of the computed atmospheric deposition of acidifying pollutants (sulfur, oxidized nitrogen and reduced nitrogen) at the Petrohan site for the period 1885- 2005 has shown a clear increase between 1950 and 1980, especially for sulfur which deposition has ranged from about 20 $eq.ha^{-1}.yr^{-1}$ in 1885 to approximately 1500 $eq.ha^{-1}.yr^{-1}$ in 1975 (Fig. 6).

The real measured deposition of acidifying pollutants under the crowns of the forest cover (beech and spruce) at the study catchment area at the Petrohan site for the period 1994- 2013 has demonstrated decreasing trends for oxidized nitrogen and sulfur (NO_3^- and SO_4^{2-}) considered as main acidifying pollutants in the study region. The deposition of reduced nitrogen (NH_4^+) has oscilated around 800 $eq.ha^{-1}.yr^{-1}$, but there was a very clear increase in the deposition of Cl^- from 500 $eq.ha^{-1}.yr^{-1}$ in 1994 to 1600 $eq.ha^{-1}.yr^{-1}$ in 2012 (Fig. 7).

3.2. Acidity and stream water chemistry at the Petrohan site

Taking into consideration the acidity of the surface running water of the main "Barzia" river, included in tabl.1, it could be seen that there was not significant difference between the values of pH for the same period. The mean acidity of the surface water for 12 years period (1986- 1997) consists of 6,81 pH units against 6,67 for 2013. Taking into account that water resources in thy study region are used mainly for drinking water supply and that the limit for the acidity is from 6,5 to 8,5 pH units it could be mentioned that all measured values, except in 1986, have been very close to the lowest border of the limit.

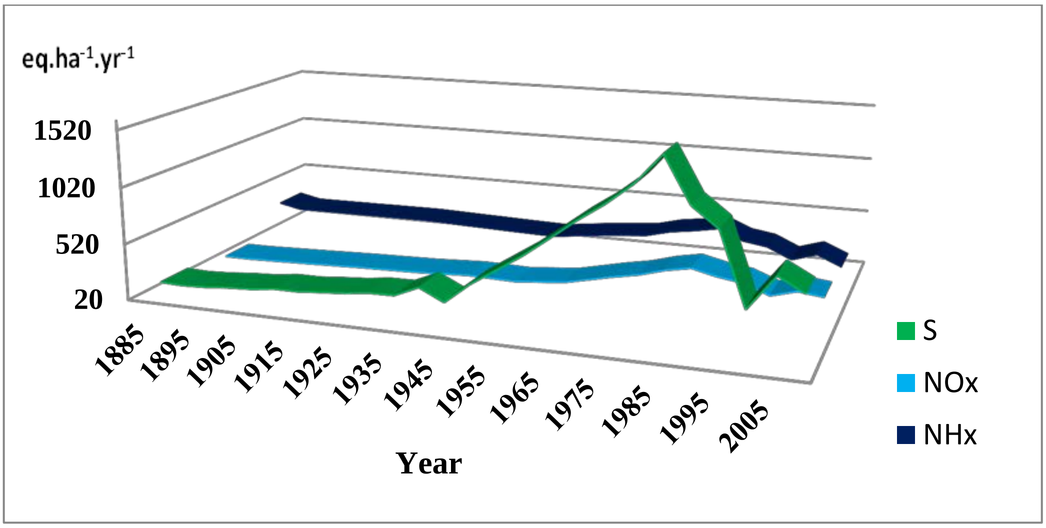

Fig. 6. Trend of atmospheric deposition of sulfur (green), oxidized nitrogen (blue light) and reduced nitrogen (blue dark) at the Petrohan site for the period 1885 – 2005,

eq.ha^{-1}.yr^{-1} (Source: ICP "Modelling and Mapping" www.unece.org/workinggroups.)

