RAPPORT L.NR. 6643-2014

ICP Waters Report 117/2014

Proceedings of the 29th Task Force meeting of the ICP Waters Programme in Český Krumlov, Czech Republic 1st –3rd October, 2013

International Cooperative Programme on Assessment
and Monitoring Effects of Air Pollution on Rivers and Lakes

Convention on Long-Range Transboundary Air Pollution

Norwegian Institute for Water Research
– an institute in the Environmental Research Alliance of Norway

REPORT

Main Office	**Regional Office, Sørlandet**	**Regional Office, Østlandet**	**Regional Office, Vestlandet**	**Regional Office Central**
Gaustadalléen 21	Jon Lilletuns vei 3	Sandvikaveien 59	Thormøhlensgate 53 D	Høgskoleringen 9
0349 Oslo	4879 Grimstad	2312 Ottestad	5006 Bergen	7034 Trondheim
Telefon (47) 22 18 51 00	Telefon (47) 22 18 51 00	Telefon (47) 22 18 51 00	Telefon (47) 22 18 51 00	Telefon (47) 22 18 51 00
Telefax (47) 22 18 52 00	Telefax (47) 37 04 45 13	Telefax (47) 62 57 66 53	Telefax (47) 55 31 22 14	Telefax (47) 73 54 63 87
Internett: www.niva.no				

Title Proceedings of the 29th Task Force meeting of the ICP Waters Programme in Český Krumlov, Czech Republic 1st –3rd October, 2013.	Report No.. SNO 6643-2014 ICP Waters report 117/2014	Date March 2014
	Project No. O 10300	Pages 63 Price
Editors Heleen de Wit (NIVA), Bente M. Wathne (NIVA) and Jakub Hruśka (Czech Geological Survey) (editors)	Topic group Air pollution	Distribution
	Geographical area Europe and North America	Printed NIVA

Client(s) Norwegian Environment Agency (Mildir) United Nations Economic Commission for Europe (UNECE)	Client ref.

Abstract

The report contains Proceedings of the 29th Task Force meeting of the ICP Waters Programme in Český Krumlov, Czech Republic, October 1 – 3, 2013, including national contributions from Armenia, Canada, the Czech Republic, Italy, Norway and Russia and Switzerland

4 keywords, Norwegian	4 keywords, English
1. Overvåking	1. Monitoring
2. Ferskvann	2. Surface Waters
3. Luftforurensning	3. Air Pollution
4. Internasjonalt samarbeid	4. International Cooperation

Heleen de Wit	*Øyvind Kaste*	*Claus Beier*
Project Manager	Research Manager	Research Director

ISBN 978-82-577-6378-7

CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING EFFECTS OF AIR POLLUTION ON RIVERS AND LAKES

Proceedings of the 29th Task Force meeting of the ICP Waters Programme in Český Krumlov, Czech Republic, October 1 – 3, 2013

Prepared at the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, January 2014

Preface

The international cooperative programme on assessment and monitoring of air pollution on rivers and lakes (ICP Waters) was established under the Executive Body of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) in July 1985. Since then, ICP Waters has been an important contributor to documenting effects on surface waters of implementing Protocols under the Convention. Numerous assessments, reports and publications covering the effects of long-range transported air pollution have been published over the years.

The ICP Waters Programme Centre is hosted by the Norwegian Institute for Water Research (NIVA), while the Norwegian Environment Agency leads the programme. The Programme Centre's work is supported financially by the Norwegian Environment Agency.

The main aim of the ICP Waters Programme is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters. More than 20 countries in Europe and North America participate in the programme on a regular basis.

ICP Waters is based on existing surface water monitoring programmes in the participating countries, implemented by voluntary contributions. The ICP Waters site network is geographically extensive and includes long-term data series (more than 30 years) for many sites. The programme conducts annual chemical and biological intercalibrations.

At the annual Programme Task Force meeting, ongoing national activities from participating countries are presented. This report presents national contributions from the 29th Task Force meeting of the ICP Waters programme, held in Český Krumlov, Czech Republic, October 1 – 3, 2013. In addition, the Minutes of the Task Force meeting are published here.

Heleen de Wit
ICP Waters Programme Centre

Oslo, January 2014

Contents

1. Introduction

The International Cooperative Programme on Assessment and Monitoring of Rivers and Lakes (ICP Waters) is a programme under the Executive Body of the Convention on Long-Range Transboundary Air Pollution. The main aims of the programme are:

- *To assess the degree and geographic extent of the impact of atmospheric pollution, in particular acidification, on surface waters;*
- *To collect information to evaluate dose/response relationships;*
- *To describe and evaluate long-term trends and variation in aquatic chemistry and biota attributable to atmospheric pollution.*

The national contributions on ongoing activities that were presented during the ICP Waters Task Force meeting in Český Krumlov, Czech Republic, October 1 – 3, 2013 were grouped thematically. A short summary of each presentation is given in the Minutes (Chapter 9). The list below contains the presentations that are included in the Proceedings of the meeting.

Water chemistry
- Streamwater chemistry at Lysina (CZ 07). *Pavel Krám et al., Czech Republic*
- The Acidification and Interaction of Metal Ions with Humus Substances in Natural Waters. *M. Dinu et al., Russia*

Biological response
- Benthic macroinvertebrates of the acidified Bohemian Forest lakes, their inflows and outflows. *Kateřina Kolaříková et al., Czech Republic*

Heavy metals and POPs
- Assessment of the air pollution impacts on waters of the trans-boundary Debed River. *Marine Nalbandyan, Armenia*
- No decline detected in mercury concentrations of large-bodied fishes in Northern Ontario, Canada lakes. *John M. Gunn and Thomas A. Johnston, Canada*

Dynamic modelling / Critical Loads
- An application of the MAGIC model to four high altitude lakes in Ticino, Switzerland communities. *M. Rogora (Italy), S. Steingruber, L. Colombo (Switzerland)*

Ecosystem services
- Drinking water treatment adaptation to increasing levels of DOM and changing DOM quality under climate change (DOMQUA). *Heleen de Wit, Programme Centre, Norway*

2. Streamwater chemistry at Lysina (CZ 07)

Pavel Krám[1,2,*], Oldřich Myška[1,2], Jakub Hruška[1,2], Jan Čuřík[1,2], František Veselovský[1], Tomáš Navrátil[3], Jan Rohovec[3]

[1] *Czech Geological Survey, Klárov 3, 118 21 Prague 1, Czech Republic,*
[2] *Global Change Research Centre, Academy of Sciences of the Czech Republic, Bělidla 4a,*
603 00 Brno, Czech Republic
[3] *Geological Institute, Academy of Sciences of the Czech Republic, Rozvojová 269,*
165 00 Prague 6, Czech Republic

[*]pavel.kram@geology.cz

Keywords: **forest catchment, acidification recovery, sulfate, alkalinity, aluminum, mercury**

Introduction

Eight sites from the Czech Republic are currently in the ICP Waters network, six glacial lakes (CZ 01-06) in the Bohemian Forest (Soldán et al. 2012) and two streams: Lysina, Slavkov Forest, CZ 07 and Uhlířská, Jizera Mountains, CZ 08 (Oulehle et al. 2008).

Study site and methods

The Lysina catchment (0.27 km^2, 50^{o}N, 829-949 m a.s.l.) is situated in the Slavkov Forest (Majer et al. 2005), western Bohemia, Czech Republic. It is underlain by granite and is forested by dense Norway spruce (*Picea abies*) plantations (Krám et al. 2012). It is in the GEOMON network of Czech catchments (Oulehle et al. 2008), in the International Cooperative Programs – Integrated Monitoring (ICP IM; Holmberg et al. 2013) and the ICP Waters (Velle et al. 2013, Garmo et al. 2014), and in the International Long-Term Ecological Research network (ILTER; http://www.lter.cz; http://www.lter-europe.net/sites-platforms/lter-europe-map). Lysina became one of the Critical Zone Observatories of the SoilTrEC project (Banwart et al. 2012). Streamwater was monitored since 1989 at Lysina, samples were usually collected weekly for chemical analysis. Laboratory methods of water analyses performed mostly in the Czech Geological Survey were described previously in detail (Krám et al. 2009, 2012).

Results and discussion

In response to decreased atmospheric deposition of anthropogenic sulfur mainly in 1990s, the Lysina streamwater exhibited steep decline of sulfate concentrations (Fig. 1), slightly increasing but still extremely low alkalinity (Fig. 2, Fig. 3) and pH (not shown) and correspondingly very high inorganic monomeric aluminum (Ali) concentrations (Fig. 4). Concentrations of Ali were usually above the toxic level for fish (0.05 mg l^{-1}) and benthic macroinvertebrates (0.14 or 0.3 mg l^{-1} for different species). Extremely high mean concentrations of potentially toxic Ali (0.7 mg l^{-1}) were observed in stream water at Lysina in the first half of the 1990s (Krám et al. 2009). These Ali concentrations were among the highest values reported in literature (Driscoll and Postek 1995). Recent concentrations of mercury in streamwater was elevated, in the range of 1-20 ng L^{-1}, with mean 8 ng L^{-1} (Buchtová et al. 2013). The strongly anthropogenically acidified drainage waters at Lysina exhibited incomplete neutralization of acidic atmospheric deposition mostly due to low weathering rates (Krám et al. 2012). Taxonomic richness of macroinvertebrates was very low in the Lysina stream (Krám et al. 2008, Traister et al. 2013, Horecký et al. 2013) in comparison with sites with higher streamwater pH values.

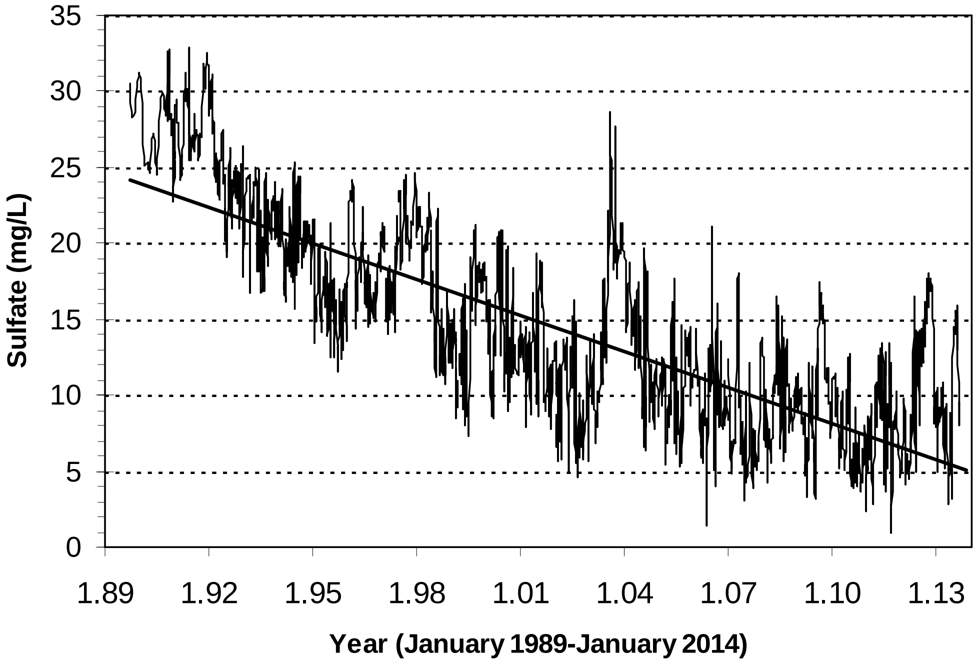


Figure 1. Temporal patterns of streamwater sulfate concentrations at Lysina in September 1989-September 2013.

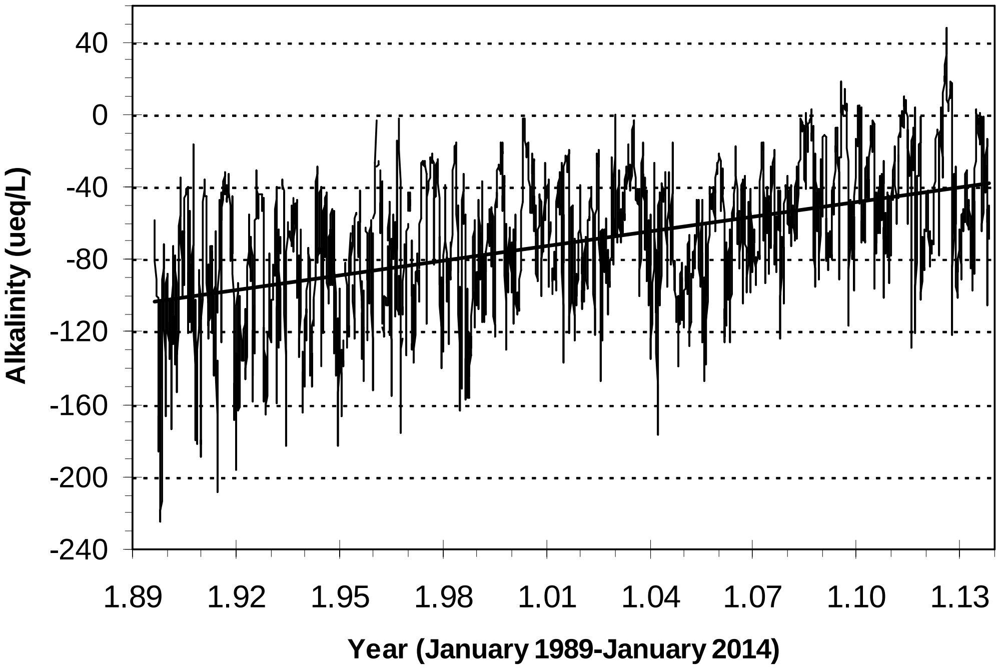


Figure 2. Temporal patterns of streamwater Gran titration alkalinity at Lysina in September 1989-November 2013.

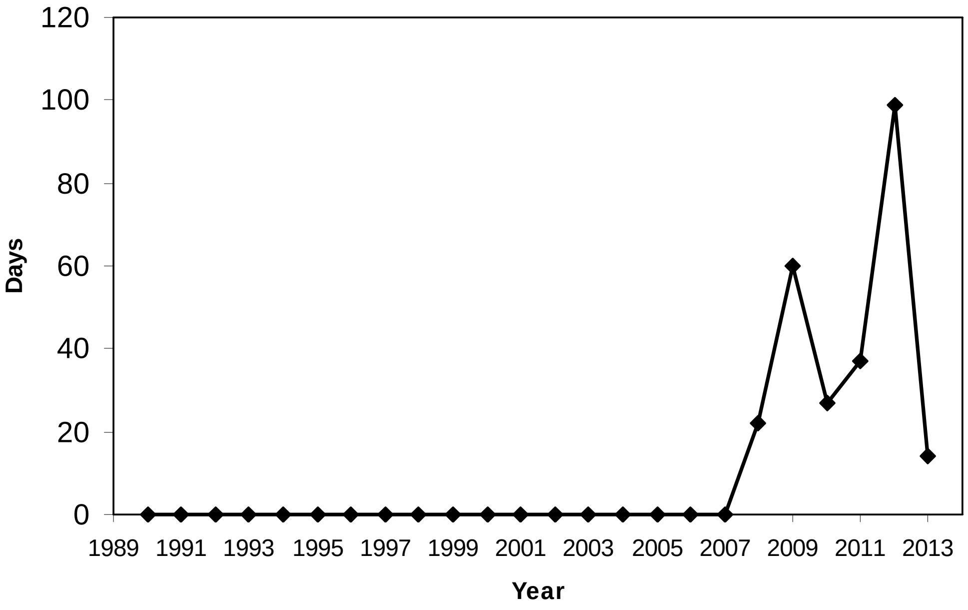


Figure 3. Number of days with streamwater alkalinity above the threshold 0 μeq L^{-1} at Lysina.

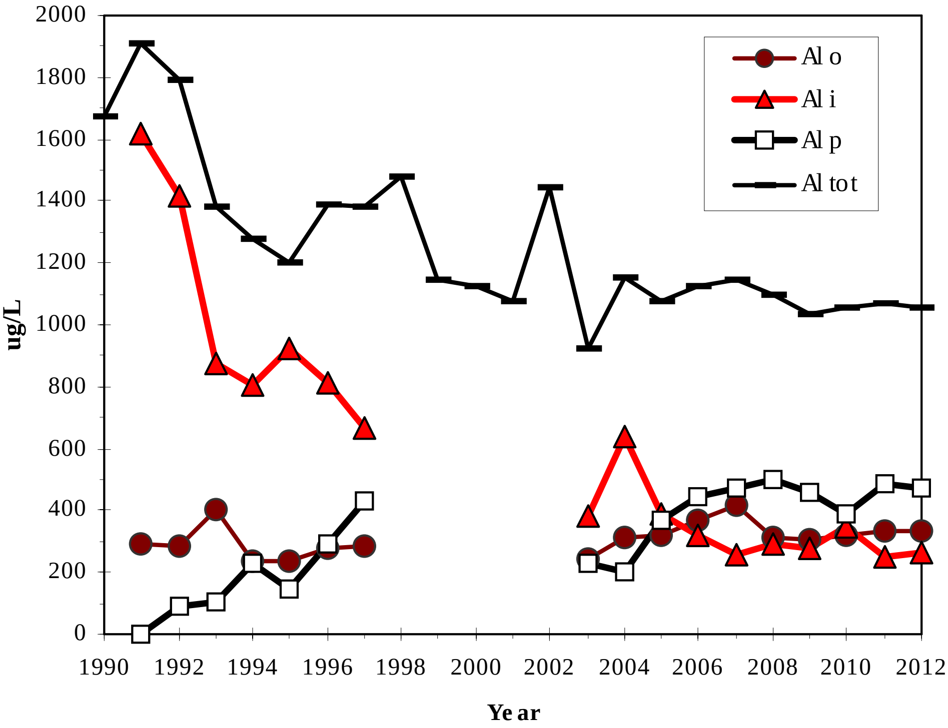


Figure 4. Discharge-weighted annual mean streamwater concentrations of aluminum fractions (Krám et al. 2009) at Lysina. Alo organic monomeric Al (reactive non-labile Al), Ali inorganic monomeric Al (reactive labile Al), Alp particulate Al, Altot total Al.

Acknowledgements

The most recent research was supported by the European Commission (FP7 SoilTrEC 244118), the GAČR (P210/11/1369) and the EU Operation Programme (CzechGlobe – CZ.1.05/1.1.00/02.0073).

References

Banwart, S., Menon, M., Bernasconi, S., Bloem, J., Blum, W., de Souza, D.M., Davidsdottir, B., Duffy, C., Lair, G., Krám, P., Lamačová, A., Lundin, L., Nikolaidis, N., Novák, M., Panagos, P., Ragnarsdottir, K.V., Reynolds, B., Robinson, D., Rousseva, S., de Ruiter, P., van Gaans, P., Weng, L., White, T., Zhang, B. 2012. Soil processes and functions across an International Network of Critical Zone Observatories: introduction to experimental methods and initial results. Comptes Rendus Geoscience 344: 758-772.

Buchtová, J., Navrátil, T., Rohovec, J., Matoušková, Š., Myška, O., Krám, P., Tesař, M. 2013. Total mercury in stream water of selected catchments within the Czech Republic. 11th Conference on Mercury as a Global Pollutant Abstracts, Jul 28-Aug 2, Edinburgh, UK, M69.

Driscoll, C.T., Postek, K.M. 1995. The chemistry of aluminum in surface waters. In Sposito, G. (Ed.) The environmental chemisty of aluminum. CRC Press, Boca Raton, Florida, USA, 363-418.

Garmo, Ø.A., Skjelkvåle, B.L., de Wit, H.A., Colombo, L., Curtis, C., Fölster, J., Hoffmann, A., Hruška, J., Høgåsen, T., Jeffries, D.S., Keller, W.B., Krám, P., Majer, V., Monteith, D.T., Paterson, A.M., Rogora, M., Rzychon, D., Steingruber, S., Stoddard, J.L., Vuorenmaa, J., Worsztynowicz, A. 2014. Trends in surface water chemistry in acidified areas in Europe and North America from 1990-2008. Water, Air, and Soil Pollution, in press.

Holmberg, M., Vuorenmaa, J., Posch, M., Forsius, M., Lundin, L., Kleemola, S., Augustaitis, A., Beudert, B., de Wit, H., Dirnbock, T., Dubakova, I., Evans, C., Frey, J., Grandin U., Krám, P., Pompei, E., Schulte-Bisping, H., Srybny, A., Váňa, M. 2013. Relationship between critical load exceedances and empirical impact indicators at Integrated Monitoring sites across Europe. Ecol. Indicators 24: 256-265.

Horecký, J., Rucki, J., Stuchlík, E., Krám, P., Křeček, J., Bitušík, P. 2013. Benthic macroinvertebrates of headwater streams with extreme hydrochemistry. Biologia 68: 303-313.

Krám, P., Traister, E., Kolaříková, K., Oulehle, F., Skořepa, J., Fottová, D. 2008. Stream benthic macroinvertebrates of nine selected catchments of the GEOMON network (In Czech, English abstract). Geoscience Research Reports for 2007, Czech Geol. Survey, Prague, 160-166.

Krám, P., Hruška, J., Driscoll, C.T. Johnson, C.E., Oulehle F,. 2009. Long-term changes in aluminum fractions of drainage waters in two forest catchments with contrasting lithology. Journal of Inorganic Biochemistry 103: 1465-1472

Krám, P., Hruška, J., Shanley, J. B. 2012. Streamwater chemistry in three contrasting monolithologic catchments. Applied Geochemistry 27: 1854-1863.

Majer, V., Krám, P., Shanley, J.B. 2005. Rapid regional recovery from sulfate and nitrate pollution in streams of the western Czech Republic- comparison to other recovering areas. Environmental Pollution 135: 17-28.

Oulehle, F., McDowell, W.H., Aitkenhead-Peterson, J.A., Krám, P., Hruška, J., Navrátil, T., Buzek, F., Fottová, D. 2008. Long-term trends in stream nitrate concentrations and losses across watersheds undergoing recovery from acidification in the Czech Republic. Ecosystems 11: 410-425.

