

**Pirkko Kortelainen**

**Contribution of organic acids to the acidity of Finnish lakes**

Yhteenveto: Orgaanisten happojen merkitys Suomen järvien happamuuteen



# 13

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## Contents

1	Introduction	5
1.1	Peatlands and forested catchments as the source of organic carbon in surface waters	5
1.2	Organic acids and approaches for estimating organic acidity	6
1.3	Development of research on organic acidity	8
1.3.1	Unreliable ion balance calculations	8
1.3.2	Problems in alkalinity determinations	9
1.3.3	Overemphasis of natural acidification	9
1.3.4	Research on organic acidity in Finnish lakes	10
1.4	Objectives of this study	11
2	Materials and methods	12
2.1	The Finnish Lake Survey	12
2.1.1	Selection of lakes and field sampling	12
2.1.2	Catchment characteristics	12
2.1.3	Chemical measurements	12
2.2	Other data bases	13
2.3	Approaches for estimating organic acidity	14
2.3.1	Model approach	14
2.3.2	Empirical measurements	14
2.3.3	Ion balance calculations	16
2.4	Estimation of the organic anion contribution to Gran alkalinity	17
3	Organic carbon concentrations in Finnish lakes vs. catchment	18
3.1	Organic carbon concentrations in the lakes	18
3.2	Relationships between TOC, colour and $COD_{Mn}$	21
3.3	Catchment characteristics as predictors of lake TOC content	21
4	Organic acidity in lakes	23
4.1	Acid/base characteristics of organic carbon and the dissociation of organic acids	23
4.2	Comparison and uncertainties of the organic acidity approaches	25
4.3	Impact of acidification on organic carbon concentrations and on the dissociation of organic acids	28
4.4	Contribution of organic acids to the acidity of Finnish lakes	29
4.4.1	Acid deposition vs. organic acids from the catchments	29
4.4.2	Regional acidification of Finnish lakes	30
4.4.3	Major anion ratios in lakes: organic anion vs. non-marine sulphate	32
4.5	The effect of organic carbon on alkalinity	34
5	Conclusions	37
	Acknowledgements	38
	Yhteenveto	39
	References	40
	Summarized publications	48



## CONTRIBUTION OF ORGANIC ACIDS TO THE ACIDITY OF FINNISH LAKES

Pirkko Kortelainen

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This study provides a comprehensive assessment of the contribution of organic carbon and organic acids to the acid-base status of Finnish lakes, summarizing empirical organic acidity measurements (from 16 lakes) combined with the Finnish Lake Survey data set (978 lakes sampled in autumn 1987). Due to the random selection of the lakes the high median total organic carbon (TOC=12 mg l<sup>-1</sup>) and colour (100 mg l<sup>-1</sup> Pt) can be considered representative for small lakes in Finland. Latitude and the proportion of the catchment covered by peatlands were the most important catchment variables determining TOC concentrations in the lakes. In northern regions TOC concentrations were low compared with central and southern Finland, despite a high proportion of peatlands. Organic carbon in Finnish lakes was dominated by organic acids, averaging about 84 % of DOC (dissolved organic carbon) with smaller amounts of neutral and basic components. In forested, peatland-dominated regions the mean annual leaching of organic acids was calculated to exceed the mean annual deposition of anthropogenic acids. The average total acidity of organic carbon (at pH values existing in natural waters) was 9.7 µeq (mg DOC)<sup>-1</sup>. The average dissociation of organic acids increased with increasing pH from about 48 % at pH 4 to about 92 % at pH 7, supporting the use of pK<sub>a</sub> 4 as an average pK<sub>a</sub> value for organic acids. Organic acids reduce pH (median pH 6.3) and total buffer capacity in Finnish lakes. Each milligram of TOC per liter was estimated to lower Gran alkalinity by about 5 µeq. The median acid-neutralizing capacity provided by organic anions during Gran alkalinity titrations was estimated to be 1.6 µeq (mg TOC)<sup>-1</sup>. Considerable effort was devoted to the development of an empirical model for organic anion, the dissociation product of organic acids, based on fractionations of DOC and titrations of isolated organic acids. Using the Finnish Lake Survey data base the developed model well agreed with the two most widely used methods of estimating organic acidity: 1) the charge balance approach and 2) the model of Oliver et al. (1983). Organic anion, estimated by any of the three approaches, was the dominant anion in Finnish lakes. In most areas in Finland catchment-derived organic acidity in lakes exceeded the anthropogenic acidity. In the highest deposition area in southern Finland minerogenic acidity was more important.

Keywords: Organic carbon, organic acidity, buffer capacity, lakes, catchment

### 1 INTRODUCTION

#### 1.1 Peatlands and forested catchments as the source of organic carbon in surface waters

Humic brown coloured lakes are common in temperate and cold regions in the boreal

landscape. Terrestrial ecosystems are the primary source of aquatic humus, although decomposition products of aquatic organisms may be important in some cases (Wetzel 1975, Thurman 1985, Mulholland et al. 1990). Vegetation and hydrological conditions are important factors contribu-

ting to the leaching of organic carbon. Wetlands are proposed as the dominant organic carbon source for surface waters (Hemond 1990b, Mulholland et al. 1990). Due to a high water content throughout the year subsurface runoff is dominant, which facilitates leaching of organic carbon.

High organic carbon concentrations are also frequently found in the soil solutions in the organic horizon of mineral soils, especially in coniferous forests (e.g. Cronan and Aiken 1985). The highest concentrations are found in subsurface horizons (Hemond 1990b). Concentrations decline sharply in lower soil horizons, primarily because of adsorption/co-precipitation in mineral soils with iron and aluminium (e.g. McDowell and Wood 1984). Organic carbon concentrations in runoff waters from well drained mineral soils are, however, usually much lower than in those from wetlands (Mulholland and Kuenzler 1979, Hemond 1990b, David and Vance 1991). Organic carbon adsorption in mineral soils has been suggested to be an important mechanism controlling organic carbon transport and leaching, and consequently the buffering of dissolved organic carbon concentrations in surface waters (e.g. Jardine et al. 1989, Hemond 1990b, Vance and David 1991, David et al. 1992). The primary source of organic carbon reaching surface waters is organic-rich surface soils, whereas the lower soils appear to be a sink. The pathways by which water, and consequently organic carbon is transported from terrestrial environments are still incompletely quantified (Hemond 1990b, Mulholland et al. 1990). Most studies have concentrated on only one environment: either wetlands, soils, groundwater or surface waters. Consequently, many of the linkages and transformation processes require further study.

The vast majority of aquatic ecosystems in the world have dissolved organic carbon (DOC) concentrations falling within the range of 0.5 to 50 mg l<sup>-1</sup>. The variability of DOC concentrations is lower than that of many other water quality parameters (Mulholland et al. 1990). Small aquatic ecosystems, e.g. small rivers are more variable in DOC concentrations than large rivers (Sedell and Dahm 1990). Organic carbon is a typical runoff-dependent variable, the variations of which are strongly affected by patterns of DOC transport from terrestrial to aquatic ecosystems (Cronan 1990).

High humic matter concentration can impart several physical and chemical characteristics that are not found in clearwater habitats. These may have major implications for ecosystem structure and function. Humic matter has a strong influence on the optical properties of surface waters, and consequently on photosynthetic processes. The recent results of the research project "Food chains of humic lakes" have shown that dissolved organic matter provides a major energy source in aquatic ecosystems (Salonen et al. 1992). Complexation of humic matter with nutrients, metals and trace elements strongly regulates their transport, biological availability and toxicity (e.g. Reuter and Perdue 1977, Bergkvist et al. 1989, Kukkonen 1991, LaZerte 1991).

## 1.2 Organic acids and approaches for estimating organic acidity

Organic acids are the most important fraction of the total pool of dissolved organic matter and dissolved organic carbon in natural waters (e.g. McKnight et al. 1985, David and Vance 1991). The bulk of the DOC and the highly complex mixture of organic acids is made up of complex substances that are commonly known as humic and fulvic acids. The basic definitions of humic substances are operational, based on the procedures used for their isolation. The classification is based on the solubility of humic substances in acids and bases; fulvic acids (soluble at all pH values) and humic acids (soluble above pH 2). The simple low molecular weight compounds such as acetic, oxalic, and lactic acids typically account for only a few percentage of the DOC and a correspondingly small fraction of the organic acidity (McKnight et al. 1990).

The role of catchment derived organic acids in the acidification of surface waters has been widely debated. This controversy is largely due to an inability to accurately characterize these complex constituents. There is no method presently available for the direct determination of "total organic acids" (Glaze et al. 1990). Numerous workers have found organic acidity in surface waters to correlate with DOC. Reasonable data bases including DOC exist; however, if the data base is restricted to those measurements explicitly intended to assess organic acidity, far less



information is available. DOC or TOC (total organic carbon) can, however, be considered as bulk parameters for organic molecules similar to conductivity for inorganic compounds.

Humic substances have an effect on the anion-cation charge balance among dissolved solutes. The various acids in surface waters can be identified by measuring the corresponding anions. The main source of strong acid anions, sulphate and nitrate, is anthropogenic deposition. Organic anion representing the natural acidity is derived from peatlands or organic soils in catchments. Because all empirical methods of measuring organic acidity are laborious and consequently not applicable to routine water sample analysis, the contribution of organic acids to surface water acidity has been estimated indirectly. Large-scale surveys both in North America and northern Europe that have documented the contribution of organic acids to the surface water acidity have used two indirect approaches, based on different assumptions, either a charge balance approach or the model of Oliver et al. (1983). In Norway (Henriksen et al. 1988a, 1988b) the charge balance approach was used. In the Eastern Lake Survey in the U.S.A. (Brakke et al. 1988, Eilers et al. 1988a, Eilers et al. 1988b, Driscoll et al. 1989) and in Canada (e.g. Jeffries et al. 1986, Wilkinson et al. 1992) results using both the methods have been presented.

Ion balance calculations are based on the principle of electroneutrality. In clear water lakes the concentrations of inorganic anions and cations are balanced. Using solution cation-anion charge balances, an estimate of the organic anion contribution to the acidity can be defined by the anion deficit. This approach is based on the assumption that the positively charged cations which are not balanced by inorganic anions are derived from organic anions, the dissociation product of organic acids. The model of Oliver et al. (1983) is based on an organic acid dissociation model (Gamble 1970, Perdue et al. 1980) that was calibrated from titrations of isolated organic acids. It requires only DOC and pH measurements from a natural water sample and provides an estimate for organic anion.

The empirical approach for determining organic acidity usually includes the following steps: fractionation, isolation, concentration, purification and titration. The isolation and purification of DOC is essential to separate

organic solutes from inorganic salts and contaminants. The above steps are also essential because many experimental methods are not sensitive enough to measure properties of organic acids at natural concentration levels, and natural organic acid mixtures are too complex to characterize in bulk (Glaze et al. 1990). A wide range of procedures have been used to fractionate and isolate organic acids from natural waters. For over a decade, the method of choice for isolation of the organic acids from surface waters has been sorption onto XAD-8 macroporous resins (Aiken 1985). For example, the isolation of humic and fulvic acids is based on XAD-8 resins. Moreover, the model of Oliver et al. (1983) was based on titrations of isolated humic and fulvic acids. When the XAD extracts are titrated with standard base to pH 7–8 the acidity is mainly due to carboxylic acids. If the titration is continued to over pH 10, additional weak acids such as phenols are neutralized (e.g. Perdue et al. 1984).

The XAD-8 resin technique has been criticized because it extracts only about 45–70 % of the total dissolved carbon (Shuman 1990). The fraction that passes through the resin has high carboxyl acidity. In the early 1980's Leenheer (1981) developed a procedure for isolation and fractionation of DOC from natural waters based on an earlier fractionation procedure (Leenheer and Huffman 1976, 1979). This procedure using the XAD-8 method in combination with cation- and anion-exchange resins provides fractionation of organic carbon into acidic, basic, and neutral components as well as isolation of acidic components. The advantage of this procedure is that a higher percentage of DOC can be isolated compared with the frequently used humic-fulvic acid isolation. Moreover, the most acidic part of DOC, the hydrophilic acids, are not lost.

Since the work of Oliver et al. (1983), there has been only a few attempts to measure organic acidity empirically. McKnight et al. (1985) presented an empirically measured organic anion for two samples from Thoreau's Bog. Recently David and Vance (1991) developed an empirical measure for organic anion in a water sample relying on fractionations of DOC and titrations of isolated organic acids following a modified procedure of Leenheer (1981). The same empirical approach has been used by David et al. (1991), Vance and David (1991), Kortelainen et al. (1992) and Roila et al. (1993a).

### 1.3 Development of research on organic acidity

Since Oden (1968) recognized the widespread ecological consequences of long-range transport of acidic air pollutants, understanding of the environmental effects of acidic deposition has grown tremendously. Over the past two decades acidification (defined as the loss of acid neutralizing capacity) has been one of the central issues in environmental research. Extensive research programmes have been conducted in many European and North American countries. The long-range transport of pollutants has made acidification an international problem, and has resulted in extensive cooperation in both research and environmental policy. Lake acidification is recognized as a severe environmental problem e.g. in some parts of Sweden (Naturvårdsverket 1986), Norway (Henriksen et al. 1988b, Henriksen et al. 1989), Canada (e.g. Jeffries et al. 1986, Neary and Dillon 1988) and the United States (Landers et al. 1988, Schindler et al. 1989). The experimental acidification of lakes by Schindler and his colleagues (Schindler et al. 1980, 1985) and of entire catchments by Wright and his coworkers (Wright et al. 1988) has provided important new insights.

Research on anthropogenic acidification of susceptible freshwaters and soils is well documented, but early research on natural ecosystem acidification is much less well known (Gorham 1989). Thaer (1810) first thought of sour humus as a distinct acid. The presence of more complex "humic" acids in soil was demonstrated by Sprengel (1826) and Oden (1912). Salisbury (1922) found that in forest soil, organic matter declines sharply downward in soil profiles resulting in the highest acidity and lowest pH at the surface. Causes of acidity in humic waters have long been argued. Carbon dioxide was designated as the major cause by Stremme (1908), but later workers, dealing with well stirred surface pools in bogs with pH around 4, found that acidity changed little on boiling or stirring with CO<sub>2</sub>-free air or nitrogen. Thompson et al. (1927) observed a distinct correlation between acidity and both organic matter and colour in bog waters. They concluded that the amount of organic matter appears to be the controlling factor of acidity.

#### 1.3.1 Unreliable ion balance calculations

The importance of humic substances for the ion balance of natural waters was already recognised in the 1950's (Ohle 1955). However, the charge balance approach for the estimation of organic anion concentrations in surface waters has been used successfully only during the past decade since reliable ion chromatographic results for sulphate and chloride have been available. Coloured organic matter can cause interference in many analytical methods based on colorimetric measurements. In the acidification research this has been especially obvious in the case of sulphate. Earlier colorimetric methods for sulphate have been shown to be inaccurate for coloured waters and thus cannot be compared with the present measurements based on ion chromatography (Cronan 1979, Cheam et al. 1984, Kerekes et al. 1984, Gorham and Detenbeck 1986, Jones et al. 1986). In recent studies many colorimetric methods have been shown to overestimate the true sulphate concentrations in coloured waters, whereas ion chromatographic results from organic coloured waters have been shown to be reliable (Cheam and Chau 1987).

The problems in sulphate analysis have led to a revision of ideas about the sources of acidity in bog waters (Gorham and Detenbeck 1986). In numerous earlier papers by Gorham and coworkers dealing with the dissolved major ions in ombrotrophic bog waters and in lake waters influenced by runoff from bogs (e.g. Gorham 1956, 1957a, b, c, Gorham and Cragg 1960, Tolpa and Gorham 1961), sulphate was measured by the colorimetric Mackereth's method (Mackereth 1955). In a recent paper Gorham and Detenbeck (1986) concluded that coloured organic anions are measured along with sulphate by Mackereth's method, and that the inferences made earlier by Gorham, concerning sulphuric acid as a major cause of acidity in pristine bogs, are invalid.

Using reliable ion chromatographic results for sulphate in conjunction with other inorganic cation/anion measurements, it was demonstrated that North American bog waters also exhibited a distinct deficit in anion that correlated significantly with dissolved organic carbon. Organic anions, estimated by anion deficit, have been found to be the dominant anion in many bog waters (e.g. Hemond 1980, Gorham et al. 1985).

Furthermore, following oxidation of organic compounds by UV-radiation, the cation and inorganic anion sums have become essentially equal. Moreover, the pH of the samples in which organic matter has been decomposed clearly increased (Hemond 1980, Gorham et al. 1985, Eshleman and Hemond 1985). These results have been considered as indicating that organic acids are responsible for most of the observed acidity in such waters.

### 1.3.2 Problems in alkalinity determinations

Acid neutralizing capacity (ANC) is generally regarded as a more suitable index of a natural water's acid-base status than pH because it is considered not to vary with transient (e.g. diurnal) changes in total inorganic carbon content (e.g. Hemond 1990a). Acidic waters have been defined as having ANC values less than zero, and acidification is often quantified by decreases in ANC. Operationally, ANC has been defined as the equivalent sum of all bases in a solution that can be titrated with standardized strong acid to a preselected end point (Stumm and Morgan 1981), i.e. the amount of acid consumed is the measure of the amount of alkalinity present. The endpoint of the titration is either assumed to occur at a fixed endpoint pH (generally pH 4.5) or the equivalence point is determined using Gran titration (Gran 1952).

In low alkalinity waters the equivalence point in Gran titration is difficult to determine. The equivalence pH of the alkalinity titration depends on the CO<sub>2</sub> concentration at this point, whereas the CO<sub>2</sub> concentration itself depends on the total concentration of the carbonate system. Consequently, the endpoint of the alkalinity titration depends on the alkalinity to be determined and the equivalence pH is a function of the alkalinity (Henriksen 1982, Reynolds and Neal 1987). In waters containing high concentrations of total inorganic carbon, the endpoint is close to pH 4.5. However, in waters with alkalinity of 100 µeq l<sup>-1</sup> the equivalence pH is 5.15 (Henriksen 1982). At the low alkalinities normally encountered in areas sensitive to acidification the earlier widely used fixed end-point method (titration to pH 4.5) thus overestimates the true bicarbonate alkalinity (Henriksen 1982, Reynolds and Neal 1987).