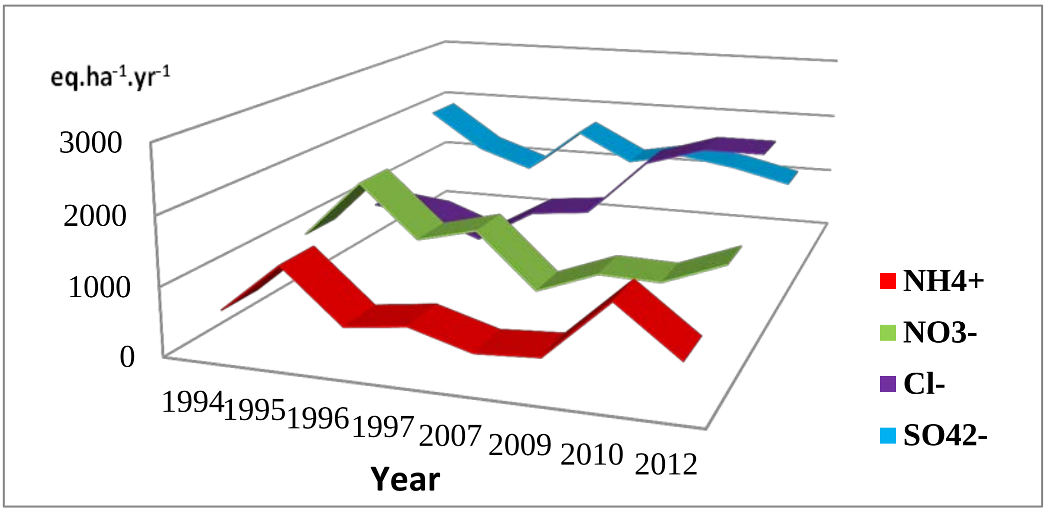

Fig. 7. The deposition trend of NH_4^+ (red), NO_3^- (green), Cl^- (blue dark) and SO_4^{2-} (blue light) by throughfall for the period 1994- 2012 at the Petrohan site eq.ha^{-1}.yr^{-1}

Table 1 Stream water chemistry for the period 1986- 2013 (Barzia river), mgdm^{-3}

Year	**pH**	**NH_4^+**	**NO_3^-**	**Cl^-**	**SO_4^{2-}**	**K^+**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**
1986	7,32	0,12	0,26	4,40	6,08	2,72	3,63	7,79	2,67
1994	6,80	0,68	2,02	6,95	23,60	1,01	4,57	14,70	3,43
1995	6,73	2,03	1,98	3,19	5,01	0,94	1,67	5,26	1,10
1996	6,55	0,50	3,17	3,11	10,58	1,22	2,10	3,70	0,86
1997	6,67	0,56	1,40	4,04	12,91	0,51	1,60	4,49	0,91

Mean for 1986-1997	**6,81**	**0,78**	**1,77**	**4,34**	**11,64**	**1,28**	**2,71**	**7,19**	**1,79**
2013	**6,67**	**0,08**	**5,23**	**11,22**	**4,22**	**0,83**	**2,92**	**9,72**	**1,83**

The concentration of acidifying NO_3^- and Cl^- in the stream water has increased dramatically. The mean concentration of NO_3^- for the period 1986- 1997 has been 1,77 mg.dm^{-3} whereas it has reached 5,23 mg.dm^{-3} in 2013.The similar increase could be seen for Cl^- ranging from 4,34 mg.dm^{-3} to 11,22 mg.dm^{-3}. At the same time there has been significant decrease in the concentration of NH_4^+ (from 0,78 to 0,08 mg.dm^{-3}) and SO_4^{2-} (from 11,64 to 4,22 mg.dm^{-3} respectively). When comparing the concentrations of Base cations (K^+, Na^+, $Ca^{2+}$and Mg^{2+}) for the above mentioned periods the result shows that the values are very close (Table 1).

3.3. Comparative study on the acidity and water chemistry of spring and stream water bodies

Based on the results obtained for the atmospheric deposition of acidifying pollutants as well as for the acidity and water chemistry of the main water body of “Barzia” river for 27 years period (1986-2013) it can be concluded that this information is not enough for the risk assessment of acidification of the water resources at the Petrohan site. This was the reason to compare the acidity and water chemistry of the spring and stream water at the catchment area of concern. As it is shown in table 2 the mean annual value of pH of 4 spring water bodies has been averaged as 5,99 pH units, ranging from 4,76 for the “Petrohan” spring to 6,79 for the “Small Barzia” spring in 1997. During the same one-year period the mean acidity of 9 stream water bodies at the same catchment area has reached 6,62 pH units. The computed values have been situated between 6,01 and 7,29. A comparison of the water chemistry of springs and streams has revealed that the concentration of all measured base cations and acidifying anions has been smaller in stream water than in spring one. Although the spring water has been more acid than stream one it has been found that the mean annual concentration of neutralizing base cations has been higher in spring water bodies compared to streams (K^+- 2,71 mg.dm^{-3} in springs agains 0,72 mg.dm^{-3} in streams; Ca^{2+}- 12,20 mg.dm^{-3} and 7,36 mg.dm^{-3} respectively). At the same time the concentration of SO_4^{2-}, Cl^- and NO_3^- in streams has remained lower which corresponds to their lower acidity.

16 years later, in 2013, the mean annual values of pH for the same spring (6,26) and stream (6,74) water bodies at the Petrohan site have been very close to ones measured in 1997 (5,99 and 6,62), even a little higher (Table 3).

