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INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

Proceedings of the 18th meeting of the ICP Waters Programme Task Force in Moscow, October 7-9, 2002

Prepared the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, March 2003
Preface

The International Cooperative Programme on Assessment and Monitoring of Rivers and Lakes (ICP Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body also accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. Berit Kvæven, Norwegian State Pollution Control Authority, has led the ICP Waters programme. The Norwegian State Pollution Control Authority (SFT) provides financial support to the work of the Programme Centre.

At the annual Programme Task Force, national ongoing activities in many countries are presented. This report presents some of the national contributions from the 18th Task Force meeting of the ICP Waters programme, held in Moscow, October 7-9, 2002.

Oslo, March 2003

Brit Lisa Skjelkvåle
Project manager
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1. Assessment of water acidification in European part of Russia: variations along a north-south transect

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Introduction

In last 10 years several institutes in Russia (Institute of the Global Climate and Ecology, Institute of Biology of Inland Waters, Institute of Water Problems, Institute Lakes Research, Karelian Institute of Water Problems, and Institute North Industrial Ecology Problems of Kola) have conducted studies on water acidification. Data on anthropogenic acidification were obtained from the Kola peninsula, Karelia, Leningrad, Arkhangelsk and Vologda areas. These investigations, however, were not systematic. The extensive monitoring network for waters in Russia focuses on large water systems subject direct inputs of local pollution and thus poorly covers those lakes and streams that are potentially vulnerable to acidification.

Officially there is no water acidification in Russia. On the contrary, alkalisation takes place in waters near industrial centres due to the emissions of dust. Systematic and quality-assured investigations over large regions, however, have not been carried out. The most detailed investigation of water acidification has been carried out in the area of Kola North. This region is characterised high vulnerability to acidification due to climatic and geological factors, and since the mid-1900’s has had a high acid sulphur load due to two large copper-nickel smelters (the Severonickel and Pechenganickel Co.).

Water acidification in Kola North is manifest in three ways: i) the decrease of buffer capacity in soils; ii) the occurrence of episodes of acidification during floods in small streams, and iii) the acidification of small lakes (Moiseenko, 1994). Of 460 lakes surveyed in 1995 10% were acidified (pH<6) and 30 % were in a critical state (alkalinity < 50 µeq/1) (Henriksen et al., 1998). Paleoeocological data show that initial acidification of waters in the Arctic region began about 1900 and was connected with transboundary transport of acid-forming substances from industrial Europe. Acid deposition in the area has increased dramatically due to emissions by local industry in the mid-1900’s (Moiseenko et al., 1999).

The situation for most of Russia, however, remained unclear. In 2001-2002, therefore a pilot survey of lakes was conducted along a north-south transect from the tundra zone through the forest tundra, northern, middle and southern taiga, mixed forests, forest-steppe to steppe.
Methods

The lakes were selected from topographic maps (1:100 000). Sites included 282 small lakes (area <20 km²) located from 69.62°N to 52.93°N. The lakes are not subject to pollution sources within the catchment. The lake selection closely followed the approach used in the 1995 Northern Lake Survey (Henriksen et al., 1998). The number of lakes in each ecoregion varied due to the large region to be covered and the non-uniform distribution of lakes; in the south lakes are less common in comparison with the north (Table 1).

Samples were collected during or shortly after autumn overturn, from end of September to November. The samples were analysed for pH, conductivity, silicon, calcium, magnesium, sodium, potassium, chloride, sulphate, nitrate, alkalinity, organic, dissolved organic carbon (DOC) by standard methods according to procedures of the 1995 Northern Lake Survey (Henriksen et al., 1998). The analytical methods are subject to quality control through the intercalibration tests run by the International Cooperative Program on Acidification of Lakes and Rivers (Hovind, 2002).

Results and discussion

The chemical composition of the lakewater shows significant variations across the European part of Russia. From the north to south the concentrations of major cations and buffer capacity increase and are highest in the mixed forest and steppes ecoregions. Some lakes with low concentrations of major cations, however, are found in every zone except steppe. Such lakes are vulnerable to acid precipitation (Figure 1a) The concentrations of anthropogenic sulphate (excess sulphate SO₄* corrected for seasalt sulphate) in lakewater are high in the northern areas (situated in forest-tundra) due to the proximity of the Kola copper-nickel smelters (the Severonickel and Pechenganickel Co.). SO₄* concentrations also increase in southern regions, where industry is higher (Figure 1b) The lowest concentrations of SO₄* are found in the taiga ecoregions; here lakes are remote from industrial air pollution sources.

The ratio of alkalinity to SO₄* (Alk/SO₄*) shows that in every zone, including steppe, lakes with sulphate as the dominant anion are found (Figure 2a) The distribution of nitrate (NO₃) concentrations reveals a pattern similar to that of SO₄*; concentrations increase in the southern lakes. Lakes with high NO₃ concentrations are present also in taiga. Southern regions are characterised by more industry and agriculture, and these contribute to nitrogen inputs to lakes. For assessment of the contribution of NO₃ to water acidification, the KNS indicator was used (Traaen and Stoddard, 1995) (Figure 2b):

\[ \text{KNS}=\frac{\text{NO}_3^-}{(\text{SO}_4^{*}+\text{NO}_3^-)} \]

where units are in µeq/l. Analysis of distribution of KNS in the different zones shows high values for some lakes. This indicates a large impact of nitrogen impact on the water chemistry of these lakes.

The distribution of pH values in different zones shows that lakes with low pH value are observed in humid ecoregions (Figure 3). In the northern part of tundra 9% of lakes have pH < 6, and 6% with pH <5. The latter are acidified lakes with low ionic strength and high transparency, and SO₄* is the dominant anion.
Lakes with reduced pH values (5.5-6.0) are also found in the middle taiga zone. About 6% of lakes have pH <6 and low concentrations of DOC. In the southern taiga some lakes have low ionic strength. These lakes have very low pH (4.7-6.0), and SO$_4^*$ is the dominant anion. 15% of investigated lakes in that zone have pH <6.

In mixed forest zone lakewater pH is 6-6.5, in forest-steppe pH 7-9, and in the steppe zone pH 9-9.5.