Organic carbon in natural waters is both a

natural background source of acidity and a pH buffer in low alkalinity waters (e.g. Perdue and Gjessing 1990). The acid-base properties of the organic acid mixture have been difficult to describe quantitatively (Perdue 1985). Organic acids are a complex mixture of different acids which dissociate across a wide pH range but are never totally dissociated and never totally protonated at any pH value in natural waters. Strong acids are always completely dissociated in aqueous solutions. At a given pH weak acids are defined as those acids which are less than 100 % dissociated (see Publication I for a review). The dissociation of weak acids is determined by their pK<sub>a</sub> values. The dissociation of an organic acid mixture (in natural waters and during acid/base titrations in the laboratory) is a function of the pK<sub>a</sub> value distribution of the acidic functional groups (Perdue et al. 1984).

In some studies ANC has been calculated as a difference between base cations and strong acid anions. The discrepancy between calculated and measured alkalinity has been found to be greatest for waters with high concentrations of DOC and aluminium (Sullivan et al. 1989). The interference of humic matter in the titrimetric determinations of inorganic carbon content of natural waters was recognized previously by Wilson (1979). However, only very recently, when the large-scale acidification research programmes in most countries had already finished, was the organic carbon contribution to Gran alkalinity titrations examined by theoretical calculations (Cantrell et al. 1990, Hemond 1990a).

### 1.3.3 Overemphasis of natural acidification

Rosenqvist (1978) and Krug and Frink (1983) suggested that lakes and streams in the north-eastern United States and southern Scandinavia that have high mineral acidity had, before acidic deposition, high concentrations of DOC and were acidified by natural organic acids. Rosenqvist (1978) proposed that natural acid-forming processes in the soil (such as carbonic and organic acid formation and the uptake of base cations by vegetation) often far exceed acid inputs in acid precipitation. He suggested that these processes can lead to surface water acidification, and argued that soil-derived acids themselves can cause surface water acidification and that acid

precipitation is not required to explain it. Krug and Frink (1983) proposed a 2-step hypothesis for the changes in soil water caused by acid deposition: 1) increased acidity decreases the solubility of humic acids, and 2) sulphuric acid in rain should increase the flux of sulphate and decrease the flux of organic anions, with little or no measurable change in pH. They therefore suggested that decreasing acid deposition will not significantly affect runoff pH, but that anthropogenic mineral acidity would be replaced by natural, mostly organic, acidity.

Natural acidification of soils by evolution of vegetation is without doubt an important source of surface water acidification, but it cannot be accepted as the only cause. Natural acidification in freshwaters and in their catchments is a rather well documented process. Wetlands provide a rich medium for the production and accumulation of acid organic matter. In many upland catchments, evolution of highly acidic soils and drainage waters is a natural process, particularly in the case of podzolization (e.g. Petersen 1980). The development of coniferous woods, which is favoured by cool climates, also results in accumulation of coarse, acid humic materials in the soil.

Many studies have demonstrated that the chemistry of many surface waters is dominated by organic acidity. On an extensive scale, however, the evidence points towards a prominent role for atmospheric deposition in controlling surface water acidity in sensitive high deposition areas (Jones et al. 1986). This evidence for recent acidification comes from both paleolimnological studies (e.g. Davis et al. 1983, Battarbee et al. 1985, Dixit et al. 1988, Steinberg et al. 1988) and recent regional surveys. Analyses of extensive data sets show reasonably good relationships between estimated sulphate deposition and lake sulphate levels (Rapp et al. 1985, Thompson and Hutton 1985, Henriksen et al. 1988b, Neary and Dillon 1988, Sullivan et al. 1988). Evidence from field studies generally does not support the proposal of Krug and Frink (1983) that soil and surface water pH changes little or not at all with acid deposition due to a complete replacement of organic anions by sulphate. Although some replacement of organic anions by sulphate appears to occur, its importance is probably less than that suggested by Krug and Frink (1983). Moreover, a shift from organic acid controlled low or negative

ANC to mineral acidity is generally accompanied by a large change in toxicity to biota, e.g. due to a shift from organically complexed Al to free and inorganically complexed forms (Marmorek et al. 1989).

#### 1.3.4 Research on organic acidity in Finnish lakes

In Finland the cold climate and flat topography provide favourable conditions for organic matter accumulation. Peatlands cover about one third of the land area, a higher percentage of the total land area than in any other country. Ditching and draining of peatlands has also been more extensive than in other countries. The area drained for forestry, including paludified upland forests is approximately 5.7 million ha (Päivänen and Paavilainen 1990), which is almost half the area of peatlands drained for forestry in boreal and temperate regions. Coniferous forests are predominant, and 87 % of the total land area is presently classified as forestry land (Aarne 1992). Mineral forest soils are mainly podzols or are podzolized, and derived from base-poor rocks, mainly granite.

Awareness of the potential importance of dissolved organic matter in surface waters developed relatively early in Finland. A classification scheme for lakes developed by Järnefelt (1952) was based on eutrophy and colour. High TOC, colour or  $\text{COD}_{\text{Mn}}$  (chemical oxygen demand) concentrations have been demonstrated in Finnish rivers (Laaksonen 1970, Wartiovaara 1978, Alasaarela and Heinonen 1984, Pitkänen 1986, Heikkinen 1992) and in runoff waters from small lakeless catchments (Kauppi 1975, Sallantausta 1986). The mean total organic carbon concentration was above  $10 \text{ mg l}^{-1}$  in 18 out of the 21 rivers flowing to the Baltic Sea during the years 1974–76 (Wartiovaara 1978). The catchments of these rivers cover about two-thirds of the total land area of Finland. In North American rivers organic carbon concentrations higher than  $10 \text{ mg l}^{-1}$  are reached mainly in peat-rich areas such as Florida, South Carolina and Ontario (Mulholland and Watts 1982).

Laaksonen (1970) found a negative relationship between  $\text{COD}_{\text{Mn}}$  and pH or alkalinity in Finnish rivers. The lowest pH values were found in regions where  $\text{COD}_{\text{Mn}}$  contents were the highest.

Moreover the lowest pH values were found during time periods when  $\text{COD}_{\text{Mn}}$  concentrations were highest. Using monitoring data from large lakes in Finland, Laaksonen and Malin (1984) concluded that the concentration of cations was 4.0 % higher than that of anions during the period 1968–1970, but that by 1981–1983 this discrepancy had increased to 11.5 %. They ascribed this to the adherence of the "excess cations" on the surface of humus colloids; during the observation period water colour increased by an average of 8.2 %. The important role of humic matter in the acidity of small Finnish lakes was suggested by Kortelainen and Mannio (1987). They calculated charge balances for 73 forest lakes and found anion deficits in humic lakes. Including the organic anions estimated by the model of Oliver et al. (1983) yielded good ion balances for humic lakes. In a literature review by Kortelainen (1987) the current knowledge about different approaches for organic acidity assessment as well as the role of organic acidity in surface water acidification were summarized. Paleolimnological studies have indicated that some acidic lakes in high deposition areas in southern Finland have only recently been acidified. In low deposition areas in central and northern Finland naturally acidic lakes were more common (e.g. Simola et al. 1985, Tolonen et al. 1986, Huttunen et al. 1990). Recently, Sallantausta (1992) has emphasized the dominant role of organic acidity in runoff waters from peatlands.

The Finnish Acidification Research Programme, HAPRO, was launched in 1985. Studies conducted under the HAPRO programme as well as some earlier smaller-scale studies have shown that acidification of surface waters is common throughout the country in sensitive terrains (see Forsius 1992 for a review). A lake survey based on statistically selected lakes covering the entire country was conducted in 1987 as part of the HAPRO programme. The selection of lakes, regional estimates of lake acidification, critical loads and trace metal distribution in the lakes have been extensively evaluated (Forsius et al. 1990a, Forsius et al. 1990b, Verta et al. 1990, Forsius et al. 1992, Mannio et al. 1992, Kämäri et al. 1993, Posch et al. 1993). Forsius (1992) calculated that acidic lakes ( $\text{ANC} \leq 0$ ) in Finland constitute a significant proportion of the total number of lakes (12 % of the frame population). The critical load for sulphur was exceeded in

about one third of the lakes and the critical load for nitrogen in about 10 % of the lakes.

#### 1.4 Objectives of this study

High organic carbon concentrations in Finnish surface waters suggested an important role of humic matter to the acidity of the lakes. Consequently a comprehensive assessment of the contribution of organic acids to the acidity of Finnish lakes was outlined. On the basis of an earlier small-scale study (Publication II) the Finnish Lake Survey was designed to evaluate the contribution of organic acidity to the acidity of the lakes and to assess the impact of catchment characteristics on lakewater quality. Because of the large data base of the Finnish Lake Survey the assessment of the role of organic acidity was based on indirect approaches. After the Finnish Lake Survey considerable effort was devoted to the development of a model for organic acidity based on empirical measurements. As a response to the increasing knowledge regarding organic alkalinity contribution to the Gran alkalinity in the 1990's, the contribution of organic anions to the buffer capacity in Finnish lakes was estimated.

The objectives of this study were 1) to describe the statistical distribution of TOC concentrations in small Finnish lakes, 2) to determine the most important catchment characteristics controlling TOC concentrations in the lakes, 3) to develop an empirical estimate for organic acidity in Finnish lakes and to compare this with indirect approaches and 4) to assess the contribution of organic carbon and organic acids to the acidity and buffer capacity of Finnish lakes. Publications I-V and VII summarized in this paper were initiated during the HAPRO programme and III, IV, V, and VII were based on the Finnish Lake Survey. Publications I and II were based on earlier, smaller data sets. In Publication VI some preliminary results of the project connected with the Finnish Research Programme on Climate Change (SILMU) are summarized. Publications I-VII are listed at the end of this paper. In the Publications II-V organic acidity contribution was estimated indirectly either using ion balance calculations or the model of Oliver et al. (1983). The assessment of the acid-base characteristics of organic carbon and the development of an

empirical estimate for organic acidity in Finnish lakes were conducted after the HAPRO programme. These new results are summarized in this paper.

## 2 MATERIALS AND METHODS

### 2.1 The Finnish Lake Survey

#### 2.1.1 Selection of lakes and field sampling

The lakes for the Finnish Lake Survey were randomly selected by a two-stage cluster sampling from two separate subregions which together covered the entire country. The selection was weighted by lake density. The selection methodology implies that the probability of selection of a lake was the greater the more lakes there were in that particular area. Lakes of sizes 0.01–10 km<sup>2</sup> were included in the statistical sampling of southern and central Finland (Subregion 1). In northern Finland (Subregion 2), only lakes of sizes 0.1–10 km<sup>2</sup> were included. Moreover, the sampling intensity for northern Finland was set lower than that for southern and central regions. The final number of lakes in the data set is 789 for Subregion 1 and 189 for Subregion 2. The lake set represents about two percent of the total number of lakes in the size range 0.01–10 km<sup>2</sup> in Subregion 1, and five percent of the lakes with surface areas 0.1–10 km<sup>2</sup> in Subregion 2. A detailed description of the statistical sampling design is given in Forsius et al. (1990b).

Autumn was selected as the sampling time because during circulation a single sample is most representative of the chemistry of the whole lake water body. The period of field sampling was from August 25 to November 23, starting in northernmost Finland. The sampling generally coincided with the autumn turnover period. Most of the lakes were sampled by boat, but in northern Finland about 130 lakes were sampled by helicopter. Water samples from each lake were collected from a depth of one meter at least 30 meters from the lakeshore, using Ruttner-type water samplers.

#### 2.1.2 Catchment characteristics

Lakes were classified into four groups according to their hydrologic type by visual examination of the topographic maps: seepage (no inlets, no outlet), closed (inlets, no outlet), headwater (no inlets, outlet), and drainage lakes (both inlets and outlet). Catchment area and lake surface area, and the proportion of the catchment area covered by peatlands, fields, exposed bedrock and upstream lakes were determined on topographic maps with a scale of 1: 50 000. For catchments larger than 1 000 km<sup>2</sup>, maps with a scale of 1:200 000 were used.

Stepwise multiple linear regression was used to model the relationship between TOC concentration and catchment variables. Many of the variables used in the correlation and regression analyses were log-transformed in order to increase the normality of the distribution.

#### 2.1.3 Chemical measurements

Twenty-three chemical variables were measured from each lake water sample. Twelve measurements which are affected by long storage times were measured at the district laboratories of the National Board of Waters and the Environment on the day after sampling. These measurements included pH, Gran alkalinity and the main nutrients. The main cations and fluoride analyses were carried out at the Research Laboratory of the National Board of Waters and the Environment in Helsinki. Chloride and SO<sub>4</sub> measurements were performed at the Water Conservation Laboratory of the City of Helsinki. TOC and aluminium were analyzed at the Norwegian Institute for Water Research.

TOC was measured from deep-frozen samples by UV-persulfate oxidation followed by IR gas measurements (ASTRO model 2850 TOC/TC Analyzer). The acidified samples were bubbled with nitrogen to remove inorganic carbon (CO<sub>2</sub>). Organic compounds were oxidized, under UV-radiation, with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to CO<sub>2</sub>, and determined by infrared spectrophotometry. Colour (mg l<sup>-1</sup> Pt) was determined by comparison with standard platinum cobalt chloride disks. Chemical oxygen demand (COD<sub>Mn</sub>) was determined titrimetrically following oxidation with KMnO<sub>4</sub>.

The major inorganic cations, Ca, Mg, Na, and

K were measured by flame-AAS, and Cl and  $\text{SO}_4$  by ion-chromatography. Fluoride was measured using an ion-selective electrode.  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were determined colorimetrically. Total monomeric Al and non-labile monomeric Al were measured by the method of Røgeberg and Henriksen (1985). Labile monomeric Al was calculated as the difference between total monomeric Al and non-labile monomeric Al, and it was assumed to have a charge value of 3 in ion balance calculations. pH was measured with Radiometer combination electrodes, and the Gran method (obtained using pH 3.7–4.4 regression results) was used for alkalinity determinations. Conductivity was based on conductometric determination and total N, total P and total Fe were measured colorimetrically following oxidation with  $\text{K}_2\text{S}_2\text{O}_8$ .

It is generally thought that sea salts are transported in the atmosphere in proportions similar to those in seawater. Non-marine sulphate and base cations (denoted by the prefixed asterisks as:  $^*\text{SO}_4$ ,  $^*\text{Ca}$ ,  $^*\text{Mg}$ ,  $^*\text{K}$ ,  $^*\text{Na}$ ) were derived as the differences between total and marine concentrations, the latter being estimated on the basis of ratios to chloride in seawater.

The quality assurance and quality control procedures for analytical methods were performed according to established methods of the laboratories of the National Board of Waters and the Environment. These laboratories are continuously included in an extensive internal quality control programme, and the procedures were carried out in each laboratory during the survey. The verification procedure for the chemical data was carefully performed on a sample-by-sample basis including examination of the cation-anion charge balance. Outliers were also identified by regression analyses and examination of scatter plots between related variables. A more detailed description of the analytical methods and quality assurance used in the Finnish Lake Survey is given by Forsius et al. (1990b).

## 2.2 Other data bases

The water quality data in Publication I was based on samples from 26 lakes collected during

autumn 1985 and in Publication II on 78 lakes sampled during autumn 1983, 1985 or 1986. The water samples were taken from the depth of 1 m. In these earlier studies  $\text{SO}_4$  was measured by an automatic colorimetric thiorin method and Cl by automatic spectrophotometry (National Board of Waters 1981). Alkalinity was titrated potentiometrically to pH values of 4.5 and 4.2 with hydrochloric acid (American Public Health Association 1980). In Publication I aluminium was measured from samples preserved with sulphuric acid by a colorimetric method based on reaction with pyrocatechol (Dougan and Wilson 1974). All other analyses were carried out using the same methods as in the Finnish Lake Survey.

The selection of the study areas in Publication VI was based on an assessment of the water quality data retrieved from the national water quality data base. The selection criteria for the study catchments ( $n=13$ ) were: high peatland percentage, low percentage ( $< 5\%$ ) of agricultural fields, and the availability of long-term water quality data. The size of the catchments ranged from 2.5 to 56.3  $\text{km}^2$ , the peatland percentage from 37 to 87 and the proportion of ditched peatlands from 0 to 100 % of the total peatland area. The annual leaching of TOC from the five catchments with available water quality and daily runoff data over a 8–14 year time period was calculated using four different methods (Rekolainen et al. 1991).

Empirical measurements of the acid-base characteristics of organic carbon in Finnish lakes were carried out during autumn 1991 and spring 1992. Samples from 16 lakes (12 during autumn 1991 and 4 during spring 1992) were fractionated into acidic, neutral and basic components. Organic acids were isolated from 10 lakes (6 lakes during autumn 1991 and 4 lakes during spring 1992). DOC (filtered through Whatman GF/F glass fiber filter) measurements were based on catalysed combustion at 900 °C (Dohrman DC-90 Analyzer). Dissolved inorganic carbon (DIC) was determined as  $\text{CO}_2$  with an IR gas analyzer after converting carbonates to free  $\text{CO}_2$  with nitric acid (Salonen 1981). Bicarbonate concentrations for ion balance calculations were calculated using DIC and pH measurements and the equilibrium constants for the  $\text{CO}_2$ – $\text{H}_2\text{O}$  system (Hillman et al. 1986). Al was measured by flameless AAS (in ion balance calculations a charge value of 2+ was used for Al). Other cation

and anion analyses were carried out using the same methods as in the Finnish Lake Survey.