Table 2. Acidity and water chemistry of spring and stream water bodies at the LTER Petrohan site, **1997**, mg dm^{-3}

Water body	pH	NH_4^+	NO_3^-	Cl^-	SO_4^{2-}	K^+	Na^+	Ca^{2+}	Mg^{2+}
Spring Petrohan	4,76	2,19	1,43	3,69	3,95	0,87	0,62	3,25	0,60
Dry spring	6,11	0,52	0,49	7,38	5,35	0,77	2,18	11,90	1,45
Spring Yanina	6,32	0,52	3,81	11,68	22,04	8,14	12,00	20,15	3,45
Spr. Small Barzia	6,79	0,12	1,77	7,38	6,05	1,06	4,10	13,58	3,08
Mean Springs	**5,99**	**0,84**	**1,88**	**7,53**	**9,35**	**2,71**	**4,73**	**12,20**	**2,15**
Stream Ginska	6,01	1,92	0,98	4,92	5,00	0,74	1,65	5,25	1,05
Reserv. Petrohan	6,11	0,52	0,49	1,84	5,35	0,77	2,18	11,90	1,45
Str. Kadyiska	6,72	0,06	0,98	2,46	7,65	0,73	0,74	4,50	0,55
Gavaneshnica	6,50	0,76	0,24	2,16	7,83	0,75	1,21	5,85	0,85
Fish stream	7,14	1,00	1,67	4,94	8,01	0,87	1,81	7,20	0,90

Str. Berberska	6,72	0,06	0,98	2,07	7,65	0,73	0,74	4,50	0,55
Small Selt Str.	7,29	0	1,46	2,46	7,11	0,51	1,23	12,50	2,83
Stream Shirine	6,44	0	4,15	4,92	8,01	0,89	2,30	10,08	1,80
Stream Barzia	6,67	0,56	1,40	4,04	12,91	0,51	1,60	4,49	0,91
Mean Streams	**6,62**	**0,54**	**1,37**	**3,31**	**7,72**	**0,72**	**1,50**	**7,36**	**1,21**

Table 3. Acidity and water chemistry of spring and stream water bodies at the LTER Petrohan site, **2013**, mg dm^{-3}

Water body	**pH**	**NH_4^+**	**NO_3^-**	**Cl^-**	**SO_4^{2-}**	**K^+**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**
Spring Petrohan	4,92	0,08	13,49	10,37	2,78	5,15	0,46	1,70	0,38
Dry spring	7,08	0,00	6,06	3,91	3,98	0,73	1,96	8,17	1,39
Spring Yanina	6,48	0,69	6,06	3,98	5,65	0,95	2,02	5,57	1,25
Spr. Small Barzia	6,54	0,69	2,55	18,46	4,93	1,05	4,50	8,22	2,40
Mean Springs	**6,26**	**0,37**	**7,04**	**9,18**	**4,34**	**1,97**	**2,24**	**5,92**	**1,36**
Stream Ginska	6,43	2,76	16,60	2,13	3,50	0,82	0,45	3,45	0,50
Reserv. Petrohan	7,24	2,55	13,09	2,27	3,74	0,52	1,58	3,00	0,79
Str. Kadyiska	6,38	0,48	4,83	3,05	3,98	0,86	2,02	7,87	1,39
Gavaneshnica	6,38	1,51	4,04	10,30	4,93	0,89	2,85	8,20	1,20
Fish stream	7,12	0,00	4,83	2,63	5,17	0,78	1,40	4,10	0,80
Str. Berberska	6,48	0,00	5,66	3,05	4,33	0,68	1,46	3,75	0,73
Small Selt Str.	7,26	0,00	6,27	3,12	4,22	0,57	1,60	4,20	0,89
Stream Shirine	6,72	0,69	4,20	2,84	4,69	0,48	1,48	2,76	0,74
Stream Barzia	6,67	0,00	5,23	11,22	4,22	0,83	2,92	9,72	1,83
Mean Streams	**6,74**	**0,89**	**7,19**	**4,51**	**4,31**	**0,71**	**1,75**	**5,23**	**0,99**

Despite the concentration of base cations has been again higher in spring water than in streams in 2013 the difference between them is not as significant as in 1997 due mainly to the decrease in their concentration in spring water bodies. For example the mean annual concentration of Ca^{2+} in spring water consists of 12,20 mg.dm^{-3} in 1997 against 5,92 mg.dm^{-3} in 2013. This ratio has been similar for K^+- 4,72 mg.dm^{-3} in 1997 and more than two times lower (1,97 mg.dm^{-3}) in 2013 as well as for Mg^{2+}- 2,15 mg.dm^{-3} in 1997 and 1,36 mg.dm^{-3} in 2013 (Table 3).

Concerning acidifying pollutants, only the concentration of Cl^- has been lower in streams (4,51 mg.dm^{-3}) than in springs (9,18 mg.dm^{-3}) in 2013, but other concentrations (SO_4^{2--} and NO_3) have remained similar or even higher (NH_4^+).

This discussion aims to confirm the idea that only the acidity and water chemistry are not good tools for risk assessment of water resources acidification.

3.4. Ratio between base cations and acidifying pollutants

The next step of the investigation the potential risk of water resources acidification has been the calculation the ratio between the sum of base cations as a parameter of the buffering capacity of the water environment and the sum of acidifying pollutants. The results obtained in 1997 have shown that the sum of base cations in the most acid spring water body (spring "Petrohan") has been two times lower than the sum of acidifying pollutants with a ratio between them 0,47. For all other spring waters the sum of neutralizing base cations has been higher than the sum of acid ions and the ration between two sums have been more than 1 with an average value of 1,11.