The distribution of acid neutralisation capacity (ANC) has a distribution similar to that of the major cations (Figure 4). More than 80% of lakes in tundra and forest-tundra zones have negative values of ANC. The number of lakes with low ANC level decreases to the south.

**Critical loads of acidity (CL) and its exceedence (CL$_{ex}$)** were calculated using the Steady-state Water Chemistry (SSWC) method of Henriksen et al. (1992) (Table 1). The lowest CL values are found in tundra and forest tundra lakes. Here more than 60% of investigated lakes have CL < 50 meq/m$^2$/yr. In the northern and middle zones 15-25% of investigated lakes have CL < 50 meq/m$^2$/yr. CL values are increase to the south. In mixed forest zone and steppe zone, the majority of lakes have CL > 200 meq/m$^2$/yr. These sites are not sensitive to acid deposition.

The number of lakes with exceeded CL is the highest in the northern regions. At the same time some lakes with CL exceedance are present in the southern tundra and forest-steppe zones. These regions have highly developed industry and urbanisation, which contribute to the high level of acid deposition. Thus despite high CL, in some forest lakes CL is exceeded. In the northern region CL is exceeded because of inherently low CL, whereas in the south CL is exceeded because of the high acid deposition. This pilot survey of lakes in European Russia shows that the problem of water acidification in Russia is urgent and requires further more large-scale investigation.

**Conclusion**

Acid sensitive lakes are present in all ecoregions of European Russia. The zone covers the territory within tundra and southern taiga. In these ecoregions anthropogenically acidified lakes occur as characterised by low pH and ANC with SO4* the dominant anion. In southern areas with high population density and industrial activity, lakes are characterised by high SO4* and NO3 concentrations. To the south the proportion of lakes increase in which NO3 plays a key role in water acidification. Critical loads are exceeded in northern humid ecoregions, and also in southern areas due to high levels of acid deposition to lakes of these ecoregions.

This is a pilot survey, in that the lakes selected were irregularly distributed over the territory. The data show, however, that water acidification is an important problem for Russia, especially in the humid zone which comprises 70% of the territory.
ACKNOWLEDGEMENTS

The authors thank the Russian Fund of Basic Research for financing the project (grant 01-05-) and U. Biliniak, Rasumovskiy and B. Saltankin for carrying out the fieldwork over the large territory. The authors also thank colleagues from Norwegian Institute for Water Research for assistance with methods, improvement of analytical measurements, and intercalibration.

References


Table 1. Distribution of CL and CL_{ex} (meq/m²/yr) by cumulative percent for ecoregions of European part of Russia. N=number of lakes.

<table>
<thead>
<tr>
<th>Percent of lakes</th>
<th>2.5</th>
<th>10</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>90</th>
<th>97.5</th>
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<td></td>
<td></td>
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<tr>
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<td>80</td>
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<tr>
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<td>93</td>
<td>113</td>
<td>156</td>
<td>85</td>
</tr>
<tr>
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<td>42</td>
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<td>332</td>
<td>577</td>
<td>749</td>
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<td>319</td>
<td>462</td>
<td>695</td>
<td>800</td>
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<td>99</td>
<td>192</td>
<td>300</td>
<td>440</td>
<td>550</td>
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</tr>
<tr>
<td>Tundra and forest-tundra</td>
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<td>18</td>
<td>11</td>
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<td>-205</td>
<td>-251</td>
<td>-413</td>
<td>-512</td>
<td>18</td>
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</table>

Figure 1. North-to-south variation in concentrations of the major cations (a) and \( \text{SO}_4^* \) (b) in lakes in the European part of Russia.
Figure 2. North-to-south variation in concentrations of the ratio of alkalinity to $\text{SO}_4^{2-}$ ($\text{Alk}/\text{SO}_4^{2-}$) (a) and KNS (b) in lakes in the European part of Russia.
Figure 3. Distribution of lakes (%) by pH in ecoregions in the European part of Russia.
Figure 4. Distribution of lakes (%) by ANC in ecoregions in the European part of Russia.
2. Recent trends in acid-sensitive populations of surface waters in the U.S., 1990-2000

John Stoddard, EPA, US

NHEERL Fact Sheet
Report on Assessment of Surface Water Chemistry (“Acid Rain”) to be Released

Impact Statement:
- A report entitled “Response of surface water chemistry to the Clean Air Act Amendments of 1990” assesses changes in surface water chemistry in the northern and eastern United States. The assessment was conducted to determine if there have been reductions in the level of acidity in lakes and streams affected by “acid rain”, resulting from pollutants emitted from coal-powered plants and other sources of combusted fossil fuels.
- The results of this study indicate that improvements in surface water chemistry (lower sulfate concentrations and decreases in acidity) have resulted from emissions regulations enacted as part of the Clean Air Act Amendments of 1990. This may be the first example of a monitoring program and assessment produced in direct response to the requirements of the Government Performance and Results Act (GPRA).

Background:
- In response to Title IV of the 1990 Clean Air Act Amendments (CAAA), the Office of Research and Development (ORD) began working with the Office of Air and Radiation (OAR) to determine if expected improvements in surface water chemistry occurred. The resulting monitoring and research effort was funded by ORD through the TIME (Temporally Integrated Monitoring of Ecosystems) and LTM (Long-Term Monitoring) projects.
- This study reports on the results of that monitoring effort over the 11-year period 1990-2000.
- Study Description:
  - Because consistent recovery across a regional population of streams or lakes would provide the strongest evidence for the success of controls on acidic deposition, TIME and LTM are designed to estimate chemical trends in surface waters at regional scales.
  - Monitoring results from a total of 145 lakes and 147 streams represent all of the major acid sensitive regions of the northern and eastern U.S.
  - ORD designed and implemented this program in collaboration partners from OAR, the University of Maine, U.S. Geological Survey, Adirondack Lake Survey Corporation, Vermont Department of Environmental Conservation, Pennsylvania State University, University of Virginia, Syracuse University, and Oregon State University.
Results:

- The CAAA has resulted in a large and widespread decrease in the deposition of sulfur. Wet sulfate deposition declined by approximately 40% in the 1990s. In the same period, surface water sulfate declined in all regions except the Ridge and Blue Ridge provinces (Virginia).