## 2.3 Approaches for estimating organic acidity

The contribution of organic anion, the dissociation product of organic acids, to the acidity of Finnish lakes was estimated 1) by the charge balance approach (II, III, IV, V), 2) using the model of Oliver et al. (1983) (III) and 3) by developing an empirical model for organic anion. The empirical model was based on titrations of isolated organic acids (providing the dissociation of organic acids as a function of pH in 10 lakes) combined with the fractionation of DOC from 16 lakes following the empirical methods recently developed by David and Vance (1991). The results of the three approaches are compared in this study.

### 2.3.1 Model approach

The model of Oliver et al. (1983) is based on the chemical equilibrium model presented by Gamble (1970) and Perdue et al. (1980), where the dissociated organic anion concentrations  $[A^-]_{OTM}$  ( $\mu\text{eq l}^{-1}$ ) are estimated using the equation:

$$[A^-]_{OTM} = K_a [C_T] / (K_a + [H^+]) \quad (1)$$

where  $K_a$  is the mass action quotient of fulvic and humic acids,  $[C_T]$  is the total organic (fulvic + humic) acid concentration (titrated to pH 7) and  $[H^+]$  the hydrogen ion concentration in the sample. All the concentrations and  $K_a$  are expressed in  $\mu\text{eq l}^{-1}$ .

Oliver et al. (1983) determined total acidity ( $[C_T]$  in equation 1) using titration results of isolated fulvic and humic acids (XAD-8 resins) from samples from rivers, streams, lakes, wetlands and groundwater, collected from a variety of climatic and geologic environments throughout the continental United States, Hawaii and Canada. Oliver et al. (1983) titrated isolated humic and fulvic acids to pH 7 and found that despite the diversity of the samples, only small

variations in these mainly carboxyl groups were observed. The carboxyl content of all samples ranged from 5.1 to 13.4  $\mu\text{eq (mg DOC)}^{-1}$  with an average of 10.5  $\mu\text{eq (mg DOC)}^{-1}$ . The average carboxyl content for fulvic acids was 10.7  $\mu\text{eq (mg DOC)}^{-1}$  and for humic acids 7.7  $\mu\text{eq (mg DOC)}^{-1}$ . Oliver et al. (1983) concluded that the carboxyl content of aquatic humic substances, in general, is close to 10  $\mu\text{eq (mg DOC)}^{-1}$ . Consequently,  $[C_T]$  in equation (1) was determined as sample DOC concentration ( $\text{mg l}^{-1}$ ) multiplied by 10  $\mu\text{eq (mg DOC)}^{-1}$ .

Oliver et al. (1983) found that the mass action quotient changed with pH over the course of the titration, and that fulvic acids from two different aquatic sources exhibited almost identical dissociation behaviour as a function of pH, which was in good agreement with the results of earlier studies (Gamble 1970, Perdue et al. 1980). On the basis of these two samples Oliver et al. (1983) obtained the following equation for the  $pK_a$  value:

$$pK_a = a + b(\text{pH}) + c(\text{pH})^2 \quad (2)$$

where  $a=0.96$ ,  $b=0.90$ , and  $c=-0.039$ . This equation, when substituted into equation (1), allows the prediction of organic anion concentration as a function of pH and DOC.

In later papers some (e.g. LaZerte and Dillon 1984) or all (Driscoll et al. 1989, Kortelainen 1992, Wilkinson et al. 1992) of the model coefficients  $a$ ,  $b$ ,  $c$ , and  $m$  ( $[C_T] = m \cdot \text{DOC}$ ) in the model by Oliver et al. (1983) have been recalibrated on the basis of field data from surface waters in Canada, Finland and the U.S.A. Unlike in the original approach of Oliver et al. (1983), no attempt was made in these studies to isolate and characterize the organic acids.

### 2.3.2 Empirical measurements

A modified procedure of Leenheer (1981) based on XAD-8, anion-exchange (Duolite A-7), and cation-exchange (AG-MP-50) resins was used to fractionate dissolved organic carbon into hydrophobic acids and neutrals, and hydrophilic acids, bases and neutrals. Hydrophobic bases were not measured because of insufficient quantities in lake waters (Bourbonniere 1989, Easthouse et al. 1992). The fractionation procedure was stan-



standardized by adjusting each sample to a similar DOC concentration. Samples with a DOC concentration below 5 mg l<sup>-1</sup> were flash evaporated (30–39 °C) to increase the concentration to about 10 mg l<sup>-1</sup>, whereas samples with a DOC concentration > 13 mg l<sup>-1</sup> were diluted to 10 mg l<sup>-1</sup> with distilled water.

Duplicate fractionations were made with three samples, with variation between replicate analyses < 7 %. The reproducibility of the fractionation procedure was determined with two synthetic acids: oxalic acid, which is mainly hydrophilic and benzoic acid which is mainly hydrophobic. 99 % of the oxalic acid was recovered as hydrophilic acids, and 98 % of the benzoic acid as hydrophobic acids.

The dominant DOC fractions, hydrophobic (HPO-A) and hydrophilic acids (HPI-A), were isolated using two different procedures. Hydrophilic and hydrophobic acids were isolated from two lakes using the modified procedure of Leenheer (1981). Samples were filtered and passed through a cation-exchange resin, acidified to pH 2.0 and pumped through columns of XAD-8 and anion-exchange resins connected in sequence. Hydrophobic acids were eluted from the XAD-8 column using NaOH and protonated by passing through cation-exchange resin. Hydrophilic acids were eluted from the anion-exchange column with NaOH, passed through a cation-exchange column, acidified to pH 2.0, and reabsorbed on XAD-8. Adsorbed hydrophilic acids were then removed following the procedure outlined for collection of hydrophobic acids.

Another slightly different isolation procedure (Malcolm and McCarthy 1992) was used for the other eight lakes. Samples were filtered and passed through a cation-exchange resin, acidified to pH 2.0 and pumped through columns of XAD-8 and XAD-4 connected in sequence. Hydrophobic acids were eluted from the XAD-8 column and hydrophilic acids from the XAD-4 column, respectively, using NaOH. Both hydrophilic and hydrophobic acids were protonated by passing through a cation-exchange resin. Detailed descriptions of the fractionation method and the isolation methods are given in David and Vance (1991) and Kortelainen et al. (1992).

The isolated acids were base titrated to obtain organic acid dissociation as a function of pH. Titrations were conducted on an Orion 960

Autochemistry unit using 0.1 or 0.05 N KOH. Ionic strength was adjusted to 0.01 using KCl and samples were bubbled with N<sub>2</sub> gas before and during the base titrations. The DOC concentrations of the titrated hydrophobic and hydrophilic acids were about 400 and 200 mg l<sup>-1</sup>, respectively.

A first derivative analysis was applied to the titration data to compute total acidity, charge density and the average pK<sub>a</sub> values for hydrophobic and hydrophilic acids. The titration results were compensated with residual anions and cations in the isolated sample according to David and Vance (1991). Total acidity is defined here as the total concentration of acidic groups of DOC titrated to the equivalent point and charge density as the dissociated organic acids per milligram of DOC at a given pH. Total acidity is mostly due to carboxylic acids, because the equivalent point in the titrations was between pH 7.5–8.7.

Using the proportions of hydrophobic and hydrophilic acids of total DOC associated with the total acidity of these acid fractions in each isolated sample (n=10), an empirical estimate for the average total organic acidity [ $\overline{C}_{\text{tot}}$ ] (µeq (mg DOC)<sup>-1</sup>) for Finnish lakes was developed:

$$[\overline{C}_{\text{tot}}] = \sum_{i=1}^{10} (d[C_{\text{HPO-A}}] + e[C_{\text{HPI-A}}])/10 \quad (3)$$

where d and e are the shares of hydrophobic and hydrophilic acids of total DOC in the sample, respectively, and [C<sub>HPO-A</sub>] and [C<sub>HPI-A</sub>] are the total acidity of hydrophobic and hydrophilic acids per milligram of DOC, respectively. [ $\overline{C}_{\text{tot}}$ ] represents the acidic functional groups in aquatic organic carbon that could potentially dissociate in pH values existing in natural waters.

Fractionation and titration results were used to calculate an empirical estimate for dissociated organic anions. An empirical measure for organic anion [A<sup>-</sup>]<sub>EMP</sub> (µeq l<sup>-1</sup>) was developed separately for the 10 lakes using titration results of isolated hydrophobic and hydrophilic acids (second order equations as a function of pH) combined with the fractionation results:

$$[A^-]_{\text{EMP}} = d \cdot \text{DOC}(a + b\text{pH} + c(\text{pH})^2) + e \cdot \text{DOC}(a' + b'\text{pH} + c'(\text{pH})^2) \quad (4)$$

where a, b and c are coefficient values in the second-order regressions from titration analysis

for hydrophobic acids and a', b' and c' for hydrophilic acids, respectively. DOC is expressed in mg l<sup>-1</sup>.

The combined data set of the titrations of isolated acids from 10 lakes gives the following equations for the charge density of hydrophobic [CD<sub>HPO-A</sub>] (µeq (mg DOC)<sup>-1</sup>) and hydrophilic [CD<sub>HPL-A</sub>] acids in Finnish lakes:

$$[CD_{HPO-A}] = -10.1 + 5.02pH - 0.312(pH)^2 \quad (5)$$

$$[CD_{HPL-A}] = -11.3 + 5.78pH - 0.371(pH)^2 \quad (6)$$

These second order equations can be used to determine the average charge density of organic acids at any pH between pH 4.0 and 7.0. The proportion of hydrophobic acids increased with increasing DOC whereas the proportion of hydrophilic acids decreased with increasing DOC. On the basis of fractionation results a linear equation was developed for the relationships between the shares of hydrophobic and hydrophilic acids, d<sub>f</sub> and e<sub>f</sub>, respectively, of total DOC as a function of DOC (r<sup>2</sup>=0.558, P<0.001 and r<sup>2</sup>=0.379, P<0.01 for hydrophobic and hydrophilic acids, respectively):

$$d_f = 0.426 + 0.00991DOC \quad (7)$$

$$e_f = 0.373 - 0.00387DOC \quad (8)$$

Using these equations the sum of d<sub>f</sub> and e<sub>f</sub> is 1.0 (i.e. organic acid percentage of the total DOC is 100 %) when the sample DOC is 33.3 mg l<sup>-1</sup>. Consequently d<sub>f</sub> and e<sub>f</sub> were determined to be 0.756 and 0.244, respectively (corresponding the values of d<sub>f</sub> and e<sub>f</sub>, respectively when DOC=33.3 mg l<sup>-1</sup>) at TOC concentrations higher than 33.3 mg l<sup>-1</sup>. Equations (7) and (8) were combined with equations (5) and (6) when developing an empirical equation for dissociated organic anion [A<sup>-</sup>]<sub>FIN</sub> in Finnish lakes:

$$[A^-]_{FIN} = d_f DOC [CD_{HPO-A}] + e_f DOC [CD_{HPL-A}] \quad (9)$$

Equation (9) simplifies the estimation of the acidic contribution of organic acids in natural waters to measuring DOC and pH of the sample. This equation was applied to the Finnish Lake Survey data set and compared with organic anion estimated by the charge balance approach and by the model of Oliver et al. (1983).

Equation (9) divided by the sample DOC can be used to calculate the average charge density of DOC at a given pH:

$$[CD] = [A^-]_{FIN} / DOC \quad (10)$$

The average dissociation share of organic acids at any pH in Finnish lakes can be calculated by dividing the average charge density (equation 10) by the total acidity (equation 3):

$$DISS = [CD] / [\overline{C}_{tot}] \quad (11)$$

When applying equations (9) and (10) as well as the model of Oliver et al. (1983) to the Finnish lake survey data set TOC measurements were used instead of DOC. In many studies, total organic carbon is partitioned into dissolved (DOC) and particulate (POC) components by filtration through a 0.45 µm pore filter. The separation of organic carbon into different classes is more for analytical convenience than a reflection of the true relations of the constituents in natural waters (Schlesinger and Melack 1981). The majority of organic carbon in lakes is dissolved, and particulate carbon contributes only minor part of the total organic carbon (Thurman 1985). The average difference between TOC and DOC was only about 0.5 mg l<sup>-1</sup> in 1 m samples from 36 small Finnish lakes with TOC concentrations comparable with those in the Finnish Lake Survey (Kortelainen et al., unpublished). It can be assumed that the proportion of particulate organic carbon compared with total organic carbon was small in the present study.

### 2.3.3 Ion balance calculations

The anion deficit [A<sup>-</sup>]<sub>AD</sub> (µeq l<sup>-1</sup>) used as an estimate for the dissociated organic anion concentration in Publications III, IV and V was:

$$[A^-]_{AD} = 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] + [NH_4^+] + 3[Al^{3+}] + [H^+] - 2[SO_4^{2-}] - [Cl^-] - [NO_3^-] - [F^-] - [ALK]_{GRAN} \quad (12)$$

where all the ion concentrations were expressed in µeq l<sup>-1</sup>. If Gran alkalinity was < 0 it was defined to be 0 in ion balance calculations. The assumption that Ca, Mg, Na and K exist as free cations, i.e. that they are not appreciably complexed with the

dissolved organic matter, is consistent with their known aqueous chemistry (Morel 1983, Eshleman and Hemond 1985). On the basis of the model calculations Tipping et al. (1991) concluded that only small amounts of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are organically bound at the pH values existing in natural waters. Iron was not included in the ion balance calculations, as it exists predominantly as an Fe(II)-organic complex at the pH values of most natural waters; concentrations of dissolved inorganic Fe are negligible in most oxic, high DOC waters (Reuter and Perdue 1977).

It is difficult to determine the uncertainty associated with the anion deficit approach. Organic anions are determined through the analysis of many ions, and therefore uncertainty in these estimates is a result of uncertainty associated with the analysis of each individual ion. Assuming errors associated with sample collection and analysis are randomly distributed, uncertainty in the determination of cationic solutes may be offset to some extent by uncertainty in the determination of anionic solutes in charge balance calculations.

#### 2.4 Estimation of the organic anion contribution to Gran alkalinity

In the Finnish Lake Survey acid neutralizing capacity was determined using Gran alkalinity titrations ( $[\text{ALK}]_{\text{GRAN}}$ ). Alkalinity can also be calculated as a difference between non-hydrogen cation concentrations and strong acid anion concentrations as follows:

$$[\text{ALK}]_{\text{CB}} = 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + 2[\text{Al}^{2+}] - 2[\text{SO}_4^{2-}] - [\text{Cl}^-] - [\text{NO}_3^-] - [\text{F}^-] \quad (13)$$

where all the concentrations are expressed in  $\mu\text{eq l}^{-1}$ . This charge balance alkalinity ( $[\text{ALK}]_{\text{CB}}$ ) is compared with the titrimetrically measured alkalinity in section 4.5.

In Publications III, IV and V the Gran alkalinity results ( $[\text{ALK}]_{\text{GRAN}}$  in equation 12) were used as an estimate for bicarbonate, although recent studies have shown that these measurements include some organic alkalinity in addition to bicarbonate

(Sullivan et al. 1989, Cantrell et al. 1990, Hemond 1990a). This causes an underestimation of the organic anion concentration calculated as the difference between the cations and inorganic anions (equation 12). To estimate the organic contribution in Gran titrations the following calculations were made. A fraction of organic carbon behaves as a base during Gran alkalinity titration (in the pH range: sample pH – end point pH in Gran titration). Using equation (9) the dissociated organic anion at the sample pH ( $[\text{A}^-]_{\text{pH}}$ ) and at the titration end point pH ( $[\text{A}^-]_{\text{endpH}}$ ) was calculated, separately, and the following equation for the titrated organic anion concentrations during Gran alkalinity titrations,  $[\text{A}^-]_{\text{GRAN}}$ , was developed:

$$[\text{A}^-]_{\text{GRAN}} = [\text{A}^-]_{\text{pH}} - [\text{A}^-]_{\text{endpH}} \quad (14)$$

In section 4.5 equation (14) is used as an estimate for organic alkalinity in the Finnish Lake Survey. If sample pH was < titration end point pH,  $[\text{A}^-]_{\text{GRAN}}$  was defined to be 0.

At pH values existing in natural waters acid neutralizing capacity can be simplified as follows (e.g. Schnoor and Stumm 1985):  $\text{ANC} = [\text{HCO}_3^-] + [\text{ORG}^-] - [\text{H}^+]$ , where  $[\text{HCO}_3^-]$  is bicarbonate alkalinity,  $[\text{ORG}^-]$  is organic alkalinity and  $[\text{H}^+]$  is the free acidity at the titration endpoint pH. Carbonate alkalinity as well as other alkalinity sources, e.g. aluminium, borate, phosphate, silicate, ammonia and sulfides, are often excluded because of minor contributions (e.g. Wissmar et al. 1990). Consequently the bicarbonate in the Finnish Lake Survey can be estimated as follows:

$$[\text{HCO}_3^-] = [\text{ALK}]_{\text{GRAN}} - [\text{A}^-]_{\text{GRAN}} + ([\text{H}^+]_{\text{pH}} - [\text{H}^+]_{\text{endpH}}) \quad (15)$$

where  $[\text{HCO}_3^-]$  is the titrated bicarbonate,  $[\text{ALK}]_{\text{GRAN}}$  is the measured Gran alkalinity,  $[\text{H}^+]_{\text{pH}}$  is the  $\text{H}^+$  concentration at the sample pH and  $[\text{H}^+]_{\text{endpH}}$  is the  $\text{H}^+$  concentration at the titration endpoint pH (free acidity at the titration endpoint pH). If calculated  $[\text{HCO}_3^-]$  was < 0, it was defined to be 0 in ion balance calculations. A second-order regression for  $[\text{H}^+]_{\text{endpH}}$  as a function of TOC was developed using Table 2 in Cantrell et al. (1990):

$$[\text{H}^+]_{\text{endpH}} = 2.27 + 0.837\text{TOC} - 0.0161(\text{TOC})^2 \quad (16)$$

Replacing Gran alkalinity ( $[ALK]_{GRAN}$ ) in equation (12) by an estimate for titrated bicarbonate ( $[HCO_3^-]$ ; equation 15) a corrected estimate for the free organic anion concentration in Finnish lakes can be calculated:

$$[A^-]_{ADFREE} = [A^-]_{AD} + [ALK]_{GRAN} - [HCO_3^-] \quad (17)$$

In Cantrell et al. (1990), based on theoretical calculations,  $H^+$  concentration at the titration endpoint pH was calculated as a function of DOC, whereas in the present study it was calculated as a function of TOC. Moreover, the pH range in Gran titration in Cantrell et al. (1990) was 3.5–4.5 compared with 3.7–4.4 in the Finnish Lake Survey. Further uncertainty is caused by the fact that Gran alkalinity in the Finnish Lake Survey was determined manually, which cannot be considered as reliable as Gran alkalinity carried out by an automatic titrator. This causes uncertainty both in Gran alkalinity results in the Finnish Lake Survey as well as in the estimated organic alkalinity and bicarbonate contribution in Gran titrations.