For running surface water in the streams the sum of acidifying anions has been higher than the sum of base cations and the values of their ratio have been situated between 0,40 for Barzia river and 0,88 for the stream "Shirine". As a result the mean annual ratio has been calculated as 0,83 (Table 4).

Table 4. Acidity and ratio between sum of base cations (∑**BC**) and sum of acidifying pollutants (∑**N, S, Cl**) in spring and stream water bodies at the Petrohan site in **1997**

Water body	**pH**	**Ca^{2+}/Cl^-**	**∑BC**	**∑N, S, Cl**	**∑BC/∑N, S, Cl**
Spring "Petrohan"	4,76	0,88	5,34	11,26	0,47
"Dry" spring	6,11	1,61	16,30	13,74	1,19
Spring "Yanina"	6,32	1,73	43,74	38,05	1,15
Spring "Small Barzia"	6,79	1,84	21,82	15,32	1,42
Mean Spring Water	**5,99**	**1,62**	**21,80**	**19,59**	**1,11**
Stream "Ginska"	6,01	1,07	8,69	12,82	0,68
Reservoir "Petrohan"	6,11	6,47	16,30	8,20	1,99
Stream "Kadyiska"	6,72	1,83	6,52	11,15	0,58
Stream "Gavaneshnica"	6,50	2,71	8,66	10,99	0,79
"Fish" stream	7,14	1,46	10,78	15,62	0,69
Stream "Berberska"	6,72	2,17	6,52	10,76	0,61
"Small Selt Stream"	7,29	5,08	17,07	11,03	1,55
Stream "Shirine"	6,44	2,05	15,07	17,08	0,88
Stream "Barzia"	6,67	1,11	7,51	18,91	0,40
Mean Stream Water	**6,62**	**2,22**	**10,79**	**12,95**	**0,83**

Table 5. Acidity and ratio between sum of base cations (**∑BC**) and sum of acidifying pollutants (**∑N, S, Cl**) in spring and stream water bodies at the Petrohan site in **2013**

Water body	**pH**	**Ca^{2+}/Cl^-**	**∑BC**	**∑N, S, Cl**	**∑BC/∑N, S, Cl**
Spring "Petrohan"	4,92	0,16	7,69	26,72	0,29
"Dry" spring	7,08	2,09	12,25	13,95	0,88
Spring "Yanina"	6,48	1,40	9,79	16,38	0,60
Spring "Small Barzia"	6,54	0,45	16,17	26,63	0,61
Mean Spring Water	**6,26**	**1,03**	**11,48**	**20,92**	**0,55**
Stream "Ginska"	6,43	1,62	5,22	24,99	0,21
Reservoir "Petrohan"	7,24	1,32	5,89	21,65	0,27
Stream "Kadyiska"	6,38	2,58	12,14	12,34	0,98
Stream "Gavaneshnica"	6,38	0,80	13,14	20,78	0,63
"Fish" stream	7,12	1,56	7,08	12,63	0,56
Stream "Berberska"	6,48	1,23	6,62	13,04	0,51
"Small Selt Stream"	7,26	1,34	7,26	13,61	0,53
Stream "Shirine"	6,72	0,97	5,46	12,42	0,44
Stream "Barzia"	6,67	0,87	15,30	20,67	0,74
Mean Stream Water	**6,74**	**1,37**	**8,68**	**16,90**	**0,51**

Keeping almost the same sum of acid anions, the sum of base cations has decreased two times in spring water bodies 16 years later, which has been followed by decreasing the ratio between them two times from 1,11 in 1997 to 0,55 in 2013. The meaning of this change is that the buffering capacity of spring water has decreased which can increase the risk of acidification of water resources in the region. Similar ratio between the sum of base cations and the sum of acidifying pollutants has been found for surface water bodies (0,51) because of increasing the sum of acid anions from 12,95 $mg.dm^{-3}$ to 16,90 $mg.dm^{-3}$ for the study period (Table 5).

Special attention has to be paid to the ratio between the concentration of Ca^{2+} and Cl^-. As it has been mentioned previously the increasing trend of the deposition of Cl^- by the throughfall at the catchment area of concern has been found for the period 1994- 2012 (Fig. 7).

In consequence the ratio Ca^{2+}/Cl^- has decreased from 1,62 in 1997 to 1,03 in 2013 for spring water bodies as well as from 2,22 to1,37 respectively for streams (Tables 4 and 5). The most dramatic decrease of this ratio from 6,47 to 1,32 has been calculated for the reservoir"Petrohan" collecting the water resources produced in the region.