Soldán, T., Bojková, J., Vrba, J., Bitušík, P., Chvojka, P., Papáček, M., Peltanová, J., Sychra, J., Tátosová, J.. Aquatic insects of the Bohemian Forest glacial lakes: diversity, long-term changes, and influence of acidification. Silva Gabreta 18: 123-283.

Traister, E.M., McDowell, W.D., Krám, P., Fottová, D., Kolaříková, K. 2013. Persistent effects of acidification on stream ecosystem structure and function. Freshwater Science 32: 586-596.

Velle, G., Telford, R.J., Curtis, C., Eriksson, L., Fjellheim, A., Frolova, M., Fölster, J., Grudule, N., Halvorsen, G.A., Hildrew, A., Hoffmann, A., Indriksone, I., Kamasová, L., Kopáček, J., Orton, S., Krám, P., Montheit, D.T., Senoo, T., Shillhand, E.M., Stuchlík, E., Wiklund, M.L., de Wit, H., Skjelkvåle, B.L. (2013) Biodiversity in freshwaters: temporal trends and response to water chemistry. ICP Waters Report 114/2013, Rapp. L.NR. 6580-2013, NIVA, Oslo, Norway, 1-66.

3. The Acidification and Interaction of Metal Ions with Humus Substances in Natural Waters

Dinu M.[1], Moiseenko T.[1], Gashkina N.[1], Kremleva T.[2]

[1] Vernadsky Institute
[2] Tyumen State University

Introduction

Anthropogenic acidification of the water is a complex process and is accompanied not only by reducing the pH. It is preceded by complex geochemical processes in the catchment, related to the direct and indirect effects of deposition of acidifying substances. Acid deposition decreases the base saturation of soils in the catchment area, and therefore the concentrations of base cations in surface and groundwater. Also, alkalinity of water is reduced due to displacement of hydrocarbons by stronger acids. Acid deposition leads also to increased leaching of metals from rocks forming the watersheds, related to weathering (Al, Cd, Zn, Mn , etc.). In the European territory of Russia (ETR) and Western Siberia (WS) in boreal zones, forest and wetland watersheds, as shown in Fig. 1, formed colored water with high contents of humus substances. These lakes had more than 100 water color °Pt-Co-scale and were characterized by low pH waters (Table 1). In oligotrophic or dystrophic lakes, organic anions can occupy a dominant position. This fact is crucial to the interactions of the individual metals with humus substances in natural waters of various natural zones. For example, as shown in Fig. 2 in high color and low pH 6-7 manganese content is higher than Fe and Al. The Fe content of above at pH 6-7 and high color, Al - vice versa.

Although some authors suggest that acidification processes are not typical for natural waters in Russia, our studies of natural waters show a significant influence anthropogenic and natural acidification on water quality (Moiseenko, Gashkina et al., 2013). Here, we focus on the question: "How does acidification influence interactions between metals and humus acids (HA), and how do HA decrease metals toxicity? What is the mechanism of HA destruction?"

Fig. 1. *The scheme of study points to the European territory of Russia (ETR) and in Western Siberia (WS)*

Water chemistry

The basis of the work was a generalization of the original results of the small lakes chemical composition in the European part of Russia and West Siberia. Pioneering research in the ETR were conducted in 2003-2008, they covered 280 lakes in different climatic zones (from the tundra to the arid). Regional studies of lakes in the Legislative Assembly were held in 2012 under the same principles and methods that were used in the study of lakes in the ETR, only 137 lakes have been surveyed climatic zones unified methodical scheme (Moiseenko, Gashkina et al., 2013).

Surveyed Lake ETR located on the East European Plain, which is the average height of 170 m above sea level, and the hill rising to 300-400 m and more. The main feature of the plains is the tectonic structure: in the northern part of the Kola Peninsula and Karelia Archean-Proterozoic crystalline basement comes to the surface, forming the Baltic Shield and the southern part of the valley is covered powerful Upper Proterozoic and Phanerozoic sedimentary cover.

Table 1. *Distribution of lakes (%) by the values of pH and color of water in the climatic zones of the European part of Russia and Western Siberia.*

pH	Color, °Pt-Co						Color, °Cr-Co					
	<10	10-30	30-60	60-100	>100	*n*	<10	10-30	30-60	60-100	>100	*n*
	THE EUROPEAN PART OF RUSSIA						WESTERN SIBERIA					
Tundra - taiga zone (tundra and forest tundra. northern and middle taiga)												
<4	1.0	0.5	0.5	0	1.0		0	0	0	0	0	
4-5	1.0	1.4	0	1.4	1.0		0	0.9	0	2.8	6.5	
5-6	3.8	2.9	1.4	1.0	3.3		6.5	7.4	15.7	8.3	5.6	
6-7	3.3	22.4	26.2	12.9	3.3		8.3	18.5	3.7	6.5	2.8	108
7-8	0.5	3.3	7.6	0	0.5	210	2.8	0.9	0.9	0	1.9	

The lakes studied by us in WS are located in various zones of the western Siberian lowland plain, which is characterized by a flat relief and strong paludification. The mean lake surface elevation is 40–60 m a.s.l. The surface area of the plain is completely covered by rather thick (300–400 m and more) unconsolidated.

<u>Chemical analyzes</u> of water samples were performed by a single method in accordance with the recommendations (Standart Methods 1992; Wathne BM, Mosello R., 1998; Mosello et al., 1996; ICP-Water report 105/2010, 2010).

Water samples from lakes in the *ETR* were analyzed in the laboratories of the Institute of North Industrial Ecology Problems of the KSC RAS, Institute of Water Problems, Russian Academy of Sciences and the Institute of Geochemistry and Analytical Chemistry by V.Vernadsky RAS. *Samples* of water from the lakes of *WS* have been analyzed in the Laboratory for Environmental Research of the Tyumen State University.

Chemical analysis of samples was performed according to standard procedures listed on the National Register of methods of quantitative chemical analysis and assessment of the state of the environment, and in accordance with the recommendations to the measuring instruments used.

<u>Chemical experiments:</u> in the course of detailed experiments have been studied humus substances (HS) - alkaline extract of the soil (catchment), alkali- and acid soluble fraction of humus substances – fulvic (FA) and humic acids (HA) in different natural zones. With the help of electrochemical methods of analysis have been investigated processes of complex metal ions with HS and their factions. Were selected following metal ions: Fe^{3+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}, Ca^{2+}, $Mg^{2+,}$ Sr^{2+}, Al^{3+}.

Isolation of samples was carried out using the procedure of leaching from soils (catchment), HS fall into water due to leaching (Orlov, 1996). They contain a proportion of fulvic acids, which are well soluble in water and alkalis, and humic acids, which are soluble in alkalis.

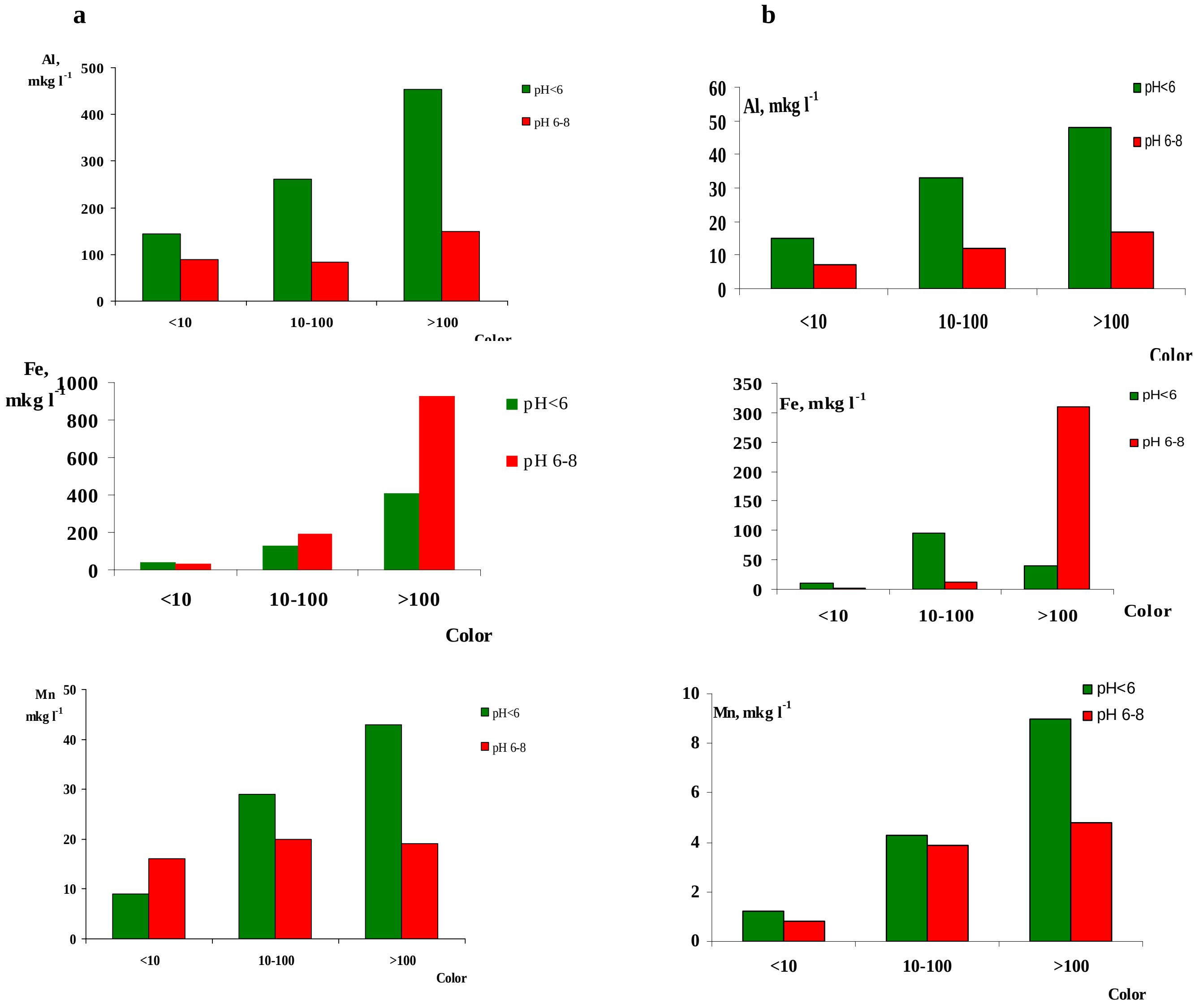


Fig. 2 *The metal content (mkg l^{-1}) in the water of lakes (taiga zone) depends on color and acidity (pH): a -* ***THE EUROPEAN PART OF RUSSIA*** *b -* ***WESTERN SIBERIA***

The study of fractions - humic and fulvic acids were held for more in-depth examination of complex formation with the functional characteristics of each fraction (These, 2004; These, 2005; Cristl, 2001). Studies of complex FA as dominant components HS, revealed the metal ions that have an affinity for oxygen functional groups, as well as to compare the obtained stability constants of metal complexes with FA with numerous data in the literature, most of which is devoted to the study of this fraction HS. Study of complex formation of metal ions with a humic acids which are necessarily present in natural waters, but in lower concentrations as compared with FA revealed differences in the mechanisms for the complexation of these fractions (Tipping, 1993).

Physical-chemical methods used to study the complexation of metal ions with HS presented in Figure 3. As can be seen from the figure, the qualitative features of soil acids have been studied by IR and NMR spectrometric techniques that allow you to get information about the functional groups, causing the connection to a particular metal ion.

According to Moiseenko, Gashkina et al., 2013 observed a significant correlation (99%) between the amount of organic matter in natural waters (HS) and values permanganate oxidation, so the concentration of HS and their fractions were determined by method of permanganatomety.

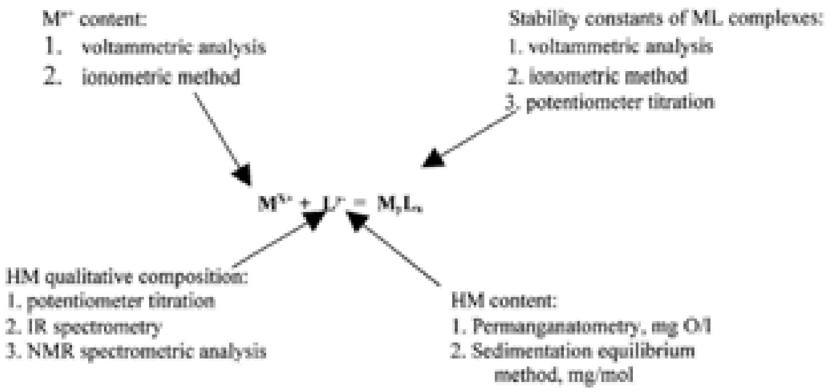


Fig. 3 *Main methods of metal and soil humic matter (HM) complexing (M^{x+} is metal cations. L^{y-} is the humus matter anion and M_y–L_n is the complex of metal with humic matter)*

The average molecular weight HS were found by sedimentation equilibrium (Orlov, 1996). Using the obtained molecular weights were calculated molar concentrations of HS and fractions which are used in further calculations conditional stability constants of complexes. For the obtained of acidity constants as the main characteristics of the acid-base properties of HS was use methods of titrometry and three methods of calculation: a graphical method, the "buffering" and Berumms method (calculation carried out in the program MathCad).

The stability constants of metal complexes with HS have been identified by various physical and chemical methods. The main physical-chemical method used in the work - voltammetry (VA). Potentiometric titration method was used to study the interaction of the ions Ca^{2+}, Mg^{2+}, Sr^{2+}, Al^{3+} with HS. Application of the method ionometry to determine the stability constants of metal complexes with HS was performed in the form as a direct ionometry and ionometric titration.

In the final stage of the experiment was checked the stability constants of the complexes with help modeling systems - several metal cations and HS or fraction. We measured ion and complexing metal forms. Processes have also been considered with complexing metal ions HS in competitive binding as in natural water, i.e. in the presence of several cations or anions that approximate the composition of the waters as the natural systems. The concentrations of cations and anions were chosen according to the chemical composition of natural waters, as reflected in the works (Moiseenko, Gashkina et al., 2013).

Table 2. *The logarithms of the acidity constants (-lgK) of humic substances ($P=0.95$; $n=15$, $\Delta<0.3$)*

The dissotiation degree	pH<6			pH=6-7		
	Humus acid	**Fulvic acid**	**Humic acid**	**Humus acid**	**Fulvic acid**	**Humic acid**
1	3.0	3.0	5.0	2.0	1.4	3.0
2	6.0	7.3	10.0	4.0	5.7	5.0
3	10.8	12.0	-	4.3	9.0	-
4	13.4	15.0	-	10.0	15.0	-

At last step of our investigation was calculations of metal forms base on obtaining constant, to do this, we used the material balance equation, the equation of electrical neutrality, the equations of proton equilibrium (calculation carried out in the program MathCad). All calculated date was verified with field data from the literature and our measurements.

Results

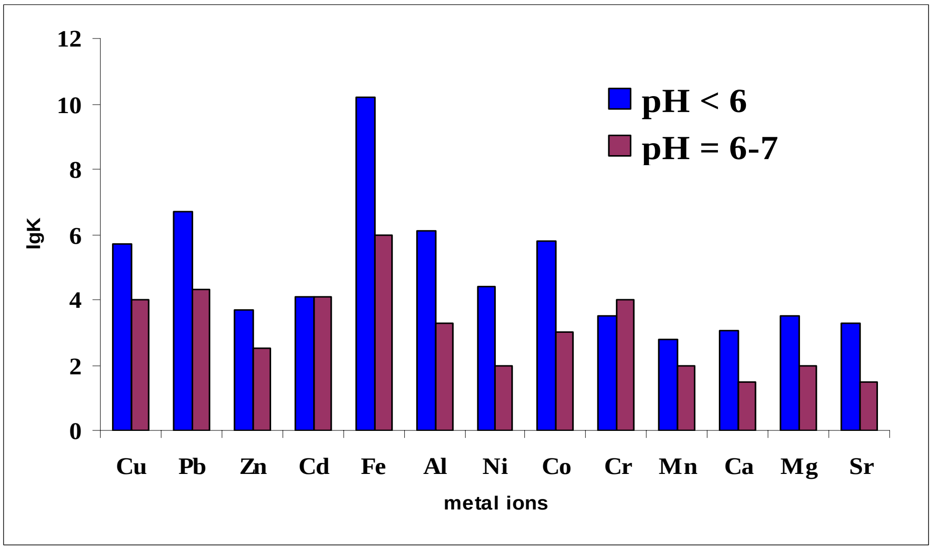


Fig. 4 *The conditional stability constants of the complexes (at different pH), P=0.95; n=25, Δ<0.25*

According to our data, the decrease in pH of the system is accompanied by an increase in the acidity constant and conditional stability constants of the complexes. Figure 4 reflects the change in the stability constants of the complexes at different pH for the zone of northern taiga ETR. During acidification humic substances decompose and dissociate to form lower molecular weight fragments, as evidenced by the data of spectral analysis. For most metals complexes with humic substances (M<50 kDa) are more durable than high molecular weight. And the higher molecular weight complexes of Fe, Al, Cu, characterized by low values of conditional stability of the complexes constant (Fig. 4).

Conditional stability constants of the complexes are important, but defining fracture in the forming of metals. A larger value provides the material balance of the system and the competitive reaction to it.

Table 3. *The calculated form of metal migration in some lakes of the Kola North to the basis of the bulk of experimental data*

Lakes	n	Ca(II)	Mg(II)	Cu(II) K_1	Cu(II) K_2	Ni(II)	Co(II)	Zn(II)	Sr(II)	Pb(II)	Cd(II)
pH<6	5	0 0	0 0	5.11 0.01	28.68 0.24	0.26 0	6.44 0	0.05 0	0 0	38.97 0.06	0.16 0
pH 6-7	10	0.21 0	0.14 0	0.03 0	1.24 0	2.83 0	33.30 0	0.01 0	0.14 0	0.25 0	2.95 0

Table 3 presents the migration forms of some metals as complexes with HS (natural waters of the Kola Peninsula), it can be concluded about the differences in the degree of complexation at different conditions. As we can see, Ni more active in complexation with HS at pH=6-7 according Table 3 then according Figure 4. It can mean that a lot of factors influence on migrations forms every metal. All our results were verified with measured in natural waters forms of metals (our measurements). For example, Figure 5 show date about complexing forms of Fe in Kola North some lakes.

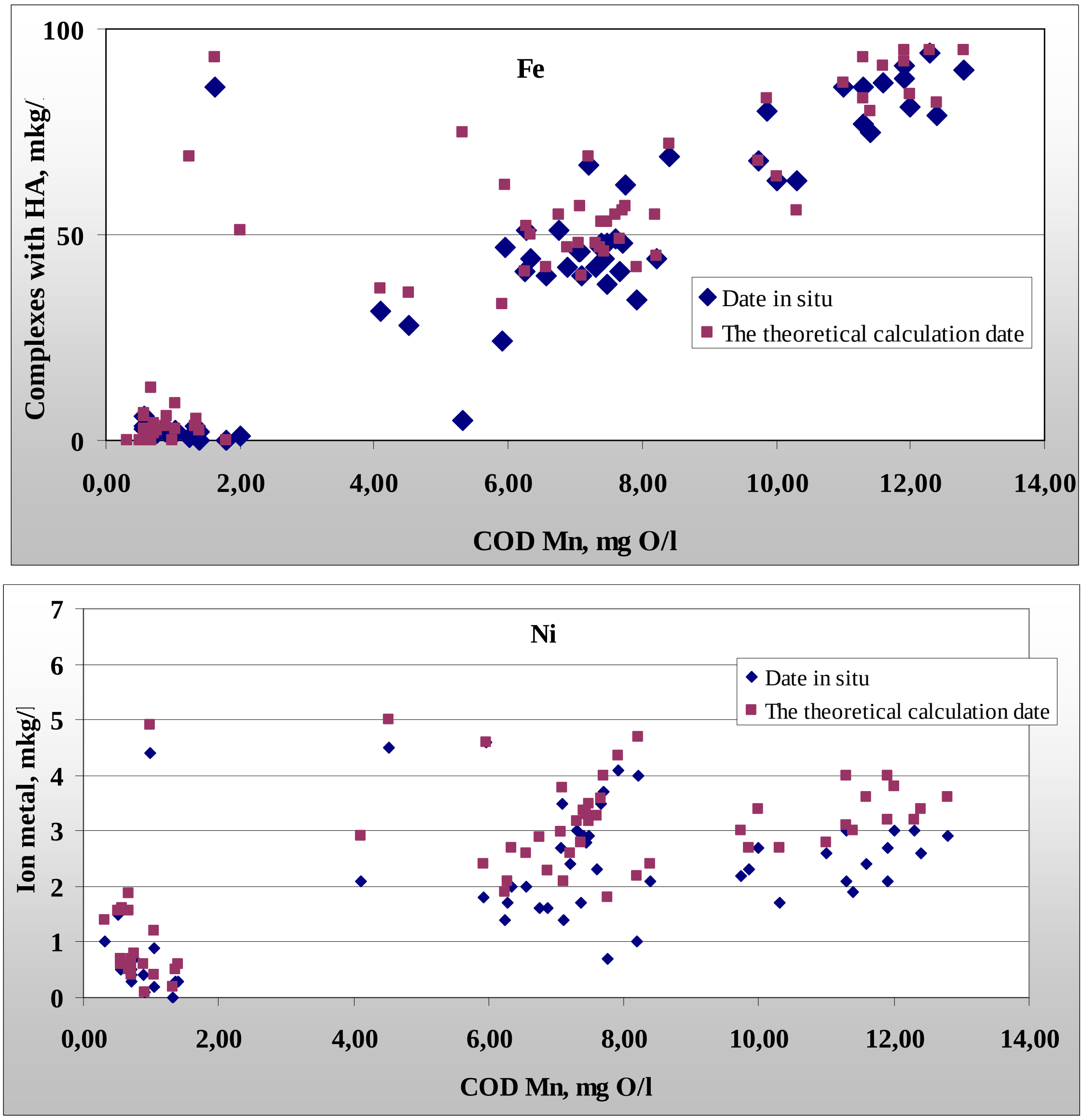


Fig. 5 *The correlation between the calculated amount of metal complexes with humic substances and measured at pH 6-7 (Kola Peninsula), r=0,97; 0,95*

Because of the differences in the complexation of metal in the model experiment and in the natural environment, we can talk about different "in the ranks of the metal activity in complexation reactions". According to Table 3 and Figure 4 can be represented by the following series of complex metal HS (for zone of northern taiga):

1. Fe> Cu > Pb> Al> Co> Ni> Cd> Zn> Cr> Mg> Sr> Ca> Mn
(According to the stability constants of the complexes)
2. The taiga zone are characterized by a wide variety of metals, the simultaneous presence of which, along with sufficient alkalinity, cause the following pattern in an advantageous distribution of metals bound to organic complexes:
Fe> Al> Pb> Co> Ni> Zn> Cd> Cu> Mg> Ca> Cr> Mn> Sr
3. In the area of water present facilities in which the total alkalinity is zero, in which case the distribution of metals in forms primarily depends on the stability constants of complexes concentrations HS and has the following sequence:
Fe> Al> Cu> Co = Ni> Pb> Zn> Cd> Cr> Mn> Ca> Mg> Sr

Conclusions

1. Acidification affects the form of metal migration mainly due to changes in the qualitative composition of humic substances
2. Change in the qualitative composition of humic substances is accompanied by a decrease in the molecular weight, the formation of additional free functional groups
3. Most metals form more stable complexes with low molecular weight humic substances. This fact is important for the calculation of the distribution of metals in forms
4. In natural waters, metal affinity laws to HS do not coincide with the stability constants of complexes those obtained in model systems. This is due to differences in the chemical composition of the water of certain natural areas. Accounting for physical-chemical parameters of natural waters, including the experimentally determined stability constant of the complex, allows obtaining reliable calculation of metal-humus complexes.

