

**European Mountain lake Ecosystems: Regionalisation,
diaGnostics & socio-economic Evaluation**

EMERGE

04

**CHEMICAL ANALYSIS OF MAJOR IONS
AND NUTRIENTS
ANALYTICAL QUALITY CONTROL**

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Chemical Analysis of Major Ions and Nutrients

Analytical Quality Control

1. Chemical analyses, major ions and nutrients

1.1 Variables considered

Atmospheric deposition

The variables taken into account for each precipitation event, and their relative units, are:

- a. name and site code
- b. starting and ending dates of the sampling
- c. volume of precipitation (mm)
- d. pH
- e. conductivity ($\mu\text{S cm}^{-1}$ at 25°C)
- f. ammonium, nitrate ($\mu\text{g N l}^{-1}$)
- g. sulphate ($\text{mg SO}_4 \text{l}^{-1}$)
- h. alkalinity ($\mu\text{eq l}^{-1}$)
- i. calcium, magnesium, sodium, potassium, chloride (mg l^{-1})

The measurement of reactive or total phosphorus, which may give indications on the contamination of the sample (e.g. by bird droppings), is optional.

Surface waters

The total analytical programme includes the components listed in table 3 with their relative units.

Measurement of colour is recommended where there may be influence from bogs or marsh in the watershed.

1.2 Handling of samples

The greatest care and the most accurate analytical quality control (AQC) are needed for the analyses of atmospheric deposition and water samples at/from remote sites, as in general these samples present the lowest ionic concentrations. All containers used for collecting,

transporting or analysing samples must be free of any important quantity of determinands. Several checks of the cleanliness of the containers must be made, using the purest de-ionised water. Samples after collection should be stored in the dark at about 4°C and transferred to the laboratory as soon as possible.

Sample identification and documentation of the sampling must be accurately maintained for every sample. This documentation is an integral part of the sample information and must be entered into the laboratory data base. Any lack or confusion of documentation may invalidate the resulting data.

1.3 Analytical methods

The very low concentrations of these samples require the most accurate analytical techniques available. Ion chromatography (IC) is at present the most reliable technique for both anion and cation measurements; equally reliable is the use of atomic absorption spectrophotometry for the analysis of cations. In the absence of IC, wet spectrophotometric determinations may be used for anions, but they must be performed with the greatest care and applying all the internal AQC criteria (e.g. blank checking and control charts at low concentration levels).

The suggested analytical methods are summarized in table 1. See table 1 for the references on the different analytical methods. Recommendations for performing some of the measurements are given below.

pH

It must be measured in unstirred water after calibration of the electrode with two buffers covering a range of values which includes the expected value of the sample. Buffers with low ionic strength should be used. For all measurement details and for temperature correction follow the instructions accompanying the equipment.

Conductivity

The cell constant must be recalculated yearly, following the indications, e.g. APHA, AWWA, WEF (1992).

Alkalinity

The measurement of alkalinity at the very low levels normally detected in atmospheric precipitation or in high altitude lakes **requires** the use of an automatic titrator and the use of Gran's titration or the two end-point technique (Gran 1950, 1952; A.P.H.A., A.W.W.A., W.E.F. 1992). Alternatively Henriksen's technique may be used (Henriksen 1982), but the results must be corrected for the excess of acid necessary to shift the pH value from the equivalent point (5.2-5.6 in relation with inorganic carbon concentration) to the end point of 4.5. Titrations performed through the colorimetric detection of the equivalent point are in most cases affected by systematic overevaluation of values (Kramer & Tessier 1982; Kramer *et al.* 1986; Mc Quaker *et al.* 1983; Mosello *et al.* 1993).

Ion chromatographic determinations

Quantification of low concentrations of solutes requires careful AQC. Six-eight standard solutions of known concentrations are needed for the calibration every batch of analyses. As the instrument signal may not be linear, quadratic or cubic regressions must be used (Tartari *et al.* 1995). Quality controls should include:

- a. test of de-ionised water
- b. release of base cation from the glass of vials
- c. pollution of calibration standards, easy because of the low concentration

- d. cleanliness of plastic- and glass-ware
- e. use and regular check of in-laboratory standards of known and stable concentrations, in the range of those present in the samples
- f. vials must be rinsed with de-ionised water and then with the sample
- g. check vial glass for release of Na and K in the sample

Spectrophotometric determination

The analytical methods suggested for each variable are given in table 1.

General recommendations are, that when the calibration curve is performed on 6-8 points in standard conditions, calibration is generally stable for several months, but a check every 3-4 months is suggested.

As sample concentrations are often very low, it is important to verify the lower detection limit (LOD, defined as the smallest amount that can be detected above the noise in a procedure and within a stated confidence limit) and the lower quantification limit (LOQ) (A.P.H.A., A.W.W.A., W.E.F. 1992). The quantification of concentrations is possible only for values higher than LOQ.

Atomic absorption spectrophotometry (AAS) determination

A multi point calibration should be used for every batch of measurements. Linearity must be checked in the range of concentrations considered. It is essential to check to LOD and LOQ, and to use of internal standards of known concentrations, and control charts, to guarantee the reliability of results.