### 3 ORGANIC CARBON CONCENTRATIONS IN FINNISH LAKES VS. CATCHMENT

#### 3.1 Organic carbon concentrations in the lakes

The size range of the lakes in the Finnish Lake Survey was 0.01–7.5 km<sup>2</sup>. The median lake surface area in Subregion 1 was 0.07 km<sup>2</sup>, and 0.20 km<sup>2</sup> in Subregion 2. Catchments of the lakes were also larger in Subregion 2, resulting in only a slight difference between the two subregions with respect to catchment to lake area ratio (Table 1). Drainage lakes were the major lake type in both subregions (69 % in Subregion 1 vs. 75 % in Subregion 2) followed by headwater lakes (Table 1). Headwater lakes were more common in Subregion 1 than in Subregion 2 (18 % vs. 12 %) which is probably related to the fact that lakes with area smaller than 0.1 km<sup>2</sup> were excluded in Subregion 2.

The median TOC, colour and  $COD_{Mn}$  in the Finnish Lake Survey were 12 mg l<sup>-1</sup> (range 0.5–47 mg l<sup>-1</sup>), 100 mg l<sup>-1</sup> Pt and 15 mg l<sup>-1</sup> O<sub>2</sub>, respectively. The percentage of lakes with TOC concentrations  $\geq 5$  mg l<sup>-1</sup> in the whole country was 93 % (III). The median TOC values in drainage, headwater and closed lakes were almost identical (13 mg l<sup>-1</sup>, 11 mg l<sup>-1</sup> and 12 mg l<sup>-1</sup>, respectively). In seepage lakes, TOC concentrations were lower (median 7.1 mg l<sup>-1</sup>). The highest organic carbon concentrations were found in lakes with the highest iron, nitrogen and phosphorus concentrations and the lowest pH (Table 2, VII). Moreover, the concentrations were predominantly highest in the smallest lakes. The significant positive relationships between organic carbon and total iron, total nitrogen and total phosphorus suggest that large proportions of these elements are transported into Finnish lakes together with organic carbon.

One major trend in Finnish lakes is low TOC, colour and  $COD_{Mn}$  concentrations in northern regions compared with central and southern parts of the country. In northern Finland many other water quality parameters, e.g. phosphorus, nitrogen, iron and conductance also had low values compared with southern and central regions (Table 1). Lakes had high values of TOC (Fig. 1), colour and  $COD_{Mn}$ , especially in central regions. In many lakes located in flat, peatland-dominated areas near the Gulf of Bothnia TOC concentrations were  $\geq 25$  mg l<sup>-1</sup> (IV). In Subregion 1, TOC concentrations were higher than 10 mg l<sup>-1</sup> in 70 % of the lakes, and colour values were higher than 100 mg l<sup>-1</sup> Pt in 54 % of the lakes. In Subregion 2, these percentages were much lower, 16 % and 6 %, respectively (VII). The median TOC in lakes of Subregion 2 (6.4 mg l<sup>-1</sup>) was only half of that (11.9 mg l<sup>-1</sup>) in lakes larger than 0.1 km<sup>2</sup> in Subregion 1. However, the fact that lakes with area smaller than 0.1 km<sup>2</sup> were excluded in Subregion 2 probably emphasized the high number of high TOC lakes in southern Finland compared with northern Finland.

An important reason for the lower TOC, colour and  $COD_{Mn}$  concentrations in northern Finland is probably the colder climate compared with southern Finland, which results in a longer soil frost period and lower primary production and decomposition in the catchments. This agrees with results from lakes in Labrador (Engstrom

Table 1. Median characteristics of the lakes and catchments in the two subregions and in the whole country.

		Subregion 1	Subregion 2	Finland
<b>Hydrologic lake type (%)</b>				
Drainage		69	75	70
Headwater		18	12	17
Seepage		10	10	10
Closed		3	3	3
		100	100	100
<b>Median catchment characteristics</b>				
Lake area	(km <sup>2</sup> )	0.07	0.20	0.09
Catchment area	(km <sup>2</sup> )	1.6	4.2	2.0
Catchment/lake ratio		20	17	19
Percent peatland		16	20	17
Percent field		1.7	0	0.46
Percent exposed bedrock		0.27	0.45	0.30
Percent upstream lakes		0	1.1	0
<b>Median chemical characteristics</b>				
TOC	(mg l <sup>-1</sup> )	14	6.4	12
Colour	(mg l <sup>-1</sup> Pt)	120	40	100
COD <sub>Mn</sub>	(mg l <sup>-1</sup> O <sub>2</sub> )	17	6.7	15
pH		6.1	6.8	6.3
ANC	( $\mu$ eq l <sup>-1</sup> )	69	90	75
Conductivity	(mS m <sup>-1</sup> )	3.4	2.2	3.1
Total P	( $\mu$ g l <sup>-1</sup> )	18	8.0	15
Total N	( $\mu$ g l <sup>-1</sup> )	510	270	450
Total Fe	( $\mu$ g l <sup>-1</sup> )	560	120	460
*[Ca+Mg+Na+K]	( $\mu$ eq l <sup>-1</sup> )	270	180	250
Labile Al <sup>1)</sup>	( $\mu$ eq l <sup>-1</sup> )	1.9	<1.1	1.6
NH <sub>4</sub>	( $\mu$ eq l <sup>-1</sup> )	1.0	0.4	0.8
*SO <sub>4</sub>	( $\mu$ eq l <sup>-1</sup> )	90	35	71
Cl	( $\mu$ eq l <sup>-1</sup> )	31	20	25
NO <sub>3</sub>	( $\mu$ eq l <sup>-1</sup> )	1.5	0.2	1.1
F	( $\mu$ eq l <sup>-1</sup> )	<5	<5	<5
HCO <sub>3</sub>	( $\mu$ eq l <sup>-1</sup> )	35	68	46
[A <sup>-</sup> ] <sub>AD</sub> <sup>a)</sup>	( $\mu$ eq l <sup>-1</sup> )	99	58	89
[A <sup>-</sup> ] <sub>ADFREE</sub> <sup>b)</sup>	( $\mu$ eq l <sup>-1</sup> )	127	75	114
[A <sup>-</sup> ] <sub>FIN</sub> <sup>c)</sup>	( $\mu$ eq l <sup>-1</sup> )	110	53	96
[A <sup>-</sup> ] <sub>OTM</sub> <sup>d)</sup>	( $\mu$ eq l <sup>-1</sup> )	123	61	108
$\Sigma$ [Cat]/ $\Sigma$ [An] <sup>e)</sup>		1.6	1.5	1.6
$\Sigma$ [Cat]/( $\Sigma$ [An]+[A <sup>-</sup> ] <sub>FIN})</sub>		1.0	1.1	1.0
$\Sigma$ [Cat]/( $\Sigma$ [An]+[A <sup>-</sup> ] <sub>OTM})</sub>		0.98	1.1	1.0

<sup>1)</sup> Labile monomeric Al (Røgeberg and Henriksen 1985) assumed to have a charge value of 3 in ion balance calculations

<sup>a)</sup> values corrected for marine contribution

<sup>b)</sup> Organic anion calculated by equation (12) (Anion deficit)

<sup>c)</sup> Organic anion calculated by equation (17) (Corrected anion deficit)

<sup>d)</sup> Organic anion calculated by equation (9) (Finnish equation)

<sup>e)</sup> Organic anion calculated by equation (1) (Oliver et al. model)

<sup>e)</sup>  $\Sigma$ [Cat]/ $\Sigma$ [An] =  $(2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + 3[\text{Al}^{3+}] + [\text{H}^+]) / (2[\text{SO}_4^{2-}] + [\text{Cl}^-] + [\text{NO}_3^-] + [\text{F}^-] + [\text{HCO}_3^-])$

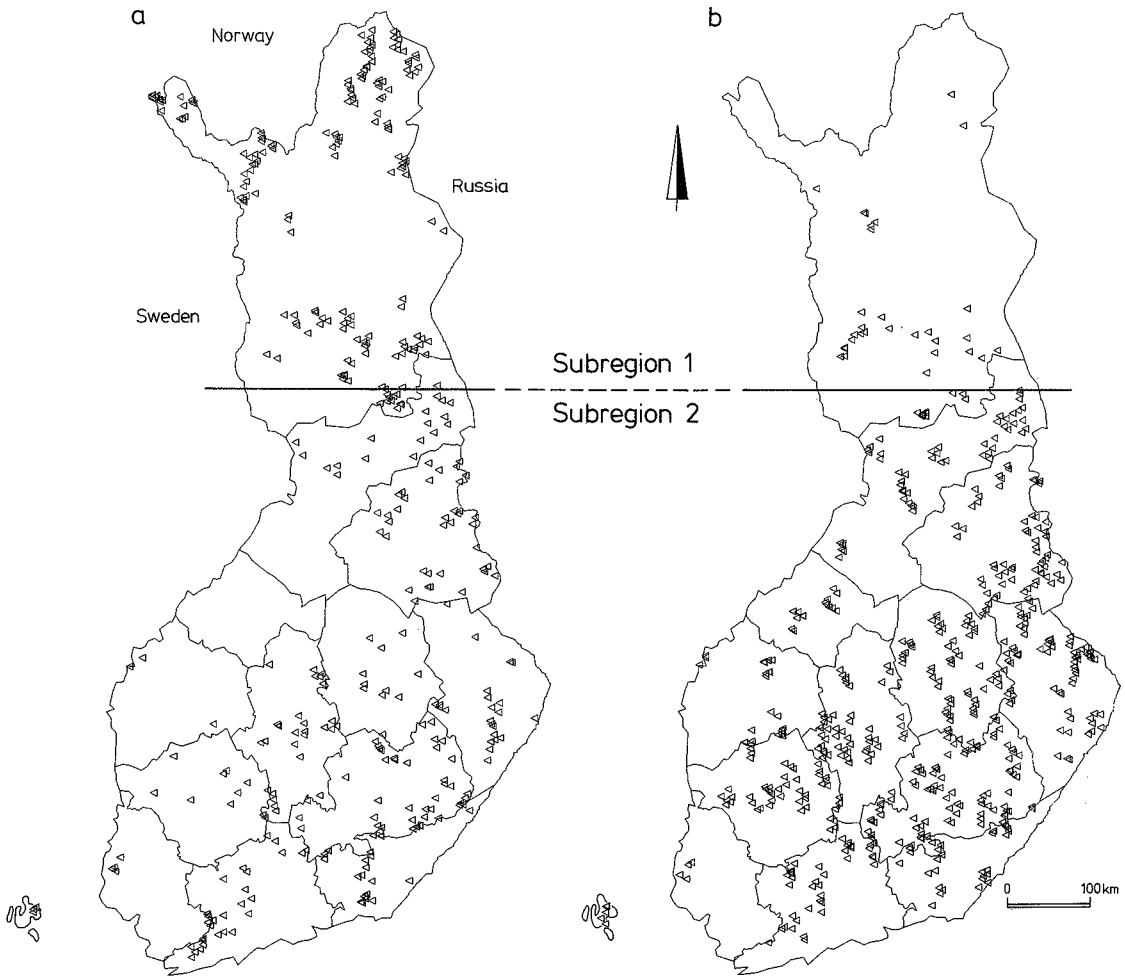


Fig. 1. The location of the lakes with TOC concentrations (a)  $< 10 \text{ mg l}^{-1}$  ( $n=397$ ) and (b)  $\geq 10 \text{ mg l}^{-1}$  ( $n=581$ ). The borders of the 13 Water and Environment Districts in Finland are presented.

1987), where colour increased clearly from north to south due to differences in humic matter loading from catchments. Moreover, in northern Finland soils and peat deposits are thinner and less disturbed; for example the ditching of peatlands has not been as intensive as in southern parts of the country (Aarne 1992).

Annual precipitation in northern Finland is lower compared with southern Finland, and a larger proportion of the precipitation is snow. The summer of 1987 prior to autumn sampling was exceptionally cold and rainy in southern and central Finland, whereas in northern Finland the precipitation was closer to normal (Hydrological yearbook 1987–1988). In rainy years, rainwater

does not penetrate very deeply into the soil because of a high groundwater table. Surface runoff is likely to be high, which increases organic carbon concentrations in surface waters. Monitoring results from Finnish lakes and the results of Kerekes (1974), Howell (1986) and Mulholland et al. (1990) suggest that the results of the Finnish Lake Survey may slightly emphasize high TOC, colour and  $\text{COD}_{\text{Mn}}$  concentrations in southern and central Finland and that autumn sampling may slightly emphasize high TOC, colour and  $\text{COD}_{\text{Mn}}$  concentrations compared with studies conducted during other periods of the year (IV).

### 3.2 Relationships between TOC, colour, and $\text{COD}_{\text{Mn}}$

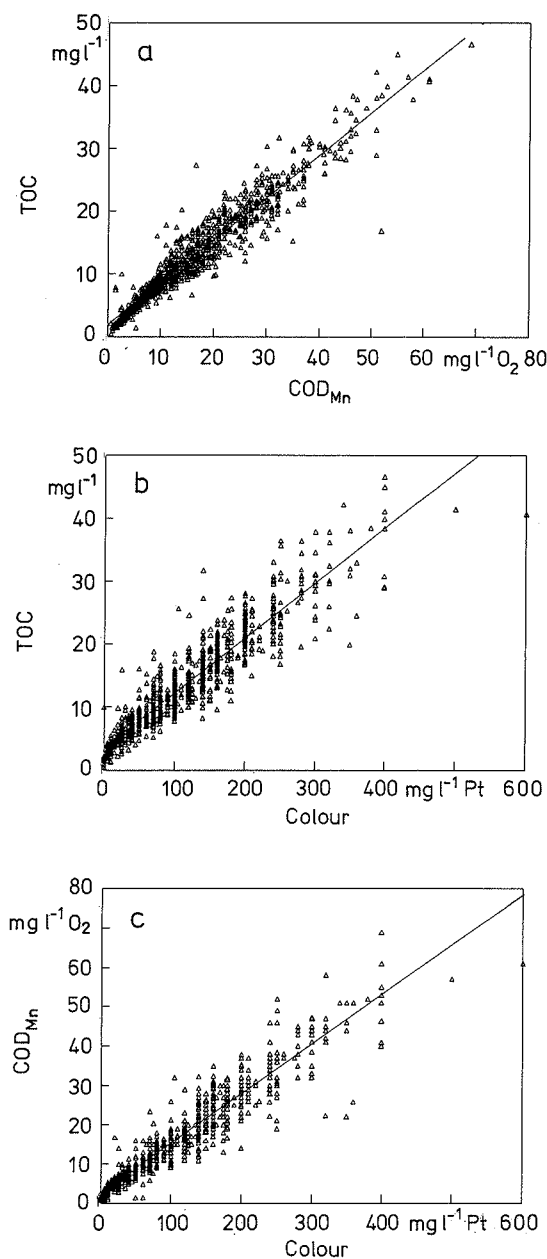
Significant positive relationships among TOC,  $\text{COD}_{\text{Mn}}$ , and colour were found (Fig. 2). These variables are generally used to describe humic matter concentrations in surface waters, although TOC is a measure for total organic carbon concentration,  $\text{COD}_{\text{Mn}}$  for the amount of chemical oxygen consumption of the organic matter under the conditions of the test, and colour for the amount of coloured substances. Dissolved substances other than organic carbon may also influence colour. For example iron is to a high degree complexed with organic carbon and can make a high contribution to the colour values (e.g. Pennanen and Frisk 1984). Similarly variations in plankton densities can affect colour (Eloranta 1978, 1983). Thurman (1985) concluded that humic substances from wetlands are most coloured, followed by rivers and streams; humic substances from eutrophic lakes are the least coloured per unit carbon.

The relationships between TOC,  $\text{COD}_{\text{Mn}}$  and colour in the Finnish Lake Survey were comparable with those in Canadian and Swedish lakes (VII). Rather good agreement between the three methods supports the usability of the regressions based on  $\text{COD}_{\text{Mn}}$  or colour (Fig. 2) as approximate estimates for TOC in Finnish lakes when organic carbon measurements are not available.

### 3.3 Catchment characteristics as predictors of lake TOC content

Lakes with the highest organic carbon concentrations are mainly small lakes, with a relatively large catchment area and a high proportion of peatlands in the catchment (Table 2), located in central or southern parts of the country where the topography is flat. Although it is easy to identify areas where TOC concentrations are highest, it is also typical that over large areas of southern and central Finland clear-water lakes and humic lakes can occur in close proximity to each other (IV).

According to correlation analysis the pro-



- (a)  $\text{TOC} = 0.675\text{COD}_{\text{Mn}} + 1.94$        $r^2=0.92$     $n=975$   
 (b)  $\text{TOC} = 0.0872\text{Colour} + 3.55$        $r^2=0.86$     $n=976$   
 (c)  $\text{COD}_{\text{Mn}} = 0.126\text{Colour} + 2.79$        $r^2=0.89$     $n=974$

Fig. 2. The relationship between (a)  $\text{COD}_{\text{Mn}}$  and TOC, (b) colour and TOC, and (c) colour and  $\text{COD}_{\text{Mn}}$ .

portion of the catchment covered by peatlands was the most important catchment variable determining TOC concentrations in Finnish lakes (VII). In lakes with TOC concentrations lower than  $5 \text{ mg l}^{-1}$  the median percentage of peatlands in the catchment was 6.5, increasing to 28 in lakes with TOC concentrations higher than  $20 \text{ mg l}^{-1}$ . In the full set of lakes the correlation coefficients between TOC and single catchment variables were rather low, although often statistically significant due to the large data base, indicating that many interacting factors contribute to the final concentration.