- Acid neutralizing capacity (ANC) is a key indicator of recovery. ANC increased in three of the regions (Adirondacks, Northern Appalachian Plateau and Upper Midwest) and was unchanged in New England and the Ridge/Blue Ridge region. Modest increases in ANC have reduced the number of acidic lakes and stream segments in some regions:
  - In the Adirondacks, 8.1% of the lakes (150 lakes), are currently acidic. In the early 1990s, 13% (240 lakes) were acidic.
  - In the Upper Midwest, an estimated 80 of 250 lakes that were acidic in mid-1980s are no longer acidic.
  - In the Northern Appalachian Plateau region, there are currently an estimated 3,393 kilometers (2,104 miles) of acidic streams in the region, or 7.9% of the total population; this compares to 5,014 kilometers (3,109 miles) of acidic streams (12%) in 1993-94.
There was no evidence of recovery in New England, or in the Ridge and Blue Ridge Provinces; the latter region is not expected to recover immediately, due to the nature of forest soils in the province.

- In the three regions showing recovery, approximately one-third of formerly acidic surface waters are no longer acidic, although still with very low ANC.

Conclusions:
- In acid sensitive regions of the northern and eastern U.S., there is evidence of recovery from the effects of acidic deposition.
- Regional declines in surface water sulfate are without question due to the declines in emissions and deposition that have occurred since the 1990 CAAA.
- Significant decreases in the number of acidic surface waters have occurred in the Adirondack Mountains, the Northern Appalachian Plateau and the Upper Midwest.

Manuscript:

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3. Assessing the recovery of lakes in southeastern Canada from the effects of acidic deposition

D.S. Jeffries, Environment Canada, Canda

Politically-mandated reductions in North American sulphur dioxide (SO₂) emissions promote expectations that aquatic ecosystems in southeastern Canada are recovering from acidification. Only lakes located near smelters that have dramatically reduced emissions meet this expectation. Lakes in the Atlantic provinces, Quebec and Ontario affected only by long range sources show a general decline in sulphate (SO₄²⁻) concentrations, but only a modest increase in pH or alkalinity. Several factors may contribute to the constrained (or likely delayed) acidity response: declining base cation concentrations, drought-induced mobilization of SO₄²⁻, damaged internal alkalinity generation mechanisms, and perhaps increasing nitrate or organic anion levels. The chemistry of recovered lakes may differ from the original (be more dilute). There is little evidence of biological recovery (nor investigation to detect it) outside of the Sudbury/Killarney area. Whole-lake experiments show that the biological characteristics of recovering lakes commonly differ from those present during acidification. This means that recovering lakes may not be restored, but rather, move to an alternate state. Chemical and biological models predict that much greater SO₂ emission reductions that presently required will be needed to promote widespread chemical and latterly, biological recovery.
4. Atmospheric deposition of nitrogen on the Lake Maggiore watershed (Italy and Switzerland): contribution to water acidification and soil N saturation

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Summary
The acidification of water bodies in the area south of the Alps is caused by the deposition of atmospheric pollutants released into the atmosphere mainly from the Po Plain (Northern Italy). Primary pollutants are oxidised compounds of sulphur (sulphur dioxide) and nitrogen (nitrogen oxides). In addition, considerable amounts of nitrogen in reduced form (ammonia), which produce acidity when oxidised, are released into the atmosphere.

This study shows the current atmospheric deposition of NH$_4^+$ and NO$_3^-$ on the watershed of Lake Maggiore where the Italian and Swiss ICP Waters sites are located. Deposition maps are extrapolated measuring concentrations of atmospheric deposition and precipitation amount. A geographical gradient and a temporal trend (in the last 20 years) of atmospheric deposition chemistry, are also illustrated. Sulphate, nitrate and ammonium oxidation, are responsible for acidification processes in the area of Lake Maggiore watershed. Finally nitrogen saturation of the watershed will be discussed.

Study Area, location of sampling sites and sampling methods
The investigated area is located in the southern part of the Alpine Chain and corresponds to the watershed of Lake Maggiore, which is very close to the most industrialised part of Italy, including cities such as Milan and Turin. Because of this location, the catchment receives high amount of orographic precipitation and deposition of anthropogenic pollutants (Barbieri et al. 2001; Barbieri & Pozzi 2001; Mosello et al. 2001; Rogora et al. 2001).

The catchment (6600 km$^2$) is located half in Italy (Piedmont and Lombardy) and half in Switzerland (Canton Ticino) (Figure 5). Most of the population (634,000) lives in the subalpine area in the southern part of the catchment where the main industrial activities are also located.

The investigated ICP Waters sites are located both in Italy (3 rivers and 2 lakes) (Mosello et al. 2000) and Switzerland (4 rivers and 20 lakes) (Barbieri et al. 2001).
In the frame of the ICP Waters activities also atmospheric deposition data are considered. There are 7 stations in Italy and 7 in Switzerland, located at an altitude between 208 and 1880 m a.s.l. Sampling frequency is weekly and made with wet-only collectors (Barbieri & Pozzi 2001; Mosello et al. 2001). Conjointly there are about 120 stations measuring precipitation amounts.

**Methods and Results**

Combining together concentrations measured in atmospheric deposition with precipitation amounts it’s possible to assess the fluxes of the major compounds and then to extrapolate deposition maps for the whole region (Figure 6).

Deposition maps in the year 2001 concerning actual acidity, sulphate, nitrate and ammonium, show a strong gradient from south to north, which depends on the distance to the main pollutant sources located in the Po Plain. Acidity deposition values lie between 10 and 30 meq m\(^{-2}\) y\(^{-1}\). Nitrogen compounds deposition shows values similar to those of sulphate, with deposition fluxes ranging between 50 and 100 meq m\(^{-2}\) y\(^{-1}\).

The comparison between ionic composition of the atmospheric deposition (Locarno, 350 m a.s.l), with that of an alpine lake (Laghetto Inferiore, 2000 m a.s.l) and of a stream (River Verzasca, 1000m a.s.l.), shows that ammonium represents an important part of precipitation ionic composition, while it almost disappears in the alpine lake and totally in the stream (Barbieri et al. 2001).

More precisely, in terms of percentage contribution, ammonium has been reduced from 40% in the atmospheric deposition to 5% in the alpine lake and has completely disappeared in the stream.