2. Analytical quality control

2.1 In-laboratory quality control

By “in-laboratory (or internal) AQC” we mean the set of rules and procedures which should be adopted to perform and check all the analytical operations, with the final aim of producing data of a pre-defined level of precision and accuracy. These rules govern many aspects of the activity of the laboratory, such as training of personnel, maintenance of laboratory equipment and facilities, choice of methods and performance of analyses, and checking and validating results (see next paragraph). A synthesis of the major points to be considered is listed in table 2. The most important part of this information (i.e. performance of the analyses, calibration, maintenance of the instruments) should be contained in a handbook which the personnel may consult easily as they work. The importance of systematic errors as part of the overall analytical error is well highlighted in inter-laboratory exercises such as intercomparisons. All the exercises performed in the framework of previous collaborations (e.g. the AL:PE project), have shown that systematic errors largely prevail over random errors (Mosello *et al.* 1995). This is usually due to faulty preparation of the calibration solutions (bad quality reagents, inaccuracy in the preparation of solutions, pollution of calibration solutions used for more than one batch of analyses).

To reduce systematic errors, and to keep them under control, is possible and is one of the aims of the program of internal AQC, which must be carefully defined by the head of each laboratory, in strict collaboration with the whole staff.

2.2 Inter-laboratory quality control

By “inter-laboratory (or external) AQC” we mean those actions aimed at achieving, maintaining and improving the laboratory AQC based on information coming from outside the laboratory, such as external standards and collaboration with other laboratories (intercomparisons).

External standards

The most common external standards are the certified reference materials (CRMs), prepared by a collective of laboratories under the control and expertise of the Community Bureau of Reference of the EU. A list of other agencies which prepare CRMs and details of the materials are given by Caroli (1993).

The concentrations of these samples are accurately determined by a group of independent laboratories, using different analytical techniques which offer a high probability of accurate results. CRMs should not be used as routine standards, but they can be used on special occasions, when high quality performance is required. They can be used for different aspects of analytical practice, for example to monitor the performance of an analytical method and demonstrate equivalence between methods, to calibrate equipment, to detect errors in the application of standardised methods.

The CRMs of interest for freshwater analyses are:

- a. CRMs 398 and 399, certified concentrations Al, Ca, Cl, K, Mg, Na, P and S (Quevauviller *et al.*, 1992 a, 1992 b)
- b. CRMs 408 and 409, major ions in rainwater (Quevauviller *et al.* 1993; Reijnders *et al.* 1994)
- c. CRMs 479 and 480 nitrate in freshwater (Quevauviller *et al.* 1996)

A catalogue of all BCR-CRMs will be sent upon request by the Community Bureau of Reference (BCR), Commission of the European Communities, Rue de la Loi 200, B-1049 Brussels.

Intercomparisons

Inter-laboratories exercises may be devoted to different aims such as the evaluation of method-performance, the certification of materials, the assessment of laboratory performance. We will consider the exercises aimed at testing the proficiency of laboratories, that is to evaluate the comparability of the results and, if possible, to point out the main causes of error. The samples used in the exercises must meet precise criteria, such as:

- a. homogeneity: samples in the bottles distributed to different laboratories must have the same concentrations
- b. stability in time: concentrations must not change for the duration of the exercise
- c. representativeness: the considered concentrations must be in the range of interest for the studies performed by the collective of laboratories

Furthermore the organizing laboratory (laboratories) must evaluate the expected concentrations, to be compared with the results provided by the participants.

The participating laboratories must give details of the analytical methods used, to evaluate and exclude the possibility of systematic errors due to the unreliability of a particular method. Furthermore in most cases two samples per exercise are considered, to allow an evaluation between random and systematic errors. The evaluation is made through the use of Youden's graph (Youden 1959; Youden & Steiner 1975).

In the EMERGE the intercomparisons exercise will be organized by NIVA.

2.3 Data checking

The following data controls should be carried out at the laboratory producing the data, and should become a routine operation for all the analyses performed. The same controls will be repeated by the EMERGE elaborating centre (surface water: NIVA Institute, atmospheric deposition: CNR-Istituto Italiano di Idrobiologia), before discussing the data.

Any data that may be in error should result in a new analysis of the sample, if possible. Comparison with previous values measured at the same site or with a range of values obtained for other sites is recommended.

Data should be sent on the diskette annexed to this document, briefly described below. If this is not possible, please use the transmission form (Tab. 3), paying attention to the recommended units.

These quality controls should be performed both on lake and atmospheric deposition data.

Ion balance

The basic assumption for this quality control is that the measurement of pH, ammonium, calcium, magnesium, sodium, potassium, bicarbonate, sulphate, nitrate and chloride accounts almost completely for the ions present in solutions. This can be incorrect in the case of lake water with pH lower than 5, where aluminium and other trace metals may be present in ionic forms. Fluoride is in most cases negligible in terms of ionic balance. On the other hand ionic balance can be influenced by the presence of high amounts of organic matter. In the case of atmospheric deposition, formic and acetic acid may have a minor role in ion balance both in urban and remote areas.

The control is based on the electro neutrality of water samples (lake or atmospheric deposition). The total number of negative and positive charges must be equal. This can be checked using milli (or micro) equivalents per litre (meq l^{-1} or $\mu\text{eq l}^{-1}$) as the concentration unit. The constants necessary to transform the units used in the EMERGE research in $\mu\text{eq l}^{-1}$ are listed in table 4.

Alternatively, the ionic balance may be evaluated using an electronic sheet; in the interests of uniformity, we recommend the sheets prepared in the enclosed diskette for lake (LAKEFORM.XLS) and atmospheric deposition (RAINFORM.XLS) results.