Because of lack of acid stream water bodies in Bulgaria simultaneous study on the acidity, Ca^{2+} and SO_4^{2-} has been carried out for "Barzia" river (pH 6,74) at the Petrohan site and acid stream "Basse des Loges" in the Voges (France) (pH 4,23). Although the pH values of the open field precipitation and throughfall have been lower showing higher acidity at the Petrohan site than in the "Voges" mountains, the stream water has been more acid in France than at the Petrohan catchment (Fig. 8 top). Higher concentration of SO_4^{2-} has been measured for all water compounds at the Petrohan site than the "Basse des Loges" catchment (Fig. 8 midle). It means that nowdays the acid deposition are not the main acidifying factor for surface water in France because the acidity of stream water is higher than the acidity of both open field precipitation and throughfall.

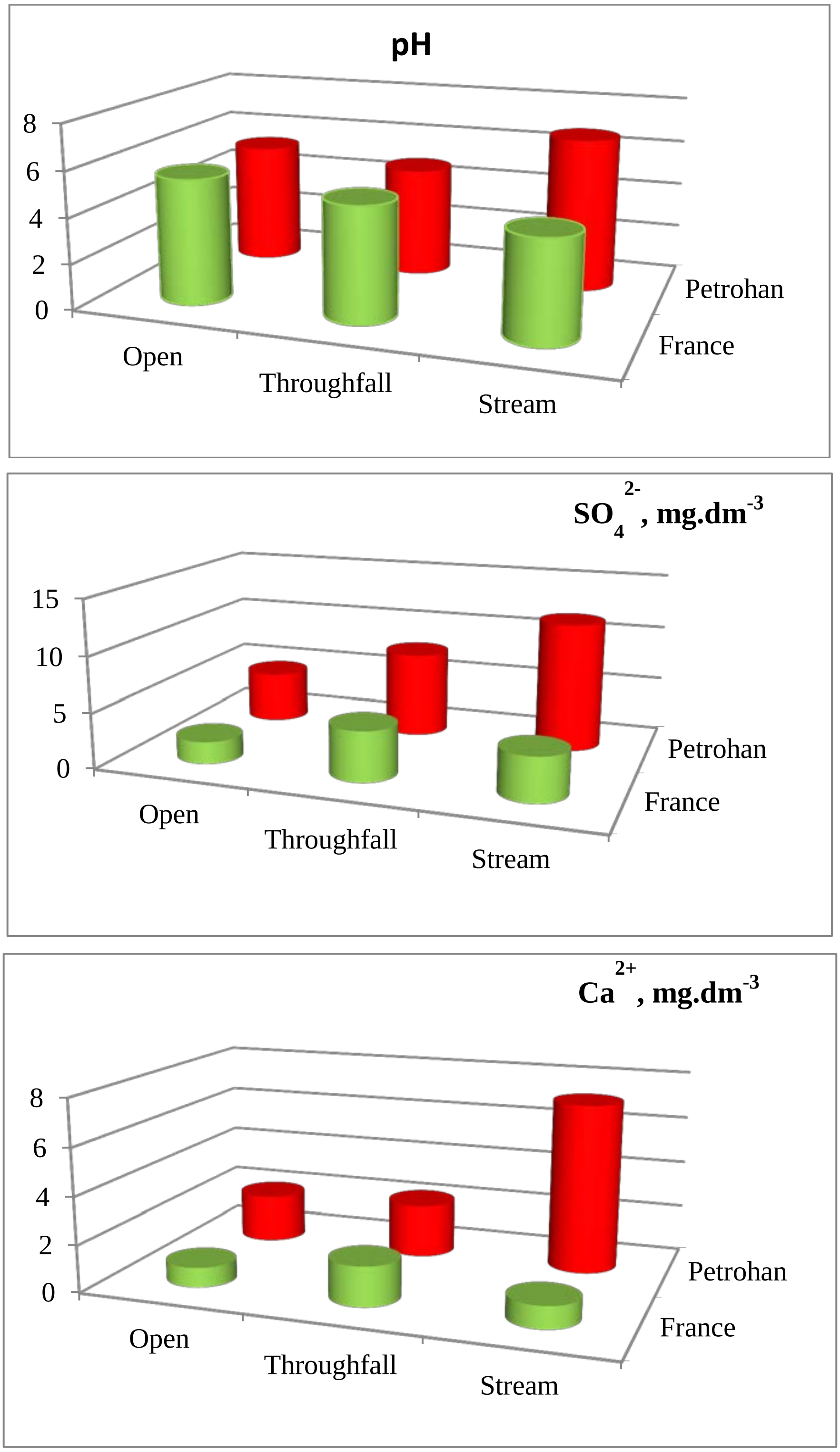

Fig. 8. Acidity (top), sulfates (midle) and calcium (bottom) in the open field precipitation, throughfall and stream water at the Petrohan site (red) and France (green)