During the last 20 years the trends for actual acidity and potential acidity pointed out a clear drop; this general decreasing trend is mainly affected by the reduction in the actual acidity rather than the dropping in the acidity derived from ammonium ion. Actual and potential acidity can be described as follows:

**Estimated actual acidity** \( (A) = [H^+] - [HCO_3^{-}] \)

**Potential Acidity** \( \text{Apot} = (A) + 2 [NH_4^{+}] = [H^+] - [HCO_3^{-}] + 2[NH_4^{+}] \)

Median annual pH values in the wet depositions of the three reference sites located south, in the middle and north of the study area, respectively, highlight a considerable increase from 4.2 to 4.8 in the last twenty years. At the same time sulphate concentration shows a strong decrease from 120 to 50 µeq l\(^{-1}\). The oxidised and reduced forms of nitrogen compounds don’t show any significant trends and their concentrations remain quite constant (Figure 7) (Barbieri & Pozzi 2001).

In order to estimate the contribution of ammonium to the potential acidity it is necessary to consider two different processes:

- the protons coming from sulphuric and nitric acid in the atmosphere which are neutralised by ammonia;
- and the protons produced by ammonium transformation in the ecosystem. In our approach we have considered two protons released for one equivalent of ammonium.
The relative contribution of sulphuric acid to potential acidity has dropped; nitric acid and the protons produced by ammonium transformation are responsible of more than 60% of total potential acidity. The acidity derived only from ammonium corresponds to about 40% of the total.

As regards the N saturation of watersheds the Stoddard’s approach (Stoddard & Traaen 1994) has been used. It emerges that most of the watersheds considered in Italy and Switzerland are oversaturated with respect to nitrogen and this condition leads to acidification. Most of the measurements, carried out in all the seasons, show that values of nitrate are higher than the threshold of 50 µeq l⁻¹ (Figure 8).

In the Po valley, where the Lake Maggiore watershed is located, there are other, very important lakes, like lakes Lugano, Como, Iseo and Garda. In these lakes nitrate shows an increasing trend, with the exception of Lake Garda, because of its long residence time (Figure 9). In Lake Maggiore concentrations of nitrate have increased twice, from 30 to 60 µeq l⁻¹, from 1955 to the 90’s mainly because of the increase of N load from atmosphere (Mosello et al. 2001).

Conclusions
Lake Maggiore area receives high atmospheric input of N, both oxidised and reduced, with a \( \text{NH}_4^+:\text{NO}_3^- \) ratio of about 1:1. Once ammonium has reached the aquatic or terrestrial ecosystem, it is rapidly transformed into nitrate or organic N, increasing acidification. While the contribution of sulphate deposition to acidification has decreased during the last 20 years, that of \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) has remained constant representing more than 60% of total acidity.

Surface waters in the study area show high concentrations of nitrate, as a consequence of the N saturation of the catchments; this situation interests a wide area in Northern Italy and Southern Switzerland in Canton Ticino and affects also the water chemistry of the major subalpine lakes (Mosello et al. 2001).

References
Barbieri, A., S.Pozzi, 2001. Acidifying Deposition (Southern Switzerland), Environmental Documentation 134 – Air, SAEFL


*Figure 5.* Lake Maggiore watershed and ICP Waters investigated sites (rivers and lakes).
Figure 6. Actual acidity, sulphate, nitrate and ammonium deposition maps (year 2001).
Figure 7. Trends of pH, sulphate, nitrate and ammonium values at Orta-M.Mesma, Locarno and Piotta.
Figure 8. Application of Stoddard’s approach to Italian and Swiss rivers (mean values of 2000–2001).

Figure 9. Trend of nitrate concentrations in deep subalpine lakes.
5. Changes in the water chemistry of 49 West of Ireland Lakes

Jim Bowman
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Introduction
Acid sensitive water bodies in Ireland are found mostly along the western seaboard and in Co. Wicklow on the east coast, area with slow weathering bedrock formations principally of granite, quartzite and schist overlain with associated soils. The surface waters in these areas are characterised by their natural acidity and low alkalinity and a consequent poor capacity to neutralise acid inputs.

Regular annual monitoring, carried out in December and April, of the chemical and biological characteristics of three lakes and their inflowing streams: Loughs Veagh (Donegal), Maumwee (Galway) and Glendalough Lake Upper (Wicklow), representative of the larger acid-sensitive areas in the State, has been on-going since 1984. These waters form part of the ICP monitoring Programme and were also the subject of a detailed investigation, to examine the impact of acid precipitation, in the period 1987-89 (Bowman, 1991).

In addition to the detailed monitoring outlined above, a physico-chemical examination of 80 lakes was carried out in both July and December in the period 1987-9 (Bowman, 1991) in the immediate region adjoining Lough Maumwee in Galway in the west of Ireland. A sub-set of these lakes was selected for re-examination as part of the National Lakes Monitoring Programme in 2000. Sampling was performed annually in May /June (27 lakes) and in December (22 lakes).

These lakes are predominantly located in areas of granite and schist bedrock overlain with blanket peat soils. They are lowland (<100m asl), shallow (mean depth <5m), and small (<50 ha) with, in most instances, a high degree of acid sensitivity as indicated by alkalinity values <10 mg CaCO₃/l.

Results
A comparison is given, in Table 1, of the ranges and medians of measurements of pH, oxidised nitrogen, total and non-marine sulphate, alkalinity, magnesium and calcium made in the summer and winter between 1987-9 and 2000-2. The mean of the three-year values in both the summer and winter in the two periods for selected parameters in individual lakes, are presented graphically.

A marked tendency towards increased mean pH values and reduced mean non-marine sulphate concentrations in both the winter and summer data sets is apparent for the individual lakes (Figure 10 and Figure 11). During the winter in the 1987 - 89 period the majority of the lakes had pH values in the pH range 6.20 - 6.50, whereas the corresponding range for the recent period is 6.40 - 6.80. The increase is more notable for the summer samples with the majority of the lakes in the pH range 6.20 - 6.60 in the former period and from 6.80 to over
7.00 for the years 2000 - 02. A pronounced reduction is noted in the winter data for non-marine sulphate with the concentrations in the majority of lakes in the years 2000 – 02 <0.6 mg SO₄/l; the values in the period 1987 - 89 were mostly in the range 1 - 3 mg SO₄/l.