The limit of acceptable errors varies with the total ionic concentrations and the nature of the solutions. Indicating with Σcat and Σan the concentrations ($\mu\text{eq l}^{-1}$) of cations and anions respectively, we can define percent difference as:

$$\text{PD} = 100 * (\Sigma\text{cat} - \Sigma\text{an}) / (0.5 * (\Sigma\text{cat} + \Sigma\text{an}))$$

where:

$$\begin{aligned}\Sigma\text{cat} &= [\text{Ca}] + [\text{Mg}] + [\text{Na}] + [\text{K}] + [\text{H}^+] \\ \Sigma\text{an} &= \text{Alk} + [\text{SO}_4] + [\text{NO}_3] + [\text{Cl}]\end{aligned}$$

As mentioned above, in the case of lake water with pH below 5, Al in ionic form can be important. High amounts of organic matter also need to be taken into consideration when present. To enable the ionic balance (IB) to be calculated as correctly as possible, calculations are made in two versions. In the first version ($\text{pH} > 5.0$), IB is calculated on the basis of all the major ions; in the second version ($\text{pH} < 5.0$), Al, NH_4 and TOC are also considered.

$$\Sigma_{\text{cat}} = [\text{Ca}] + [\text{Mg}] + [\text{Na}] + [\text{K}] + [\text{H}^+] + [\text{NH}_4] + \text{Al}$$

$$\Sigma_{\text{an}} = \text{Alk} + [\text{SO}_4] + [\text{NO}_3] + [\text{Cl}] + \text{OA}$$

OA is calculated from the TOC value taking into account weak organic acids. It may be evaluated from the following empirical equation (Oliver *et al.* 1983):

$$\text{OA} = 4.7 - 6.87 * \exp(-0.322 \text{ TOC})$$

In normal conditions, for dilute lake water samples, a PD lower than 3% should be achieved. Higher values can indicate a lack of precision in one or more analytical techniques, or the omission of important ion/s, or both. In the case of atmospheric deposition, in the EMEP quality assurance plan (Schaug 1988) a score is given to the chemical analyses, on the basis of PD and IS ($\text{IS} = \Sigma_{\text{cat}} + \Sigma_{\text{an}}$; unit: $\mu\text{eq l}^{-1}$), table 5.

An example of a plot of Σ_{cat} vs Σ_{an} for the AL:PE lakes is shown in figure 1.

Comparison between measured and calculated conductivity

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This possibility depends on the type and concentrations of ions and on the temperature of measurement. It is defined as:

$$K = G * (L/A)$$

where $G = 1/R$ is the conductance (unit: ohm^{-1} or siemens; ohm^{-1} is sometime written as mho), defined as the reciprocal of resistance (R ; unit: ohm); A (cm^2) is the electrode surface area, L (cm) is the distance between the two electrodes. The units of K are $\text{ohm}^{-1} \text{cm}^{-1}$. In the International System of Units (SI) conductivity is expressed as millisiemens per meter (mS m^{-1}); this unit is also used by the IUPAC and accepted as Nordic standard. In practice the unit $\mu\text{S cm}^{-1}$, where $1 \text{ mS m}^{-1} = 10 \mu\text{S cm}^{-1} = 10 \mu\text{mho cm}^{-1}$, is also commonly used.

Conductivity depends on the type and concentration (activity) of ions in solution; the capacity of a single ion to transport an electric current is given in standard conditions and in ideal conditions of infinite dilution by the equivalent ionic conductance (λ_i ; unit: $\text{S cm}^2 \text{equivalent}^{-1}$). Values of equivalent conductance of the main ions at 20 and 25°C are presented in table 4.

In the **EMERGE** research, conductivity units used are mS m^{-1} at 25°C. If other units are currently used in the different laboratories (e.g., $\mu\text{S cm}^{-1}$), the transformation is easy, while a problem does exist if a different reference temperature is used. In fact, the variation of equivalent conductance with temperature is not the same for all the ions (e.g. Pungor 1965), so that the function of conductivity with temperature will depend on the chemical composition of the solution. An example is given in figure 2, where the variation of conductivity with temperature for Lake Maggiore (buffered water), for an alpine lake (poorly buffered water) and for an acidic sample of atmospheric deposition are compared. The ion concentrations of the three samples are presented in table 6. The different slopes of the two straight lines clearly indicate different relationships $K = f(T)$. The values of correction of conductivity for temperature are therefore a simplification, performed assuming a “standard composition” for surface water (e.g. Rodier 1984); this can introduce a systematic error in the case of a different chemical composition, as is the case for atmospheric deposition chemistry. Of course this is also true if the correction is made automatically by the conductivity meter. For this reason the suggestion is to make the measurement as close as possible to 25°C (e.g. in the range 24-26°C), and not to try measuring at 20°C and then transforming the value to 25°C with a constant. If conductivity is also measured at 20°C, for reasons of comparison and continuity with past data or with data of other samples, please send to the elaboration centre at NIVA the values at both 20 and 25°C.

A careful, precise conductivity measurement is a further means of checking the results of chemical analyses. It is based on a comparison between measured conductivity (CM) and the conductivity calculated (CE) from individual ion concentrations, multiplied by the respective equivalent ionic conductance (λ_i)

$$CE = \lambda_i C_i$$

The ions are those considered in the ionic balance; the values of λ_i for the different ions are given in table 4, referred to 20 and 25°C. The same values are used in the calculation performed in the electronic sheet in the diskette. The percent difference, CD, is given by the ratio:

$$CD = 100 * |(CE-CM)/CM|$$

Also in this case it is possible to score the results on the basis of CD (Schaug 1988), as shown in table 7.

At low ionic strength (below 0.1 meq l⁻¹) of high altitude lakes or atmospheric deposition samples, the discrepancy between measured and calculated conductivity should be no more than 2% (Miles & Yost 1982). Ionic strength (Ic), in meq l⁻¹, can be calculated from the individual ion concentrations as follows:

$$Ic = 0.5 \sum c_i z_i^2 / w_i$$

where:

- c_i = concentration of the i-th ion in mg l⁻¹;
- z_i = absolute value of the charge for the i-th ion;
- w_i = gram molecular weight for the i-th ion.