Reference

T. Moiseenko, N. Gashkina, M. Dinu et. al. (2013) Aquatic Geochemistry of Small Lakes: Effects of Environment Changes. Geochemistry International, 13, 1031-1148

Standard Methods for the Examination of Water and Wastewater American Public Health Association,Washington, (1992)

B. M. Wathne and R. Mosello, (1998) Quality Control of the Chemical Data Norwegian Institute for Water Research – C.N.R. Instituto Italiano di Idrobiologia, Oslo.

ICP_Water. Programme Manuel. Programme Centre. An International Programme for Surface Water Monitoring (NIVA_Report, Oslo, 2010).

D. S. Orlov, O. N. Biryukova, and N. I. Sukhanova, (1996) Organic Matter in Soils of the Russian Federation Nauka, Mir

A. These, M. Winkler, C. Thomas, et. al., (2004) “Determination of molecular formulas and structural regularities of low molecular weight fulvic acids by size exclusion chromatography with electrospray ionization quadrupole time_of_flight mass spectrometry” Mass Spectrom. 18, 1777–1786.

A. These and T. Reemtsma, (2005) “Structure dependent reactivity of low molecular weight fulvic acid molecules during ozonation,” Environ. Sci. Technol. 39, 8382–8387.

I. Christl, C. J. Milne, D. G. Kinniburgh, et. al., (2001) “Relating ion binding by fulvic and humic acids to chemical composition and molecular size,” Environ. Sci. Technol. 35, 2512–2517.

E. Tipping, (1993) “Modelling ion binding by humic acids. Colloid and surfaces,” Physicochem. Eng. Asp. 73, 117–131.

4. Benthic macroinvertebrates of the acidified Bohemian Forest lakes, their inflows and outflows

Kateřina Kolaříková, Takaaki Senoo, Lenka Ungermanová& Evžen Stuchlík

Institute for Environmental Studies, Faculty of Science, Charles University, Benátská 2, 12843 Prague, Czech Republic

Abstract

The structure of littoral macroinvertebrates was studied in eight glacial lakes, their inflows, and outflows in the Bohemian Forest in 2007, on both the Czech and German sides. All lakes were atmospherically acidified mainly in the 1960s-1980s and have since been recovering from acidification. Water pH varied from 4.58 to 5.71 in all lakes, from 4.24 to 5.55 in main inflows, and from 4.53 to 5.58 in outflows. Concentrations of dissolved reactive Al and labile Al ranged from 118 to 973 μg/l and from 0 to 664 μg/l, respectively. A positive relationship was found between pH and the number of taxa in particular lakes whereas in lake streams any significant relationship was found.

Background

The Bohemian Forest lake district (at the border between the Czech Republic and Germany; Fig. 1) was one of the mountain areas which witnessed the most pronounced changes in acidic deposition and water composition among all European lake districts (Evans et al. 2001), due to steep increases in emission and deposition fluxes of sulphur and nitrogen compounds in the 1950s-1980s and their abrupt reduction after 1989 (Kopáček et al. 2001). The Bohemian Forest lakes currently exhibited a rapid chemical recovery from acification, with increasing water pH and declining Al concentrations (Majer et al. 2003, Veselý et al. 2003, Oulehle et al. 2012). Changes in lake biota have been, however, more delayed than the chemical recovery of the Bohemian Forest lakes, nevertheless the first signs of zooplankton and macrozoobenthos recovery have already been documented (Vrba et al. 2003, Nedbalová et al. 2006, Soldán et al. 2012).

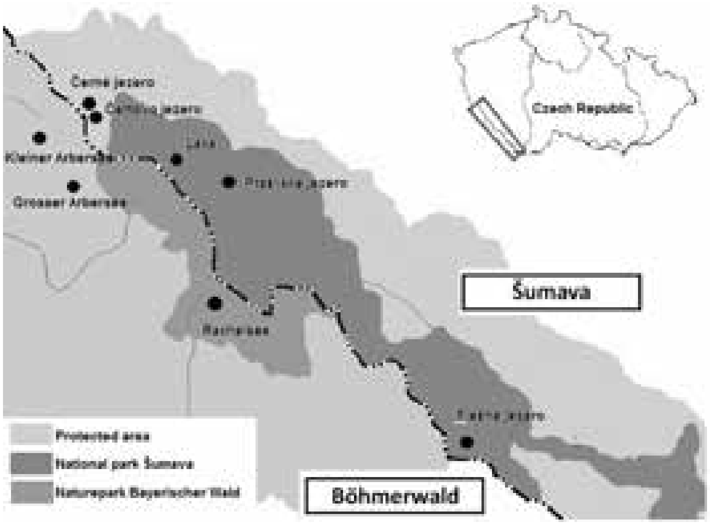


Fig.1. The location of the Bohemian Forest lakes on the Czech side (Šumava) and the German side (Böhmerwald). Map source: www.sumava.xf.cz (modified).

Results and discussion

All eight glacial lakes (Fig. 1), both in its Czech part: Černé jezero (CN), Čertovo jezero (CT), Plešné jezero (PL), Prášilské jezero (PR), and Laka (LA), and German part (Böhmerwald): Rachelsee (RA), Grosser Arbersee (GA), and Kleiner Arbersee (KA), differ in their pH, thus providing a gradient of pH. The lake water pH was about 4.5 in the 1980s except Laka, but more or less neutral pH was in the middle of the 20th century. The bedrock in lake catchments is sensitive to acid atmospheric deposition and forests around the lakes are dominated mainly by mature Norway spruce. All the Bohemian Forest lakes are fishless at present (Vrba et al. 2003).

In 2007, study on macroinvertebrates was performed in lakes and their outflows and main inflows. These data were the first obtained using a homogenous sampling method in all eight lakes and should server as a basis for future comparisons and assessments of the ongoing process of recovery.

Water pH varied from 4.58 to 5.71 in all lakes, from 4.24 to 5.55 in main inflows, and from 4.53 to 5.58 in outflows. It is obvious that the lake inflows are source of H+ and the lakes water then reduce its acidic character. Concentrations of dissolved reactive Al (R-Al) and labile Al (L-Al) ranged from 118 to 973 µg/l and from 0 to 664 µg/l, respectively. The increasing proportion of L-Al to R-Al was related to decreasing pH in the lakes in our data (Fig. 2) and previously by Fott et al. (1994). The highest proportions of L-Al to R-Al were in the most acidic CN, CT, and PL (90%, 85% and 78%, respectively). This L-Al are mostly ionic and potentially toxic forms of Al. A significant correlation ($p<0.05$) was found between the water pH and number of macroinvertebrate taxa in autumn samples from the lakes (Fig. 3) whereas the correlation was not found in inflows and outflows. It is most probable that abiotic factors influence the occurrence of macroinvertebrates with higher intensity in lake streams than in standing water in the lakes.

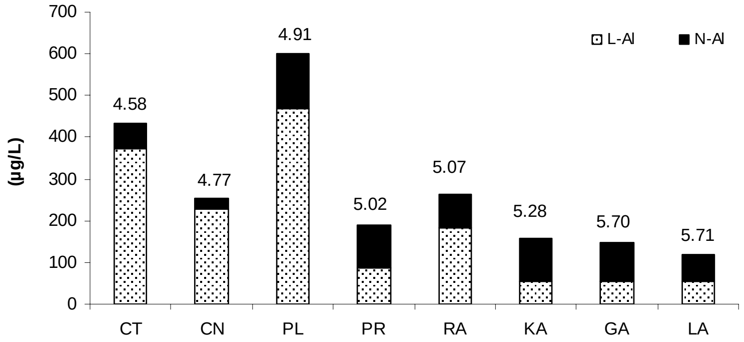


Fig.2. Contribution of L-Al and N-Al to the total R-Al in relation to pH in the lakes.

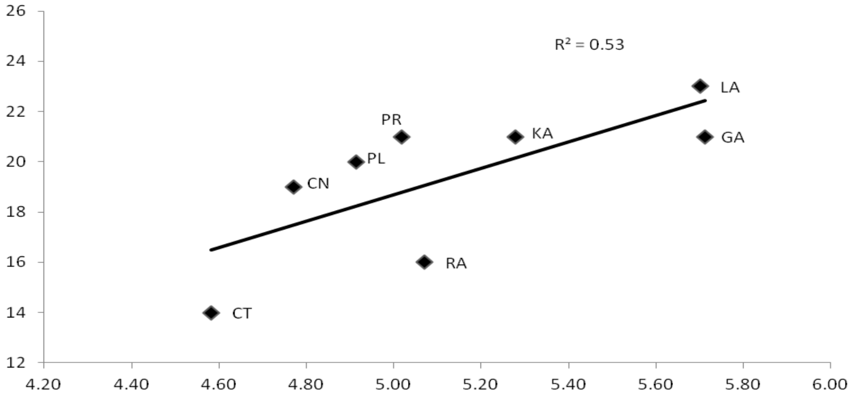


Fig. 3. Correlation of water pH with the number of benthic macroinvertebrate taxa in the lakes.

Relative abundances differed substantially among lakes, inflows, and outflows. The most abundant insects in inflows were stoneflies Plecoptera (74%, mostly Nemouridae and Leuctridae), Diptera (20%, mostly Chironomidae) and Trichoptera (5%, mostly Plectrocnemia sp.), whereas in outflows, the most dominant groups were Diptera (49%, mostly Chironomidae), Plecoptera (30%, mostly Nemouridae and Leuctridae) and Trichoptera (7%, mostly Plectrocnemia sp.) (Fig.4). The only found Ephemeroptera (12%) was Leptophlebia vespertina, its relative abundance was much higher in outflows than in their inflows (1%). Diptera dominated mostly in the lakes (68%), followed by Ephemeroptera (18%) and Trichoptera (5%).

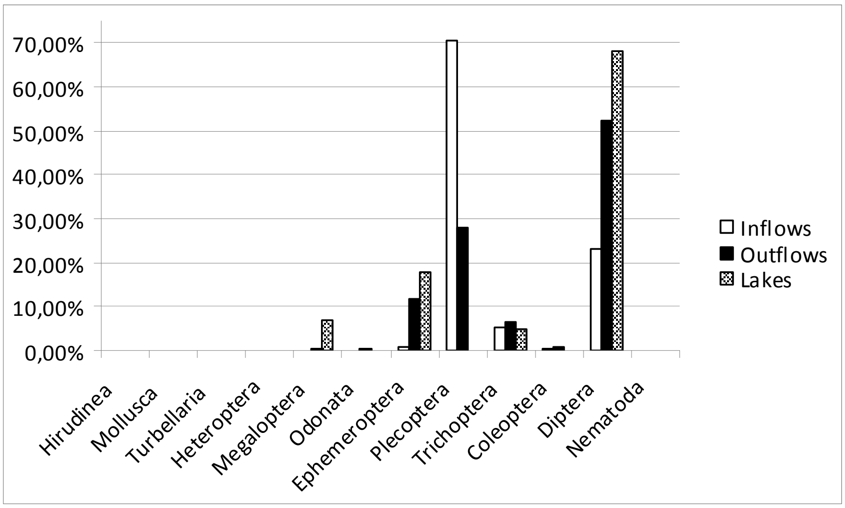


Fig. 4 Relative abundance of the particular taxa group in lakes and lake streams.

Within this study, there were several interesting findings:

- Water beetle ***Nebrioporus assimilis*** (first record in the CR since 1960).
- Mollusk ***Pisidium casertanum*** found only in the LA and GA (highest pH).
- Mayflies ***Cloeon dipterum*** and ***Leptophlebia marginata*** (in Bohemian Forest lakes only recently); ***Ameletus inopinatus***, ***Siphlonurus lacustris*** (in Bohemina Forest lakes occurred even before the acidification period).
- Stonefly ***Diura bicaudata*** in inflows and one outflow – usually not found in strongly acidified waters pH<4.5 (in PL 4.25).
- Stonefly ***Siphonoperla torrentium***: does not survive over the long period in water pH<5 (in outflows of PR, RA, LA, KA, GA: pH ~ 5 and higher).
- Flatworm ***Crenobia alpina***: found in PL inflow with pH slightly <4.5 and Al ~664 µg/l (species is strongly acid-sensitive). One of the 10 subspecies which could be less acid-sensitive???

Acknowledgement

This research was supported by the Czech Science Foundation (GACR grants No. 526/09/0567 and 206/07/1200), the Environment Project of the European Commission EURO-LIMPACS (GOCE-CT-2003-505540), the Ministry of the Environment of the Czech Republic in the framework of the Convention of Long-Range Transboundary Air Pollution (LRTAP), and by the Grant Agency of Charles University (GAUK No. 264711).

References

Evans C.D., Cullen J.M., Alewell C., Marchetto A., Moldan F., Kopáček J., Prechtel A., Rogora M., Vesely J. & Wright R.F. 2001. Recovery from acidification in European surface waters. Hydrol. Earth System Sci. 5 (3): 283–297.

Fott J., Pražáková M., Stuchlík E. & Stuchlíková Z. 1994. Acidification of lakes in Šumava (Bohemia) and in the High Tatra Mountains (Slovakia). Hydrobiologia 274: 37–47.

Kopáček J., Veselý J. & Stuchlík E. 2001. Sulphur and nitrogen fluxes and budgets in the Bohemian Forest and Tatra Mountains during the industrial revolution (1850-2000). Hydrol. Earth System Sci. 5 (3): 391–405.

Majer V., Cosby B.J., Kopáček J. & Veselý J. 2003. Modelling reversibility of central European mountain lakes from acidification: Part I - The Bohemian Forest. Hydrol. Earth System Sci., 7 (4): 494–509.

Nedbalová L., Vrba J., Fott J., Kohout L., Kopáček J., Macek M. & Soldán T. 2006. Biological recovery of the Bohemian Forest lakes from acidification. Biologia 61, Suppl. 20: 453–466.

Oulehle F., Cosby B.J., Wright R.F., Hruška J., Kopáček J., Krám P., Evans C.D. & Moldan F. 2012. Modelling soil nitrogen: The MAGIC model with nitrogen retention linked to carbon turnover using decomposer dynamics. Environ. Pollut. 165: 158–166.

Soldán T., Bojková J., Vrba J., Bitušík P., Chvojka P., Papáček M., Peltanová J., Sychra J. & Tátosová J. 2012. Aquatic insects of the Bohemian Forest glacial lakes: Diversity, long-term changes and influence of acidification. Silva Gabreta 18 (3): 123–283.

Veselý J., Kopáček J. & Norton S.A. 2003. Increasing temperature decreases aluminium concentrations in Central European lakes recovering from acidification. Limnol. Oceanogr., 48: 2346–2354.

Vrba J., Kopáček J., Fott J., Kohout L., Nedbalová L., Pražáková M., Soldán T. & Schaumburg J. 2003. Long-term studies (1871–2000) on acidification and recovery of lakes in the Bohemian Forest (central Europe). Sci. Total Environ. 310: 73–85.

5. Assessment of the air pollution impacts on waters of the trans-boundary Debed River

Marine Nalbandyan

The Institute of Geological Sciences of the National Academy of Sciences of Armenia
e-mail:marinen3@yahoo.com

Introduction

Armenia is a country with developing economy, where water management requires an integrated approach. For low water resources of Armenia, anthropogenic pollution and eutrophication of surface waters is a serious problem.

In the study of aquatic ecosystems, particular importance is given to pollution and degradation of cross-border water resources. From this perspective, the study of the cross-border Khrami-Debed River, which flows through the area of three states (Armenia, Azerbaijan, Georgia) is of interest (Fig.1.). The Debed River, which belongs to the basin of the Kura River, is of great importance not only for Armenia, but also for the whole region (Fig.1,a).

Problems of pollution of surface waters have retained their urgency in Armenia. Insufficient control of pollution sources and absence of any treatment facilities represent the main causes of pollution of rivers and lakes in the country. Negative effects of the mining industry activities have been most strongly felt in the north and in the south of the country, where the environment has been continuously affected by both wastewater, and air pollution discharges. In particular, the increasing rate of production intensity within the Debed River basin has led to the observed increase of heavy metal pollution, and even first signs of surface water acidulation are revealed.

1. Study area.

1.1. General characteristics of the Debed River and its Pambak tributary

The Debed River forms as a result of confluence of two major tributaries - the Pambak River and the Dzoraget River. The Debed River has the highest water level among all rivers in the Northern Armenia. The river is 178 km long, and its watershed covers an area of 4,050 km^2. Mean annual water discharge is 35.8 m^3/sec.

Twenty-one settlements are located along the river banks, including the cities of Spitak, Vanadzor, and Alaverdi. The Akhtala mining and dressing plant and the Alaverdi copper-smelting group of enterprises operate within the limits of the basin. River feeding is of combined character, the ground feeding coefficient varying from 34 to 56%.The Pambak - one of the major tributaries of the Debed River – forms near the Jajour tunnel and flows into the Dzoraget River nearby the Toumanian station. The river is 86 km long, and the mean annual water discharge makes 11.7m^3/sec.

1.2. *Sampling sites description.*

Debed River – Ayrum Village Sampling Site. The station, which is the terminal one in the Debed River basin, is located within the area of the Ayrum railway station, at $41^0$13'N/$44^0$53'E, 10 km far from the border to Georgia. Mean annual discharge is 32.4 m^3/sec, daily max. - 759 m^3/sec, min. summer-fall – 5.80 m^3/sec. The river bed is straight and made up of boulders, pebble and gravel. The river banks are 1-3 m high, gentle, non-inundated. In winter, some shore ice is common.

Pambak River - Shirakamut Village Sampling Site is situated near the riverhead, at $40^0 51^{'}$ N / $44^0 14^{'}$E. Mean annual water discharge for this section is 2.42 m^3/sec, max. mean daily - 45.6 m^3/sec, min. summer - 0.10 m^3/sec. There are not any man-made impacts within the Armenia's section of the station area. On the sampling site section, the river bed is straight and is made up of pebble and boulder –containing gravel. The banks are 3-5m high, but can be 15-20 m high in places, sheer and steep and are made up of volcanic rocks. Fifty meters farther upstream from the sampling point, the Pambak River flows into the Chanakchi River, which transports with it huge amounts of sediments. In winter, shore ice, ice jam, hanging dams, sludge ice and ice run are common in the Pambak River, but the river freezes-up rarely. In low-water periods, water discharge is measured fording the river all over the hydrological section, and during high-water period - from a small bridge located 2.5 km downstream the post.

Pambak River Sampling Site falls within the city of Vanadzor, and is located in the outskirts of Vanadzor, at $40^0$48'N / $44^0$30'E.

The mean annual water discharge at this river section makes 5.60, maximum daily rate is 83.5 m^3/sec, and the minimum for summer-fall is 0.37 m^3/sec. The river bed is straight and is made up of boulders, pebble, gravel and sand. The river banks are precipitous and 1-1.5 m high. Due to warm discharges upstream the post, some shore ice and sludge ice are common in winter.

2. Material and methods

The material of the study included the quarterly average data on the content of sulfates, hydrocarbonates, nitrites and nitrates in the water of the Pambak River and Debed River, as well as the monthly average data on the air content of sulfur oxide. The following indices, each having certain advantages and limitations, were applied by this study as criteria to assess acidulation processes.