Stepwise multiple regression was used to model the relationship between TOC concentration and catchment variables. In the full set of lakes the latitude, catchment to lake area ratio and the proportion of the catchment covered by peatlands, upstream lakes and fields explained 55 % of the variation in TOC. For TOC, 61 % of the variation was explained by catchment variables in drainage lakes, 59 % in headwater lakes, 52 % in

closed lakes, and 32 % in seepage lakes. Separation of the lakes regionally into subgroups improved the predictive power of the regression models. In northern Finland, where human impact in the catchments (e.g. ditching) has not been as extensive as in southern parts of the country, the proportion of the catchment covered by peatlands explained 53 % of the variation in TOC. When latitude and catchment to lake area ratio were included in the model, the variation explained was increased to 66 % (VII). The proportion of the variation in TOC concentration explained by catchment variables in the present study is comparable with that obtained by Rapp et al. (1985) and Rasmussen et al. (1989). They predicted lake colour from catchment variables in smaller data bases from the northern United States and Canada, respectively.

Podzolic soils under coniferous forests are probably also an important source of organic carbon for Finnish lakes. There are also lake (e.g. mean depth) and catchment characteristics (e.g.

Table 2. Median chemical and physical characteristics of lakes with  $\text{TOC} < 10 \text{ mg l}^{-1}$  and  $\text{TOC} \geq 10 \text{ mg l}^{-1}$ .

		$\text{TOC} < 10 \text{ mg l}^{-1}$	$\text{TOC} \geq 10 \text{ mg l}^{-1}$
Lake area	( $\text{km}^2$ )	0.14	0.067
Catchment/lake ratio		13	24
Percent peatland		12	23
pH		6.6	6.0
ANC	( $\mu\text{eq l}^{-1}$ )	88	64
Conductivity	( $\text{mS m}^{-1}$ )	2.6	3.4
Total P	( $\mu\text{g l}^{-1}$ )	10	21
Total N	( $\mu\text{g l}^{-1}$ )	310	570
Total Fe	( $\mu\text{g l}^{-1}$ )	140	740
*[Ca+Mg+Na+K]	( $\mu\text{eq l}^{-1}$ )	210	270
* $\text{SO}_4$	( $\mu\text{eq l}^{-1}$ )	54	84
$[\text{A}^-]_{\text{AD}}$ <sup>a)</sup>	( $\mu\text{eq l}^{-1}$ )	57	115
$[\text{A}^-]_{\text{ADFREE}}$ <sup>b)</sup>	( $\mu\text{eq l}^{-1}$ )	75	144
$[\text{A}^-]_{\text{FIN}}$ <sup>c)</sup>	( $\mu\text{eq l}^{-1}$ )	54	134
$[\text{A}^-]_{\text{OTM}}$ <sup>d)</sup>	( $\mu\text{eq l}^{-1}$ )	63	148
$\Sigma[\text{Cat}]/\Sigma[\text{An}]^{\text{e)}$		1.4	1.9
$\Sigma[\text{Cat}]/(\Sigma[\text{An}]+[\text{A}^-]_{\text{FIN}})$		1.1	1.0
$\Sigma[\text{Cat}]/(\Sigma[\text{An}]+[\text{A}^-]_{\text{OTM}})$		1.0	0.98

a) Organic anion calculated by equation (12) (Anion deficit)

b) Organic anion calculated by equation (17) (Corrected anion deficit)

c) Organic anion calculated by equation (9) (Finnish equation)

d) Organic anion calculated by equation (1) (Oliver et al. model)

e)  $\Sigma[\text{Cat}]/\Sigma[\text{An}] = (2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + 3[\text{Al}^{3+}] + [\text{H}^+]) / (2[\text{SO}_4^{2-}] + [\text{Cl}^-] + [\text{NO}_3^-] + [\text{F}^-] + [\text{HCO}_3^-])$



slope of the catchment, land use: ditching), as well as variables affecting runoff and consequently leaching of organic carbon, which were not evaluated in the Finnish Lake Survey, but which could probably also improve predictions in multiple regressions. Lakes in Finland are predominantly shallow due to the flat topography. In shallow lakes the catchment-derived organic matter is diluted into a small volume of water resulting in higher TOC concentrations compared with deep lakes. In large and deep lakes, with long residence times, the degradation and sedimentation processes affecting organic matter are also likely to be more complete, resulting in lower organic carbon concentrations (e.g. Eloranta 1973, Engstrom 1987).

The median percentage of peatlands in the catchment of the study lakes was higher in Subregion 2 than in Subregion 1 (20 % vs. 16 %, Table 1). The same percentage of peatlands in northern Finland, however, results in lower TOC concentrations than in southern Finland. The regional differences in the TOC-peatland relationship may be connected to differences in climatic and hydrological conditions. Furthermore, different wetland types as well as differences in land use have been found to produce different DOC concentrations (e.g. Moore 1987, Eckhardt and Moore 1990). Ditching can be considered as the largest-scale human impact in the catchments of Finnish watercourses during this century (Metsä- ja turvetalouden vesiensuojelutoimikunnan mietintö 1987). Ditching was already intensive in the late 1950's and peaked at the end of the 1960's. In southern Finland ditching activity has been more extensive than in northern Finland (about 71 % and 37 % of the peatland area, respectively) (Aarne 1992).

The large lakes and rivers in Finland have been monitored since the early 1960's. Sampling frequency in the national monitoring programmes has not been very high and the focus has mainly been on lakes and rivers loaded by several sources: domestic waste waters, agriculture, fish farming, peat production. Consequently forestry impacts are difficult to separate from changes in other loading sources. No major changes in the mean values of  $\text{COD}_{\text{Mn}}$  and colour in the large rivers (Laaksonen 1970) and in the annual leaching of  $\text{COD}_{\text{Mn}}$  in unloaded large rivers (Alasaarela and Heinonen 1984) have been found during this century. In case studies the leaching of

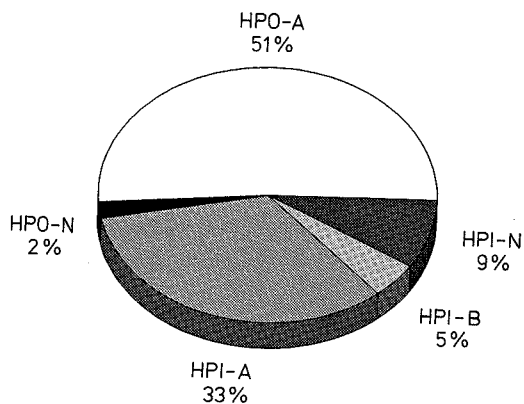
organic carbon has been found to increase during and immediately after ditching (Heikurainen et al. 1978, Ahtiainen 1988). However, ditching is usually performed to lower the groundwater table, which can in the long-term result in decreased leaching of organic carbon (Heikurainen et al. 1978, Moore 1987).

Upstream lakes reduced the TOC concentrations significantly in a selected lake group (II) in accordance with earlier Finnish studies (Laaksonen 1970, Wartiovaara 1978, Pitkänen 1986). Upstream lakes are likely to increase the sedimentation and the residence time of water, which is reflected as decreasing TOC concentrations. The catchment taken up by water bodies is lost as a source of organic matter, and excess rainwater that falls directly onto lakes also dilutes organic matter concentrations originating from terrestrial drainage (Engstrom 1987). Thus large upstream water bodies in the catchment tend to reduce water colour by dilution while also reducing temporal and annual variations (Kerekes 1974). Small lakes mainly have lakeless catchments, which is consistent with the observation that small lakes have the highest organic carbon concentrations.

## 4 ORGANIC ACIDITY IN LAKES

### 4.1 Acid/base characteristics of organic carbon and the dissociation of organic acids

The lakes for DOC fractionation studies had a wide range of DOC (1.6–27.6 mg l<sup>-1</sup>, mean 11 mg l<sup>-1</sup>) and pH (4.5–6.3). In every sample, the proportion of organic acids was dominant compared with neutral and basic components. The hydrophobic and hydrophilic acids averaged 51 % (range 24–66 %) and 33 % (range 28–43 %) of DOC, respectively. The remaining DOC fractions (bases plus neutrals) reached a minimum of 6.6 % and a maximum of 33 % of the DOC. This demonstrates that organic carbon in Finnish lakes is dominated by organic acids (mean 84 %, range 67–95 %), with much smaller amounts of neutral and basic components (Fig. 3). No



- HPO-A:** Hydrophobic acids  
**HPO-N:** Hydrophobic neutrals  
**HPI-A:** Hydrophilic acids  
**HPI-B:** Hydrophilic bases  
**HPI-N:** Hydrophilic neutrals

Fig. 3. Average percentages of acidic, basic and neutral fractions of DOC in 16 Finnish lakes.

relationship between organic acid proportions and sample pH was found. However, differences in DOC fractions were found between lakes with low and high DOC. Low DOC lakes had smaller proportions of their DOC as hydrophobic acids and higher proportions of hydrophilic acids and neutrals compared with high DOC lakes. The proportion of organic acids increased with increasing DOC concentrations. The proportions of acidic, neutral and basic components in Finnish lakes were comparable with the proportions in Maine lakes (David and Vance 1991, David et al. 1991) and in the HUMEX project study area, Lake Skjervatjern, in Norway (Kortelainen et al. 1992). In Maine lakes the organic acid contribution varied from 60 to 92 % of DOC (David and Vance 1991). In forest floor solutions with higher DOC concentrations the organic acid contribution was generally higher, averaging 92 % (Vance and David 1991).

Hydrophobic and hydrophilic acids, the dominant DOC fractions, were isolated from 10 lakes with a DOC range from 3.7 to 22.3 mg l<sup>-1</sup> and pH range from 4.7 to 6.3. Organic acids were

negatively charged over the entire pH range of the acid-base titration and the dissociation of organic acids clearly increased with increasing pH. The charge density of hydrophobic acids as a function of pH in the 10 Finnish lakes was close to each other and comparable with the titration results of fulvic acids in the model of Oliver et al. (1983). The model of Oliver et al. (1983) was based on humic/fulvic acid isolation procedure, in which the isolated acids would be classified as hydrophobic acids. Slightly more variation in the dissociation of hydrophilic acids was observed compared with hydrophobic acids, although no systematic differences between the two different isolation procedures were found (Fig. 4). The titrations of Finnish lakes as well as the studies of McKnight et al. (1985), David and Vance (1991) and David et al. (1991) show that hydrophilic acids are more acidic than hydrophobic acids, which is reflected in higher charge density values for hydrophilic acids at a given pH (Fig. 4). Using <sup>13</sup>C-NMR spectra Vance and David (1991) showed that hydrophobic and hydrophilic acids are primarily carboxylic acids, with a higher content of carboxylic functional groups per milligram of DOC in hydrophilic acids than in hydrophobic acids.

The average pK<sub>a</sub> values for hydrophobic and hydrophilic acids in the Finnish lakes were 4.11 (the range for average pK<sub>a</sub> in different lakes was 3.95–4.25) and 3.82 (range 2.63–4.20), respectively. Thurman (1985) concluded that pK<sub>a</sub> values of organic acids range from 1.2 to 13, averaging 4.2. Perdue and his co-workers suggested a continuous distribution model to describe the extent of proton binding of humic matter across the whole pH range. The most frequent values were reported at pK<sub>a</sub> 3.7 and 12.5, corresponding to carboxylic and phenolic groups, respectively (Perdue et al. 1980, Perdue et al. 1984, Perdue 1985). The empirical measurements from Finnish lakes support the use of pK<sub>a</sub> 4 to represent the average pK<sub>a</sub> for carboxylic acids in surface waters, in agreement with Perdue et al. (1984) and Thurman (1985).

In Publication I the applicability of coulometric Gran titration to the separation of strong and weak acids in lake water samples was investigated. In the selected Finnish lake group 99 % of the variance in the weak acid concentration was explained by TOC, aluminium and

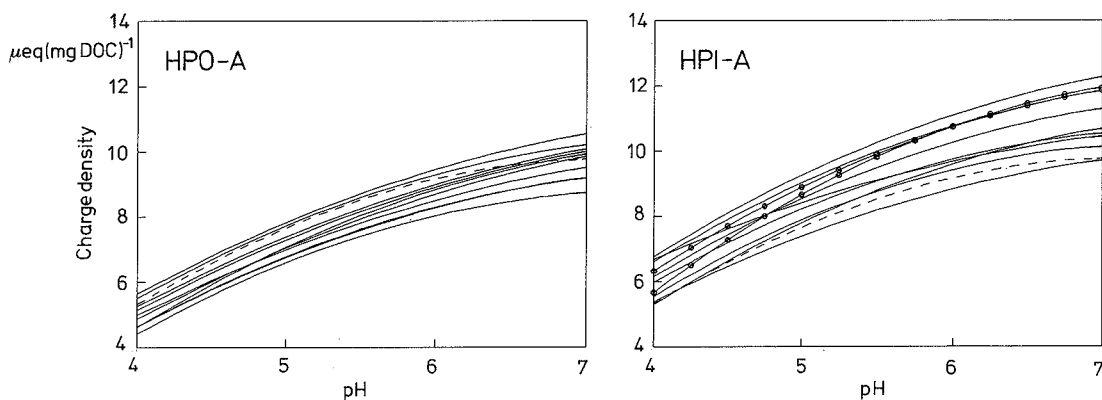


Fig. 4. Charge density of hydrophobic (HPO-A) and hydrophilic acids (HPI-A) as a function of pH in 10 Finnish lakes (continuous line). The two lakes with the different isolation procedure for hydrophilic acids are identified. Results from Oliver et al. (1983) (dashed line) are also shown for comparison.

SiO<sub>2</sub> concentrations. It was recognized that the separation of organic acids having very low pK<sub>a</sub> value from strong mineral acids by this kind of Gran titration is difficult. Recent studies (e.g. Munson and Gherini 1993) have indicated that although the organic acids in surface waters contain a continuum of acid functional groups, many of which display weak acid characteristics, a significant fraction of the organic acids can be considered as strong. This observation means that organic acids having the lowest pK<sub>a</sub> value have probably been titrated with the strong mineral acids in Publication I and in other studies using this kind of technique (Henriksen and Seip 1980, Webb 1982, Molværsmyr and Lund 1983, Røgeberg and Källqvist 1988).

Total acidity (equivalent point in titrations between pH 7.5–8.7) for hydrophobic and hydrophilic acids, respectively, averaged 10.7 μeq (mg DOC)<sup>-1</sup> (range 9.9–11.3 μeq (mg DOC)<sup>-1</sup> and 11.8 μeq (mg DOC)<sup>-1</sup> (range 10.1–13.2 μeq (mg DOC)<sup>-1</sup>). The fractionation studies connected with titrations of isolated acids allow calculation of the average total acidity of DOC (mostly carboxylic acids) for Finnish lakes (equation 3). The average value of 9.7 μeq (mg DOC)<sup>-1</sup> with a range from 8.3 to 10.6 μeq (mg DOC)<sup>-1</sup> agrees well with the value, 10 μeq (mg DOC)<sup>-1</sup>, reported by Oliver et al. (1983). In later studies 10 μeq (mg DOC)<sup>-1</sup> has generally been accepted for the average carboxyl content of aquatic humic substances (e.g. Perdue et al. 1984, Thurman 1985, Cantrell et al. 1990).

#### 4.2 Comparison and uncertainties of the organic acidity approaches

An empirical estimate for free organic anion ( $[A^-]_{\text{EMP}}$ , equation 4), the dissociation product of organic acids, was developed separately for the 10 lakes using titration results of isolated hydrophobic and hydrophilic acids combined with the fractionation results. Organic anion based on empirical measurements varied from 24 μeq l<sup>-1</sup> to 147 μeq l<sup>-1</sup> and corresponded well with the anion deficits in most lakes. In five lakes organic anion was higher than the anion deficit and in four lakes lower than the deficit. The difference between organic anion and anion deficit ranged from 0 to 41 μeq l<sup>-1</sup>, which was 0–27 % of the total amount of cations (Fig. 5).

The developed empirical model for organic anion, based on the combined data set of all fractionations and titrations ( $[A^-]_{\text{FIN}}$ , equation 9), was applied to the Finnish Lake Survey data set and compared with organic anion estimated by anion deficit ( $[A^-]_{\text{AD}}$ , equation 12) and by the model of Oliver et al. (1983) ( $[A^-]_{\text{OTM}}$ , equation 1). When applying  $[A^-]_{\text{OTM}}$  and  $[A^-]_{\text{FIN}}$  to the Finnish Lake Survey data set, TOC was used instead of DOC. If DOC results had been available these approaches would probably have given slightly lower values for organic anions. All three approaches for organic anion have limitations. Uncertainty in anion deficit is a result of uncertainty associated with the analysis

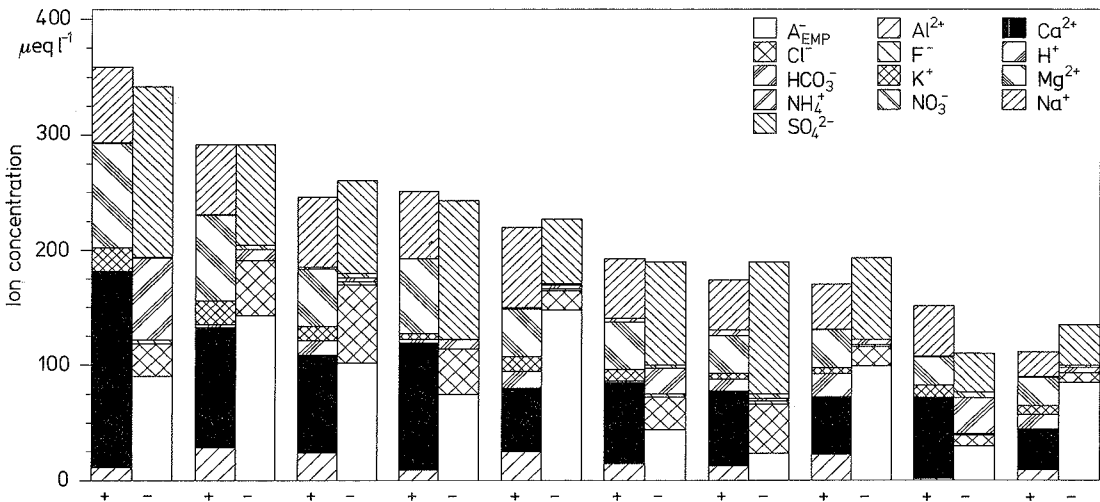


Fig. 5. Charge balances for 10 Finnish lakes with organic anion concentration ( $[A^-]_{EMP}$ ) based on empirical measurements.

of each of the 12 individual ions. Isolation and fractionation procedures are never perfect. The chemical characteristics of the material may vary between different isolation schemes (e.g. Aiken 1988, Hedges 1990, Shuman 1990). It has even been suggested that during the isolation procedure part of the material can be lost or even transformed in some way by the procedure (e.g. due to high and low pH conditions), resulting in a uniform fraction of DOC with uniform chemical properties (Shuman 1990). The model of Oliver et al. (1983) as well as equation (9) were designated to strip the acids of all complexed metals, which means that these approaches are strictly applicable only in the absence of metal-organic complexes.