For ionic strength higher than 0.1 meq l⁻¹ a correction of the activity of each ion can be used, as proposed e.g. by Stumm and Morgan (1981) and A.P.H.A., A.W.W.A., W.E.F. (1992). For the routine data checking of a set of analyses, an alternative is the plot of measured vs calculated conductivity; the departure of some results from linearity may suggest the presence of analytical errors (Fig. 3).

Comparison between measured conductivity and ion concentrations

If we consider samples with similar ionic ratios and different ionic concentrations, a linear correlation should be expected between conductivity and the sum of cations and anions. Figures 4 and 5 show an example for the analyses performed in 1993 in the AL:PE lakes. The results which depart from the linearity must be checked with care, to see if there have been any mistakes in the analyses or in the data processing, or if the values of some ions are missing from the sum.

The linearity of the relation is lost if marked chemical differences are present between the samples; for example, a sample with pH lower than 4.5 will show, at equal total ionic concentration, higher conductivity than a buffered sample (pH above 6.0), because of the high equivalent ionic conductance of hydrogen ion compared with the other ions (Tab. 4). There will also be a lack of linearity with increasing ionic strength.

3. Mailing the results to the data centre

The diskette annexed to this document contains two electronic sheets (Microsoft Excel version 5 for Windows), respectively for the transmission of surface water (NIVA) and atmospheric deposition (CNR-III) results. The variables contained in the electronic sheet are listed in table 3, as a transmission form of chemical data. The transmission forms, intended as units and number of decimals (if significative, due to the analytical technique), must be used for sending data if no computer facilities are available.

The electronic sheet calculates the ionic balance and the calculated conductivity. As an example the sheet for surface water contains the values measured in the AL:PE lakes in 1993. Furthermore, the relationships between (1) Σ_{cat} and Σ_{an} , (2) measured (CM) and calculated conductivity (CE), (3) CM and Σ_{an} , (4) CM and Σ_{cat} are plotted in the data sheet (Figs 1, 3, 4 and 5). Participants are invited to use chemical data already available in their laboratory, if possible of different origins (e.g. rain and lake water), to become familiar with the data check approach.

4. References

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Table 1a. Suggested analytical methods for the surface waters and deposition water.
IC: Ion Chromatography; AAS: Atomic Absorption Spectrophotometry.

	Suggested method	References	Alternative method	References
Ammonium	Indophenol blue spectr.	Fresenius <i>et al.</i> 1988	IC	U.S.E.P.A. 1986; Tartari <i>et al.</i> 1995
Ca, Mg, Na, K	IC	U.S.E.P.A. 1986; Tartari <i>et al.</i> 1995	AAS, ICP	A.P.H.A. 1992 (3111 B)
Sulphate	IC	A.P.H.A. 1992; Durst <i>et al.</i> 1991	Methylthymol blue spectr.	A.P.H.A. 1992 (4500-SO4-F); Coloros <i>et al.</i> 1976
Nitrate	IC	A.P.H.A. 1992; Durst <i>et al.</i> 1991	Cd reduction, Salicylate spectr.	A.P.H.A. 1992 (4500-NO3-E); Rodier 1982.
Chloride	IC	A.P.H.A. 1992; Durst <i>et al.</i> 1991	Cd reduction, Diazoreaction Ferricyanide spectr.	A.P.H.A. 1992 (4500- NO3-F); A.P.H.A. 1992 (4500-Cl-E); Zall <i>et al.</i> 1956
Reactive P	Molybden blue spectr.	A.P.H.A. 1992 (4500 -P-E)		
Total P	Digestion, molybden blue spectr.	digestion: Valderrama 1981; measure: A.P.H.A. 1992 (4500 -P-E)		
Total N	Digestion, UV spectr.	digestion: Valderrama 1981; measure: A.P.H.A. 1992 (4500 -NO3-B)		
Reactive Si	Molibdosilicate, reduction to heteropoly blue	A.P.H.A. 1992 (4500-Si-E)		
Aluminium	Spectrometric method using pyrocatechol violet	ISO 10566:1994		
Aluminium fractions	Automatic Method for Fractionation and Determination of Aluminium Species in Fresh-Waters..	E.J.S. Røgeberg and A. Henriksen. Vatten 1985, 41 (1), 48 - 53		

Table 1b. International standard methods recommended in the draft ICP manual:

- EN-ISO 7887:1994 Water quality- Examination of colour.
- EN 25 813:1992 Water quality- Determination of dissolved oxygen- Iodometric method.
- EN 25 814:1992 Water quality- Determination of dissolved oxygen- Electrochemical probe method.
- EN 27 888:1993 Water quality- Determination of electrical conductivity.
- ISO 9963-2:1994 Water quality- Determination of alkalinity. Part 2. Determination of carbonate alkalinity.
- ISO 9964-1:1993 Water quality- Determination of sodium and potassium. Part 1. Determination of sodium by atomic absorption spectrometry.
- ISO 9964-2:1993 Water quality- Determination of sodium and potassium. Part 2. Determination of potassium by atomic absorption spectrometry.
- ISO 9964-3:1993 Water quality- Determination of sodium and potassium. Part 1. Determination of sodium and potassium by flame emission spectrometry.
- ISO 10523-1:1994 Water quality- Determination of pH.
- ISO 8245 Water quality- Guidelines for the determination of total organic carbon (TOC).
- ISO 10566:1994 Water quality- Determination of aluminium -Spectrometric method using pyrocatechol violet.
- For speciation of aluminium fractions, see e.g.: E.J.S. Røgeberg and A. Henriksen. An Automatic Method for Fractionation and Determination of Aluminium Species in Fresh-Waters. *Vatten* 1985, **41**(1), 48 - 53.
- ISO 10304-1:1992 Water quality- Determination of dissolved fluoride, chloride, nitrite, orthophosphate, nitrate and sulphate- Part 1. Method for water with low contamination.
- ISO 6878/1: 1986 Water quality- Determination of phosphorous - Part 1: Ammonium molybdate spectrometric method.
- ISO/DIS 11732: Water quality- Determination of ammonium nitrogen by flow analysis and spectrometric detection.
- ISO/DIS 13395: Water quality- Determination of nitrate and nitrite nitrogen and the sum of both by flow analysis.
- ISO/DIS 11905-1: Water quality- Determination of nitrogen - Part 1: Method using oxidative digestion with peroxodisulfate.