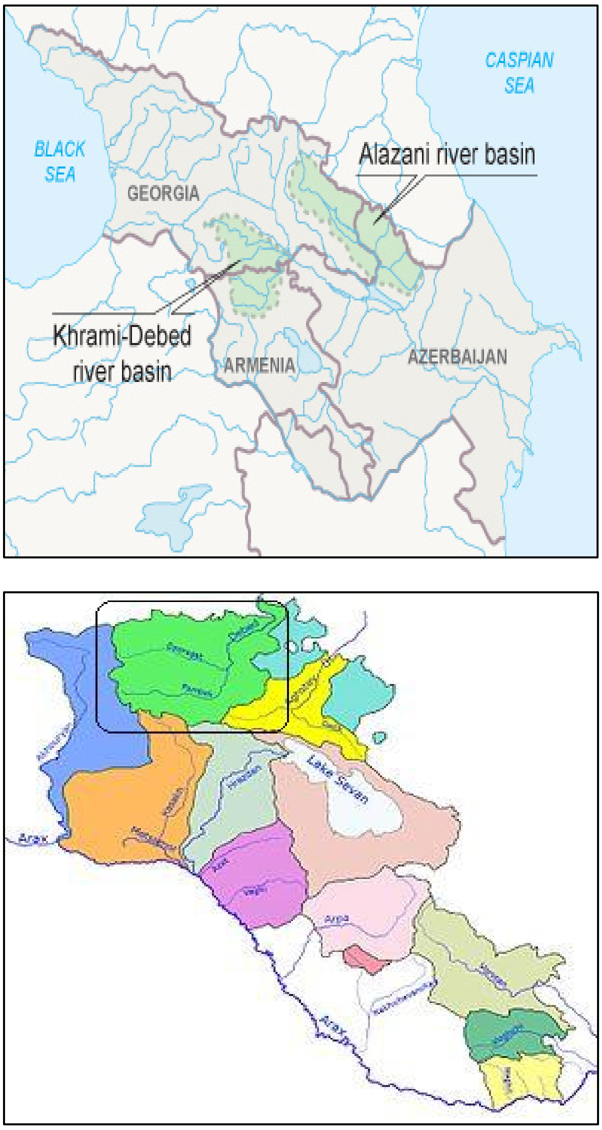


Fig.1.The location of the trans-boundary Debed-Khrami River catchment within the region (above) and Armenia (below).

1. The ratio of $\mathbf{HCO_3^-/SO_4^{2-}}$ anions was studied; this ratio reflects, on one hand, the increasing load of sulfates, but on the other hand, the reduced buffer capacity of the water. Concentrations of the anions (HCO_3^-/SO_4^{2-}) changing towards the predominance of sulfates are symptomatic and indicate water acidulation. This index is the most informative one when seasonal dynamics and many years-long trends are studied for the same objects, as these parameters are quite easily determined.

1. The **KNS** index was applied to assess the role of the contribution of sulfates and nitrates in acidulation processes; the index was estimated as the ratio of $NO_3^-/(SO_4^{2-}+NO_3^-)$, along with the **Alk/SO4 index**, reflecting the ratio of water alkalinity versus the amount of sulfates. Regions where sulfates are the determining factor of acidulation have KNS values approaching 0, increasing as the contribution of nitrates in the anionic composition of the waters builds up.

Samples were collected, conserved, transported and stored following the Standard Operational Procedures (SOPs) developed based on the methods of ISO [1]. Field measurements were done on a monthly basis. In-situ measurements included hydrogen index (pH), conductivity, turbidity, dissolved oxygen, temperature and salinity and were done using U-10 portable analyzer (Horiba).

Common SO_4, HCO_3, NO_2 and NO_3 ions in water were studied on a quarterly basis and were determined in non-acidified and filtered samples. Element and compound concentrations were measured following the developed ISO-based SOPs [2].

3. Results and discussion

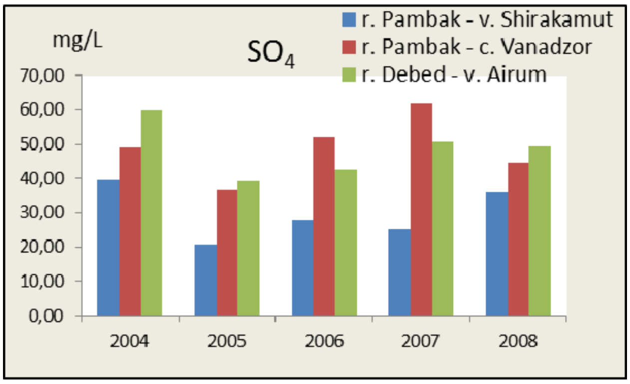


Fig. 2. Concentrations of sulfate in the Pambak River and the Debed river in 2004-2008

Fig. 3. Concentrations of sulfate in the Debed River catchment (Akhtala tributary) in summer months

According to the data, the amount of sulfur dioxide in the air within the Debed river basin, and, in particular, in the region of Alaverdi, has been 10 to 12 higher that the MPC value during the last 10 years.

As concerns sulfate contents in the river water, it should be observed that in the Akhtala river mouth and downstream from confluence with the Debed River, these contents exceeded the MPC value on average 3 to 5, and 6 to 7 times during 2009-2010, and in the last three years, respectively (Fig.3).

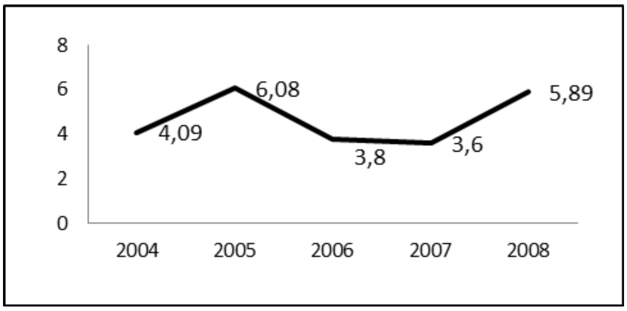
To assess water quality by the acidulation criteria, we carried out certain studies and calculations. According to the measurements carried out at the Alaverdi-Akhtala Site, it was revealed that pH varies in certain range depending on the season and the year and can change to very low values (5.9-6.2, which is the upper limit of the acidulation hazard).

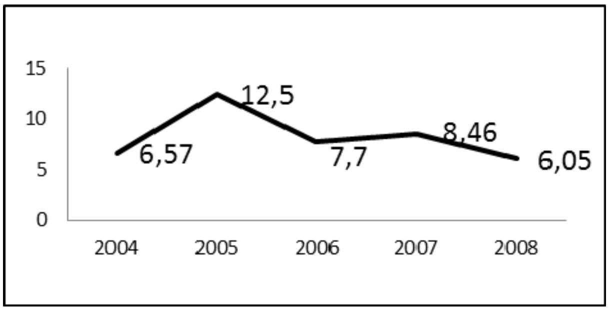
The index of KNS, calculated for the three sites in the basin, bears evidence of an increased contribution and share of sulfates in the water acidulation process. In the Shirakamout region, the index varied in the limits of 0- 0.4, in the region of the Vanadzor city it was about the range of 0-0.2, while the range established near Alaverdi was only as large as 0-0.12 (Fig.5).

In the meantime, the studies of Alk/SO4 indicated that in the mentioned study regions the ratio varied in the limits of 6.3-12.5, 4.09-6.08 and 2.1-2.52, respectively (Fig. 4.) According to the standards, the rates of the studied indices attest to onset of water acidulation process in the Alaverdi-Akhtala region, which poses potential hazard for the water ecosystem.

In the framework of the studies, data collected at various sites of the catchment area were compared. No deviations from the standards of sulfate content in water and sulfur dioxide in air were recorded in the areas where from the tributaries to the Debed River – the Dzoraghet River and the Pambak River start. Air environment pollution was recorded in the region of the Vanadzor city, although this had not been shown to have an effect on the quality of water in the Pambak River in terms of changed acidity of the river waters. The section of the Debed River from Alaverdi Town to Akhtala Town is the most vulnerable one.

The assessment of season-dependent pollution impacts showed that maximum pollution of both water, and air in the risk zone was observed during the summer months, which additionally confirms the direct impact of the polluted air on the river water quality.





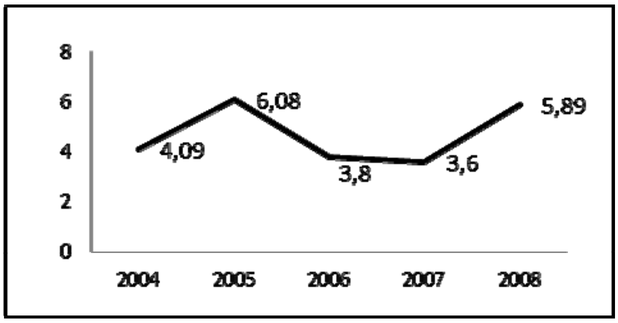


Fig. 4. ***Alk/SO4*** ratio for river water at the sampling sites – Pambak-Shirakamout, Pambak-Vanadzor and Debed –Airum.

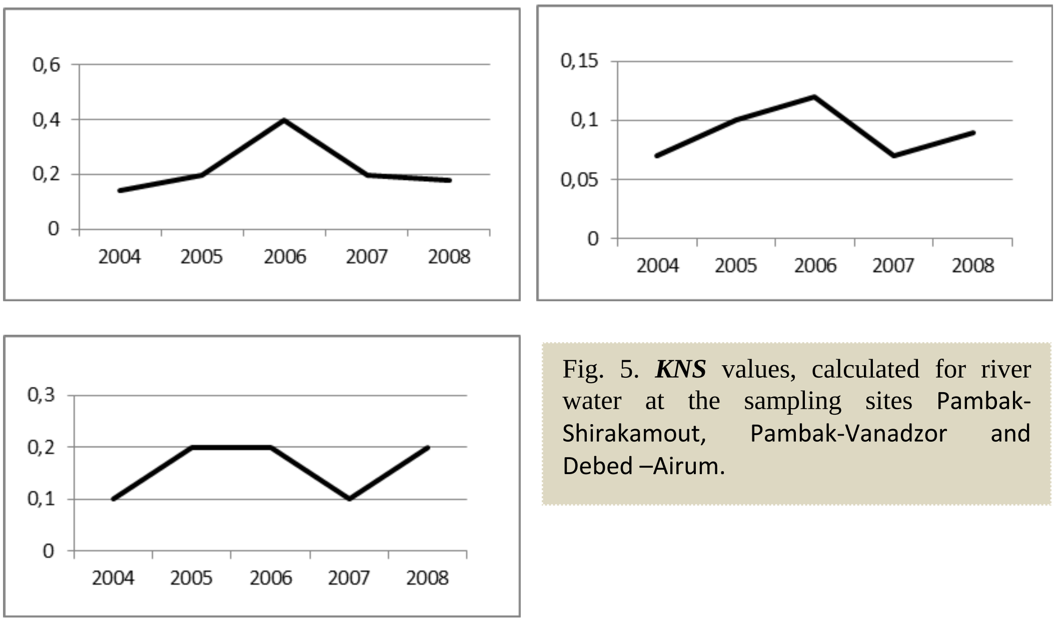


Fig. 5. ***KNS*** values, calculated for river water at the sampling sites Pambak-Shirakamout, Pambak-Vanadzor and Debed –Airum.

Conclusion

As a summary, it is stated that the onset of water acidification process is observed now in the Alaverdi-Akhtala region and this may pose potential hazard for the water environment of the river.

Regretfully, lack of information about the quality of atmospheric precipitation in the considered region does not allow us to achieve better accuracy in estimating the influx of air sulfates and the critical load imposed on the river waters. Additionally, it is also necessary to observe the distribution and movement of the polluted air masses over and beyond the catchment basin region.

Presently, Armenia is only partly involved in the program activity because of the limited funding. Efforts are undertaken to establish a coordinating centre for this international program in Armenia, which may enable realization of detailed studies.

References

1. Standard operational procedures for river water sample collection, conservation and storage. ISO-5667-1, ISO-5667-2, ISO – 5667-3. Manual for sampling methods. Manual for sample conservation and storage. 1998, pp.11-43.
2. Fomin G.S. Water. Control of chemical, bacterial and radiation safety by international standard. Standard operational procedures for determination of basic ions and biogenic elements in surface waters. Moscow. Pub.h."Protector", 2000

6. No decline detected in mercury concentrations of large-bodied fishes in Northern Ontario, Canada lakes

John M. Gunn [a] ***and Thomas A. Johnston*** [b] *******

[a] *Department of Biology, Laurentian University, Cooperative Freshwater Ecology Unit, Sudbury, Ontario P3E 2C6, Canada*

b Ontario Ministry of Natural Resources, Aquatic Research and Development Section, Cooperative Freshwater Ecology Unit, Sudbury, Ontario P3E 2C6, Canada

** Corresponding author: Tel: 705-671-3828; email: tjohnston@laurentian.ca*

ABSTRACT

We compared historic (1974-1981) and recent (2005-2010) muscle total mercury concentrations ([THg], in seven fish species (five piscivores, two benthivores) from 73 lakes in northern Ontario (Canada) using a paired-comparisons approach. There was no significant decline in mean [THg] between recent and historic time periods for any species. In fact, recent mean [THg] were slightly higher (< 0.08 ppm) than historic mean [THg] for all species, and this difference was significant for northern pike (*Esox lucius*).

1. Introduction

The objective of this study was to determine if fish Hg concentrations in Boreal Shield lakes of northern Ontario have declined over the past 30 years, during a period when atmospheric Hg inputs to northern regions may have peaked and are now declining (Butler et al., 2008; Prestbo and Gay, 2009; Slemr et al., 2003) . The Ontario Ministry of Environment (OMOE) has been monitoring fish Hg concentrations across the Ontario portion of this ecoregion for over 30 years through the Sport Fish Contaminant Monitoring Program (SFCMP)((OMOE), 2011). We utilized SFCMP data to compare fish Hg concentrations between two time periods: 1974-1981 and 2005-2010. The earlier period corresponds to a time period when atmospheric Hg deposition was probably much higher than today (Schuster et al., 2002). We assessed temporal changes in Hg concentrations in both piscivorous and benthivorous fish species from lakes covering a wide geographic area using a paired-comparisons approach. This reports findings previously published in Tang et al. (2013).

2. Materials and methods

Target species and sampling sites

Seven species of fish were selected for study: walleye, northern pike, lake trout, burbot, smallmouth bass, lake whitefish and white sucker. These are the most common large-bodied fish species found across the boreal shield ecoregion. Lake whitefish and white sucker are primarily benthivorous and generally have low Hg concentrations whereas the other species are primarily piscivorous and generally have much higher Hg concentrations. Our target group included species commonly exploited in recreational, commercial and subsistence fisheries (walleye, trout, whitefish, pike) as well as relatively unexploited species (burbot, sucker).

We used historic (1974-1981) and contemporary (2005-2011) fish Hg data from 73 medium-size (mostly <5000ha) Ontario lakes located north of 46° latitude, which largely defines the southern boundary of the boreal ecoregion (Figure 1). Only lakes with no known localized Hg issues, such as terrestrial flooding, point-source discharges of Hg or major disturbance in their drainage basins were used. During the netting surveys the individual fish were measured for total length and mass, and a sample (~30 g) of skinless axial muscle removed for analysis of total mercury concentrations ([THg]) by cold vapour-flameless atomic absorption spectroscopy (CV-FAAS) according to the OMOE protocol HGBIO-E3057 ((OMOE), 2006). Mercury analysis methods in the OMOE laboratory have remained consistent from the 1970s to the present.

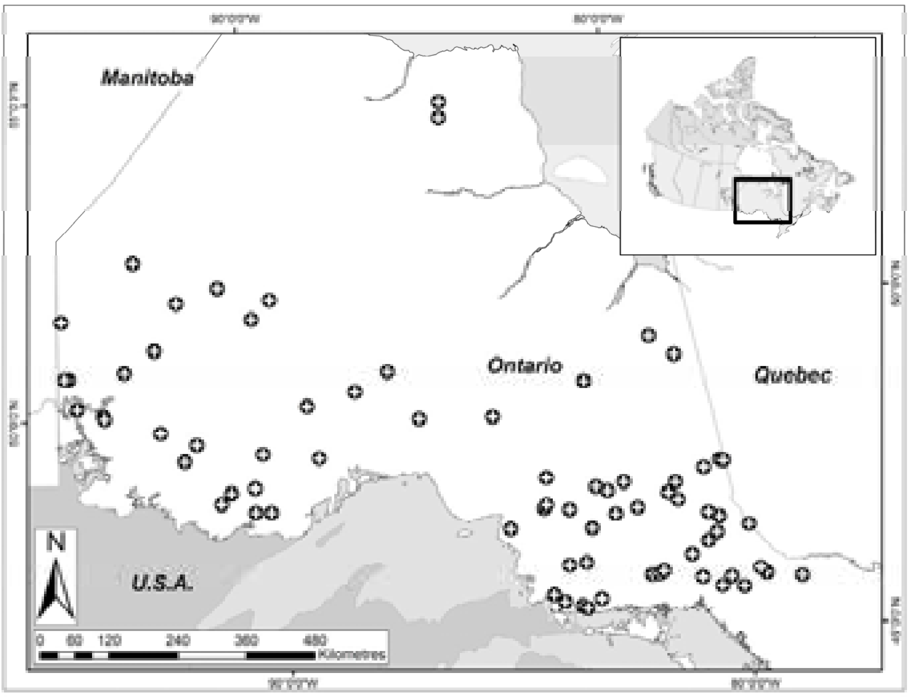


Figure 1. Distribution of study lakes in northern Ontario, Canada. Each lake contains at least one fish population with muscle [THg] data for both historic (1974 – 1981) and current (2005 – 2010) sampling periods (n ≥ 10 individuals per sample period). Figure from Tang eta l. 2013.

Statistical analyses

Through regression analysis we standardized [THg] data to a common total length for each species: walleye,482 mm; pike,563 mm; trout,507 mm; burbot,539 mm; bass,407 mm; whitefish,463 mm; and sucker,438 mm. Differences in current and historic slopes of $\log_e$[THg] vs $\log_e$TL (Δslope = $\text{slope}_{\text{current}} - \text{slope}_{\text{historic}}$) and differences in current and historic mean [THg] (Δ[THg] = $[\text{THg}]_{\text{current}} - [\text{THg}]_{\text{historic}}$) were then tested for each species using paired-comparisons t-tests (MEANS procedure).

3. Results

Temporal changes in the slope of the loge [THg] vs loge TL relationship (Δslope) varied among target species (Figure 2) but there was little evidence that the Hg bioaccumulation rate (increase with body size) changed over time. Paired-comparisons t-tests indicated that Δslope was significantly greater than 0 only for walleye (paired-comparisons t-test, $t = 2.42$, $df = 54$, $p = 0.019$). However, mean muscle [THg] increased (rather than decreased as expected) in all 7 species between the two study periods (Figure 3), but the changes (Δ[THg]) were small for all species (<0.08 ppm, Figure 3) and only statistically significant for northern pike (paired-comparisons t-tests: $t = 2.18$, $df = 28$, $p = 0.038$).

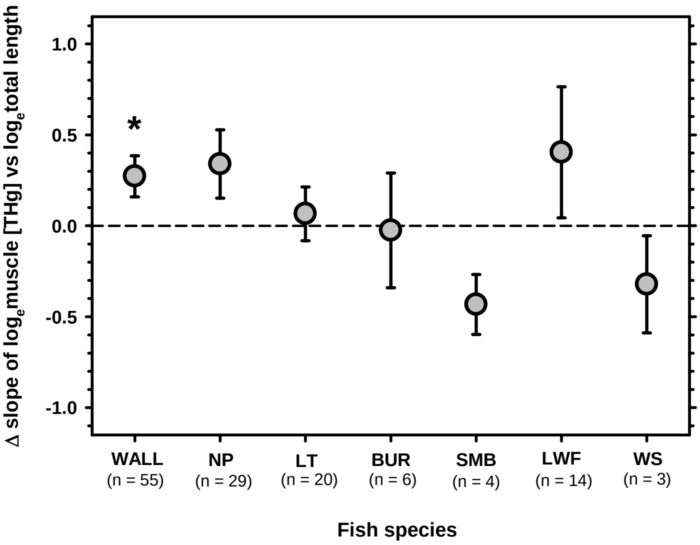


Figure 2. Temporal change (current minus historic) in the slope of the $\log_e$ muscle [THg] vs $\log_e$ total length relationship for walleye (WALL), northern pike (NP), lake trout (LT), burbot (BUR), smallmouth bass (SMB), lake whitefish (LWF), and white sucker (WS). Symbols are means ± 1 standard error (n = number of populations). Significant temporal changes (paired-comparisons t-test, $P < 0.05$) are indicated (*). Figure from Tang et al. 2013

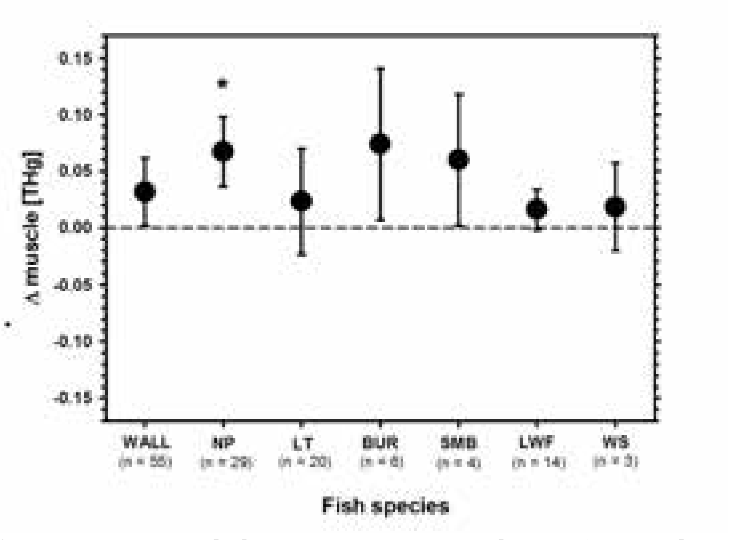


Figure 3. Temporal change (current minus historic) in predicted mean muscle [THg] at 1 kg for walleye (WALL), northern pike (NP), lake trout (LT), burbot (BUR), smallmouth bass (SMB), lake whitefish (LWF), and white sucker (WS). Symbols are means ± 1 standard error (n = number of populations). Significant temporal changes (paired-comparisons t-test, $P < 0.05$) are indicated (*). Figure from Tang et al. 2013.