Despite the limitations in different approaches, the organic anion concentrations in the Finnish Lake Survey estimated by the three methods agreed rather well (Fig. 6, Tables 1–2). The highest median organic anion ( $108 \mu\text{eq l}^{-1}$ ) was given by the model of Oliver et al. (1983), followed by the Finnish equation ( $96 \mu\text{eq l}^{-1}$ ) and the charge balance approach ( $89 \mu\text{eq l}^{-1}$ ).

#### Gran alkalinity correction in ion balances

In Publications III, IV, and V charge balance approach,  $[A^-]_{AD}$ , was used to estimate the organic anion content and the contribution of

organic acids to the acidity of Finnish lakes. In these studies Gran alkalinity was used as an estimate for bicarbonate. The satisfactory relationship between the three approaches supports the usability of the method, although it can be considered more as an underestimate than an overestimate of the true organic acidity contribution.

On the basis of titrations of isolated organic acids the contribution of organic anion in the Finnish Lake Survey Gran alkalinity results (in the pH range: sample pH – end point pH in Gran titration) was estimated using equation (14). The median organic anion fraction titrated during Gran alkalinity was  $15 \mu\text{eq l}^{-1}$ . Samples with high TOC concentrations and high pH are titrated over the widest pH range, resulting in the highest organic alkalinity contribution. For lakes averaged by pH class over 0.5 unit intervals, organic anion contribution in Gran alkalinity was highest ( $24 \mu\text{eq l}^{-1}$ ) in the pH range 6.0–6.5 (average TOC  $14 \text{ mg l}^{-1}$ ). However, the majority of high TOC samples in the Finnish Lake Survey have low pH and the sample is titrated only over a narrow range of pH, thus minimizing the organic interference. Recently Roila et al. (1993b) have calculated bicarbonate concentrations in 40 Finnish lakes (median pH 5.7, median TOC  $12 \text{ mg l}^{-1}$ ) based on TOC, DIC (dissolved inorganic carbon) and Gran alkalinity measurements. On the basis of Gran alkalinity and

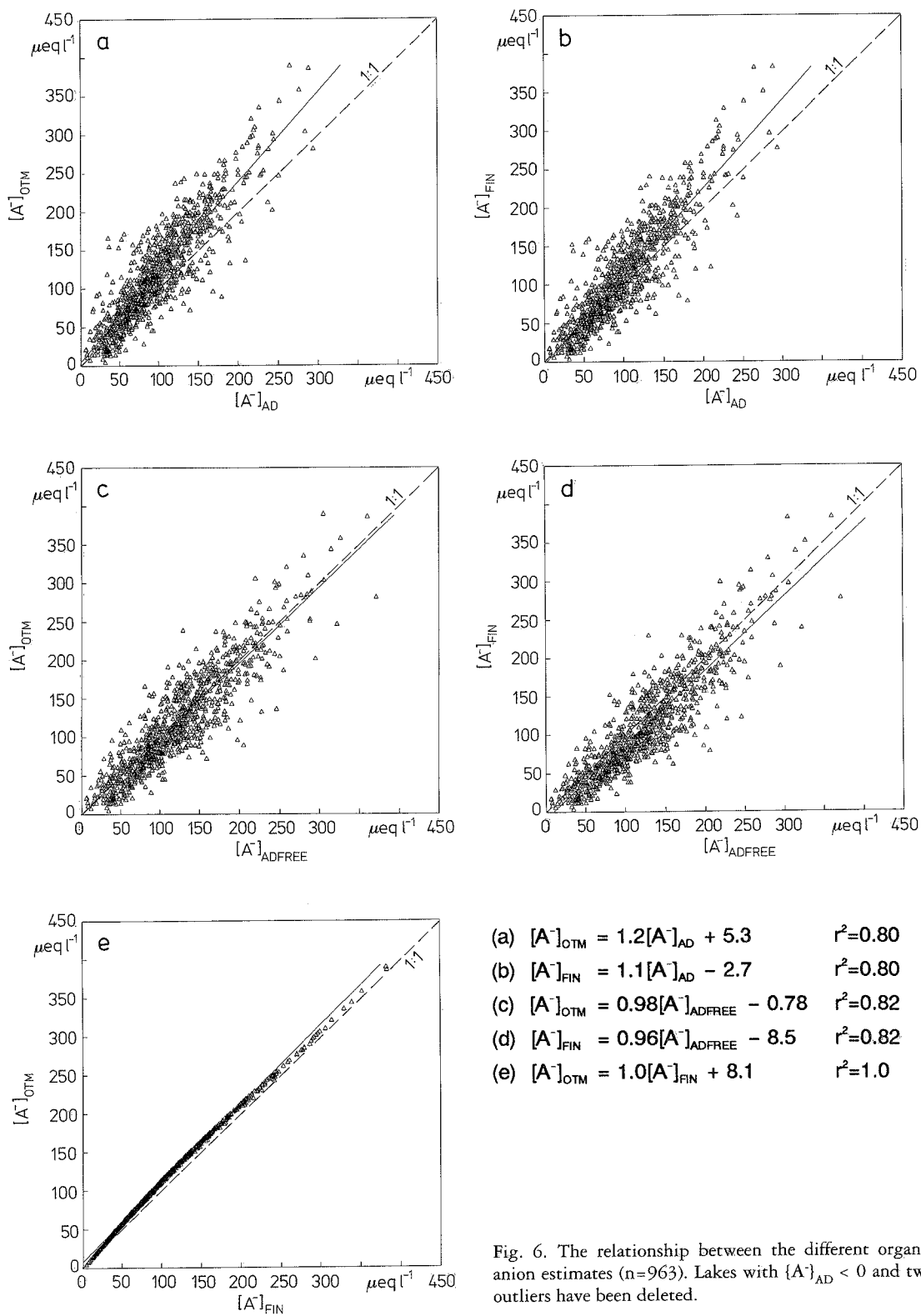


Fig. 6. The relationship between the different organic anion estimates ( $n=963$ ). Lakes with  $[A^-]_{AD} < 0$  and two outliers have been deleted.

bicarbonate concentrations the median organic anion contribution to Gran alkalinity was estimated to be  $16 \mu\text{eq l}^{-1}$ , close to median organic anion contribution in the Finnish Lake Survey. Thompson (1986) concluded that the impact of organic anions on Gran alkalinity measurements in organic-rich waters in Nova Scotia was minimal, except in the uncommon situation of combined high organic carbon concentrations and high pH. In such samples (DOC about  $21 \text{ mg l}^{-1}$ ; pH range 5.5–5.8) the organic anion contribution was found to be up to  $30 \mu\text{eq l}^{-1}$ .

When Gran alkalinity in the charge balance approach is replaced by estimated bicarbonate (equation 15), the regression line between  $[\text{A}^-]_{\text{FIN}}$  and the corrected charge balance approach,  $[\text{A}^-]_{\text{ADFREE}}$ , as well as between  $[\text{A}^-]_{\text{OTM}}$  and  $[\text{A}^-]_{\text{ADFREE}}$  is closer to the 1:1 line (Fig. 6). The corrected charge balance approach increases the median organic anion in the full set of lakes to  $114 \mu\text{eq l}^{-1}$ , higher than the median values given by  $[\text{A}^-]_{\text{OTM}}$  ( $108 \mu\text{eq l}^{-1}$ ) and by  $[\text{A}^-]_{\text{FIN}}$  ( $96 \mu\text{eq l}^{-1}$ ) (Table 1, Fig. 7). Generally at low pH values  $[\text{A}^-]_{\text{OTM}}$  and  $[\text{A}^-]_{\text{FIN}}$  give higher values than  $[\text{A}^-]_{\text{ADFREE}}$ , whereas at high pH values the corrected charge balance approach gives the highest values. At low pH values  $[\text{A}^-]_{\text{ADFREE}}$  is closer to  $[\text{A}^-]_{\text{FIN}}$ , whereas at high pH values  $[\text{A}^-]_{\text{ADFREE}}$  is closer to  $[\text{A}^-]_{\text{OTM}}$ . Oliver et al. (1983) model has generally been considered to be a slight overestimate of the free organic anion content, because it describes the dissociation behaviour of organic acids purified from all complexed cations. In a recent study by Wilkinson et al. (1992) it gave significantly lower organic anion concentrations for Quebec lakes compared with anion deficits.

The median  $\Sigma[\text{Cations}]/\Sigma[\text{Inorganic anions}]$ -ratio for the full set of lakes was 1.6. Inclusion of organic anions estimated either by the Finnish equation or by the model of Oliver et al. (1983) balanced the ion ratio to 1.0 (Table 1). In lakes with TOC concentrations higher than  $10 \text{ mg l}^{-1}$  the median  $\Sigma[\text{Cations}]/\Sigma[\text{Inorganic anions}]$ -ratio was 1.9. Inclusion of  $[\text{A}^-]_{\text{FIN}}$  gave the ion ratio 1.0 also in these high TOC lakes (Table 2). The good consistency between the different approaches for organic anion supports the usability of any of the approaches in allowing broad trends and patterns of organic acidity in Finnish lakes to be discussed. The equation (9) based on empirical measurements from Finnish

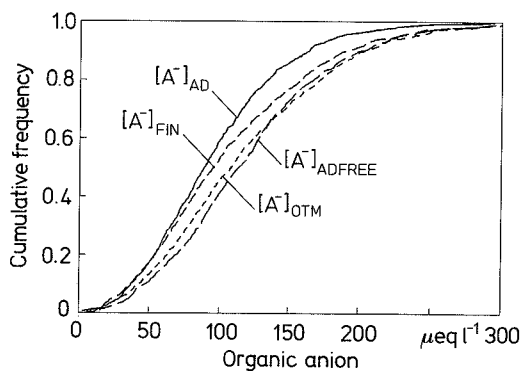


Fig. 7. Cumulative frequency distributions for the different organic anion estimates.

lakes requires only DOC and pH measurements from a natural water sample for providing an estimate for organic anion. It excludes many error possibilities inherent in different cation and anion measurements, because comprehensive cation and anion measurements are not necessary. This supports the use of equation (9) in assessing the contribution of organic acids to the acidity of Finnish lakes.

#### 4.3 Impact of acidification on organic carbon concentrations and on the dissociation of organic acids

There has been considerable controversy concerning the hypothesis that acidification has decreased organic carbon concentrations and colour values in surface waters. The two most likely mechanisms resulting in decreasing organic carbon, colour and organic anion concentrations in surface waters have been suggested to be organic acid-metal complexation (and consequent precipitation) and pH-dependent changes in the dissociation of organic acids (see Marmorek et al. 1987 for a review). A notable feature in the dissociation of the organic acids in Finnish lakes (Fig. 4) is the high anionic charge which organic acids retain even at pH 4. Moreover the dissociation increases clearly with increasing pH. At pH 4 on average 48 % of the organic acids were dissociated, whereas at pH 7 the average disso-

ciation increased to 92 % (equation 11).

Organic anion estimated by corrected charge balance approach (equation 17) was positively related to both TOC and pH. The relationship between  $[A^-]_{\text{ADFREE}}$  and TOC was evident in the full set of lakes ( $r^2=0.71$ ,  $P<0.001$ ), although stronger in discrete pH intervals. In lakes with pH value lower than 4.5 the relationship was strongest ( $r^2=0.97$ ,  $P<0.001$ ) and it decreased with increasing pH ( $r^2=0.69$  in lakes with pH > 7.0,  $P<0.001$ ). Because organic acids are a mixture of different functional groups with varying acid-base strengths, the degree of dissociation depends largely on solution pH. Over a wide range of pH, the dissociation can be expected to vary widely, whereas over small pH intervals the dissociation percentage is more nearly constant. The slope of the relationship between anion deficit and DOC increased as the interval pH increased. This reflects a larger extent of dissociation of the functional groups as the pH increases, in agreement with the titration results of isolated organic acids (Fig. 4). The pH dependent dissociation of organic acids suggests that if acidification results in decreasing pH there should be a decrease in the dissociation of organic acids, resulting in decreasing organic acidity in surface waters. On the other hand increasing pH due to more effective control strategies over acidic deposition could result in an increasing organic acidity contribution. Seasonal variations in pH can also have an impact on the dissociation of organic acids, e.g. short-term drops in pH during the snow melt period can decrease the dissociation of organic acids.

Catchment scale experiments have only recently been implemented. They offer considerable promise, as all the potentially important mechanisms (except inlake processes) are included, although the process of acidification is somewhat accelerated and spatial variation in soils within the catchment is a difficult problem. The exclusion of acid rain in a RAIN project research area increased the dissociation of organic acids (Wright 1989). A pH increase from 4.0 to 4.1 was coupled with organic anion increase (calculated using the charge balance approach) from about  $22 \mu\text{eq l}^{-1}$  in 1984 to  $49 \mu\text{eq l}^{-1}$  in 1987. This increase was concluded to be due to increased dissociation of organic acids and not to the change in TOC concentrations.

The Humic Lake Acidification Experiment

(HUMEX) is an international project launched in 1988 and coordinated by the Norwegian Institute for Water Research (Gjessing 1992). One half of the humic lake and its catchment is acidified, the other half is the reference area. The first results of the HUMEX project suggest that the contribution of organic acids to the overall lake acidity (average pH about 4.5) has slightly decreased since the acidification was started. This has been connected to the observed increase in sulphate concentrations in the acidified lake half as well as to a slight decrease in pH and organic carbon concentrations after the acidification was started (Gjessing 1992, Kortelainen et al. 1992).

Acidification can also have an impact on the leaching of organic carbon and organic acids. A decrease in the amount of DOC leached with decreasing solution pH has been suggested by Chang and Alexander (1984) and Hay et al. (1985). By contrast in some studies increased leaching of DOC and organic acids from soils as a result of additions of mineral acids has been found (McColl and Pohlman 1986). In the paleolimnological approach of Davis et al. (1985) diatoms were used to reconstruct historical concentrations of TOC, which indicated a reduction of TOC during acidification. Whereas in an experimental acidification of a brownwater stream, Hedin et al. (1990) showed that DOC concentrations were not reduced by acidification. There are still inconsistencies, and the question of acidification and surface water organic carbon concentrations is far from settled. Historical changes in the amount and type of organic carbon within a drainage basin are difficult to infer or quantify and unequivocal linkage of long-term changes in DOC to acid deposition has still to be conclusively demonstrated. In particular, distinguishing between DOC differences which are linked to varying land use patterns, vegetation and soil type from those due to strong acid deposition can be problematic (Sedell and Dahm 1990).

#### 4.4 Contribution of organic acids to the acidity of Finnish lakes

##### 4.4.1 Acid deposition vs. organic acids from the catchments

Significant relationships between pH and most of the measured catchment characteristics were

found in a selected lake group (II), emphasizing the important role of the catchment in determining the pH of Finnish lakes. A considerable part of the variation in pH of humic lakes was explained by the same predictors, which were also the best predictors for the TOC concentrations in the lakes. The proportion of peatlands in the catchment was positively related to TOC and negatively related to pH. Upstream lakes made a negative contribution to TOC and a positive contribution to pH. Together these variables explained 70 % of the variation in TOC and 46 % of the variation in pH. In stepwise multiple regression 65 % of the variation in pH was explained by lake area, the proportion of the catchment covered by peatlands, upstream lakes and latitude. Latitude, which was strongly related to lake sulphate concentrations ( $r^2=0.63$ ), was the last variable to enter the regression improving the cumulative explanation power of the model by only 1 percent. The results suggested that the pH of humic lakes in Finland is determined to a greater extent by individual catchment characteristics and organic carbon concentrations than by the geographical location of the lake, which determines the level of current atmospheric loading.

In the Finnish Lake Survey the contributions of organic vs. anthropogenic sources of acidity to the free acidity were evaluated by calculating the dependency of pH on the variables reflecting these sources. TOC was used to describe the catchment-derived acidity. This variable explained the variation of pH better than non-marine sulphate (assumed to be mostly atmospherically derived) both in the full set of lakes and in the subgroups stratified according to base cation concentrations reflecting the acid sensitivity of the lakes (III). A stepwise multiple regression analysis applied to the Finnish Lake Survey using the sum of non-marine base cations, non-marine sulphate and TOC as independent variables, explained 61 % of the variation in pH. Nitrate did not increase the proportion of variance explained. The results of the Finnish Lake Survey support the conclusions based on the earlier smaller data set (II) about the dominating role of organic acidity in Finnish lakes.