Information of the ISO/CEN methods listed above can be obtained from :

- a. The national standardisation agencies.
- b. International Organisation for Standardisation, DIN, Burggrafenstrasse 6, 10787 Berlin, Germany.
- c. ISO International Organisation for Standardisation, Case Postale 56, CH-1211 Genève, Switzerland.
- d. CEN European Committee for Standardisation, rue de Stassart 36, B-1050 Brussels, Belgium.

Table 2. Main in-laboratory Analytical Quality Control.

Testing facilities, organization and personnel	
Sampling and storage	
Assessment of the analytical methods used	<ul style="list-style-type: none"> ● interlaboratory testing programs ● reference materials
Statistical quality control	control chart (internal standards)
Apparatus, chemicals, reagents, and blanks	
Documentation	<ul style="list-style-type: none"> ● methods ● work-sheets ● notebook
Checking of results	<ul style="list-style-type: none"> ● ion balance ● comparison between measured and calculated conductivity ● relationship among ions
Reporting of results	<ul style="list-style-type: none"> ● not computerized ● computerized
Archiving of results	

Table 3. EMERGE research. Transmission form of chemical data.

	Lake	Rain	Code	Units	N. decimals	Results
Lake/site number	L	R				
Name of the lake/site	L	R				
Date starting		R	DATE			
Date ending		R	DATE			
Sampling date	L		DATE			
Number depth sampled	L					
Volume		R	Vol	mm	0	
pH	L	R	pH		2	
Conductivity 25°C	L	R	Cond	$\mu\text{S cm}^{-1} 25^\circ\text{C}$	1	
Ammonium	L	R	NH ₄ -N	$\mu\text{g N l}^{-1}$	0	
Calcium	L	R	Ca	mg l^{-1}	2	
Magnesium	L	R	Mg	mg l^{-1}	2	
Sodium	L	R	Na	mg l^{-1}	2	
Potassium	L	R	K	mg l^{-1}	2	
Alkalinity	L	R	Alk	$\mu\text{eq l}^{-1}$	0	
Sulphate	L	R	SO ₄	$\text{mg SO}_4 \text{l}^{-1}$	2	
Nitrate	L	R	NO ₃ -N	$\mu\text{g N l}^{-1}$	0	
Chloride	L	R	Cl	mg l^{-1}	2	
Total nitrogen	L		TN	$\mu\text{g N l}^{-1}$	0	
Tot. phosphorus	L		TP	$\mu\text{g P l}^{-1}$	0	
React. phosphorus		R	RP	$\mu\text{g P l}^{-1}$	0	
Tot. org. carbon	L		TOC	mg C l^{-1}	2	
Silica						
Optional components						
Tot. Aluminium	L		*TAI	$\mu\text{g l}^{-1}$	0	
React. Al	L		*RAI	$\mu\text{g l}^{-1}$	0	
Labile Al	L		*ILAI	$\mu\text{g l}^{-1}$	0	
Labile Al	L		*LAI	$\mu\text{g l}^{-1}$	0	
Fluoride	L		F	$\mu\text{g l}^{-1}$	0	
Cadmium	L	R	*Cd	$\mu\text{g l}^{-1}$	2	
Lead	L	R	*Pb	$\mu\text{g l}^{-1}$	2	
Copper	L	R	*Cu	$\mu\text{g l}^{-1}$	2	
Cobalt	L	R	*Co	$\mu\text{g l}^{-1}$	2	
Mercury	L	R	*Hg	ng l^{-1}	2	

* = some of the measurements performed by the NIVA laboratory.

** = measurement performed by the NILU laboratory

Table 4. Factors to transform concentrations used in the electronic sheet in $\mu\text{eq l}^{-1}$ and values of equivalent conductances.

	Code	Units	Factor to $\mu\text{eq l}^{-1}$	Equivalent conductance at 20°C $\text{kS cm}^2 \text{eq}^{-1}$	Equivalent conductance at 25°C $\text{kS cm}^2 \text{eq}^{-1}$
pH	pH		$10^6 * 10^{-\text{pH}}$	0.3151	0.3500
Ammonium	$\text{NH}_4\text{-N}$	$\mu\text{g N l}^{-1}$	0.07139	0.0670	0.0735
Calcium	Ca	mg l^{-1}	49.9	0.0543	0.0595
Magnesium	Mg	mg l^{-1}	82.24	0.0486	0.0531
Sodium	Na	mg l^{-1}	43.48	0.0459	0.0501
Potassium	K	mg l^{-1}	25.58	0.0670	0.0735
Alkalinity	Alk	$\mu\text{eq l}^{-1}$	1	0.0394	0.0445
Sulphate	SO_4	$\text{mg SO}_4 \text{l}^{-1}$	20.82	0.0712	0.0800
Nitrate	$\text{NO}_3\text{-N}$	$\mu\text{g N l}^{-1}$	0.07139	0.0636	0.0714
Chloride	Cl	mg l^{-1}	28.2	0.0680	0.0764
Fluoride	F	$\mu\text{g l}^{-1}$	0.05263	0.0491	0.0544

Table 5. Score of the analyses on the basis of the percent difference in ionic balance (PD) and of the total ion concentrations (IS in $\mu\text{eq l}^{-1}$; from Schaug 1988).