4. Discussion

Despite the reported decline in atmospheric Hg deposition in northern North America (Prestbo and Gay 2009), our study did not find any major changes in Hg bioaccumulation rates (slope of [THg] vs body size) or mean Hg concentration (Δ[THg] at the standard size) for most of the common large-bodied fish species across Ontario's boreal shield ecoregion over the past 30+ years. The single exceptions were a significant increase in the Hg bioaccumulation rate for walleye, and a significant increase, rather than a decrease, in the mean Hg concentration for northern pike.

Other studies have reported stable or declining concentrations of Hg in many regions of North America, but these trends have not been consistent over all time periods or all regions. For example, trend analyses on the Great Lakes show increasing fish [Hg] in some areas (e.g., Lake Erie) but declines in others (Bhavsar et al., 2010; Zananski et al., 2011), while an extensive study of northern Minnesota lakes found that muscle [THg] of walleye and northern pike had declined from the early 1980s to the mid 1990s but then increased afterwards up to 2006 (Monson, 2009). Similarly, the muscle [THg] of burbot in the lower Mackenzie River, Northwest Territories, declined slightly from 1985 to 1994 then increased sharply afterwards (Carrie et al., 2010). If a similar mid-90 inflection point existed for Northern Ontario lakes, our temporal trend study, based on only two time windows on either side of this period, may have missed detecting such a reversal.

The absence of any significant decline in fish [THg] across northern Ontario over the past 30 years may be due to in-lake processes that influence MeHg production or uptake and thus interact with the effects changing atmospheric Hg inputs. For example, MeHg production may increase in response to reduced pH (Miskimmin et al., 1992), increased anoxia (Eckley and Hintelmann, 2006; Watras et al., 1995), and increased concentrations of sulfate (Gilmour et al., 1992; Jeremiason et al., 2006; Watras and Morrison, 2008), and dissolved organic matter (Eckley and Hintelmann, 2006; Ravichandran, 2004). It is likely that several of these factors have been altered in recent decades due to changes in acid deposition and climate warming.

Acknowledgments: Financial and in-kind support for this research was provided by the Ontario Ministry of the Environment's (OMOE) Environmental Monitoring and Reporting Branch, the Ontario Ministry of Natural Resources (OMNR), the Natural Sciences and Engineering Research Council (NSERC), and Laurentian University.

References

Bhavsar SP, Gewurtz SB, McGoldrick DJ, Keir MJ, Backus SM. Changes in mercury levels in Great Lakes fish between 1970s and 2007. Environ Sci Technol 2010;44:3273-3279.

Butler TJ, Cohen MD, Vermeylen FM, Likens GE, Schmeltz D, Artz RS. Regional precipitation mercury trends in the eastern USA, 1998-2005: Declines in the Northeast and Midwest, no trend in the Southeast. Atmos Environ 2008;42:1582-1592.

Carrie J, Wang F, Sanei H, MacDonald RW, Outridge PM, Stern GA. Increasing contaminant burdens in an Arctic fish, burbot (*Lota lota*), in a warming climate. Environ Sci Technol 2010;44:316-322.

Eckley CS, Hintelmann H. Determination of mercury methylation potentials in the water column of lakes across Canada. Sci Total Environ 2006;368:111-125.

Gilmour CC, Henry EA, Mitchell R. Sulfate stimulation of mercury methylation in freshwater sediments. Environ Sci Technol 1992;26:2281-2287.

Jeremiason JD, Engstrom DR, Swain EB, Nater EA, Johnson BM, Almendinger JE, et al. Sulfate addition increases methylmercury production in an experimental wetland. Environ Sci Technol 2006;40:3800-3806.

Miskimmin BM, Rudd JWM, Kelly CA. Influence of dissolved organic carbon, pH, and microbial respiration rates on mercury methylation and demethylation in lake water. Can J Fish Aquat Sci 1992;49:17-22.

Monson BA. Trend reversal of mercury concentrations in piscivorous fish from Minnesota Lakes: 1982-2006. Environ Sci Technol 2009;43:1750-1755.

OMOE. Guide to Eating Ontario Sport Fish, 2011-2012, 26th ed. Toronto: Queen's Printer for Ontario; 2011

OMOE. The determination of mercury in biomaterials by cold vapour-flameless atomic absorption spectroscopy (CV-FAAS). Toronto: Ontario Ministry of the Environment; 2006

Prestbo EM, and Gay DA. Wet deposition of mercury in the US and Canada, 1996-2005: Results and analysis of the NADP mercury deposition network (MDN). Atmos Environ 2009;43:4223-4233.

Ravichandran M. Interactions between mercury and dissolved organic matter - a review Chemosphere 2004;55:319-331.

Schuster PF, Krabbenhoft DP, Naftz DL, Cecil LD, Olson ML, Dewild JF, et al. Atmospheric mercury deposition during the last 270 years: A glacial ice core record of natural and anthropogenic sources. Environ Sci Technol 2002;36:2303-2310.

Slemr F, Brunke E-G, Ebinghaus R, Temme C, Munthe J, Wängberg I, et al. Worldwide trend of atmospheric mercury since 1977. Geophys Res Letters 2003;30:1516.

Tang RW-K, Johnston TA, Gunn JM, Bhavsar SP. Temporal changes in mercury concentrations of large-bodied fishes in the boreal shield ecoregion of northern Ontario, Canada. Sci Tot Env 2013; 444:409-416.

Watras CJ, Bloom NS, Claas SA, Morrison KA, Gilmour CC, Craig SR. Methylmercury production in the anoxic hypolimnion of a dimictic seepage lake. Water Air Soil Pollut 1995;80:735-745.

Watras CJ, and Morrison KA. The response of two remote, temperate lakes to changes in atmospheric mercury deposition, sulfate, and the water cycle. Can J Fish Aquat Sci 2008;65:100-116.

Zananski TJ, Holsen TM, Hopke PK, Crimmins BS. Mercury temporal trends in top predator fish of the Laurentian Great Lakes. Ecotoxicology 2011;20:1568-1576

7. An application of the MAGIC model to four high altitude lakes in Ticino, Switzerland communities

M. Rogora, S. Steingruber**, L. Colombo****

*CNR Institute of Ecosystem Study, I-28922 Verbania Pallanza
**Ufficio aria, clima, energie rinnovabili, Cantone Ticino, CH-6500 Bellinzona
*** University of Applied Sciences of Southern Switzerland,SUPSI, CH-6952 Canobbio

1. Introduction

This report presents the results of a modelling exercise applied to four high altitude lakes in the Ticino region, Switzerland. In this area, acidification of high-altitude lakes situated in granitic areas was first reported in the early 1980s, as an effect of acid deposition (Mosello et al., 1992). Successively, as an effect of decreasing emission and deposition of acidifying compounds, several lakes showed signs of acidification recovery (Steingruber & Colombo, 2010a).

The aim of the modelling was to reconstruct and predict lake chemistry in response to atmospheric deposition change. The applied model is MAGIC, which was specifically developed for the long term reconstruction and future prediction of soil and surface water acidification at the catchment scale (Cosby et al., 2001).

The study lakes were selected on the basis of available data for the model application, and in order to be representative of the high altitude lake population in the Ticino region. They span a wide range of chemical characteristics and cover varying level of sensitivity to acidification, from highly (Starlaresc, Tomè) to moderately sensitive (Laghetto Inferiore, Laghetto Superiore) lakes.

This study represents the first attempt to model long term changes in lake water chemistry, trying to evaluate the effective level of recovery (in terms of pH, ANC or other key variables) with respect to pre-acidification conditions. The model allowed a reconstruction (hindcast) of lake chemistry since 1960, and a prediction (forecast) for the period 2010-2050. The projections of future lake chemistry were obtained by applying different scenarios of atmospheric deposition reduction.

2. Study lakes

The characteristics of the lakes selected for the modelling (Fig. 1) are shown in table 1, while their average chemical characteristics (mean values of 2010-2011) are shown in table 2. Lake Starlaresc (STA) and Tomè (TOM) have low pH and alkalinity values (5.6-5.7 and 3-4 µeq L-1, respectively), and may be considered representative of the category of highly sensitive lakes. Indeed ANC levels below 20 µeq l-1, as those affecting these lakes, are usually assumed as “critical” for the biota and indicative of a high acidification risk. On the other hand Laghetto Inferiore (LAI) and Superiore (LAS) may be classified as moderately sensitive, with ANC values between 30 and 40 µeq L-1.

Lake	Acronym	Lat.	Long.	Alt.	Catchment area	Lake area	Max depth	Catchment cover	
				m a.s.l.	ha	ha	m	Rocks %	Meadows %
Starlaresc da Sgiof	STA	8°46’25’’	46°16’26’’	1875	23	1.1	6	29	67
Tomè	TOM	8°41’23’’	46°21’47’’	1692	294	5.8	38	57	41
Laghetto Inferiore	LAI	8°35’ 34’’	46°28’34’’	2074	182	8.3	5.6	65	27
Laghetto Superiore	LAS	8°35’05’’	46°28’34’’	2128	125	12.7	8.3	65	29

Tab. 1 – Main characteristics of the lakes selected for the modelling and their catchments.

The study lakes have been monitored for water chemistry since the 1980s, so that a long term series of chemical data exist. Similarly, atmospheric deposition chemistry has been studied in the Ticino region since the late 1980s and a network of 9 sites is still operating (Steingruber & Colombo, 2010b).

Fig. 1: Lakes selected for the modelling. a) Starlaresc da Sgiof; b) Tomè; c) Laghetto Inferiore; d) Laghetto Superiore (Pictures by G.A. Tartari & M. Veronesi).

Lake	pH	Cond. µS cm^{-1}	Alk µeq L^{-1}	BC µeq L^{-1}	SO_4 µeq L^{-1}	NO_3 µeq L^{-1}	Cl µeq L^{-1}	Si mg L^{-1}	DOC mg C L^{-1}	Al tot µg L^{-1}
STA	5.59	7.2	4	48	26	17	3	0.73	0.9	52
TOM	5.66	7.8	3	61	27	27	3	1.0	0.4	25
LAI	6.79	8.4	36	85	27	13	2	0.75	0.6	17
LAS	6.78	7.9	35	81	23	12	3	0.66	0.7	12

Tab. 2 – Mean chemical characteristics (2010-11) of the selected lakes. Cond.: conductivity at 20 °C. Alk: alkalinity. BC: sum of base cations (Ca^{++}, Mg^{++}, Na^{+}, K^{+}). Si: Reactive silica. DOC: dissolved organic carbon.

2.1. MAGIC calibration and application to the study sites

In this study the dynamic acidification model MAGIC version 777 was used. The main peculiarities in the study area (Southern Switzerland), where the studied sites are located, are:

1. the climate features, with high amount of deposition due to the orographic effect and at the same time high load of N and S compounds due to the location of the area north to the Po plain in Italy (Steingruber & Colombo, 2010a);
2. the heterogeneity in the lithological, vegetation and soil cover in the lake catchments;

3. the chemical characteristics of lake water, showing very low solute concentrations and limited buffer capacity, due to the dominance of acidic, low weatherable rocks in the catchments.

The target year chosen for the calibration was 2010. Atmospheric deposition chemical data were mean values of 2009-2011, and precipitation volume (2200 mm) was the long-term average of the period covered by available data at Robiei (1996-2011). The hindcast period was of 150 years (1860-2010) and the forecast simulations were run for 20 years (2011-2030).

2.2. Scale factors for atmospheric deposition

The study lakes are all located in the cell i=70, j=38 of the EMEP grid (50 km x 50 km). Deposition sequences for this cell covering the period 1980-2010 are available from the WebDab-EMEP DB.

Successively, to reconstruct the scale factors for the whole hindcast period (since 1860), the "historical" deposition data, provided by the Coordinating Centre for Effects (CCE) of the ICP Modelling & Mapping, were used. These data were issued in 2011 for selected ICP WATERS sites in the framework of the so-called "ex-post analysis" (Wright et al., 2011).

Data issued by CCE also included deposition scenarios for the period 2010-2030. These scenarios are COB 2020 (current legislation), and MFR 2020 (maximum feasible reduction).

Because the study lakes in Ticino are part of the ICP WATERS network, two scenarios in the present modelling exercises were applied, so that this report may be a further contribution to the evaluation of the effects of potential future deposition reduction on surface waters. Sulphate deposition is supposed to decrease of 37% and 55% with respect to the present level (2010) under the COB and MFR scenarios respectively. A relevant reduction is foreseen also for oxidised N deposition, which will decrease of 34% and 38% under COB and MFR, respectively. On the other hand, reduced N deposition will change slightly (5%) under the current legislation; only implementing the maximum feasible technologies a 38% reduction may be achieved.

3. Results and discussion

3.1. Calibration and hindcast

Generally a good agreement between modelled and measured concentrations of SO_4, NO_3 and base cations was achieved at all sites. The study lakes showed slightly different SO_4 pattern, with the highest maxima (100-110 µeq L^{-1}) at the most acidified sites STA and TOM.

Base cations decreased in the lakes, as an effect of the acidification recovery: as simulated by the model, leaching of BC increased in correspondence with the increase of acidifying anion, and peaked in the 1980s. Afterwards a decreasing trend began, more evident at the most acidified sites.

A negative trend also affected nitrate concentrations in lakes, even if measured values are much more scattered with respect to SO_4 or BC . This is related to the fact the N compounds are affected by biological processes taking place both in the soil and in lake water.

With respect to sulphate, measured NO_3 did not show a clear decreasing trend: concentrations tend to be lower only in the last few years of the record (2008-2010). This is related to the fact that atmospheric input of N did not change as the same rate as S deposition in the study area.

The decrease of NO_3 in lake water is more evident in LAS and LAI, where concentrations passed from about 25 to 10-15 µeq l^{-1}. TOM is the lake showing the highest present concentrations of NO_3 (25 µeq $l^{-1.}$ as mean value of 2010-11). This can be due to the larger catchment area and the higher catchment.

3.2. Forecast simulation

The future changes in lake chemistry according to three different scenarios are compared in fig. 2 for Lake Starlaresc da Sgiof. MFR represents the best case scenario with the emission reduction offered by a full implementation of the best available technologies. The COB or "current Legislation" scenario reflects the current perspectives of individual countries (Cofala *et al.*, 2006).

As can be expected, the greatest improvement in the lake chemical status is foreseen under the background deposition scenario, followed by MFR and COB for all the variables considered. Under the Bkgd scenario, lakes will essentially recover to the pre-acidification condition, with pH and ANC coming back to the values of the early 1900s.

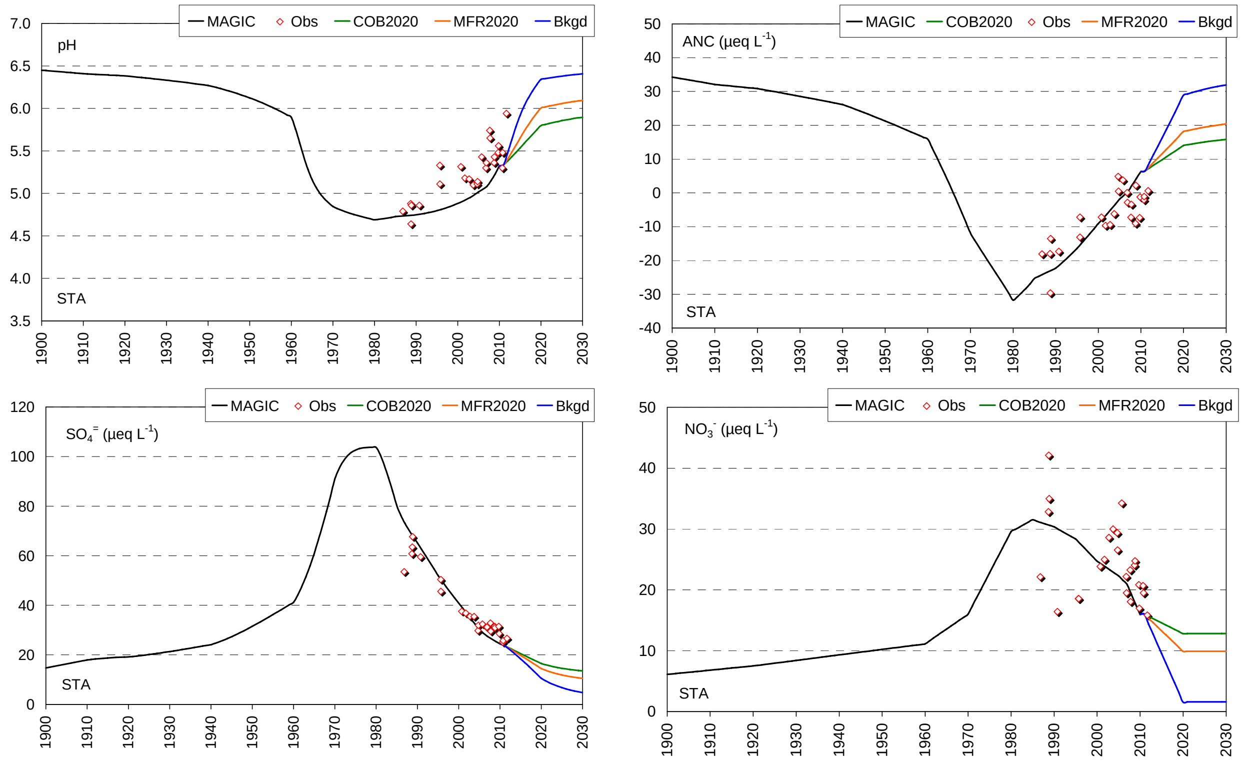


Fig. 2 – Simulated (MAGIC) and observed (Obs) pH-, ANC, sulphate and nitrate values in the Starlaresc da Sgiof lake. Three deposition scenarios are considered: COB2020 (actual legislation, including the Gothenburg Protocol), MFR2020 (maximum feasible reduction) and Bkgd (background deposition only).

The relative changes in the values of the chemical variables between 2020 and 2010 under the various scenarios are shown in tab. 3. Lakes STA and TOM, which have been affected by a more pronounced acidification in the 1980s, showed a more evident recovery pattern with respect to LAS and LAI: for instance ANC passed from strongly negative values (-20 µeq L^{-1}) to positive ones (0-5 and 0-10 µeq L^{-1} in STA and TOM, respectively). ANC will more than double by 2020 in both the two lakes (Tab. 3). However, safety values of ANC (above 20 µeq l^{-1}) would be reached only under the MFR scenario. In the more realistic hypothesis of the COB scenario the two lakes will recover to ANC values around 15 µeq l^{-1}. In Europe the value of 20 µeq L^{-1} has been identified as the level needed to meet the critical loads exceedance target under UNECE protocols and a 30 µeq L^{-1} value estimated as the pre-acidification reference value. It has to be emphasised that the most sensitive lakes STA and TOM would never reach ANC values above 40 µeq L^{-1}, even under the hypothesis of background deposition. Hence specific target values for this category of lakes (with extremely dilute, low buffered waters due to crystalline bedrock) should have been identified.

The recovery rates, in terms of pH and ANC values, have been markedly lower in LAI and LAS with respect to STA and TOM. ANC has probably never reached negative values in the lakes, and it recovered to values above 40 µeq l^{-1} in recent years (up to 60-70 µeq l^{-1} in LAS).

As to sulphate, most of the expected change in response to decreasing deposition has already taken place in the lakes (within 1980 and 2010). However, the decrease of concentration will continue also in the next two decades, and it will be of about 30-40% and 40-50% with respect to the present levels under the COB and MFR scenarios, respectively (Tab. 3).

The biggest differences among the considered scenarios are found in the forecast of NO_3 concentrations. Indeed both COB and MFR foreseen a decrease of NO_x and NH_3 emissions, but these are still far from the estimated levels of background deposition. In particular, NH_3 emissions are supposed to decrease slightly under the COB scenario (only 5% with respect to present level). NO_3 levels will decrease to about 10 µeq L^{-1} in LAS and LAI by 2020; they will remain slightly higher (13 µeq L^{-1} under the COB scenario) in STA, and above 20 µeq L^{-1} in TOM.

Lake	Scenario	ANC		SO_4		NO_3		BC	
		2020 vs 2010	2030 vs 2010	2020 vs 2010	2030 vs 2010	2020 vs 2010	2030 vs 2010	2020 vs 2010	2030 vs 2010
STA	COB	122	151	-33	-44	-20	-20	-7	-9
	MFR	187	223	-41	-57	-38	-38	-8	-12
	BKGD	358	406	-57	-81	-90	-90	-11	-17
TOM	COB	66	68	-31	-41	-19	-17	-9	-12
	MFR	120	125	-40	-55	-37	-36	-11	-16
	BKGD	256	268	-58	-80	-90	-90	-17	-23
LAI	COB	13	14	-29	-40	-20	-20	-6	-8
	MFR	22	23	-35	-49	-38	-38	-6	-10
	BKGD	45	47	-48	-67	-90	-90	-7	-12
LAS	COB	12	13	-27	-35	-20	-20	-4	-6
	MFR	19	21	-35	-46	-38	-38	-5	-7
	BKGD	39	41	-51	-68	-90	-90	-6	-10

Tab. 3 – Relative changes (%) in the values of ANC, SO_4, NO_3 and base cations (BC) in 2020 (and 2030) with respect to the present status (2010) under the three scenarios.

N deposition will be the dominant driving force in the acidification of the study lakes in the next future (Curtis *et al.*, 2005). Ammonium deposition will be particularly important, since it represents now the dominant form of N in atmospheric deposition in the study area (Rogora *et al.*, 2012).

For this reason, the MAGIC model was also run assuming (i) progressive decrease of NO_3 deposition (from -20% to -50% in 2020 with respect to 2010, and no change in NH_4 deposition) and (ii) progressive decrease of both NO_3 and NH_4 deposition (Fig. 3). Only the most sensitive lake STA was considered. The aim of this modelling exercise was indeed to put in evidence the relative gain of reducing both oxidised and reduced N deposition with respect to changing NO_3 deposition only.