The runoff water from catchments to many Finnish lakes flows generally through peatlands or acidic organic soils. The annual leaching of TOC from five peatland-dominated or forested

catchments during a 8–14 year period ranged from 1 900 to 18 000 kg km<sup>-2</sup> a<sup>-1</sup> (VI). The leaching was strongly dependent on hydrological conditions; annual leaching was closely related to annual runoff. Higher leaching values during rainy years were often a result of both high runoff and high concentrations. The mean annual runoff from the catchments increased to the north. This trend compensated for the lowest TOC concentrations recorded in the two northernmost catchments such that there was little variation in the mean annual leaching between the catchments. The mean annual leaching of total organic carbon from the five catchments located in different parts of the country ranged from 4 700 to 7 300 kg km<sup>-2</sup> a<sup>-1</sup>.

The mean annual leaching of TOC from these catchments would represent about 50–70 keq km<sup>-2</sup> leaching of organic acids using a total acidity of 9.7 µeq (mg DOC)<sup>-1</sup> (equation 3) to represent the total acidity of organic carbon, higher than the mean annual deposition of strong acids in the highest deposition areas in southern Finland. The mean annual deposition of strong acids in 50 bulk deposition monitoring stations in Finland in 1991 ranged from 3 to 32 keq km<sup>-2</sup>; in southern Finland the range was about 20–30 keq km<sup>-2</sup> (Järvinen and Vänni 1992). The average dissociation of organic acids increased with increasing pH from about 48 % at pH 4 to about 92 % at pH 7. This suggests that in forested or peatland-dominated regions the organic acid contribution at any pH in Finnish surface waters is equal to or exceeds deposition-derived strong acids.

#### 4.4.2 Regional acidification of Finnish lakes

The areas exposed to the greatest risk of anthropogenic surface water acidification are the sensitive regions receiving high levels of acidic deposition mainly in southern and north-eastern parts of the country (Kämäri 1986). Presently, the total sulphur deposition is highest in southernmost Finland (0.7–1.0 g m<sup>-2</sup> a<sup>-1</sup> S) (Rikkitoimikunta II:n mietintö 1993) and generally decreases to the north. However, there is a local maximum in the north-eastern parts of the country due to smelting emissions on the Kola Peninsula. The sulphate concentrations in the Finnish Lake Survey generally reflect the spatial sulphate



deposition pattern in Finland, i.e. the highest concentrations are observed in southern Finland (Forsius et al. 1990a, V). In a few lakes scattered throughout the country the sulphate concentrations were higher than would be expected from anthropogenic deposition. These high concentrations are most probably due to geological sources of sulphate in the catchments of these lakes (see Palko et al. 1988). Although many studies have shown that wetlands have the potential to retain sulphate (e.g. Urban et al. 1989, LaZerte 1993), wetlands have also been shown to release sulphate during dry seasons or droughts (Wieder 1985, Bayley et al. 1987, LaZerte 1993). The median nitrate concentration in the Finnish Lake Survey was close to  $1 \mu\text{eq l}^{-1}$ , suggesting that the deposition of nitrogen compounds presently plays a minor role in the long-term acidification of the lakes (Forsius 1992).

In Finland the acidifying potential of the deposition shows a much more uniform regional distribution than would be expected from the sulphate and nitrogen depositions alone (Laurila 1990). The long-term median pH of precipitation varies between 4.4 and 4.8 in southern regions and between 4.6 and 5.2 in the north (Järvinen and Vänni 1990). Although the concentrations of sulphate and nitrate in precipitation are much higher in southern Finland they are more readily neutralized by basic compounds in the deposition (Joffe et al. 1990). In high deposition areas in southern Finland soils are deeper, finer-textured and more fertile compared with those in northern Finland, resulting in higher base cation concentrations in the lakes. Moreover, the higher acidic deposition in the south has probably increased the leaching of base cations.

The present acidic deposition load over large areas of Finland is clearly above the critical load for sensitive ecosystems (Kämäri et al. 1993). The highest exceedance was estimated for lakes in southern Finland. In south-eastern parts of the country the critical load of sulphur was exceeded in more than 70 % of the lakes, whereas the corresponding values in north-eastern parts of Lapland were about 10 to 30 % (Forsius 1992). Acidic lakes occurred most commonly in south-western and central regions, and in eastern Finland along the border. Relatively few acidic lakes were observed in high-deposition areas in southern Finland, which can be attributed to high

base cation concentrations. The decreasing effect of non-marine sulphate on the pH values can be seen within separate sensitivity classes (III). There were clear differences in the relative frequencies of hydrological lake types between acidic and non-acidic lakes. Seepage and headwater lakes were more common among the acidic lakes (Forsius 1992).

The proportion of acidic lakes was higher in Subregion 1 than in Subregion 2; 13 % of the lakes had  $\text{ANC} \leq 0$  in Subregion 1, and the corresponding figure in Subregion 2 was 2 %. In Subregion 1, 11 % of the lakes had  $\text{pH} < 5.0$ , whereas in northern parts of the country no lakes with  $\text{pH}$  below 5.3 were surveyed (Forsius 1992). The fact that the lakes with area smaller than  $0.1 \text{ km}^2$  were excluded in northern Finland probably contributed to the pattern of acidic lakes. Lake area made a significant positive contribution to  $\text{pH}$  in a selected lake group ( $r^2=0.48$ ) (II). In the Finnish Lake Survey the median lake area in lakes with  $\text{ANC} \leq 0$  was  $0.038 \text{ km}^2$  compared with  $0.105 \text{ km}^2$  in the non-acidic lake group. The acidic lakes were mainly small lakes located in areas totally dominated by acidic, slowly weathering bedrock with lower concentrations of base cations compared with non-acidic lakes (median  $119 \mu\text{eq l}^{-1}$  vs.  $261 \mu\text{eq l}^{-1}$ ) (Forsius 1992). Large lakes can be expected to have larger, more complex catchments with a greater variety of bedrock types and thicker and better buffered soils. Therefore large lakes can be expected to be better buffered and higher in  $\text{pH}$ . Moreover, in the Finnish Lake Survey large lakes had predominantly lower TOC concentrations compared to small lakes which further contribute to the pattern of acidic lakes.

A number of lakes in Finland have originally been acidic due to the contribution of organic acids. On the basis of calculations using a few empirical equations including uncertainties Forsius et al. (1990a) estimated that a large proportion of the presently acidic lakes with  $\text{pH} < 5.3$  in the Finnish Lake Survey are naturally acidic (original  $\text{pH}$  levels  $< 5.3$ ). The lakes were assumed to be naturally acidic if the sum of non-marine background sulphate, fluoride and estimated organic anion concentrations exceeded estimated non-marine background base cation concentrations. 17 % of the lakes had  $\text{pH} < 5.3$ ; the proportion of these acidic lakes estimated to be naturally acidic was 56–81 %. The lakes

estimated to have become acidified recently were located mainly in the high deposition areas of southern Finland. In eastern and central regions most of the presently acidic lakes were estimated to be naturally acidic. Acid deposition has further decreased the pH in many of these already acidic lakes.

#### 4.4.3 Major anion ratios in lakes: organic anion vs. non-marine sulphate

The interaction between acidic loading and lake acidity is complex and depends on several interrelated factors: e.g. the weathering rate of the catchment soils, hydrological flow paths and inputs of catchment-derived acidity. The natural catchment-derived acidity in Finnish lakes is predominantly due to organic acids, although in some regions on the western coast the acid sulphate soils are locally important (see Palko et al. 1988). Nitrate has only a minor contribution to the acidity of Finnish lakes; the median nitrate concentration was close to  $1 \mu\text{eq l}^{-1}$  (Table 1). Consequently organic vs. minerogenic acidity in Finnish lakes can be evaluated comparing organic anion and non-marine sulphate concentrations in the lakes.

The median pH in the Finnish Lake Survey was 6.3 (range 4.1–8.0). Humic lakes were, on average, more acid than clearwater lakes. Organic acids decreased the pH values throughout the country, and acid humic lakes are also found in low deposition areas with base-poor catchments. The proportion of lakes with pH values lower than 5.5 in the whole country was 24 %. Of these low pH lakes 93 % had TOC concentrations  $\geq 5 \text{ mg l}^{-1}$  (III). 26 % of the highly humic (TOC  $> 10 \text{ mg l}^{-1}$ ) lakes with low sulphate concentrations ( $^*\text{SO}_4 < 30 \mu\text{eq l}^{-1}$ ) were acidic (ANC  $< 0 \mu\text{eq l}^{-1}$ ) (V).

Organic anion was the main anion in the Finnish Lake Survey whatever estimate for organic anion was used (Table 1). Using equation (9) the median organic anion was  $96 \mu\text{eq l}^{-1}$ , higher than median non-marine sulphate ( $71 \mu\text{eq l}^{-1}$ ). The background sulphate concentrations have been estimated to be  $10\text{--}15 \mu\text{eq l}^{-1}$  for areas of Norway and the U.S.A. containing lakes with low concentrations of base cations (Brakke et al. 1989). In Finnish lakes with higher base cation concentrations background sulphate concen-

trations are probably higher. In lakes located in northwestern Finland with minor acidic deposition non-marine sulphate concentrations were generally  $15\text{--}40 \mu\text{eq l}^{-1}$  (Posch et al. 1993). This further emphasizes the dominant role of catchment derived organic acids compared with anthropogenic acids. The contribution of organic anions to the charge balance increased with increasing TOC concentrations and decreasing pH (IV). In low TOC lakes non-marine sulphate concentrations were more comparable to organic anion concentrations (Table 2).

Organic anion (estimated by equation 9) was the dominant anion (i.e. had the highest concentration of all anions) in 51 % of the lakes (median pH 5.9) in the whole country, whereas non-marine sulphate dominated in 27 % of the lakes (median pH 6.2), and bicarbonate (estimated by equation 15) in 22 % of the lakes. Organic anion dominated in acid lakes, indicating that a substantial fraction of the overall acidity of such lakes was of natural origin. Organic anion was the dominating anion in 69 % of the lakes with ANC  $\leq 0$  (median TOC =  $15 \text{ mg l}^{-1}$ ), the other acidic lakes being dominated by sulphate. Organic anion-dominated lakes occurred throughout the country, but were concentrated in the peatland-dominated areas across central Finland (IV). The sulphate-dominated lakes were mainly concentrated in high deposition areas in the south, whereas bicarbonate dominated in northern Finland. Although the Finnish Lake Survey demonstrated that organic acids strongly affect the acidity of lakes in Finland, in the highest deposition areas in southern parts of the country the minerogenic acidity commonly exceeded the catchment-derived organic acidity. The high  $^*\text{[SO}_4\text{]}/\text{[A}^-]$  -ratio in the south is further pronounced because the peatland proportion in the southern parts of the country is not particularly high, whereas the most peatland-dominated areas are found in areas of lower deposition (IV).

The concentrations of all ions were generally lower in northern parts of the country. The median organic anion, sulphate and base cation concentrations in Subregion 1 were  $110 \mu\text{eq l}^{-1}$ ,  $90 \mu\text{eq l}^{-1}$  and  $270 \mu\text{eq l}^{-1}$ , respectively. In Subregion 2 the corresponding figures were  $53 \mu\text{eq l}^{-1}$ ,  $35 \mu\text{eq l}^{-1}$  and  $180 \mu\text{eq l}^{-1}$ , respectively (Table 1). Acidification of lakes by non-marine sulphate vs. organic anion can be further interpreted in

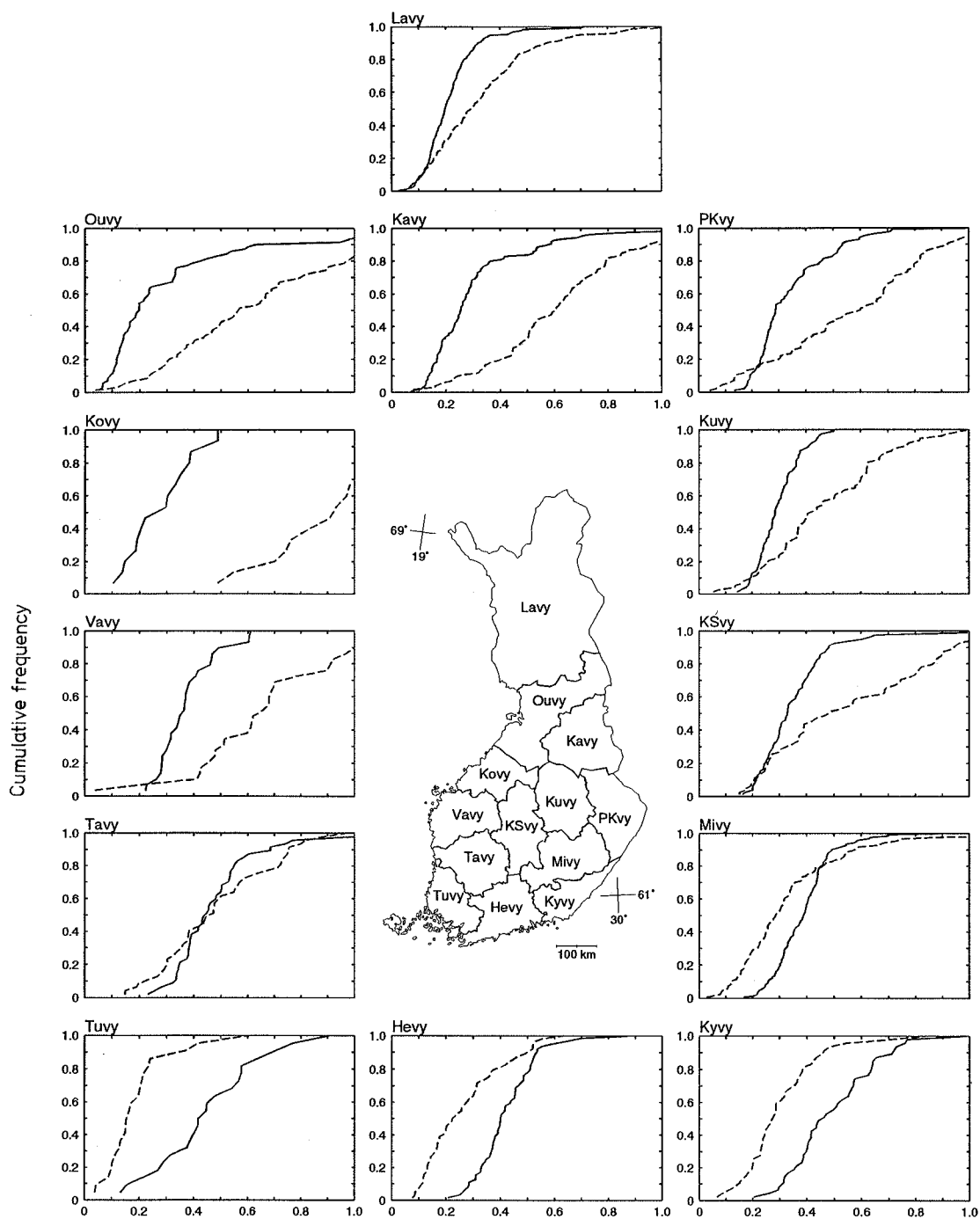


Fig. 8. Cumulative frequency distributions for base cation normalized non-marine sulphate ( $*[SO_4]/*[BC]$ ; continuous line) and organic anion ( $[A^-]_{FIN}/*[BC]$ ; dashed line) in the 13 Water and Environment Districts in Finland.

base cation normalized ratios ( $*[\text{SO}_4]/*[\text{Ca}+\text{Mg}+\text{Na}+\text{K}]$ ) vs.  $[\text{A}^-]_{\text{FIN}}/*[\text{Ca}+\text{Mg}+\text{Na}+\text{K}]$ ). In the four southernmost Water and Environment Districts non-marine sulphate exceeded organic anion concentrations. In the other nine districts organic anions dominated (Fig. 8). The dominance of organic anions was especially obvious in flat peatland-dominated areas near the Gulf of Bothnia, where TOC concentrations were also highest.

In Publications III, IV, and V the charge balance approach (equation 12) was used to estimate the organic anion content and the relative contributions of organic acids and non-marine sulphate to the acidity of Finnish lakes. The other organic acidity approaches would have resulted in higher median organic anion concentrations (Tables 1–2) still emphasizing the overwhelming role of humic matter in the acidity of Finnish lakes. Moreover, the other approaches would have increased the number of lakes classified as organic anion dominated due to higher organic anion concentrations as well as due to lower bicarbonate concentrations. The regional distribution about the dominant role of sulphate in the southernmost Finland, organic anion across large regions in central Finland and bicarbonate in the northernmost Finland is valid using any of the approaches.

In Publications I and II sulphate and chloride were measured colorimetrically. The lakes included in these earlier publications were sampled also during autumn 1987. Ion chromatography measurements during autumn 1987 gave lower concentrations for both of these ions compared with the earlier results. This was most probably due to overestimation of the true sulphate and chloride concentrations in the earlier studies. Consequently organic anion concentrations, calculated as the difference between  $\Sigma[\text{Cations}]$  and  $\Sigma[\text{Inorganic anions}]$  were underestimated in the earlier paper (see Fig. 6 in Publication II).

The contribution of organic acids to the acidity of Finnish lakes is high compared with surveys of lakes conducted in North America and Scandinavia. In most areas in the U.S. Eastern Lake Survey, organic anion concentrations were lower than sulphate concentrations (Brakke et al. 1988, Eilers et al. 1988a, Eilers et al. 1988b). In northeastern Minnesota, the upper Great Lakes area and the upper Midwest, organic anion concentrations exceeded sulphate concentrations.