These changes are strongly apparent when the ranges and medians of the summer and winter values, measured in both periods, are examined (Table 2). A statistically significant increases in the median pH values and reduction in non-marine sulphate concentrations was measured between these two datasets.

**Table 2.** Ranges and Median values for selected parameters for the periods 1987-89 and 2000-02 at 49 lakes in the West of Ireland

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ox - Nitrogen</th>
<th>Tot. Sulphate</th>
<th>NM Sulphate</th>
<th>Alkalinity</th>
<th>Magnesium</th>
<th>Calcium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>µg N/l</td>
<td>µg S/l</td>
<td>µg S/l</td>
<td>mg CaCO₃/l</td>
<td>mg Mg/l</td>
<td>mg Ca/l</td>
</tr>
<tr>
<td><strong>Summer values (27)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1987-89 Range</td>
<td>5.04 - 7.18</td>
<td>8 - 127</td>
<td>2.8 - 12.2</td>
<td>0.0 - 14.6</td>
<td>5 - 30</td>
<td>1.5 - 4.6</td>
<td>1.6 - 20.0</td>
</tr>
<tr>
<td>Median</td>
<td>6.29</td>
<td>13</td>
<td>6.1</td>
<td>1.5</td>
<td>9</td>
<td>2.6</td>
<td>3.22</td>
</tr>
<tr>
<td>2000-02 Range</td>
<td>5.45 - 7.61</td>
<td>3 - 83</td>
<td>2.8 - 10.3</td>
<td>0.0 - 16.9</td>
<td>3 - 25</td>
<td>1.1 - 4.8</td>
<td>1.6 - 27.6</td>
</tr>
<tr>
<td>Median</td>
<td>6.89</td>
<td>11</td>
<td>4.2</td>
<td>0.8</td>
<td>6</td>
<td>2.8</td>
<td>3.67</td>
</tr>
<tr>
<td><strong>Winter values (22)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1987-89 Range</td>
<td>5.76 - 6.91</td>
<td>50 - 367</td>
<td>2.8 - 6.3</td>
<td>0.8 - 4.3</td>
<td>7 - 21</td>
<td>1.0 - 2.6</td>
<td>1.5 - 7.2</td>
</tr>
<tr>
<td>Median</td>
<td>6.36</td>
<td>100</td>
<td>3.5</td>
<td>1.45</td>
<td>10</td>
<td>1.4</td>
<td>2.8</td>
</tr>
<tr>
<td>2000-02 Range</td>
<td>6.15 - 7.38</td>
<td>51 - 244</td>
<td>1.9 - 4.5</td>
<td>0.1 - 1.5</td>
<td>4 - 16</td>
<td>1.1 - 2.1</td>
<td>1.9 - 11.6</td>
</tr>
<tr>
<td>Median</td>
<td>6.67</td>
<td>72</td>
<td>2.6</td>
<td>0.6</td>
<td>5</td>
<td>1.4</td>
<td>3.2</td>
</tr>
</tbody>
</table>

When the corresponding values for oxidised nitrogen are examined, a reduction is also apparent between the two periods in the overall concentrations (Table 1) and in the individual lake data (Figure 12). However, the reduction is not as marked as that for pH and non-marine-sulphate.

A striking reduction was recorded in the alkalinity values measured in the lakes between the two periods (Figure 13). This change was most evident in the winter data where all 22 lakes registered lowered values in the recent period, while 23 of the 27 lakes examined in the summer months had reduced concentrations.

No clear pattern in the concentrations of the base cations, calcium and magnesium, in these lakes in either winter or summer data is apparent (Table 1 and Figure 14 and Figure 15) between the periods.
a) Winter values

b) Summer values

Figure 10. pH distribution for lake samples taken a) in winter and b) in summer in the periods 1987-9 and 2000-2.
a) Winter values

b) Summer values

Figure 11. Non-marine sulphate distribution for lake samples taken a) in winter and b) in summer in the periods 1987-9 and 2000-2.
a) Winter values

b) Summer values

Figure 12. Oxidised nitrogen distribution for lake samples taken a) in winter and b) in summer in the periods 1987-9 and 2000-2.
Figure 13. Alkalinity distribution for lake samples taken a) in winter and b) in summer in the periods 1987-9 and 2000-2.
Figure 14. Calcium distribution for lake samples taken a) in winter and b) in summer in the periods 1987-9 and 2000-2.
a) Winter values

c) Summer values

Figure 15. Magnesium distribution for lake samples taken a) in winter and b) in summer in the periods 1987-9 and 2000-2.
Discussion
The changes in water chemistry, outlined above, in the 49 lakes examined in the west of Ireland are relatively uniform throughout the small region. The trends and changes detailed in this study between the two periods are consistent with those noted in the detailed, continuous and long-term investigation of surface waterbodies (ICP Waters) selected to measure trends in acidity at other areas in Europe and North America (Skjelkvåle, 2002). These changes reflect the emissions reduction measures successfully operated over the past decade.

The significant reduction in the non-marine sulphate and hydrogen ion (increased pH) concentration, observed in the Irish region between 1987-89 and 2000-02, agrees with the overwhelming evidence of such a reduction in these ions in Europe over the longer period. Similarly, the less striking trend in oxidised nitrogen described above reflects a similar situation noted in Europe. The absence of a clear trend in concentrations of base cations and the obvious reduction in alkalinity in the Irish waters is somewhat at odds with the pattern emerging in Europe. The declining levels of base cations in surface waters in mainland Europe is attributed to a reduction of their concentration in emissions; however, in western Ireland the deposition of marine salts is a considerable and constant source of these base cations which would mask any reduction in the deposition of base cations of anthropogenic origin.

References

6. Heavy metals in surface waters in Latvia

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The water is an important part of the ecosystem. Different international organizations and programmes need reliable water quality data to control and minimize land-based pollution of rivers and lakes and as a result of the marine environment, to predict changes in the environment taking into consideration the quality of pollutants transmitted and climate change dynamics.