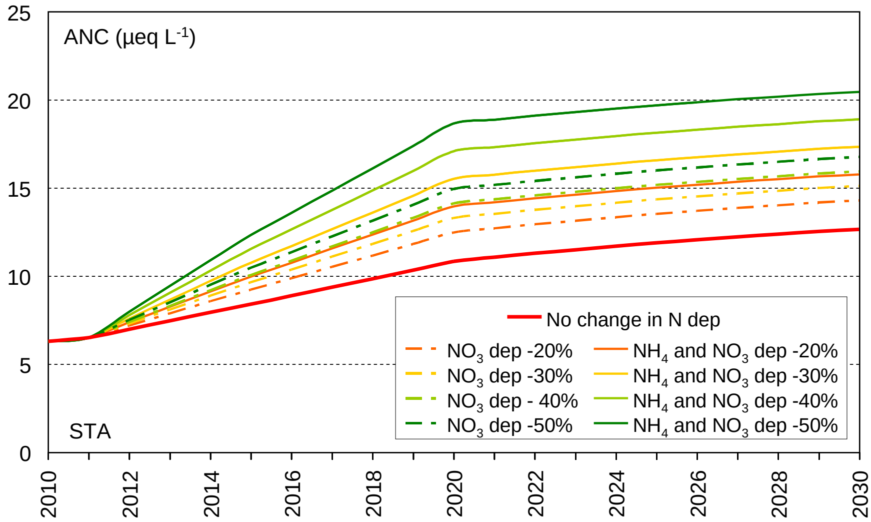


Fig. 3– Simulated changes in the ANC level of Lake Starlaresc (STA) according to different scenarios of N deposition. Changes (-20%, -30%, -40%, -50%) are decrease of deposition in 2020 with respect to 2010 levels.

The results clearly show the necessity to reduce both forms of N deposition if a significant change in the ANC levels has to be obtained. The relative gain of a coupled reduction compared to NO_3 reduction only in terms of ANC in the lake is between 1.5 (20% emission decrease in 2020) and 3.7 (50% emission decrease) µeq L^{-1}. Despite the decrease of NO_3 concentrations foreseen for the next future, NO_3 levels in the lakes will remain quite high (10-20 µeq L^{-1}). The study area is affected by high N deposition with respect to those found in other parts of the Alps or in other mountain areas of the world (Rogora *et al.*, 2006; 2008). Hence N emission in the source region located in the lowlands has necessarily to be reduced to reach a substantial decline of N deposition in the alpine and subalpine areas of both Italy and Switzerland and a further decrease of NO_3 levels in alpine lakes.

4. Concluding remarks

This modelling exercise represents the first application of the dynamic model MAGIC to high altitude lakes in the Ticino area. Previous application of MAGIC to other high altitude lakes in the Central Alps (Rogora 2004; Rogora *et al*., 2003a) as well as application of the SMB and FAB models to the Ticino lakes (Posch *et al*., 2007) already put in evidence the usefulness of dynamic modelling for both hindcast and forecast ecosystem response to atmospheric deposition scenarios.

In the Ticino area several lakes are still acidic or present a high sensitivity to acidification (Steingruber & Colombo, 2010a). MAGIC was successfully calibrated for a few lakes in this area, representative of varying levels of sensitivity to acidification. The model allowed a reconstruction of pre-acidification condition and a simulation of the future chemical changes in lake water in relation to different deposition scenarios, as those adopted in the so-called “ex-post analysis” performed within the ICP WATERS (Wright *et al*., 2011).

The output of the modelling confirmed a rather critical situation for the most sensitive lakes, with ANC values which will remain below the critical limit of 20 µeq L^{-1} in the next decades according to the most realistic scenario. This study also put in evidence that the ANC critical levels normally adopted in the evaluation of acidification recovery are probably too low for this category of lakes.

The simulations performed with MAGIC clearly demonstrated the benefits of achieving the emission reductions in both S and N agreed under the Gothenburg Protocol. But current levels of S and particularly N emissions must be reduced even more to protect freshwaters from episodic acidification and guarantee a stable recovery. The modelling results put in evidence the relevance of N deposition in determining the present status of the lakes and their chemical evolution in the next two decades.

Beside atmospheric deposition, other actors affect the long-term changes in surface water chemistry. Alpine lakes in particular have proved to be highly sensitive to climate change (e.g. Psenner & Schmidt, 1992; Rogora et al., 2003b; Hobbs et al., 2001). A further step in the modelling of high altitude lake chemistry could be an attempt to incorporate and represent climate change and its impacts using dynamic modelling, as done for instance by Wright et al. (2006).

References

Boggero A., A. Marchetto, A. Barbieri, A. Sassi, M. Conedera, G.A. Tartari, R. Mosello. 1996. Idrochimica dei laghi alpini del Canton Ticino (Alpi Centrali) in relazione con la chimica delle precipitazioni. Docum. Ist. Ital. Idrobiol., 57: 273 pp.

Cofala J., Amann M., Mechler R. 2006. Scenarios of World Anthropogenic Emissions of Air Pollutants and Methane up to 2030. International Institute for Applied Systems Analysis.

Cosby, B.J., R.C. Ferrier, A. Jenkins & R.F. Wright. 2001. Modelling the effects of acid deposition – fifteen years of MAGIC: refinements, adjustments and inclusion of nitrogen dynamics. Hydrol. Earth System Sci., 5: 499-517.

Curtis, C.J., I. Botev, L. Camarero, J. Catalan, D. Cogalniceanu, M. Hughes, M. Kernan, J. Kopáček, A. Korhola, R. Mosello, R. Psenner, M. Rogora, E. Stuchlík, M. Veronesi, R. Wright. 2005. Acidification in European mountain lake districts: a regional assessment of critical load exceedances. Aquatic Sciences 67: 237-251.

Hobbs, W.O., R. D. Vinebrooke, A.P. Wolfe. 2011. aBiogeochemical responses of two alpine lakes to climate change and atmospheric deposition, Jasper and Banff National parks, Canadian Rocky Mountains. Canadian Journal of Fisheries and Aquatic Sciences, 2011, 68(8): 1480-1494.

Posch M., Eggenberger U., Kurz D., Rihm B. 2007: Critical Loads of Acidity for Alpine Lakes. A weathering rate calculation model and the generalized First-order Acidity Balance (FAB) model applied to Alpine lake catchments. Environmental studies no. 0709. Federal Office for the Environment, Berne. 69 S.

Psenner R., Schmidt R. 1992. Climate-driven pH control of remote alpine lakes and effects of acid deposition. Nature 356, 781 – 783.

Rogora, M. 2004. Acidification and recovery at mountain lakes in Central Alps assessed by the MAGIC model. J. Limnol., 63(1): 133-142, 2004.

Rogora, M., A. Marchetto & R. Mosello. 2003a. Modelling the effects of the deposition of acidity and nitrogen on selected lakes and streams in Central Alps (Italy). Hydrol. Earth System Sci. 7: 540-551.

Rogora, M., J. Massaferro, A. Marchetto, G.A. Tartari, R. Mosello. 2008. The water chemistry of Northern Patagonian lakes and their nitrogen status in comparison with remote lakes in different regions of the globe. J. Limnol. 67 (2): 75-86.

Rogora, M., R. Mosello, S. Arisci, M.C. Brizzio, A. Barbieri, R. Balestrini, P. Waldner, M. Schmitt, M. Stähli, A. Thimonier, M. Kalina, H. Puxbaum, U. Nickus, E. Ulrich & A. Probst. 2006. An overview of atmospheric deposition chemistry over the Alps: present status and long-term trends. Hydrobiologia 562: 17-40.

Steingruber S., Colombo L. 2010b. Acidifying Deposition in Southern Switzerland. Assessment of the trend 1988–2007. Environmental studies no. 1015. Federal Office for the Environment, Bern. 82 pp.

Steingruber, S.M., L. Colombo. 2010a. Effect of Acid Deposition on Chemistry and Biology of High-Altitude Alpine Lakes. In: U. Bundi (ed.). Alpine Waters, Hdb Env Chem 6: 119–140.

Wright R.F., R. Helliwell, J. Hruska, T. Larssen, M. Rogora, D. Rzychon, B.L. Skjelkvale. 2011. Impacts of Air Pollution on Freshwater Acidification under Future Emission Reduction Scenarios; ICP Waters contribution to WGE report. ICP Waters Report 108/2011: 27 pp.

Wright, R.F., J. Aherne, K. Bishop, L. Camarero, B.J. Cosby, M. Erlandsson, C.D. Evans, D. Hardekopf, R. Helliwell, J. Hruska, A. Jenkins, F. Moldan, M. Posch and M. Rogora. 2006. Modelling the effect of climate change on recovery of acidified freshwaters: sensitivity of individual processes in the MAGIC and SMART models. Sci. Tot. Environ. 365: 154-166

8. Drinking water treatment adaptation to increasing levels of DOM and changing DOM quality under climate change (DOMQUA)

Heleen de Wit

Norwegian Institute for Water Research, Gaustadalléen 21, 0349 Oslo, Norway

Lakes and rivers are the source of drinking water for most people in Norway, Sweden and Finland. In recent years, concentrations of dissolved organic matter (DOM) in lakes and rivers have increased and associated with this, surface waters have become browner (Monteith et al., 2007). This poses a major challenge to drinking water providers, as removal of DOM is a key step in drinking water treatment.

While reduced acid deposition appears to be the main cause of increasing DOM in headwater catchments (De Wit et al., 2007; Monteith et al., 2007; Vuorenmaa et al., 2006), interannual variations of hydrology impact variations in DOM (De Wit et al., 2007; Erlandsson et al., 2008; Vuorenmaa et al., 2006) while temperature also affects long-term trends in DOM (Weyhenmeyer and Karlsson, 2009). Water color has increased more than DOM (Haaland et al., 2010), implying that DOM quality is even more sensitive to environmental change than DOM quantity. In rivers, strong correlations have been found between hydrology and water color (Bomo et al., 2007). Climate change leading to increased temperatures and changed precipitation patterns, with likely impacts on DOM in surface waters used as drinking water sources.

Adaptation measures needed are likely to raise costs of water treatment and require long-term investments. In order to maintain good drinking water quality in the future, municipalities and other stakeholders urgently need science-based projections of raw water quality under climate change as well as information about the possibilities for, and costs of adaptation.

Nordforsk, under the Nordic Council of Ministers, has financed the research project “DOMQUA” under the The Top-level Research Initiative, the programme on ‘Effect studies and adaptation to Climate Change’, for the period 2014-2016. Research partners include Norwegian, Swedish and Finnish research institutes and universities, while stakeholders are several drinking water facilities and national branch organisations.

The main aims of the DOMQUA project are the following:

- predict concentrations and quality of DOM in surface waters in the Nordic countries under climate change
- evaluate the capacity and suitability of current drinking water treatment in the light of expected changes in DOM quality and quantity
- recommend adaptation strategies to stakeholders in the drinking water industry, in cooperation with major drinking water suppliers, and analyse socio-economic costs and benefits of adaptation strategies

The scientific participants in DOMQUA have strong expertise in understanding and modelling of DOM in catchments, lakes and rivers, and in studying effects of climate change and treatment technology on quality of drinking water sources and treated drinking water. Social scientists will be involved to make a socioeconomic analysis of adaptation in collaboration with natural scientists and stakeholders.

Results will be shared with stakeholders through Nordic and national trade conferences, seminars and journals.

For more information, visit the homepage of DOMQUA at www.niva.no/domqua or contact project leader Heleen de Wit at the Norwegian Institute for Water Research.

References

Bomo, A.M., Tryland, I., Liltved, H., 2007. Vil rent vann også være rent i fremtiden? Effekter av ekstremvær på drikkevannskvalitet. Vann 2, 143-149.

De Wit, H.A., Mulder, J., Hindar, A., Hole, L., 2007. Long-term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition. Environmental Science & Technology 41, 7706-7713.

Erlandsson, M., Buffam, I., Folster, J., Laudon, H., Temnerud, J., Weyhenmeyer, G.A., Bishop, K., 2008. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. Global Change Biology 14, 1191-1198.

Haaland, S., Hongve, D., Laudon, H., Riise, G., Vogt, R.D., 2010. Quantifying the Drivers of the Increasing Colored Organic Matter in Boreal Surface Waters. Environmental Science & Technology 44, 2975-2980.

Monteith, D.T., Stoddard, J.L., Evans, C.D., de Wit, H.A., Forsius, M., Hogasen, T., Wilander, A., Skjelkvale, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopacek, J., Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450, 537-U539.

Vuorenmaa, J., Forsius, M., Mannio, J., 2006. Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. Science of the Total Environment 365, 47-65.

Weyhenmeyer, G.A., Karlsson, J., 2009. Nonlinear response of dissolved organic carbon concentrations in boreal lakes to increasing temperatures. Limnology And Oceanography 54, 2513-2519.

9. Task Force minutes of the twenty-ninth meeting of the Programme Task Force held in Český Krumlov, Czech republic, October 1-3, 2013

CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

Working Group on Effects

International Cooperative Programme
on Assessment and Monitoring of the Effects of Air Pollution on Rivers and Lakes

MINUTES

of the twenty-ninth meeting of the Programme Task Force
held in Český Krumlov, Czech republic, October 1-3, 2013

Key messages from the Task Force meeting

Ecosystem services

Through ecosystem service valuation, different environmental effects and their societal impacts can be evaluated in monetary and non-monetary values. In the initial phases of the LTRAP convention, non-monetary values were crucial but recently, monetary valuation of ecosystem services has received more attention although not for freshwaters. Sports fishing is the freshwater ecosystem service that is most affected by acidification, resulting in large monetary losses.

Biodiversity

Invertebrate biodiversity of rivers and lakes in ICP Waters sites in the Czech Republic, Germany, Latvia, Norway, Sweden and the UK has increased in the past 30 years, likely as a result of reduced sulphur deposition. Monitoring data on water- and sediment-dwelling insects paired with water chemical records were analysed statistically, where biodiversity was quantified with Shannon’s index. Thus, reduced sulphur emissions to the atmosphere have resulted in improved biodiversity of acid-sensitive waters.

Biological recovery

Monitoring data from the Czech Republic show strong positive relations between water acidity and number of invertebrate species, implying that improved water chemical status is expected to lead to biological recovery. However, the waters are still extremely acidic due to soil base cation depletion. Despite huge reductions in sulphur deposition, biological recovery could suffer from a long delay.

Nitrogen

Inorganic nitrogen species in some Czech catchments have declined, probably as a response to increased nitrogen uptake in recovering forests. A bark beetle attack that killed most forest reversed this trend. The insect attack may be linked to extreme drought in previous years, illustrating climate as a confounding factor for recovery from acid deposition.

Sulphur

Water chemical records show strong negative trends in sulphate concentrations of acid-sensitive waters, as a response to reduced sulphur deposition.

Mercury

Mercury levels in freshwater fish in Canada and Sweden exceed limits adviced for human consumption. Some fish species have significant increases in mercury over time. Reductions in mercury emissions do not result in declines of mercury in fish. Factors driving trends in mercury in aquatic biota are speculated to be related to reduced sulphur deposition, increased concentrations of dissolved organic carbon and climate warming.

Dynamic modeling

Water chemistry in four acid-sensitive high altitude lakes in Switzerland was hindcast and predicted with the MAGIC model using several emission scenarios, indicating a critically low acid neutralizing capacity (ANC) of these lakes in the future despite considerably reduction of emissions of sulphur and nitrogen. The simulations demonstrated the benefits of achieving the emission reductions for both sulphur and nitrogen, as agreed under the Gothenburg protocol.

EECCA countries

Water chemical monitoring data from the Debed river in Armenia show increased sulphate concentrations, possibly related to emissions from industrial activity in Armenia and its surroundings. Deposition stations in background areas are not established, limiting the assessment of effects of air pollution in Armenia.

1. The meeting of the International Cooperative Programme on Assessment and Monitoring of the Effects of Air Pollution on Rivers and Lakes (ICP Waters) was attended by 29 experts from the following Parties to the Convention on Long-range Transboundary Air Pollution (CLRTAP): Armenia, the Czech Republic, Estonia, Finland, Italy, Latvia, Norway, Russia, Sweden, Switzerland and the United Kingdom. In addition a representative for ICP Integrated Monitoring participated. The list of participants is attached as **Annex I.**

Introductions

2. Ms. Barbora Cimbálníková from the Czech Ministry of the Environment welcomed all participants to the ICP Waters meeting in Český Krumlov. Ms. Barbora Cimbálníková expressed appreciation for the work that ICP Waters had done through the years in relation to the implementation of the Convention on Long Range Transported Pollutants.
3. Mr. Gunnar Skotte (Norway), Chair of the Programme Task Force, thanked Ms. Barbora Cimbálníková for opening the meeting and the warm welcoming words. He thanked Mr. Jakub Hruśka (Czech Republic) for inviting us and hosting the meeting. Then he welcomed all participants to the 29th Task Force Meeting of ICP Waters in Český Krumlov. He announced that Ms. Brit Lisa Skjelkvåle had withdrawn as leader for the Progamme Centre because of a new position and thanked for her services to ICP Waters over the years. He then announced that Ms. Heleen de Wit (Norway) would take over as new leader for the Programme Centre.
4. Ms. Heleen de Wit (Norway) from the Programme centre expressed regards and warm greetings to the Task Force from Ms. Skjelkvåle, who regretted that she could not attend the meeting.
5. The Task Force adopted the agenda of the meeting (**Annex II**).
6. Mr. Jakub Hruśka (Czech Republic) welcomed us to Český Krumlov and gave general information on the meeting and the excursion.
7. Mr. Jakub Hruśka (Czech Republic) then gave a presentation on 30 years of recovery of Bohemian Forest lakes and bark beetle infestation as confounding factor. The Bohemian lakes showed significant chemical recovery related to reduced deposition, between 1984 and 2006. Forest dieback after a bark beetle infestation in 2007 reversed chemical recovery owing to increased NO_3 leaching related to reduced forest N uptake. Biological recovery of zooplankton, benthic invertebrates and macrophytes was not strongly affected by the NO_3 pulse after deforestration. Model simulations with the MAGIC model indicate slow chemical recovery in the future, and the potential for natural re-establishment of fish in lake Laka in the next decade.
8. Ms. Heleen de Wit commented that Mr. Hruśka's presentation illustrates the value of long time series of both chemical and biological parameters. She pointed out that the effect of the bark beetle infestation could exemplify impacts of climate change on water chemistry and ecology, and she emphasised the value of these time series for assessment of base line and reference states of acid-sensitive waters, for instance through modeling.
9. Mr. Gunnar Skotte (Programme chair) reported from the Working Group on Effects (WGE), and the review of the ICPs. The WGE meeting in September 2013 was attended by 30 parties to the convention, in addition to representatives from EMEP,

WGSR and EB. At the WGE meeting, the 2014-2015 workplan was presented and discussed. The new plan is more focused on deliverables than plans from previous years. According to the plan, ICP Waters should

- “Identify the (i) state of surface water ecosystems and their long-term changes with respect to the impact of selected air pollutants including effects on biota; and
- (ii) changes in biodiversity and climate in surface water ecosystems”.
- Expected deliverables are “Report on trends in surface water chemistry and biology up to 2011, and ecosystem response to emission reductions”.

10. Mr. Skotte continued with reporting from the review of ICP’s which was presented and discussed at the WGE meeting. The document can be found at www.unece.org. The final version of the review will be submitted to the EB meeting in December. In general, the review acknowledged the useful work done by the ICPs under the convention, and most recommendations from the review were received with approvement at the WGE meeting. It was mentioned that the effect programmes needed more feedback from EB on the deliveries made to EB, and the need for information in EB. General recommendations from the review were to aim for common data standards, and improve data access via the web. Also, summary brochures aimed at policy makers could accompany ICP reports, but ICPs should also continue to publish in scientific journals as this provides the Convention with scientific legitimacy. More cooperation between NFCs would be welcomed, and more integrated meetings between ICPs and scientific communities with topical workshops should be considered. Specific comments for ICP Waters were to shift focus from acidification to more comprehensively assessments of impacts of nitrogen, heavy metals, and POPs, but to continue periodic trend assessments. Also, ICP Waters should pursue interaction with other international programmes for monitoring of waters, e.g. UNEP, GEMS, etc.

11. In the following discussion, several points were raised such as

    - The ICP Waters database has no data on metals and POPs and it may be difficult to include such data in the database. Possibly, other databases have such data. Alternatively, assessments based on literature could be considered. This point should be clarified.
    - It was pointed out that ICP Waters already does extensive work on nitrogen.
    - Upon a question on the importance of annual Task Force meetings, national focal centres responded that annual meetings were important for the progress of the work. However, integrated TF meetings and topical workshops was perceived as a good idea.
    - It was suggested that the ICP Waters website could include an option where every nation could report papers, activities etc.
    - An additional topic that was raised was how ICP Waters could increase cooperation with ICP IM. It was suggested that especially on nitrogen and Hg there is potential for cooperation, in addition to trend analyses.

12. Mr. Jussi Vuorenmaa (Finland) reported from the ICP Integrated Monitoring Programme (ICP IM). He described the purpose, extent and priorities of the programme. Present work includes assessment of baseline, budgets and critical loads of heavy metals. Element budgets indicate continued accumulation and exceedance of

CL, particularly for Hg. Findings from recent papers based on ICP IM work were presented. Planned work for 2014-2015 includes report and paper on long-term trends in ecosystem effects of S and N. An important part will probably be effects on water chemistry.

Reports from the ICP Waters Programme activities 2012/2013

13. Ms. Heleen de Wit (Norway) from the Programme centre reported on the status of the ICP Waters programme and on common work for effect-oriented programmes under the WGE. She gave a résumé of the main results from the last TF meeting, showed the aims of the Programme and described its main activities. The status of participation and data collection as of October 2013 is shown **Annex III.** The participation in the Task Force meeting is declining slightly, but the number of sites for which data are delivered is stable or slightly increasing. Participation in the chemical intercomparison and biological intercalibration is stable.