In the reverse case of Ca^{2+}, the concentration of this neutralizing cation in the stream water in France is two times lower than in the troughfall deposition whereas it has been measured ten times higher values in the “Barzia” river at the Petrohan site than in the troughfall deposition (Fig. 8 bottom). At the same time the concentration of Ca^{2+} in the throughfall at the Petrohan site has been complitely equal to its concentration in the throughfall in French site. It revials the very important role of Ca^{2+} in keeping the buffering capacity of the surface water in order to avoid the acidification. The high concentration of Ca^{2+} in the water of "Barzia" river has protected the surface water against acidification

3.5. Critical loads of Acidity, Sulfur and Nitrogen for surface water and their exceedances

In general, a critical load of pollutants indicates only the sensitivity of an ecosystem against the anthropogenic input of the pollutant of interest. Higher values of critical loads indicate high tolerance and low sensitivity of receptors to pollutants. As mentioned above, the deposition of NH_4^+, NO_3^-, Cl^- and SO_4^{2-} was very high in beech and spruce forest at the catchment area for the period 1994-2012 (Fig.7), but these deposition rates are not suitable for assessing the risk of harmful effects of these pollutants to water ecosystems, because the pH values for some of water bodies have been lower than 6 but for another part of them the acidity has corresponded to the limit with pH values higher than 7. In addition the concentration of the acidifying SO_4^{2-} in the throughfall in France has been lower than in Petrohan but the stream water has been much more acid in French catchment than in Bulgarian one.

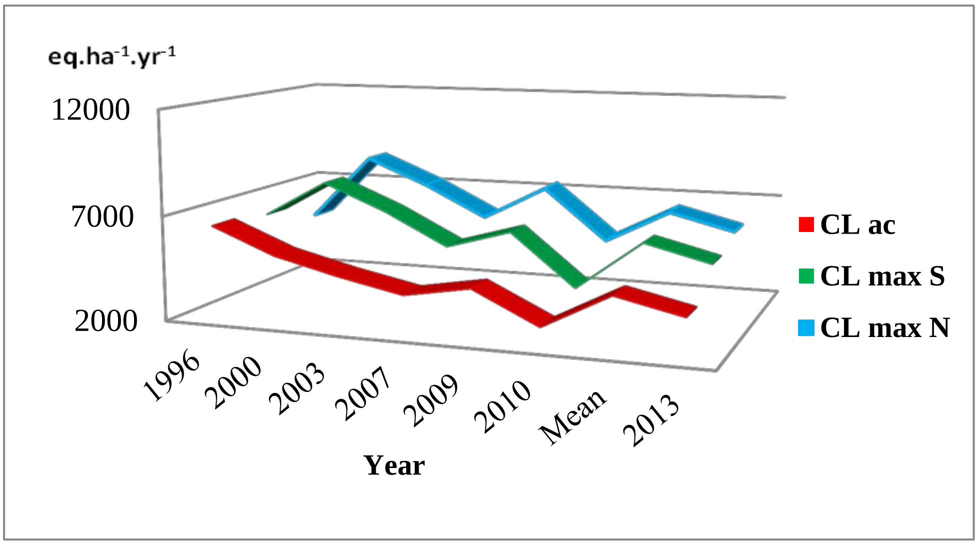

Fig. 9. Trend of critical loads of acidity (red), sulfur (green) and nitrogen (blue) for the period 1996-2013 r., eq.ha^{-1}.yr^{-1}

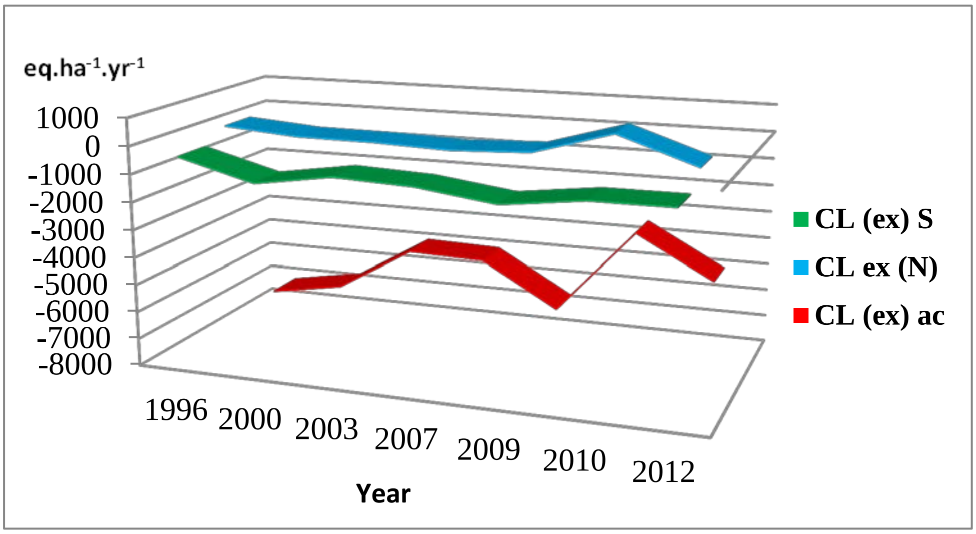

Fig. 10. Exceedances of critical loads for acidity (red), sulfur (green) and nitrogen (blue) for the period 1996-2012, eq.ha^{-1}.yr^{-1}