Heavy metal measurement results from the national water quality network available since 1972 have been used under different international programmes.

The present material provides the heavy metal measurement results in surface waters in Latvia in the period 1996-2000, with reference to the Lielupe and Daugava rivers.

- Heavy metal concentrations in the Daugava and Lielupe basins correspond to the good water quality requirements.
- The distribution of heavy metals in the Daugava showed concentrations in the frontier areas equal to those in towns or higher due to pollutant arrival from Belarus; for the Lielupe, the transboundary impact is less pronounced, with heavy metal maxima in the estuary.
- A comparison of heavy metal measurement results from two basins and the background station shows that the concentrations in both basins are higher than on the background station, excluding Cd in the Lielupe basin.
- Heavy metal concentrations have not greatly changed in the period 1996-2000, with somewhat decrease of Zn from 1997 and increase of Pb in 2000.
- The calculated inflow of heavy metals to the Gulf of Riga and from the frontier areas showed a considerable heavy metal inflow to the Daugava basin from Belarus; the heavy metal inflow to the Lielupe basin from Lithuanian was insignificant; inflow of heavy metals would depend on the river run-off.
7. Effects of meteorological condition changes on the water quality of Csorret Reservoir, Hungary

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Introduction

The Csorret Reservoir is the only ICP site in Hungary concerning the International Cooperative Program on assessment and Monitoring of Acidification of Rivers and Lakes. In 2002 we launched a project to collect water samples from both the reservoir and the small streams feeding the reservoir. Sampling was carried out during May – December with monthly frequency. The goal of the assessment was to determine the effects of meteorological conditions on the water quality changes of Csorret Reservoir. In the samples, collected from the reservoir and its feeding streams, 23 chemical compounds, temperature and electric conductivity were measured. In this paper we are concerned with temperature, pH, electric conductivity, alkalinity, aluminum and manganese concentrations, as these parameters proved to be affected significantly by changes in meteorological conditions.

Another goal of the project was to examine the effect of the feeding streams on the water quality of the reservoir. The transformation of the nitrogen compounds was also to be analyzed. The results of the eight sampling occasions (monthly between May – December) showed that to track such processes with sufficient accuracy requires more data (i.e. more sampling). Thus this study does not include any further analyzes of nitrogen compounds.

The Csorret Reservoir

The Csorret Reservoir is located in the northeastern mountain region of Hungary, at an altitude of 534 m. The reservoir was created in 1973 by constructing a dam across the valley, to supply the nearby holiday resorts. The capacity of the reservoir at operating water level is 1 million m³, with an area of 12.8 ha, and a maximum depth of 22.5 m. The 8.38 km² catchment area is vegetated by deciduous and coniferous forests in approximately equal ratio. The catchment is intact from anthropogenic influence. The reservoir has five permanent inflows (see map). The five streams contribute 1.5 million m³ water annually. The most important inflows are stream “2”, “3”, and “4” (see map), which bring 38, 11 and 29% of the total, respectively. Another 0.3-0.4 million m³ comes from surface and subsurface flows. 1.02 million m³ water is withdrawn for drinking water supply.
**Meteorological conditions and sampling**

During May – December 2002 samples were collected with monthly frequency from the reservoir and its feeding streams. The samples from the reservoir were collected in 40 m distance of the dam at the water intake facility. Five depths were sampled with a submersible pump (depth are relative to the bottom): W4: 1 m (bottom), W3: 3.5 m, W2: 7.0 m, W1: 10.5 m, W0: surface (14-16 m). The streams were sampled at a fixed section between 10-50 m from the mouth of the stream. When sampling, much care was taken to exclude sediments from the water samples.

The first half of 2002, until the second half of July, was extremely dry. As a consequence, the water level of the reservoir decreased several meters below the operating water level. In the end of July and in the beginning of August unusual heavy rains came, followed by another dry period. Until the end of the year two significant precipitations occurred: in the end of September (which was a cold rain) and in the beginning of December. In the beginning of November there was a 3-5 cm thick snow-cover on the catchment. Sample collections were scheduled in a way that the effect of the precipitations already appeared in the samples.

**Analyzes**

Immediately after sampling, temperature, pH, and electric conductivity of the water sample were measured. Part of the sample was filtered through 0.45 µm membrane filter for measuring suspended solid concentration. The filtrate, and a sub-sample from the original sample were conserved with concentrated HNO₃ and stored for later analyzes of dissolved and total heavy metal concentration, respectively.

The samples were analyzed for the following conventional parameters: KOIₚₑₛ, NH₄⁺, NO₂⁻, NO₃⁻, organic nitrogen, SO₄²⁻, Cl⁻, alkalinity, Ca²⁺, Mg²⁺, Na⁺, and K⁺. The concentrations of metals (Hg, Cd, Pb, Cu, Cr, Ni, Al, Zn, Fe, and Mn) were determined by atomic absorption spectrophotometry, using the graphite-furnace method.

**Temperature in the reservoir**

The temperature of the water essentially affects the biological and chemical processes taking place in water, e.g. their speed. Its effect can directly be observed in the water quality parameters.

The reservoir has a maximum depth of more than 20 m, and a mean depth of almost 10 m. Due to the relatively small surface area of the reservoir the wind can only mix the upper few meters of the reservoir water. This results in stratification of the water layers. Due to the meteorological conditions two turnovers occur annually. Thus the reservoir is a dimictic deep lake in limnological terms. The stratification is clearly visible in . The water level of the reservoir was very low in the beginning of the study period, but the heavy rains in the end of July and in the beginning of August filled it up to normal level (actually, some of the water had to be released). The rains even affected the stratification: the difference in the temperature of the different layers decreased. The remaining differences were equalized by the cold rains in the end of September, thus the stratification ended entirely.
Figure 1. Temperature in the reservoir

Figure 2. pH in the reservoir
pH in the reservoir

The pH of the water showed a definite tendency during the investigation period. High values, even above pH 8.5, measured in the beginning of the period decreased continuously: in August, after the rainy period, pH values were only about 6.5 at each sampling depth (Figure 2). From October pH increased again until it reached pH 7.5-8.0 in December. According to the measurements high pH values stabilized in the long, dry period, but decreased in the rainy period due to the diluting effect and acidic character of the rain.