14. Ms. Heleen de Wit (Norway) reported on representation of ICP Waters in other bodies/meetings under the Convention:

    - Oct 12: JEG-meeting, Sitges, Spain. JEG applauded the efforts of ICP Waters in putting together a 30-year time series of invertebrate data from seven countries across Europe
    - Feb 13: WGE, Extended Bureau, Geneva
    - April 13: CCE WS, Copenhagen
    - May 13: ICP IM, Obninsk
    - June 13: Saltsjøbaden Workshop, Gothenburg
    - Sept 13: WGE, Extended Bureau, Geneva

15. At the upcoming JEG meeting on dynamic modelling in October 2013, the ICP M&M call for data (as specified on the CCE website www.wge-cce.org) on outputs of dynamic modelling on biota will be discussed, for terrestrial and for aquatic ecosystems. A representative for ICP Waters will attend the meeting.

16. Ms. Heleen de Wit (Norway) provided information on the most important 2012 and 2013 publications presenting the results of ICP Waters. The following documents were mentioned:

    - ICP Waters Report 115/2013 - Effects of long-range transported air pollution on freshwater ecosystem services. Holen, S., R.F. Wright, I. Seifert. ICP Waters Report 114/2013
    - ICP waters report 114/2013 (finalized but not yet in press). Biodiversity in freshwaters: temporal trends and response to water chemistry. Velle, G., Telford, R.J., Curtis, C., Eriksson L.,Fjellheim A., Frolova M., Fölster J., Grudule N., Halvorsen G.A., Hildrew A., Hoffmann A., Indriksone I., Kamasová L., Kopáček J., Orton S., Krám P., Monteith D.T., Senoo T., Shilland E.M., Stuchlík E., Wiklund M.L., de Wit, H., Skjelkvaale B.L.
    - ICP Waters Report 113/2013 - Biological intercalibration: Invertebrates 1612. Fjellheim, A., Johannessen, A. and Landås, T.S.
    - ICP Waters Report 112/2013 Proceedings of the 28th Task Force meeting of the ICP Waters Programme in Verbania Pallanza, Italy, October 8 – 10, 2012. Skjelkvåle, B.L., Wathne, B.M., de Wit, H. and Michela Rogora (eds.)

- ICP Waters report 111/2012 Intercomparison 1226: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn. Dahl I.
- Manuscript submitted to Water Air and Soil Pollution: on trends in surface water chemistry between 1990 and 2008.
- Some other written contributions were also mentioned, such as the contribution to the WGE joint report on biodiversity and ecosystem services.

The 2013 ICP Waters report: Ecosystem services

17. Mr. Richard Wright (Norway) from the Programme Centre gave a presentation on ecosystem services of fresh water ecosystems in Europe and North America. The final ICP Waters report is now available. The history and content of the report was presented. “Ecosystem services” is an anthropocentric concept that separates between monetary and non-monetary values of services that ecosystems supply to people. Cases presented included cost-benefit analyses of the UNECE LRTAP history and the EU-2010 revision of the Natural emission ceilings directive. Mr. Wright asked the Task Force meeting about their opinion on the relevance of ecosystem service analyses under the convention.
18. In the subsequent discussion, it was mentioned that concerns about effects of pollutants on human health have been more important than ecosystem services for the introduction of conventions limiting emissions of pollutants. An example of a paradoxical conclusion that might be inferred from an anthropocentric view and extensive use of monetisation is that money can be saved on water treatment by keeping concentrations of natural organic matter low through acidification. However, it was also emphasised that the concept of “ecosystem services” has been included in international environmental policy and that ICP Waters should contribute to further quantification and assessment of ecosystem services rendered by acid-sensitive aquatic ecosystems.
19. Ms. Heleen de Wit introduced the Domqua project - a Nordic cooperation on increased DOM and drinking water quality. She described the background and objectives of the project, and invited interested parties to show their interest. The project will start up next year.

The 2013 ICP Waters report: Biodiversity

20. Mr. Gaute Velle (Norway) from the Programme subcentre gave a presentation on freshwater biodiversity in a changing environment and the final results from the ICP Waters biodiversity report. Two important potential sources of errors were pointed out: 1) Non-consistent taxonomic resolution through time and 2) non-consistent season of sampling. There are interesting diverging pattern between littoral and sub-littoral sones in lakes and between lakes and rivers. The question of whether biological recovery means a return to the original state or to a different state was raised. Mr.Velle argued that the dataset should be explored further because there is more to be learned from it. He also pointed out the relevance of such studies for society, the added value for funding agencies and how such studies demonstrate the importance of performing monitoring. Mr.Velle suggested that the data analyses could be repeated with only acid sensitive sites and using continuous variables, that the spatial trends in diversity should be analysed further, that more environmental data should be included, and that

it could be useful for modelling, backward extrapolation using paleolimnology and analyses of trends in functional biodiversity.

21. The following points were raised in the subsequent discussion, i.e. on the importance of aluminium for biological recovery, on the meaning of the concept of “no net loss of biodiversity” (i.e., the aim of the EU biodiversity strategy up to 2020, which will allow compensating the loss of biodiversity in one area by balancing with gain elsewhere in the EU), the difference between acidification and biodiversity indexes, on useful indicators for communication to policy makers. There could also be instances where increased biodiversity is negative, e.g. in case of invasive species.

22. Ms. Heleen de Wit (Norway) thanked Mr. Velle for the thorough data analysis and important report. She mentioned that several presentations addressed changes in biological responses, but using different concepts. There is a challenge with communication of changes in biodiversity using biodiversity indices to policy makers.

Water chemistry

23. Mr. Pavel Kram (Czech Republic) gave a presentation on trends in water chemistry from the Lysina catchment (Site CZ 07) in ICP Waters. It has the lowest pH and taxa richness of 9 catchments in the GEOMON network. Recent papers were mentioned Trends between geochemically contrasting sites were compared. Depth profiles of soil water and results of MAGIC simulation were presented. Water chemistry has improved considerably because of large decrease of SO_4. Results from simulations of future hydrological scenario were presented.

24. Ms. Marine Nalbandyan (Armenia) gave a presentation on the assessment of the air pollution impacts on waters of transboundary river Debed. She introduced the river basin and described water related problems in the area. The river flows through 3 countries and its problems are of transboundary nature. Data presented were from Armenia. Ms. Nalbandyan described the anthropogenic disturbances in the catchment. Extremely high concentrations of SO_4 in the water were shown. Results from monitoring of urban air pollution were also presented. There is a lack of data on deposition and Ms. Nalbandyan is interested to get funding for investigations. Copper smelting plant are the most important source of air pollution, but there are also possible sources of pollution in Georgia and Azerbadjian. A question was raised on how maximum permissible concentration of pollutants in the rivers were determined, and whether any policy is implemented to limit exceedance of those maximum concentrations.

25. Mr. Øyvind Garmo (Norway) from the Programme centre gave a presentation on plans for the coming trend report. He pointed out that it is now possible to compare trends in water chemistry from none-overlapping periods of more than 10 years. He invited the Task Force meeting to provide ideas on new approaches for the trend analysis. It was suggested to i) compare current water chemical status with pre-industrial status (from models), and quantify variations in water chemical status (related to climate rather than deposition) in order to be able to define pre-industrial status as an interval rather than a point; ii) compare trends with critical load exceedances (from (dynamic) modelling) for different deposition scenarios; iii) seek cooperation with other ICPs (ICP M&M, ICP IM); iv) link exceedances of critical loads with biological status (fish, zooplankton).

Intercalibration/intercomparison

26. Ms. Bente Wathne (Norway) from the Programme centre presented the results from the chemical intercomparison, for which the report is in press. Next year's communication with participating laboratories will be by web and email only. Sixty laboratories from 28 countries participated. All the usual variables were included, and also aluminium and TOC. The quality of results was similar to former years. 76% of results were acceptable, but pH and Zn were the parameters with the lowest performance. The best results were obtained for Na, Ca, Al, Cd, Cu and Ni. Nitrate was not included in the Youden test because of problems that appeared to be caused by stability in the sample. Improvements should be made for some variables. Also, concentrations close to the detection limit can give problems, suggesting that some laboratories should employ more sensitive methods. It is suggested to ship the samples earlier (May rather than June). The revised manual is still in line with existing practice at most laboratories. There was a question regarding declining number of laboratories participating. The reasons for this are not clear. It was suggested that the results for pH should be categorized according to pH(, e.g. stirred and unstirred).

27. Mr. Arne Fjellheim (Norway) from the Programme subcentre presented the results from the biological intercalibration, for which the report is not yet printed. Four laboratories participated in the biological intercalibration 2013. The laboratories identified a high portion of the individuals in the test samples, usually > 95% of the total number of species, which were the best results ever. The quality of the identification of the different groups was above the level of acceptance for all laboratories. The taxonomic quality was sufficient for stating the acidity index. The average Quality assurance index ranged between 96.2 and 99, well above the value 80 - indicating good taxonomic work.

Biological response

28. Mr. Bjørn Olav Rosseland (Norway) gave a presentation on the nearly 40-year search for an explanation of the sensitivity of Atlantic salmon smolts to acid waters. Early incidents of fish deaths (pre 1900s) had been registered but were not understood. The perceptions regarding the most sensitive life stage of salmon has changed through the years. In the 1980s there were politically charged arguments concerning the sensitivity of salmon to aluminium. It was shown that spawners were very sensitive to acidification. The discovery of mixing zone effects in estuarines indicated the extreme sensitivity to aluminium of the smolt stage of salmon. Research into the physiological mechanisms and significance for marine survival and population level has reached an advanced level. Mr. Rosseland finished with an assessment of current threats to Atlantic salmon.

29. Ms. Kateřina Kolaříková (Czech Republic) gave a presentation on macroinvertebrates of the acidified Bohemian Forest lakes and their inflows and outflows. The study sites were 5 Czech lakes and 3 German lakes close to the southwestern border between the Czech republic and Germany. The sampling was done in the spring and autumn of 2007. Lakes had pH between 4.58 and 5.71. Inflows were more acidic, outflows were less acidic. The concentration and relative distribution of labile and non-labile Al was highly dependen on the pH. The number of benthic macroinvertebrate taxa was correlated to pH. The correlation coefficient between pH and number of taxa was high in inflow but not in outflow. This could be caused by wider range of pH in inflow. Leuctridae, Nemouridae (streams) and Chironomidae and Ceratopogonidae (lakes) were the dominating taxa.

30. In the subsequent discussion the question of whether calcium levels could be important for explaining the difference in acid sensitivity of species between different regions was raised.

Heavy metals and POPs

31. Mr Staffan Åkerblom (Sweden) gave a presentation on trends in Hg concentrations in deposition and fish in Sweden. He gave an overview of temporal trends of Hg concentrations in biota and deposition over the last 30 years and discussed potential drivers for the observed patterns. It is unclear whether reduced Hg emissions would result in rapid decline of Hg concentration in biota.

32. Mr. Bjørn Olav Rosseland (Norway) gave a presentation on behalf of Mr. John Gunn (Canada) regarding temporal trends in mercury concentrations of large-bodied fishes in northern Ontario Lakes. The aim of the work was to examine temporal trends in fish mercury accumulation in boreal shield lakes over the last 30 years, by comparing current Hg data to historic Hg data. Data from 73 lakes were analysed. The findings indicate that Hg concentrations in fish from Ontario’s northern lakes were not correlated to declines in Hg emissions in North America. Topics for further work include the role of climate change, watershed alterations, changes in fish growth rates or community composition, and of new sources of Hg (e.g. Asian).

33. The discussion following the two presentations on Hg included the following topics: The importance of measurements of stable isotopes of C and N to determine trophic status, the role of forest in the watershed for mercury in freshwaters, differences between clear and brown water lakes. The possibility of doing a regional trend analysis of mercury in freshwaters and biota for the Nordic countries and North America should be considered.

34. Ms. Marina Dinu (Russia) gave a presentation on the interaction of metal ions with humic substances in natural waters. The study included more than 500 samples from the European part of Russia and from Western Siberia. The experimental work included determination of acidity constants of humic acids, conditional stability constants of metal complexes with humic acids, and other properties of humic substances. Theoretical work included modelling of metal speciation in natural waters. The presentation focused on the effect of pH and colour on metal speciation.

Dynamic modelling / Critical Loads

35. Mr. Luca Colombo (Switzerland) presented an application of the MAGIC model on four high altitude lakes in Switzerland. The study was cooperation between the NFCs of Italy and Switzerland. The aim was to estimate original lake water chemistry and simulate effects of future scenarios for deposition. The four lakes were selected because they span a range of acid sensitivity that was considered representative for the lake population in the Ticino region. The lakes have very dilute and clear waters. Three deposition scenarios (COB 2020, MFR 2020 and background) were selected for the simulations. The results show good agreement between modelled and measured concentrations of SO_4, NO_3 and base cations at all four sites. Hindcast of charge balance ANC agreed fairly well with calculated values, but agreement for pH was poor. The simulations suggest that ANC in the most sensitive lakes will remain below the critical limit. It was suggested that the critical level set for ANC could be too low for these lakes. The simulations further demonstrated the benefits of achieving the emission reductions for both sulphur and nitrogen agreed under the Gothenburg

protocol. The modelling results show the relevance of N deposition for determining the present status of the lakes and their chemical evolution in the next two decades

36. Ms. de Wit (Norway) praised the collaboration between the NFCs of Italy and Switzerland, and mentioned that such national activities are important in the ICP Waters work. The WGE has asked for a higher visibility of national contributions, and the Programme Centre would like to present such national activities at suitable arenas such as the WGE meeting. Also, it is possible to create more visibility for such activities by publishing reports (or links to reports) on the ICP Waters homepage. It is important to write in the acknowledgements in such reports and papers that the work was done at ICP Waters sites, or something along those lines.

Workplan 2014-2015

37. Ms. Heleen de Wit (Norway) presented the 2014 – 2015 Workplan for ICP Waters **(Appendix IV).**
38. Support the work under the various protocols.
39. Finalise new trend report with data up to 2011. Several ideas for new trend report were discussed at the meeting.
40. The possible themes for 2014 were presented, such as the preparation of a new report on biodiversity and climate. Possible approaches were discussed. It was discussed how temperature effects might be included, and whether it was possible to discern climate effects from deposition effects. It was suggested to use an analogue approach, by using regional differences as a proxy for changes over time. It was mentioned that extreme effects of climate and deposition can have large effects on biology.
41. The Programme Centre will add papers to the list of papers published by ICP Waters at the webpage, but these papers should acknowledge ICP Waters (or mention ICP Waters in the materials and methods).
42. Contribute on common workplan items from WGE.
43. Prepare proceedings Abstracts by December 1st
44. New chemical and biological intercalibration reports.
45. Run the programme centre. Maintenance of web pages and database. Participate in meetings.
46. The Task Force approved the Workplan.

Other Business

47. Mr. Jens Fölster (Sweden) offered to investigate the possibility for holding the next Task Force meeting in Uppsala.
48. Mr. Gunnar Skotte (Norway), Chair of the Programme Task Force, thanked the hosts and organising committee for excellent organisation of the Task Force meeting. The delegates from the Programme centre, and especially Ms. de Wit who on short notice stepped in as leader, were thanked for setting the agenda for the meeting and for their efforts during the meeting.
49. The Task Force expressed its appreciation to the Programme Centre for its scientific and coordinating work and acknowledged its important contribution to the programme’s successful implementation. It again stressed the importance of the

continuing contributions of the National Focal Centres and cooperating institutes and the essential role in ensuring the high quality of the overall programme results.

Adoption of the minutes

50. The Task Force meeting adopted the Minutes.

Annex I: Participants at the ICP Waters 29th Task Force meeting

Armenia

Ms. Marine Nalbandyan
Institute of Geological Sciences
The National Academy of Sciences of Armenia
24, Marshall Baghramian Avenue
0019 Yerevan, Republic of Armenia
marinen3@yahoo.com

Czech Republic

Ms. Barbora Cimbálníková
Ministry of the Environment of the Czech republic
Vršovická 65
100 10 Praha 10,
Czech Republic

Ms. Zuzana Hořická
Charles University in Prague
Faculty of Sciences
Benátská 2
128 01 Prague 2
Czech Republic
zhoricka@hotmail.com

Mr. Jakub Hruška
Czech Geological Survey
Klarov 3
118 21 Prague 1, CZ
Czech Republic
Jakub.hruska@geology.cz

Ms. Kateřina Kolaříková
Charles University
Faculty of Science
Institute for Environmental Studies
Benatska 2
128 01 Prague 2, CZ
Czech Republic
katerina.kolarikova@natur.cuni.cz

Mr. Pavel Krám
Czech Geological Survey
Klarov 3
118 21 Prague 1, CZ
Czech Republic
pavel.kram@geology.cz

Mr. Vladimír Majer
Czech Geological Survey
Klarov 3
118 21 Prague 1, CZ
Czech Republic
vladimir.majer@geology.cz

Mr. Filip Oulehle
Czech Geological Survey
Klarov 3
118 21 Prague 1, CZ
Czech Republic
filip.oulehle@geology.cz

Ms. Irena Skořepová
Czech Geological Survey
Klarov 3
118 21 Prague 1, CZ
Czech Republic
irena.skorepova@geology.cz

Mr. Jaroslav Vrba
University of South Bohemia
Faculty of Science
Branišovská 31a
370 05 České Budějovice, CZ
Czech Republic
vrba@hbu.cas.cz

Estonia

Ms. Reet Talkop
Analysis and planning department
Ministry of the Environment of Estonia
Narva mnt 7a

15172 Tallinn, Estonia
reet.talkop@envir.ee

Finland

Mr. Jussi Vuorenmaa
Finnish Environment Institute (SYKE)
P.O. Box 140
FIN-00251 Helsinki, Finland
jussi.vuorenmaa@ymparisto.fi

Italy

Ms. Michela Rogora
CNR, Institute of Ecosystem Study
Largo Tonolli 50-52
I-28922 Verbiana Pallanza, Italy
m.rogora@ise.cnr.it

Latvia

Ms. Iveta Indriksone
Latvian Environment, Geology and Meteorology
Agency
165 Maskavas str.
LV-1019 Riga, Latvia
iveta.indriksone@lvgmc.lv

Norway

Mr. Arne Fjellheim
Stavanger Museum
Musegt. 16
N-4010 Stavanger, Norway
arne.fjellheim@stavanger.museum.no

Mr Øyvind Garmo
Norwegian Institute of Water Research (NIVA)
Sandvikavegen 59
NO-2312 Ottestad, Norway
oyvind.garmo@niva.no

Mr. Bjorn Olav Rosseland
Norwegian Institute of Water Research (NIVA)
Gaustadalléen 21
N-0349 Oslo, Norway
bjorn.rosseland@umb.no

Mr. Gunnar Skotte
Norwegian Environment Agency
Strømsveien 96
0663 Oslo, Norway
gunnar.skotte@miljodir.no

Mr. Gaute Velle
LFI - University of Bergen
Allegt. 42
N-5007 Bergen
Norway
gaute.velle@bio.uib.no

Ms. Bente M. Wathne
Norwegian Institute of Water Research (NIVA)
Gaustadalléen 21
N-0349 Oslo, Norway
bente.wathne@niva.no

Ms. Heleen de Wit
Norwegian Institute of Water Research (NIVA)
Gaustadalléen 21
N-0349 Oslo, Norway
heleen.de.wit@niva.no

Mr. Richard Wright
Norwegian Institute of Water Research (NIVA)
Gaustadalléen 21
N-0349 Oslo, Norway
richard.wright@niva.no

Russia

Ms. Marina Dinu
V.I.Vernadsky Institute of Geochemistry and
Analytical Chemistry RAS (Geokhi Ran)
Kosygin Street 19, 119991 Moscow, Russia
marinadinu@rambler.ru

Sweden

Mr. Jens Fölster
Swedish University of Agricultural Sciences
Dep. of Aquatic Sciences and Assessment
P.O.Box 7050 – S-750 07 Uppsala, Sweden
Jens.Folster@ma.slu.se

Ms. Magda-Lena Wiklund
Swedish University of Agricultural Sciences
Dep. of Aquatic Sciences and Assessment
P.O.Box 7050 – S-750 07 Uppsala, Sweden
Magda-Lena.wiklund@slu.se

Mr. Staffan Åkerblom, SLU
Institutionen för vatten och miljö
Lennart Hjelms väg 9
P.O. Box 7050
S - 750 07 UPPSALA, Sweden
staffan.akerblom@slu.se

Switzerland

Mr. Luca Colombo
Ufficioprotezione aria, Sezioneprotezione aria,
acqua e suolo
Via S. Salvioni 2A
6500 Bellinzona, Switzerland
luca.colombo@ti.ch

Ms. Sandra Steingruber
Ufficio protezione aria, Sezione protezione aria,
acqua e suolo
Via S. Salvioni 2A
6500 Bellinzona, Switzerland
sandra.steingruber@ti.ch

United Kingdom

Mr. Chris Evans
Centre for Ecology & Hydrology
Environment Centre Wales
Deiniol Road
Bangor
Gwynedd
LL57 2UW
United Kingdom
cev@ceh.ac.uk

Annex II: Agenda for the 29th Task Force ICP Waters October 1-3, 2013

1. Introductions

- Meeting welcome: Barbora Cimbálníková, *Czech Republic* and *Jakub Hruśka, Czech Republic*
- Adoption of the agenda, *Gunnar Skotte, ICP Waters Chairperson*
- General information about the meeting and excursion, *Jakub Hruśka, local host*
- 30 years of recovery of Bohemian Forest lakes and bark beetle infestation as confounding factor, *Jakub Hruśka, Czech Republic*
- Reports from the Working Group on Effects, including the Review on the ICPs, *Gunnar Skotte, ICP Waters Chairperson*
- Reports from ICP IM, *Jussi Vuorenmaa, Finland*
- Reports from other ICPs

2. Reports from the ICP Waters Programme activities 2012/2013

- Status of the ICP Waters programme, and report on common work for effect-oriented programmes under the Working Group on Effects, *Heleen de Wit, Programme centre*

3. The 2013 ICP Waters report: Ecosystem services

- Ecosystem services of fresh water ecosystems in Europe and North America, *Richard Wright, Programme centre*
- Domqua - a Nordic cooperation on increased DOM and drinking water quality, *Heleen de Wit, Programme centre*