The obtained values of critical loads for Acidity, Sulfur and Nitrogen have demonstrated high tolerance and low sensitivity of water ecosystems at the Petrohan site to the deposition of acidifying pollutants because all calculated values of critical loads have been higher than 2000 $eq.ha^{-1}.yr^{-1}$. As shown in figure 9, water bodies at the Petrohan site could withstand the acid deposition between 2800 $eq.ha^{-1}.yr^{-1}$ and 8200 $eq.ha^{-1}.yr^{-1}$ without harmful effects. When comparing these values of critical loads with the results for other European countries, it should be mentioned that more often than not the calculated critical loads are less than 1000 $eq.ha^{-1}.yr^{-1}$ demonstrating high sensitivity to acidifying pollutants (Hettelingh et al., 1995, 2004; Posch et al., 2005).

Although the high tolerance of water ecosystems at the Petrohan site to the acid deposition, the trend of their critical loads for acidity, sulfur and nitrogen for the period 1996- 2013 has shown a clear decreasing wich means an increasing of the sensitivity of the water bodies to the acidifying pollutants. This decreasing of the values of critical loads can be considered as an important indicator for the tolerance and sensitivity but not for potential risk of acidification of the water resources.

A real risk of damage for the studied water ecosystems is possible only when the critical load is exceeded. A comparison of the critical loads with the present deposition rates of acid pollutants revealed that there were no exceedances of critical loads for both acidity and sulfur for water ecosystems for the entire study period, hence the studied water ecosystems were not at risk of damages due to H^+ and SO_4^{2-} pollution. Unfotunately it is not the case for nitrogen which deposition has been very close to the critical loads of nitrogen and the exceedance of critical loads has been found in 2011 (Fig. 10). In order to avoid future damage to water bodies, special efforts have to be done for decreasing the emissions of nitrogen in the studied region.

However, only keeping the deposition of nitrogen less than its critical load will not lead to exceedance of their critical limits in the long run. From this point of view the exceedances of critical loads of acid pollutants could be successfully used as an indicator for assessment the risk of water acidification.

The negative values of exceedances at the Petrohan site suggest that the water ecosystems there could withstand more additional deposition of acidity (from -7500 to – 1800 $eq.ha^{-1}.yr^{-1}$) and sulfur (from -2000 to -1000 $eq.ha^{-1}.yr^{-1}$) before reaching the critical loads. Unlike for acidity and sulfur, the negative values of exceedances of critical loads for nitrogen are very close to 0 (from -320 to -58 $eq.ha^{-1}.yr^{-1}$) and critical load could be easily exceeded with a small increasing the deposition of nitrogen (Fig. 10).

Although the critical load of acidity has not been exceeded the trend of calculated exceedances has shown decreasing of the negative values for the study period. If the water bodies could accept additionaly without any harmfull effects about 7500 $eq.ha^{-1}.yr^{-1}$ of acidity befor reaching the critical load in 1996, this possibility has progressively decreased and has consisted of only 1800 in 2011 (Fig. 10). The exceedance of critical loads of acidifyingpollutants means that critical limits will be exceeded in the future, but not necessarily at present. In case when this decrease of the values of exceedances will keep the same rate, probably critical load of acidity will be exceeded in coming years and it will be a real risk of harmful effects and damages of acidification for water resources at the Petrohan site in the future.

4. CONCLUSIONS

The current measured deposition of acid pollutants for the last 27 years has shown a decreasing trend for sulfur and nitrogen but significant changes in the acidity of both spring and stream water bodies have not been found at the Petrohan site.

A comparative study has demonstrated that spring water has been more acid than the streams because of the lower ration between Ca^{2+} and Cl^-.

It has been found that the ratio between the sum of Base Cations and the sum of Acidifying pollutants has been decreased for the period 1986- 2012 in both spring and stream water which reduces their buffering capacity to acid deposition.

Long term hydrochemical study has shown that the sensitivity of water ecosystems to acidity has been increased during the last 20 years due to the decrease of critical loads of acidifying pollutants at the Petrohan site.

The real risk of stream water acidification can be assessed by determining the exceedances of critical loads of acidifying pollutants by their real deposition at the catchment area.

Special attention has to be paid to Nitrogen which critical load has been exceeded at the catchment area and this increases the risk of acidification of the drinking water in this region.

There is a potential risk of acidification of stream water at the Petrohan site because of acid spring water in combination with the decreased concentration of base cations for the period 1980 – 2012, increased sensitivity of stream water to the acidity and exceedances of critical loads of Nitrogen at the catchment area.

In order to protect drinking water against an acidification the investments in reducing the emissions of acidifying pollutants, especially nitrogen, must be addressed to this region.