Sample category	1	2	3
IS < 50	PD ≤ 60	PD > 60	-
50 ≤ IS < 100	PD ≤ 30	30 < PD ≤ 60	PD > 60
100 ≤ IS < 500	PD ≤ 15	15 < PD ≤ 30	PD > 30
IS > 500	PD ≤ 10	10 < PD ≤ 20	PD > 20

Table 6. Chemical composition of the sample of Lake Maggiore and of atmospheric deposition used for the evaluation of the relationship between conductivity and temperature. Temperature coefficient of the ion mobility ($^{\circ}\text{C}^{-1}$, from Pungor 1965). (For units see table 4.)

Variables	Rain	L. Maggiore	Alpine lakes	% Diff. / $^{\circ}\text{C}$
pH	4.28	8.10	6.48	
Cond	37	128	11	
H^+	52	0	0	1.54
Ca^{++}	14	958	65	2.54
Mg^{++}	8	251	11	2.54
Na^+	26	106	10	2.44
K^+	3	30	6	2.17
N-NH_4^+	41	0	0	2.08
Alk	0	709	17	
SO_4^-	79	541	44	2.30
N-NO_3^-	41	49	26	2.05
Cl^-	27	50	3	2.16
Σ An	147	1349	90	
Σ Cat	144	1345	92	

Table 7. Score of the analyses on the basis of the percent difference between measured and calculated conductivity (CD), in relation with measured conductivity ($\mu\text{S cm}^{-1}$ at 20°C , from Schaug 1988).

Sample category	1	2	3
$\text{CM} \leq 30$	$\text{CD} \leq 30$	$\text{CD} > 30$	-
$\text{CM} > 30$	$\text{CD} \leq 20$	$20 < \text{CD} \leq 40$	$\text{CD} > 40$

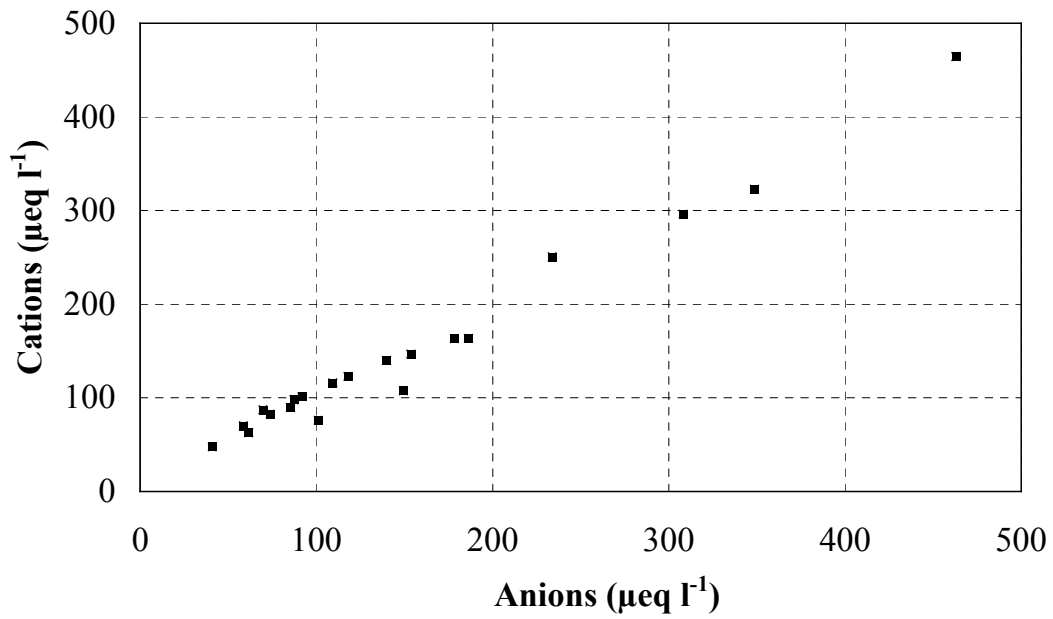


Figure 1. Plot of Σ cations vs Σ anions for the AL:PE lakes (data collected in 1993).