• The 2012 ICP Waters report: Biodiversity

- Freshwater biodiversity in a changing environment, final results from the ICP Waters biodiversity report *Gaute Velle, Programme subcentre*

4. Water chemistry

- Trends in water chemistry from the Lysina catchment, *Pavel Kram, Czech Republic*
- Assessment of the air pollution impacts on waters of transboundary river Debed, *Marine Nalbandyan, Armenia.*
- The coming trend report with data up to 2012 – *Øyvind Garmo, Programme centre*

5. Intercalibration/intercomparison

- Chemical intercomparison, *Bente Wathne, Programme centre*
- Biological intercalibration, *Arne Fjellheim, Programme subcentre*

• Biological response

- A near 40 year search to explain the sensitivity of Atlantic salmon smolts to acid waters, *Bjørn Olav Rosseland, Programme centre*

- Macroinvertebrates of the acidified Bohemian Forest lakes and their inflows and outflows, *Kateřina Kolaříková, Czech Republic*

6. Heavy metals and POPs

- Trends in Hg concentrations in deposition and fish in Sweden, *Staffan Åkerblom, Sweden*
- Temporal trends in mercury concentrations of large-bodied fishes in northern Ontario Lakes, *John Gunn, Canada.* Presented by *Bjørn Olav Rosseland, Programme centre*
- The interaction of metal ions with humic substances in natural waters: case study of the Kola Peninsula, *Marina Dinu, Russia*

7. Dynamic modelling / Critical Loads

- An application of the MAGIC model on four high altitude lakes in Switzerland, *Luca Colombo, Switzerland*

8. Workplan

- Draft 2014-2015 Workplan, *Heleen de Wit, Programme centre*

9. Other Business

- TF meeting 2014

10. Adoption of the minutes

Annex III: Status participation in the ICP Waters programme as of October 2013

	Chemical data	Biological data	Participation in TF meetings 2011-2013	Participating in chemical intercomparison	Participating in biological intercalibration 2011-2013
Armenia	2013		●		
Austria	2013		●	●	
Belarus	2012				
Canada	2012		●	●	
Croatia			●		
Czech Rep.	2013	2011	●	●	●
Estonia	2013		●	●	●
Finland	2013		●	●	
France				●	
Germany	2013	2010	●	●	●
Ireland	2012		●	●	
Italy	2013		●	●	
Latvia	2013	2012	●	●	●
Montenegro	2012				
Netherlands			●	●	
Norway	2013	2012	●	●	●
Poland	2013		●	●	
Russia			●	●	
Spain	2012		●	●	
Sweden	2013	2012	●	●	●
Switzerland	2013	2011	●	●	●
UK	2013	2010	●	●	●
USA	2012		●	●	
Total	**19**	**7**	**20**	**19**	**8**

Belgium				●	
Iceland				●	
Lithuania				●	
Portugal				●	
Romania				●	
Serbia				●	
Slovenia				●	

Indonesia				●	
Japan				●	
Thailand				●	
Total				**29**	

Annex IV: ICP Waters workplan for 2014–2015

2013

- Prepare proceedings from the 29th Task Force meeting
  - abstracts (2-6 pages) by **1. December 2013**
  - send to Bente Wathne: bmw@niva.no

2014

- Prepare the trend report on surface water chemistry and biology up to 2012
  - Discuss collaboration on report with other ICPs at suitable arenas
  - Draft report to be presented at the **Task Force meeting 2014**
  - Comments from Task Force meeting by **November 15 2014**
  - Special reviewers from Task Force will be contacted in **Summer 2014**
  - Finalize trend report by **February 2015**
- Discuss and prepare a short draft of the report on Biodiversity and climate
  - Draft report to be presented and discussed at the **Task Force meeting 2014**
  - Finalize report in before **Task Force meeting in 2015**
- Arrange and report chemical intercomparison 1428
  - in collaboration with all participating ICPs.
  - Invitations will be sent in **March 2014**
  - Samples will be sent by **May 15 2014**
  - Responsible person: Carlos Escudero
- Arrange and report biological intercalibration 1814
  - in collaboration with participating ICPs.
  - Send out invitations by **1 May 2014.**
  - Responsible person: Arne Fjellheim
- Arrange thirtieth meeting of the Programme Task Force, tentatively scheduled to be held in autumn 2014, and its reports
- Run the Programme Centre in Oslo and the Subcentre in Bergen, including:
  - maintenance of web-pages
    - All papers using data from ICP Waters sites shall be listed on our web on your request; one limitation: the word ICP Waters has to be mentioned in the paper somewhere.
    - Increase visibility of activity of Focal Centres on the web-page
  - maintenance of database of chemical and biological data
- Submission of data to the Programme Centre by all Focal centres**.**
  - Call for data: **June 15 2014**
  - Submission by **August 15 2014**
- Participation in meetings of relevance for the ICP Waters programme
- Report to WGE
- Contribute to the Common Workplan items of the Working Group on Effects
  - Contribute to common item “dynamic modelling, nitrogen and biological responses”
  - Other possible items to be announced
- Cooperation with other bodies within and outside the Convention
  - Evaluation of the ICP M&M manual, chapter on Critical loads for Waters (http://www.rivm.nl/media/documenten/cce/manual/mapman_5_4.pdf) by **March 2014**
  - Consider availability other water databases and cooperation with other water monitoring programmes (UNEP, GEMS, EEA)
- Cooperation with ECCCA countries (East Central Caucasus and Central Asian countries)

2015

- Finalize trend report and biodiversity and climate report

2016

- Consider new topics:
    - Dynamical modelling
    - Nitrogen trends, relation to surface water biology
    - Start a new report on a review of old and new policy relevant indicators, for instance of acidification and biodiversity
- Follow-up of ecosystem services report
- Mercury

10 Reports and publications from the ICP Waters Programme

All reports from the ICP Waters programme from 2000 up to present are listed below. Reports before year 2000 can be listed on request. All reports are available from the Programme Centre. Reports and recent publications are also accessible through the ICP Waters website; http://www.icp-waters.no/

de Wit, H., Bente M. Wathne, B. M. and Hruśka, J. (eds) 2014. Proceedings of the 29th Task Force meeting of the ICP Waters Programme in Český Krumlov, Czech Republic 1st –3rd October, 2013. **ICP Waters report 117/2014**

Escuedero-Oñate, C. Intercomparison 1327: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn. **ICP Waters Report 116/2013**

Holen, S., R.F. Wright, I. Seifert. 2013. - Effects of long-range transported air pollution (LTRAP) on freshwater ecosystem services. **ICP Waters Report 115/2013**

Velle, G., Telford, R.J., Curtis, C., Eriksson, L., Fjellheim, A., Frolova, M., Fölster J., Grudule N., Halvorsen G.A., Hildrew A., Hoffmann A., Indriksone I., Kamasová L., Kopáček J., Orton S., Krám P., Monteith D.T., Senoo T., Shilland E.M., Stuchlík E., Wiklund M.L., de Wit, H., Skjelkvaale B.L. 2013. Biodiversity in freshwaters. Temporal trends and response to water chemistry. **ICP Waters Report 114/2013**

Fjellheim, A., Johannessen, A. and Landås, T.S. 2013. Biological intercalibration: Invertebrates 1612. **ICP Waters Report 113/2013**

Skjelkvåle, B.L., Wathne, B.M., de Wit, H. and Michela Rogora (eds.) 2013. Proceedings of the 28th Task Force meeting of the ICP Waters Programme in Verbania Pallanza, Italy, October 8 – 10, 2012. **ICP Waters Report 112/2013**

Dahl, I. 2012. Intercomparison 1226: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn. **ICP Waters report 111/2012**

Skjelkvåle, B.L., Wathne B. M. and Moiseenko, T. (eds.) 2010. Proceedings of the 27th meeting of the ICP Waters Programme Task Force in Sochi, Russia, October 19 – 21, 2011. **ICP Waters report 110/2012**

Fjellheim, A., Johannessen, A., Svanevik Landås, T. 2011. Biological intercalibration: Invertebrates 1511. NIVA-report SNO 6264-2011,**ICP Waters report 109/2011.**

Wright, R.F., Helliwell, R., Hruska, J,. Larssen, T., Rogora, M., Rzychoń, D., Skjelkvåle, B.L. and Worsztynowicz, A. 2011. Impacts of Air Pollution on Freshwater Acidification under Future Emission Reduction Scenarios; ICP Waters contribution to WGE report. NIVA-report SNO 6243-2011**. ICP Waters report 108/2011.**

Dahl, I and Hagebø, E. 2011. Intercomparison 1125: pH, Cond, HCO3, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA-report SNO 6222-2011. **ICP Waters report 107/2011.**

Skjelkvåle B.L. and de Wit, H. (Eds). 2011. Trends in precipitation chemistry, surface water chemistry and aquatic biota in acidified areas in Europe and North America from 1990 to 2008. NIVA-report SNO 6218-2011 **ICP Waters report 106/2011.**

ICP Waters Programme Centre 2010. ICP Waters Programme manual. NIVA SNO 6074-2010.**ICP Waters report 105/2010**. 91 s. ISBN 978-82-577-5953-7,

Skjelkvåle, B.L., Wathne B. M. and Vuorenmaa J. (eds.) 2010. Proceedings of the 26th meeting of the ICP Waters Programme Task Force in Helsinki, Finland, October 4 – 6, 2010. **ICP Waters report 104/2010**

Fjellheim, A. 2010. Biological intercalibration: Invertebrates 1410. NIVA-report SNO 6087-2010, **ICP Waters report 103/2010.**

Hovind, H. 2010. Intercomparison 1024: pH, Cond, HCO$_3$, NO$_3$-N, Cl, SO$_4$, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA-report SNO 6029-2010. **ICP Waters report 102/2010.**

De Wit, H. A. and Lindholm M., 2010. Nutrient enrichment effects of atmospheric N deposition on biology in oligotrophic surface waters – a review. NIVA-report SNO 6007 - 2010. **ICP Waters report 101/2010**

Skjelkvåle, B.L., De Wit, H and and Jeffries, D. (eds.) 2010. Proceedings of presentations of national activities to the 25th meeting of the ICP Waters Programme Task Force in Burlington, Canada, October 19-21 2009. NIVA-report SNO 5995 - 2010. **ICP Waters report 100/2010.**

Fjellheim, A. 2009. Biological intercalibration: Invertebrates 1309. NIVA-report SNO 5883-2009, **ICP Waters report 99/2009.**

Hovind, H. 2009. Intercomparison 0923: pH, Cond, HCO$_3$, NO$_3$-N, Cl, SO$_4$, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA-report SNO 5845-2009. **ICP Waters report 98/2009.**

Ranneklev, S.B., De Wit, H., Jenssen, M. T. S. and Skjelkvåle, B.L., 2009. An assessment of Hg in the freshwater aquatic environment related to long-range transported air pollution in Europe and North America. NIVA-report SNO 5844-2009. **ICP Waters report 97/2009.**

Skjelkvåle, B.L., Jenssen, M. T. S. and De Wit, H (eds.) 2009. Proceedings of the 24th meeting of the ICP Waters Programme Task Force in Budapest, Hungary, October 6 – 8, 2008. NIVA-report SNO 5770-2009. **ICP Waters report 96/2008.**

Fjellheim, A and Raddum, G.G. 2008. Biological intercalibration: Invertebrates 1208. NIVA-report SNO 5706-2008, **ICP Waters report 95/2008**

Skjelkvåle, B.L., and De Wit, H. (eds.) 2008. ICP Waters 20 year with monitoring effects of long-range transboundary air pollution on surface waters in Europe and North-America. NIVA-report SNO 5684-2008. **ICP Waters report 94/2008.**

Hovind, H. 2008. Intercomparison 0822: pH, Cond, HCO_3, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA-report SNO 5660-2008. **ICP Waters report 93/2008.**

De Wit, H. Jenssen, M. T. S. and Skjelkvåle, B.L. (eds.) 2008. Proceedings of the 23rd meeting of the ICP Waters Programme Task Force in Nancy, France, October 8 – 10 , 2007. NIVA-report SNO 5567-2008. **ICP Waters report 92/2008.**

Fjellheim, A and Raddum, G.G. 2008. Biological intercalibration: Invertebrates 1107. NIVA-report SNO 5551 – 2008, **ICP Waters report 91/2008**

Hovind, H. 2007. Intercomparison 0721: pH, Cond, HCO3, NO3-N, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA-report SNO 5486-2007. **ICP Waters report 90/2007**

Wright, R.F., Posch, M., Cosby, B. J., Forsius, M., and Skjelkvåle, B. L. 2007. Review of the Gothenburg Protocol: Chemical and biological responses in surface waters and soils. NIVA-report SNO 5475-2007. **ICP Waters report 89/2007**

Skjelkvåle, B.L., Forsius, M., Wright, R.F., de Wit, H., Raddum, G.G., and Sjøeng, A.S.M. 2006. Joint Workshop on Confounding Factors in Recovery from Acid Deposition in Surface Waters, 9-10 October 2006, Bergen, Norway; Summary and Abstracts. NIVA-report SNO 5310-2006. **ICP Waters report 88/2006.**

De Wit, H. and Skjelkvåle, B.L. (eds). 2007. Trends in surface water chemistry and biota; The importance of confounding factors. NIVA-report SNO 5385-2007. **ICP Waters report 87/2007.**

Hovind, H. 2006. Intercomparison 0620. pH, K25, HCO3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 5285-2006. **ICP Waters report 86/2006.**

Raddum, G.G. and Fjellheim, A. 2006. Biological intercalibration 1006: Invertebrate fauna. NIVA-report SNO 5314-2006, **ICP Waters report 85/2006.**

De Wit, H. and Skjelkvåle, B.L. (eds.) 2006. Proceedings of the 21th meeting of the ICP Waters Programme Task Force in Tallinn, Estonia, October 17-19, 2005. NIVA-report SNO 5204-2006, **ICP Waters report 84/2006.**

Wright, R.F., Cosby, B.J., Høgåsen, T., Larssen, T., Posch, M. 2005. Critical Loads, Target Load Functions and Dynamic Modelling for Surface Waters and ICP Waters Sites. NIVA-report SNO 5166-2005. **ICP Waters report 83/2006.**

Hovind, H. 2005. Intercomparison 0317. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 5068-2005. **ICP Waters report 82/2005**

Raddum, G.G. 2005. Intercalibration 0307: Invertebrate fauna. NIVA-report SNO 5067-2005. **ICP Waters report 81/2005**

De Wit, H. and Skjelkvåle, B.L (eds.). 2005. Proceedings of the 20th meeting of the ICP Waters Programme Task Force in Falun, Sweden, October 18-20, 2004. NIVA-report SNO 5018-2005, **ICP Waters report 80/2005.**

Fjeld, E., Le Gall, A.-C. and Skjelkvåle, B.L. 2005. An assessment of POPs related to long-range air pollution in the aquatic environment. NIVA-report SNO 5107-2005, **ICP Waters report 79/2005.**

Skjelkvåle et al 2005. Regional scale evidence for improvements in surface water chemistry 1990-2001. *Environmental Pollution, 137: 165-176*

Hovind, H. 2004. Intercomparison 0418. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 4875-2004, **ICP Waters report 78/2004.**

Raddum, G.G. 2004. Intercalibration: Invertebrate fauna 09/04. NIVA-report SNO 4863-2004, **ICP Waters report 77/2004.**

Skjelkvåle, B.L. (ed). Proceedings of the 19th meeting of the ICP Waters Programme Task Force in Lugano, Switzerland, October 18-20, 2003. NIVA-report SNO 4858-2004, **ICP Waters report 76/2004.**

Raddum, G.G, *et al.* 2004. Recovery from acidification of invertebrate fauna in ICP Water sites in Europe and North America. NIVA-report SNO 4864-2004, **ICP Waters report 75/2004.**

Hovind, 2003. Intercomparison 0317. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 4715-2003, **ICP Waters report 74/2003.**

Skjelkvåle, B.L. (ed). 2003. The 15-year report: Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals. NIVA-report SNO 4716-2003, **ICP Waters report 73/2003.**

Raddum.G.G. 2003. Intercalibration 0307: Invertebrate fauna. NIVA-report SNO-4659-2003, **ICP Waters report 72/2003**.

Skjelkvåle, B.L. (ed.). 2003. Proceedings of the 18th meeting of the ICP Waters Programme Task Force in Moscow, October 7-9, 2002. NIVA-report SNO 4658-2003, **ICP Waters report 71/2002**.

Wright, R.F and Lie, M.C. 2002.Workshop on models for Biological Recovery from Acidification in a Changing Climate. 9-11 september 2002 in Grimstad, Norway. Workshop report. NIVA-report 4589-2002.

Jenkins, A. Larssen, Th., Moldan, F., Posch, M. and Wrigth R.F. 2002. Dynamic Modelling of Surface Waters: Impact of emission reduction - possibilities and limitations. NIVA-report SNO 4598-2002, **ICP Waters report 70/2002.**

Halvorsen, G.A, Heergaard, E. and Raddum, G.G. 2002. Tracing recovery from acidification - a multivariate approach. NIVA-report SNO 4564-2002, **ICP Waters report 69/2002**.

Hovind. H. 2002. Intercomparison 0216. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4558-2002, **ICP Waters Report 68/2002**.

Skjelkvåle, B.L. and Ulstein, M. (eds). 2002. Proceedings from the Workshop on Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact. March 18-20, 2002, Lillehammer, Norway. NIVA-report SNO-4563-2002, **ICP Waters report 67/2002**.

Raddum.G.G. 2002. Intercalibration 0206: Invertebrate fauna. NIVA-report SNO-4494-2002, **ICP Waters report 66/2002**.

Bull, K.R. Achermann, B., Bashkin, V., Chrast, R. Fenech, G., Forsius, M., Gregor H.-D., Guardans, R., Haussmann, T., Hayes, F., Hettelingh, J.-P., Johannessen, T., Kryzanowski, M., Kucera, V., Kvaeven, B., Lorenz, M., Lundin, L., Mills, G., Posch, M., Skjelkvåle, B.L. and Ulstein, M.J. 2001. Coordinated Effects Monitoring and Modelling for Developing and Supporting International Air Pollution Control Agreements. *Water Air Soil Poll.* **130**:119-130.

Hovind, H. 2001. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4416-2002, **ICP Waters report 64/2001**.

Lyulko, I. Berg, P. and Skjelkvåle, B.L. (eds.) 2001. National presentations from the 16th meeting of the ICP Waters Programme task Force in Riga, Latvia, October 18-20, 2000. NIVA-report SNO 4411-2001. **ICP Waters report 63/001**.

Raddum.G.G. 2000. Intercalibration 0005: Invertebrate fauna. NIVA-report SNO4384-2001, **ICP Waters report 62/2001**.

Raddum, G.G. and Skjekvåle B.L. 2000. Critical Load of Acidifying Compounds to Invertebrates In Different Ecoregions of Europe. *Water Air Soil Poll.* **130**:825-830.

Stoddard, J. Traaen, T and Skjelkvåle, B.L. 2001. Assessment of Nitrogen leaching at ICP-Waters sites (Europe and North America). *Water Air Soil Poll*. **130**:825-830.

Skjelkvåle, B.L. Stoddard J.L. and Andersen, T. 2001. Trends in surface waters acidification in Europe and North America (1989-1998). *Water Air Soil Poll.***130:**781-786.

Kvaeven, B. Ulstein, M.J., Skjelkvåle, B.L., Raddum, G.G. and Hovind. H. 2001. ICP Waters – An international programme for surface water monitoring. *Water Air Soil Poll*.**130**:775-780.

Wright, R.F. 2001. Note on: Effect of year-to-year variations in climate on trends in acidification. NIVA-report SNO 4328-2001, **ICP Waters report 57/2001**.

Hovind, H. 2000. Trends in intercomparisons 8701-9812: pH, K_{25}, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K and aluminium - reactive and nonlabile, TOC, COD-Mn. NIVA-Report SNO 4281-2000, **ICP Waters Report 56/2000**.

Hovind, H. 2000. Intercomparison 0014. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4281-2000, **ICP Waters Report 55/2000**.

Skjelkvåle, B.L., Olendrzynski, K., Stoddard, J., Traaen, T.S, Tarrason, L., Tørseth, K., Windjusveen, S. and Wright, R.F. 2001. Assessment of trends and leaching in Nitrogen at ICP Waters Sites (Europe And North America). NIVA-report SNO 4383-2001, **ICP Waters report 54/2001.**

Stoddard, J. L., Jeffries, D. S., Lükewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., Forsius, M., Johannessen, M., Kahl, J. S., Kellogg, J. H., Kemp, A., Mannio, J., Monteith, D., Murdoch, P. S., Patrick, S., Rebsdorf, A., Skjelkvåle, B. L., Stainton, M. P., Traaen, T. S., van Dam, H., Webster, K. E., Wieting, J., and Wilander, A. 1999. Regional trends in aquatic recovery from acidification in North America and Europe 1980-95. Nature 401:575- 578.

Skjelkvåle, B. L., Andersen, T., Halvorsen, G. A., Raddum, G.G., Heegaard, E., Stoddard, J. L., and Wright, R. F. 2000. The 12-year report; Acidification of Surface Water in Europe and North America; Trends, biological recovery and heavy metals. NIVA-Report SNO 4208/2000, **ICP Waters report 52/2000.**

Reports before year 2000 can be listed on request.

NIVA: Norway's leading centre of competence in aquatic environments

NIVA provides government, business and the public with a basis for preferred water management through its contracted research, reports and development work. A characteristic of NIVA is its broad scope of professional disciplines and extensive contact network in Norway and abroad. Our solid professionalism, interdisciplinary working methods and holistic approach are key elements that make us an excellent advisor for government and society.

NIVA
Norwegian Institute for Water Research

Gaustadalléen 21 • NO-0349 Oslo, Norway
Telephone: +47 22 18 51 00 • Fax: 22 18 52 00
www.niva.no • post@niva.no