ACKNOWLEDGMENT

This study has been funded by Sofia University of Forestry (grant 108/2008 "Effect of anthropogenic and biotic factors on health state and bio-production of Beech forest" and grant 60/2014 "Effect of atmospheric deposition on bio-production of Spruce forest"), ENVEUROPE Project and LTER network.

REFERENCES

Angeli N, Dambrine E, Boudot JP, Viville D, Nys C, Nedeltcheva T, Richter C, Party JP, Pollier B 2005. Delayed response of streams draining sandstone to changes in atmospheric deposition and whole catchment liming (Vosges NE, France). *Environmental Pollution*, p. 67-79.

Dambrine E, Nourrisson G 1992. Depot atmospherique d'elements mineraux sur le massif Vosgien. *Rapport definitif : pollution atmospherique et deperissement des forets dans les montagnes francaises*, p. 22-23.

Davies T.D, Tranter M, Wigington PJ, Eshman KN 1992. 'Acidic episodes' in surface waters in Europe. *Journal of Hydrology* 123, p. 25-69.

De Vries W, Kros J, Van der Salm C 1995: Modelling the impact of acid deposition and nutrient cycling on forest. *Ecol. Model*., 79, p. 231-254.

Hettelingh JP, Posch M, De Smet PAM, Dowining RJ 1995. The use of critical loads in emission reduction agreements in Europe. *Water Air Soil Pollution*, 85: 2381-2388.

Hettelingh JP, Slootweg J, Posch M 2004. Critical loads and Dynamic Modelling Results. *CCE Progress Report* 2004, 134 pp.

Ignatova N, Jorova K, Grozeva M, Trendafilov K, Tintchev G, Petkova T 1998. *Manual on Methodologies for calculation and mapping of critical loads for acidity, sulfur and nitrogen for soils in Bulgaria.* Sofia, Iriss, 49 p. (in Bulgarian).

Ignatova N, Jorova K, Myashkov I, Fikova R 2003. Modelling and mapping of critical thresholds in Europe. Bulgaria. *UN/ECE Status report 2003 of Coordination center for effects N 259101013*. RIVM, Bilthoven, Netherlands, p. 53-58.

Ignatova N 2005. Control on water acidification in forested catchments by using critical loads and levels for acidifying pollutants and their exceedences by present deposition. In proceeding of *International conference on "Forest Impact on Hydrological Precesses and soil Erosion*", Undola, p. 117-123

Ignatova N 2007. Hydrochemical monitoring in forested catchments in Bulgaria for assessment the risk of stream water acidification. *Proceedings of the 23 meeting of ICP Waters,* Nancy, October, 2007, p. 11-17.

Ignatova N, Damyanova S, Jorova K, Velizarova E, Fikova R, Broshtilova M, Yordanov Y 2007. *Critical loads of Nitrogen and Dynamic modeling in Bulgaria*, RIVM, Bilthoven, Netherlands, p. 115-120.

Ignatova N, Jorova K, Velizarova E, Damyanova S, Fikova R, Broshtilova M, Yordanov Y 2008. Modeling and Mapping Critical Loads in Bulgaria. *Modeling and Mapping Critical loads in Europe, Bulgarian national focal center report, CCE Progress report*, 21-25 April 2008, Bern, Switzerland, part II, p. 15-18.

Kehayov T 1986. *Underground waters in Bulgaria, mapping in 1:2000000*, BAS, Sofia, vol.V, p. 304-307.

Koleva K, Peneva R 1990. *Climatic reference book of Bulgaria*. BAS, Sofia.

Moldan F, Wright R, Lofgren S, Forsius M, Riuho-Airola T, Skjelkvale B 2001. Long-term changes in acidification and recovert at nine calibrated catchments in Norway, Sweden and Finland. *Hydrology and Earth System Sciences, vol* 5, p. 339-349.

Nilsson J, Grennfelt P 1988. Critical Loads for Sulfur and Nitrogen. *Miljorapport North 1988*:97. Nordic Council of Ministers, Copenhagen, Denmark, pp. 418

Posch M, Slootweg J, Hettelingh 2005. European Critical Loads and Dynamic Modelling. *CCE Status Report* 2005, pp. 171

Probst A., Viville D, Fritz B, Ambroise B, Dambrine E 1992. Hydrochemical budgets of a small forested granitic catchment exposed to acid deposition: the Strengbach catchment case study (Vosges Massif. France) *Water, Air and Soil Pollution* 62: 337-347.

Slootweg J., Posch M., Hettelingh J. P. 2007. Critical loads of Nitrogen and Dynamic modeling. Bulgaria. *CCE Progress Report*, RIVM, Bilthoven, 201 p.

Tsonmis G 1991. *Science and Technology of wood. Structure. Properties. Utilization*. Van Nostrand, New York.

UBA 2004. *Modelling and Mapping Critical loads and Levels and Air Pollution Effects, Risks and Trends.* UBA, text 52/04, Berlin (www.icpmapping.org).

www.unece.org/workinggroups