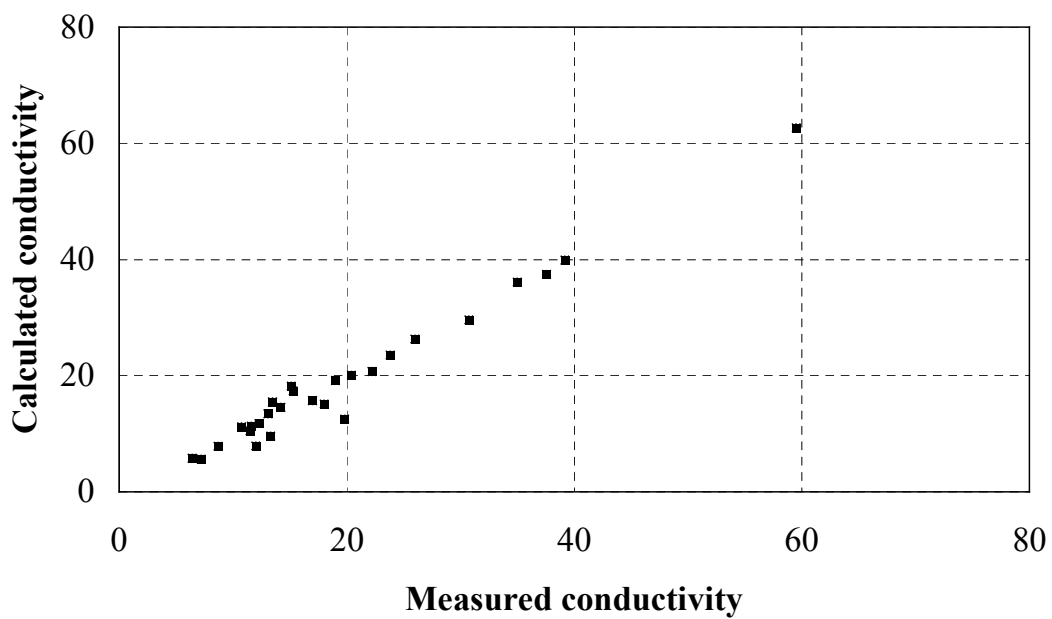


Figure 3. Plot of calculated vs measured conductivity ($\mu\text{S cm}^{-1}$ at 25°C) for the AL:PE lakes (data collected in 1993).

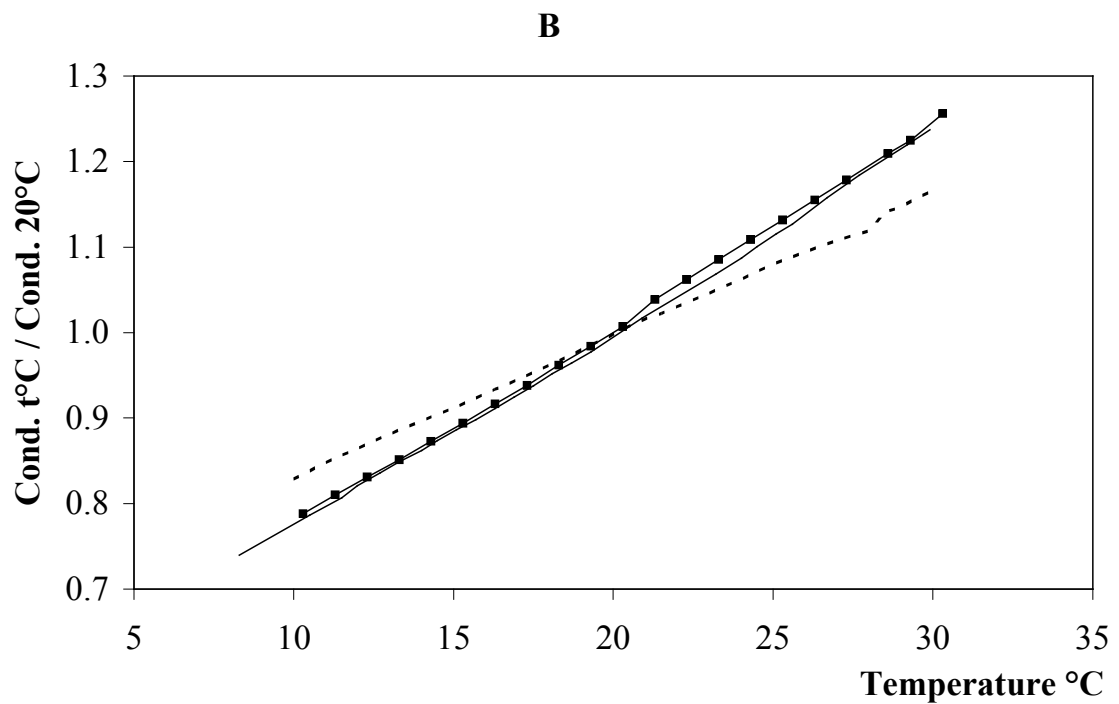
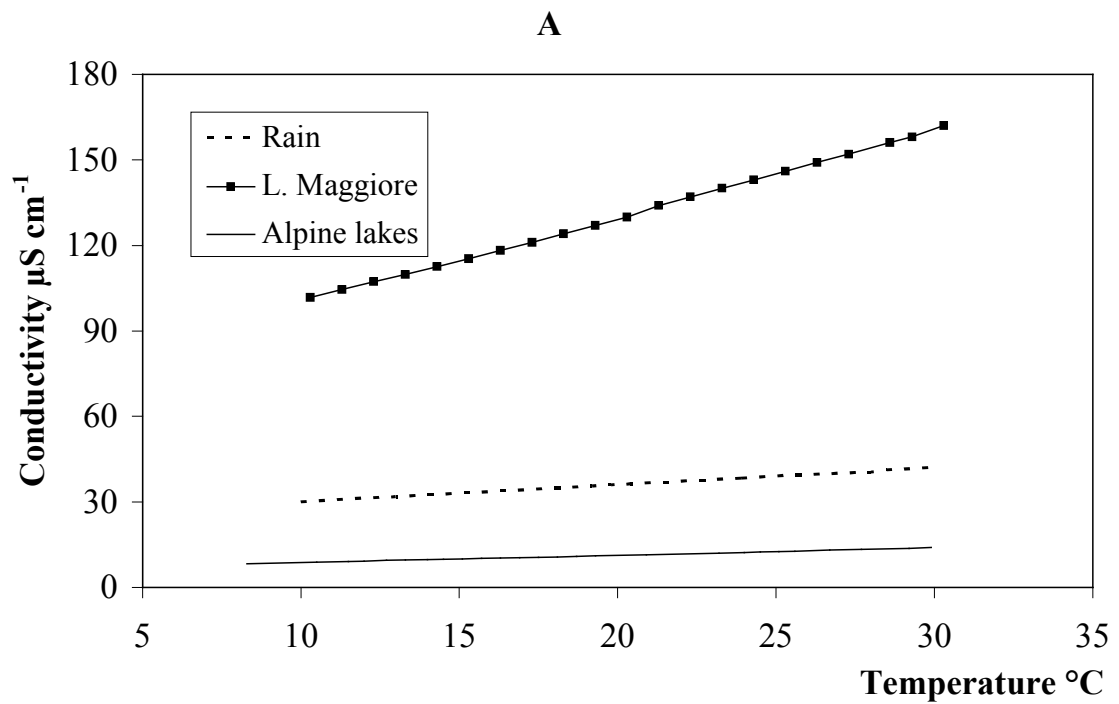