The depth profile of the pH also showed a characteristic feature. The different layers of the stratified water had different pH values: the upper layer had as much as 1-1.5 unit higher pH than the layer near the bottom of the reservoir. Highest values were always measured directly at the surface. This is probably caused by algal activity. Another phenomenon is that the pH in the bottom layer varied less during the investigation period than in the upper layer. After the rainy period in July-August the differences between the different depths had decreased (along with the decrease of the temperature differences). Later on significant difference was observed only in September, which disappeared in October.

Alkalinity in the reservoir

Alkalinity was determined by titration to pH 4.5. In the beginning of the sampling period alkalinity was between 0.75-0.85 mekv/L (Figure 3). There were only small differences between the values at different depths. The only variation in time is the effect of the July-August rainy period, which decreased alkalinity significantly. From then on alkalinity was between 0.5-0.6 mekv/L.

![Figure 3. Alkalinity in the reservoir](image-url)
Electric conductivity in the reservoir

The conductivity of the water is proportional to the dissolved salt content of the water. Different layers of the reservoir did not show significant differences in conductivity in the dry period (Figure 4). Values of around 250 $\mu$S/cm in the beginning of the sampling period changed to around 200 $\mu$S/cm after the rainy period due to the diluting effect of the rain. Different depths showed even more similar conductivity values than in the dry period.

Aluminum

Most of the aluminum in the reservoir is bind to suspended solids, however, 10-20 $\mu$g/L is in dissolved form (Figures 5 and 6). After the July-August rains there was an almost five-folds increase in the concentration of both forms (dissolved and total), which slowly decreased to the original concentration afterwards. Such an increase can be explained by the contribution of the streams feeding the reservoir. Figure 7 shows that the total aluminum concentration in the streams peaked at very high values during the rainy period. At the same time the dissolved aluminum concentration (Figure 8) had also increased significantly. Values reached 100-150 $\mu$g/L, which is a magnitude higher than in the reservoir. Regarding that the July-August rain displaced a significant volume of the reservoir, the subsequent increase in the aluminum concentration in the reservoir is understandable. It can be said that the increase in the aluminum concentration in the reservoir water is the result of large amounts of aluminum washed from the catchment area by heavy rains. Aluminum concentrations also show an expressed depth profile: highest concentrations were always measured near the bottom.
Figure 5. Total aluminum in the reservoir

Figure 6. Dissolved aluminum in the reservoir
**Figure 7.** Total aluminium in the streams

**Figure 8.** Dissolved aluminium in the streams
Manganese

According to the measurements manganese in the water of the reservoir is present almost only in dissolved form. Particulate form covers only a few percent of the total manganese concentration (Figure 9 and 10).

![Figure 9. Total manganese in the reservoir.](image)

![Figure 10. Dissolved manganese in the reservoir](image)
The concentration of manganese in the water increased gradually in spring and early summer. However, this increase is only restricted to the lower three depth – in the upper two depth the concentration remains relatively low and constant. This can be explained with that manganese dissolves into the water from the sediment under reductive conditions. According to our measurements, both the total and the dissolved manganese concentration are smaller in the
streams than in the reservoir, thus the role of the streams in supplying manganese to the reservoir is small (Figures 11 and 12). Still, the streams may have an effect on the dissolved manganese content of the reservoir. In August the manganese concentration in the reservoir decreased significantly, which can be explained with the following reasons. The water that the rain and the high-flow streams supplied to the reservoir had high dissolved oxygen content. At the same time the layers of the reservoir mixed. These two processes resulted in that the circumstances at the lake bottom became less reductive or even slightly oxidative. Thus the speed of the release of manganese from the sediment slowed down, or even dissolved manganese was precipitated. Also, the diluting effect of the streams contributed to the decrease in manganese concentration. Due to the warm weather in the second half of August and in September the bottom of the reservoir became reductive again, and the manganese concentration increased again. After the cold rain in September stratification ceased, the manganese concentration equalized at the different depth and decreased (Figures 9 and 10).

Conclusions

Our systematic measurement program, carried out at monthly frequency proved that changes in the meteorological conditions significantly affect the water quality of the Csorret Reservoir. In the dry period of late winter/early spring stratification developed in the reservoir and high pH values occurred in the water. Drastic decrease of high temperature and pH in the upper layer were caused by heavy summer rains. The 1.5 unit pH difference between the upper and lower layers decreased to almost zero. In the autumn there was an increase in the pH at all depths. At the same time there was no change in the alkalinity of the water. The increase of the pH was primarily due to microbiological and biochemical processes. The increase of aluminum concentration in the reservoir water is most probably the result of surface runoff from the catchment area with high aluminum load. Though the streams charged primarily particulate aluminum compounds into the reservoir, the concentration of the dissolved aluminum forms has also increased. After the heavy summer rains significant difference developed between the different sampling depths, which phenomenon remained for several weeks. Opposed to the aluminum, the main source of manganese is the sediment of the reservoir. Manganese was found in the water almost completely in dissolved forms. We could not prove any significant manganese runoff from the catchment area. The gradual increase of manganese concentration in the lower depths until the rainy period, and the appearance of manganese even at middle depth confirm the important role of reductive conditions in the release of manganese from the sediment. The diluting effect of the heavy summer rains and the ceasing of the reductive conditions in the near-bottom layer decreased the manganese concentration. In the autumn the difference between the manganese concentrations of the different water depths has equalized. The increase in manganese concentration is primarily due to the release of manganese from the sediment at low temperature (7-8 °C) and under reductive conditions. As reductive conditions spread upwards, the manganese could also spread upwards.
8. National monitoring of surface waters in Estonia

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Since early 1990s, certain agricultural and industrial activities have been reduced in Estonia because of the political and the economic changes. Reduced levels of sulphur (S) and nitrogen (N) pollution, decreased use of fertilizers and changes in land use are the main factors affecting our ecosystems (Saare et al, 2001). North-East Estonia is characterized by substantially increased basic cation deposition buffering the acidic deposition while in South Estonia, basic cation deposition correspond to those of the natural background and deposition reaching or exceeding the critical loads in some more sensitive areas have an acidifying impact (Oja et al, 2000).

Currently, our problems are still connected with oil-shale mining and processing. The most important contributors to air pollutants are the energy industry and transboundary air pollution. Air pollution from local stationary sources (total emission) has decreased over 2 times, emissions of solid particles and SO$_2$ have declined 74% and 60% during 1990s, respectively (Saare et al, 2001). Status of rivers and their biota has been improving during 1990s (Järvekülg, 2001).

The concentration of sulphur in precipitation was three times lower in 2000 comparing to 1996. It varied from 2 kg/ha at Vilsandi IM Site (West Estonia) to 4.5 kg/ha at Saarejärve IM Site (East Estonia) in 2000. The reduction is in good correlation with the reduction of SO$_2$ emissions.

Different pollutants (including heavy metals) emitted into the air and water remain in soil and water. Concentrations of heavy metals increases episodically in the air because of the long-range transfer from polluted areas and also by local emissions. Activity of pollutants, including heavy metals, with often high toxicity and solubility in water, depends on trends in nitrogen deposition and leaching rate of previously sorbed sulphur compounds.

Inland water monitoring is carried out in 59 river stations, 20 small lake stations, 5….13 stations on Lake Peipsi and on 2 stations of Lake Võrtsjärv and financed by state budget. There are 5 laboratories responsible for analysis in monitoring programme.

In Estonia, according to Water Framework Directive (WFD) the river classification bases on water quality monitoring data and waterbodies are divided into 5 classes. Water of I class or high quality is characterized by ingredients of natural, background water, not influenced by human activities. For the second class, water of good quality, some human impact is allowed, but water corresponds to the requirements of high quality. Rivers have to correspond to at least requirements of the good water quality.

The ICP Water site of Estonia, River Ahja-Kiidjärve, EE 02, belongs to the natural rivers in the South-East of Estonia in the drainage basin of Lake Peipsi. The total discharge of the river has been determined by ground water (51%), melting water (27%) and rain water (22%).
In hydrobiology stations of the river some changes had taken place during 5 year cycle 1994-1999: pH has been decreasing in all stations (0.1-0.7). Organic matter level has been increased. Mean concentrations of biogens have been increasing. River Ahja is mainly eutrophic (52-70 mg/m³). The content of Chl \(a\) was 1.65 times higher and the content of pheopigments 3.4 times higher in 1999 comparing to 1994. Dominants of biomass for phytoplankton have changed. By bioindication of the zoobenthos positive changes in dominant species have been observed and their biomass has been growing.

For natural rivers BOD\(_7\) during 1994-2001 was 2.8 mg O\(_2\)/L, for all rivers 3.2 mg O\(_2\)/L. Concentration of total phosphorus P\(_{tot}\) in 90% of samples of natural rivers was 0.08 mgP/L (0.09 in 1994-95), for all rivers 0.11 mgP/L. In larger rivers, as a rule, P\(_{tot}\) concentration is higher (0.17 mgP/L), but decreasing trend in P\(_{tot}\) content of rivers is remarkable (approximately 2 times)(Leisk, Loigu, 2001). The highest is the content of phosphorus and level of pollution in rivers discharging into the Gulf of Finland. P\(_{tot}\) has increased 15% at biological sites of River Ahja.

Concentration of nitrogen N\(_{tot}\) in 90% of samples of natural rivers was 2.7 mgN/L (3.0 mgN/L in 1994-95), for all rivers 4.0 mgN/L, larger rivers contain 4.9 mgN/L in 2001. Concentration of nitrogen in larger rivers is decreasing: pollution from agriculture has been decreasing for some years. Higher are concentrations in the rivers discharging to the Gulf of Finland. Denitrification and self-purification processes are higher in the discharges from Lake Võrtsjärv and Lake Peipsi. The level of N\(_{tot}\) has not been changing very much lately, but the part of nitrate concentration has become higher and part of organic nitrogen is also increasing. N\(_{tot}\) has increased 17% at biological sites of River Ahja.

The rivers are characterised by quite high buffering possibility and good conditions for denitrification processes. Nutrients are carried off from arable land in contents which are 3-5 times lower than in other countries in the region. It can not be explained only with decreasing use of fertilizers and lower productivity, but may be caused by transformation processes of nutrients and watersheds and their circulation in the water ecosystem (Loigu, 2001). Research in the field of self-purification processes may give some answers to the question, the state and behaviour of some heavy metals can also be explained by the processes.

Heavy metals (Cu, Cd, Pb, Hg) have been determined in Estonian inland waters mainly once a year. By the classification our rivers belong to good water quality. For the rivers cadmium concentration is < 0.02 µg/l, lead concentration is <0.2-0.7 µg/l, showing also good quality of water. The highest Pb concentration can be found in River Kunda (North of Estonia): 0.7 µg/l in 2001. Hg concentration is usually under detection limit <0.1 µg/l. Higher are concentrations of Cu in the rivers of industrial area Seljajõgi and Kunda, 2.4 and 2.7 µg/l, resp. In natural rivers concentrations of heavy metals are under detection limit.

The Estonian Standard Board has implemented the Quality System standard for experimental laboratories EVS_EN ISO/IEC 17025:2000 „General requirements on competence of experimental and calibration laboratories“. During 2002, all the experimental laboratories preparing for accreditation, have to implement EN ISO 17025.

In addition to the „Instruction of validation“ the instruction „Quantifying uncertainty in analytical measurement“ was compiled on the bases of EURACHEM/CITAC instruction.
Implemented and accredited quality systems need external and internal control assessment (estimation, validation): intercalibrations and audits.

For training auditors the instruction EAL-G3 „Internal audits and management reviews for laboratories“ is used.

Laboratories have participated in different international intercalibrations of Aquacheck (UK), BAM, EQUATE, NIVA, ITM; VKI_PHARE, AMOS etc. Our reference laboratories are also responsible for organising intercalibrations for surface water, waste water, ground water and drinking water for other experimental laboratories twice a year.

References


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Appendix B. Reports and publications from the ICP-Waters Programme


42. Hovind, H. 1997. Intercomparison 9711. pH, K\textsubscript{25}, HCO\textsubscript{3}, NO\textsubscript{3} + NO\textsubscript{2}, Cl, SO\textsubscript{4}, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3716-97. ISBN 82-577-3284-2.