Figure 2. Relationship between conductivity and temperature of different waters. Absolute values (A) and values relative to the temperature of 20°C (B).

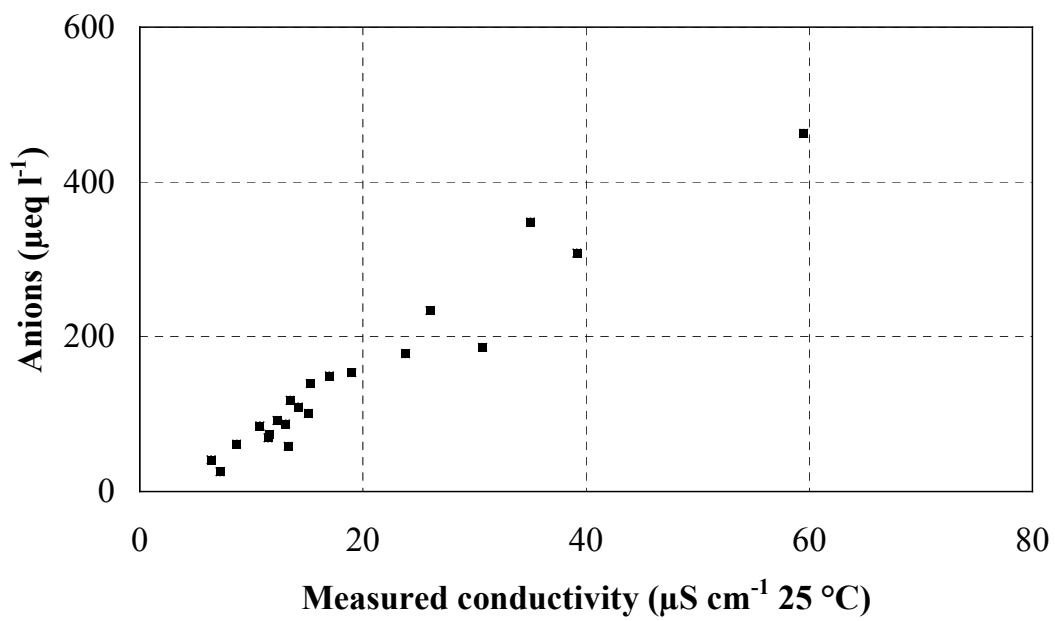


Figure 4. Plot of Σ anions vs measured conductivity for the AL:PE lakes (data collected in 1993).

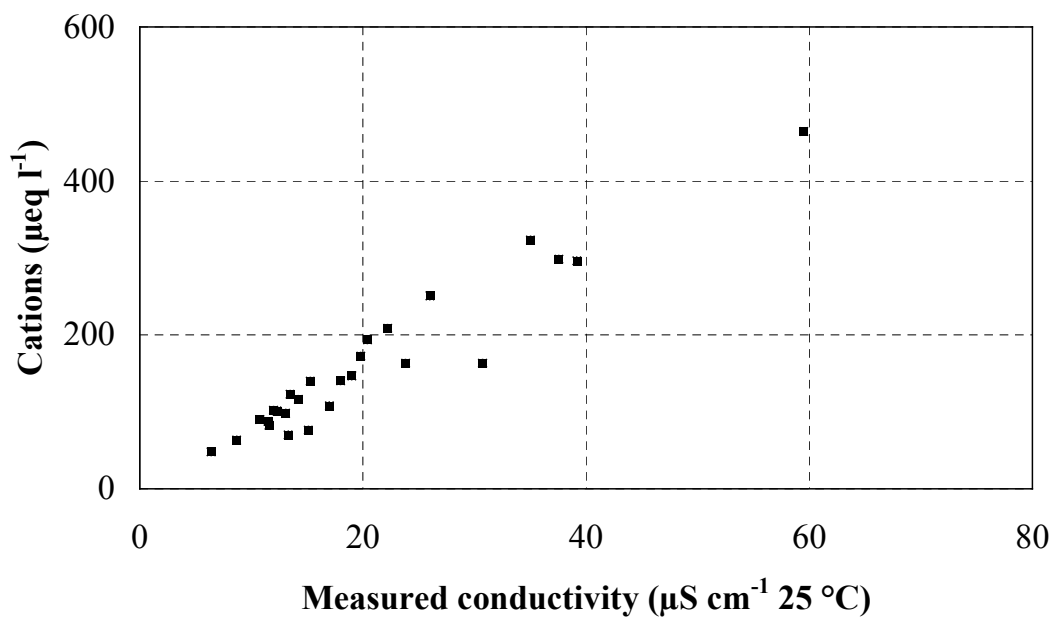


Figure 5. Plot of Σ cations vs measured conductivity for the AL:PE lakes (data collected in 1993).