In eastern Canada the role of humic matter in the acidity of lakes and streams has been studied intensively (e.g. Gorham et al. 1986, Howell 1986, Jeffries et al. 1986, Kerekes et al. 1986, Wilkinson et al. 1992). In northwestern Ontario, Labrador, Nova Scotia and Newfoundland, organic anion concentrations were higher than non-marine sulphate concentrations. In other subregions sulphate dominated (Jeffries et al. 1986). The highest median organic anion concentrations occurred in northwestern Ontario ( $94 \mu\text{eq l}^{-1}$ ) (Jeffries et al. 1986). Brakke et al. (1987) demonstrated that organic acids contribute to the acidity of humic lakes, but strong anthropogenic acids further decrease the pH, and are the primary reason for the recent acidification of coloured lakes in southern Norway. In the Norwegian 1 000 Lake Survey during the autumn overturn in 1986, organic anions represented only  $< 10 \%$  of the total anions for the full set of lakes (Henriksen et al. 1988a). The methodologies and criteria used for lake selection were different in these surveys. In Norway and in the U.S. Eastern Lake Survey the lake selection targeted areas considered most sensitive to acidification. Moreover, the inclusion of small lakes in the Finnish survey probably emphasized high TOC concentrations compared with other surveys of lakes conducted in North America and Scandinavia (IV).

#### 4.5 The effect of organic carbon on alkalinity

Brakke et al. (1987) suggested that organic acids make humic lakes more sensitive to acid deposition than clearwater lakes, for lakes with the same concentrations of base cations. The large data base of the Finnish Lake Survey supports this conclusion. In lakes stratified into subgroups according to base cation and TOC concentrations, Gran alkalinity was systematically lower in high TOC lakes compared with low TOC lakes with the same base cation levels (Table 3).

In agreement with the results of Sullivan et al. (1989), alkalinity calculated as a difference between non-hydrogen cation and strong acid anion concentrations ( $[\text{ALK}]_{\text{CB}}$ , equation 13) was in most samples higher than alkalinity measured by Gran titration ( $[\text{ALK}]_{\text{GRAN}}$ ) (Fig. 9) The discrepancy between calculated and measured alkalinity increased with increasing TOC concentrations (Fig. 10). Most of the past approaches

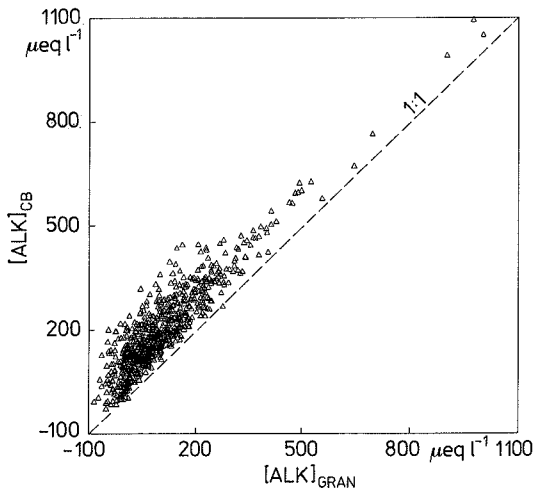


Fig. 9. Charge balance alkalinity ( $[ALK]_{CB}$ ), as a function of Gran alkalinity ( $[ALK]_{GRAN}$ ) presented for lakes with  $[ALK]_{CB} \leq 1100$ . Lakes with  $[A^-]_{ADFREE} < 0$  and two outliers have been deleted.

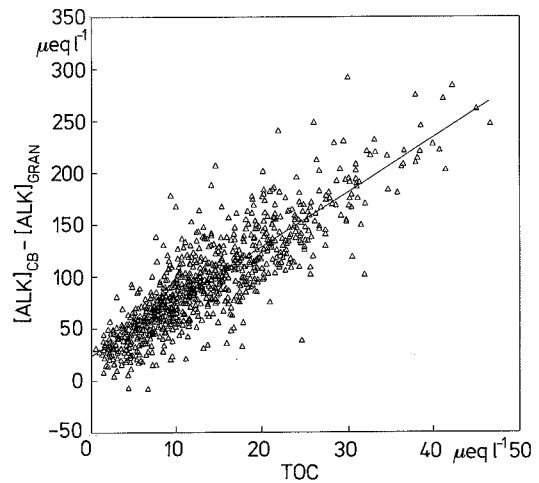


Fig. 10. The difference between  $[ALK]_{CB}$  and  $[ALK]_{GRAN}$  as a function of sample TOC concentration ( $[ALK]_{CB} - [ALK]_{GRAN} = 5.3TOC + 24$ ,  $r^2 = 0.75$ ,  $n = 964$ ). Lakes with  $[A^-]_{ADFREE} < 0$  and two outliers have been deleted.

Table 3. Gran alkalinity in lakes stratified into subgroups according to TOC and non-marine base cation concentrations ( $*[BC] = *[Ca + Mg + Na + K]$ ) ( $\mu eq l^{-1}$ ).

TOC (mg l <sup>-1</sup> )	Gran alkalinity ( $\mu eq l^{-1}$ )			
	*[BC] < 100	100 ≤ *[BC] < 200	200 ≤ *[BC] < 300	*[BC] ≥ 300
< 5	2	69	138	237
5–15	-11	51	94	187
≤ 15	-46	7	39	122

for evaluating the effects of organic acids on the acid-base characteristics of surface waters in North America and northern Europe have treated them solely as weak acids. Recently Munson and Gherini (1992, 1993) suggested that the difference between calculated and measured alkalinity can mostly be attributed to the presence of strong organic acids, which remain unprotonated in the titration procedure. The Finnish Lake Survey data base thus indicates that a fraction of the organic acid mixture at the pH values existing in natural waters can be considered strong, supporting the earlier conclusions of Brakke et al. (1987) and Driscoll et al. (1989). In natural waters these strong organic acids with low  $pK_a$  value decrease buffer capacity, making humic lakes chemically

more sensitive to acidification than clear-watered lakes when the base cation concentrations are equal. The biological impacts of acidification in humic lakes are generally, however, often less serious compared with clear water lakes because many toxic substances, e.g. aluminium, are complexed with humic matter (e.g. Henriksen et al. 1989).

Strictly defined it is analytically inaccurate to subdivide organic anions into strong and weak acids based on their titration behaviour in Gran alkalinity. The fraction of organic anions that can be protonated in an ANC titration depends on the pH at the titration endpoint. The endpoint pH in turn is a function of other factors e.g. organic and inorganic carbon concentrations and extent to which the sample solution is in equilibrium with the atmosphere (Cantrell et al. 1990). When applying Gran alkalinity results to surface water chemistry this approximate subdivision, however, clarifies the behaviour of organic acids.

Munson and Gherini (1993) studied the strength of organic acids by examining the relationship between  $[ALK]_{CB}$  and  $[ALK]_{GRAN}$  in the Adirondack lake data base and concluded that DOC contributes  $4.5\text{--}5 \mu eq (mg \text{ DOC})^{-1}$  of strong acid to water sample. In the Finnish Lake Survey the slope in the regression between

$[\text{ALK}]_{\text{CB}}$  and Gran alkalinity was 5.3 (Fig. 10). These values based on empirical lake data bases are in agreement with the theoretical calculations by Cantrell et al. (1990) and Hemond (1990a). Cantrell et al. (1990) demonstrated that a substantial fraction of the organic acids remains ionized well below pH 4 and would not be protonated in a typical alkalinity titration. Cantrell et al. (1990) proposed that the difference between charge balance alkalinity ( $[\text{ALK}]_{\text{CB}}$ ) and Gran alkalinity is the ANC of the sample at the pH of the titration endpoint and can be predicted from DOC ( $[\text{ALK}]_{\text{CB}} - [\text{ALK}]_{\text{GRAN}} = 4.48 \text{ DOC}$ ). The value 4.48 presented by Cantrell et al. (1990) was based on a lower pH range (3.0–4.0) in regression to obtain Gran alkalinity values compared with the Finnish Lake Survey (pH range 3.7–4.4). Hemond (1990a) concluded that each milligram of organic carbon per liter lowers Gran alkalinity by  $4.6 \mu\text{eq l}^{-1}$  ( $[\text{ALK}]_{\text{CB}} = [\text{ALK}]_{\text{GRAN}} + 4.6 \text{ DOC}$ ). This value was found to be quite constant over the range of organic carbon from 0 to 30 mg  $\text{l}^{-1}$ . It can be concluded that in Finnish lakes each milligram of TOC per liter lowers Gran alkalinity by about  $5 \mu\text{eq l}^{-1}$ .

In aquatic ecosystems organic carbon is both a natural background source of acidity decreasing pH and alkalinity but also a potentially significant buffer against acidic deposition in low-alkalinity waters. The median organic anion fraction titrated in Gran alkalinity in the Finnish Lake Survey was estimated to be  $15 \mu\text{eq l}^{-1}$  (equation 14). The largest amounts of organic anions were titrated in samples with high TOC concentrations and high pH (see section 4.2). However, the contribution of organic alkalinity to the total alkalinity was highest in high TOC lakes with relatively low pH, due to low bicarbonate alkalinity in such waters. The acid-neutralizing capacity provided by organic anions in the Finnish Lake Survey was  $1.6 \mu\text{eq}$  per milligram of TOC. In the study of Roila et al. (1993b) based on TOC, DIC and ANC measurements from 40 Finnish lakes the median organic anion contribution to Gran alkalinity was estimated to be  $1.9 \mu\text{eq (mg TOC)}^{-1}$ . Hedin et al. (1990) calculated that organic anions provided  $2.0 \mu\text{eq}$  acid-neutralizing capacity per milligram DOC in an empirical acidification of a brownwater stream (pH range 4.2–4.6, DOC 7–15 mg  $\text{l}^{-1}$ ). Johannessen (1980) concluded that although aluminium compounds are more effective in buffering

than humic matter, organic buffering is generally more important in natural waters because organic carbon concentrations are much higher than those of aluminium and part of the aluminium is complexed by humic matter. It can be concluded that the carbonate system in Finnish lakes is the dominant contributor to ANC. The contribution of organic buffering is emphasized in humic lakes in which bicarbonate concentrations have been decreased by the input of strong acids.

The weak-strong acid characteristics of organic acids in the Finnish Lake Survey can be summarized as follows. The strong organic acid contribution was estimated to be about  $5 \mu\text{eq (mg TOC)}^{-1}$ . These strong organic acids with low  $\text{pK}_a$  values are completely dissociated at all pH values existing in natural waters decreasing the buffer capacity and pH values in Finnish lakes. During Gran titrations the strong organic acid fraction remains unprotonated. The dissociation of weak acids with higher  $\text{pK}_a$  values is pH dependent and in natural waters the weak organic acids are a source of acidity but the corresponding anions act as a buffer against strong mineral acids, too. During Gran titrations a fraction of these anions are titrated behaving as a base. The fraction of organic anions contributing to the buffer capacity ( $15 \mu\text{eq l}^{-1}$ , equation 14) represented about 16 % of the median organic acidity contribution in the Finnish lakes ( $96 \mu\text{eq l}^{-1}$ ; equation 9).

The methodological discussion of ANC in natural waters can be summarized as follows. After intensive research during several years in both northern Europe and North America there is still no general consensus on the best measure for acid-neutralizing capacity in natural waters. The three approaches used in acidification research have been 1) titration to a fixed end-point pH, 2) Gran titration and 3) charge balance alkalinity. A complex mixture of strong organic acids (as well as some other compounds, e.g. Al, to a lesser extent) cause interference among all of these methods. Although the recent papers referred to above have significantly improved understanding, the research is still going on. As LaZerte (1993) crystallized the situation: "Although convenient, the conceptualization of alkalinity as a charge balance is not strictly correct, the proper concept is that of an acid-base balance."

## 5 CONCLUSIONS

Many catchments in Finland can be characterized by having thick organic soil horizons under coniferous forests, flat topography and a high proportion of peatlands. Peatlands and acidic soils produce large amounts of organic carbon in the shallow Finnish lakes. The leaching of organic carbon was found to be strongly dependent on hydrological conditions; annual leaching was closely related to annual runoff. Fractionation studies demonstrated that the organic carbon in Finnish lakes is dominated by organic acids, averaging 84 % of DOC with smaller amounts of neutral and basic components. Consequently, the catchment-derived organic acids represent a significant contribution to lake water acidity. In forested or peatland-dominated areas the mean annual leaching of organic acids was calculated to exceed the mean annual deposition of anthropogenic acids.

The Finnish Lake Survey with a TOC range from 0.5 to 47 mg l<sup>-1</sup> and colour range from 0 to 600 mg l<sup>-1</sup> Pt represents most of the variation found in lakes worldwide. Due to random selection of the lakes the high median TOC (12 mg l<sup>-1</sup>) and colour (100 mg l<sup>-1</sup> Pt) can be considered representative for small lakes in Finland. The survey, conducted during autumn after a rainy summer, may however, emphasize high TOC concentrations and organic acidity more than studies conducted during other periods of the year (e.g. the spring snow-melt period) or during less rainy years. Organic carbon concentrations were especially high over large regions in central Finland. Latitude and the proportion of the catchment covered by peatlands were the most important catchment variables determining TOC concentrations in Finnish lakes. In northern regions TOC concentrations were low compared with central and southern Finland, despite the high proportion of peatlands. The colder climate and consequently longer soil frost period and lower primary production and decomposition, coupled with thinner soils and peat deposits, are likely to decrease the concentrations in the north.

The majority of the world's peatlands occur in northern regions geographically coincident with lakes sensitive to acidic deposition and those receiving relatively high acidic deposition. In these areas lake acidity is a complex net effect of

several interrelated factors: e.g. anthropogenic acid load from the atmosphere, organic acid load from the catchment, weathering rate and hydrological conditions. Humic substances have several effects on water quality including anion-cation balance, pH and alkalinity. A highly complex mixture of organic acids dissociates across a wide pH range but is neither totally dissociated nor totally protonated at any pH value in natural waters. Consequently the acid-base properties of the organic acid mixture have been difficult to describe quantitatively.

This study provides an assessment of the contribution of organic acids to the acid-base status in Finnish lakes. On the basis of fractionation and isolation studies the average total organic acid content (at pH values existing in natural waters) was 9.7  $\mu\text{eq (mg DOC)}^{-1}$ , which agrees with the generally used value of 10  $\mu\text{eq (mg DOC)}^{-1}$  for carboxylic acids presented by Oliver et al. (1983). The dissociation of organic acids increased with increasing pH from about 48 % at pH 4 to about 92 % at pH 7, supporting the use of  $\text{pK}_a$  4 as an average  $\text{pK}_a$  value for organic acids. The pH-dependent dissociation of organic acids indicates that acidification and on the other hand the recovery of acidified waters can have an impact on the contribution of organic acids to the acidity of surface waters. Moreover, the dissociation pattern implies that at pH values existing in natural waters high organic acid concentrations in Finnish lakes provide both a natural background source of acidity but also a buffer against acid deposition.

Organic acids reduce pH and total buffer capacity in Finnish lakes by shifting the system to a pH range where it can be considered (chemically) more sensitive to acidic inputs due to reduced carbonate buffering. Each milligram of TOC was estimated to lower Gran alkalinity by about 5  $\mu\text{eq (mg TOC)}^{-1}$ , suggesting that at the pH values existing in aquatic ecosystems a significant fraction of organic acids can be considered strong. On the other hand, weak organic acids with higher  $\text{pK}_a$  values are a source of acidity but the corresponding anions act as a buffer against strong mineral acids, too. The average acid-neutralizing capacity provided by organic anions in Gran titrations in the Finnish Lake Survey was estimated to be 1.6  $\mu\text{eq (mg TOC)}^{-1}$ . Consequently at equal pH values humic waters buffer against pH changes more effectively

than clear water lakes. However, only a limited fraction of organic anions seem to contribute to the acid-neutralizing capacity. The fraction of organic anions contributing to the Gran alkalinity represented about 16 % of the median organic acidity contribution in the Finnish lakes.

Based on fractionations of DOC and titrations of isolated acids an empirical model for organic anion, the dissociation product of organic acids was developed. This model describes the dissociation of organic acids, requiring only pH and DOC measurements from water samples. Using the Finnish Lake Survey data base the developed model was compared with the two most widely used approaches for organic acidity, 1) the charge balance approach and 2) the model of Oliver et al. (1983). Despite the criticism presented for empirical methods and many error possibilities in the ion balance approach, the results given by the three approaches were in good consistency supporting the usability of indirect organic acidity estimates in studies, in which laborious empirical measurements cannot be used.

Organic anion, as estimated by any of the three approaches, is the dominant anion in Finnish lakes. Neglecting the contribution of organic anions to the total anionic charge can lead to serious errors in calculating the anion-cation charge balance and consequently the source of acidity in Finnish lakes. Inclusion of organic anion estimated by the developed model balances the cation/anion ratios in Finnish lakes. Organic anion-dominated lakes occurred throughout the country, but were concentrated in the peatland-dominated areas across central Finland. Compared with lake acidification surveys in other countries Finnish lakes show high concentrations of organic carbon and a high contribution of organic acidity.

In southernmost Finland the minerogenic acidity commonly exceeds the catchment-derived organic acidity. Sulphate-dominated lakes were concentrated in southern Finland for two reasons. Firstly, sulphate deposition in southern Finland is higher than in central Finland, and secondly, the lakes had lower organic anion concentrations because catchments in southern Finland are less peatland dominated. Despite the dominant influence of organic acids from natural sources, the effects of acidic deposition on Finnish lakes are clear and can be expected to be pronounced during the snow melt periods.

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## YHTEENVETO

Suomen kylmä ilmasto ja tasainen topografia luovat suotuisat edellytykset orgaanisen aineen akkumuloitumiselle. Suomen maapinta-alasta noin kolmasosa on soita, joista noin puolet on ojitettu lähinnä metsätalouden tarpeisiin. Sekä soiden osuus maa-alasta että ojitettujen soiden osuus soiden alasta ovat Suomessa suurempia kuin missään muussa maassa. Havumetsät ovat vallitsevia ja 87 % maapinta-alasta luokitellaan metsätalousmaaksi. Soilta ja metsäisten valuma-alueiden happamilta podsolimailta huuhtoutuu vesistöihin suuri määrä humusta.

Tässä julkaisussa esitetään kokonaisvaltainen arvio orgaanisen hiilen ja orgaanisten happojen osuudesta Suomen järvien happamuuteen ja puskurikykyyn. Tutkimuksessa kehitettiin kokeellisiin mittauksiin perustuva malli orgaanisten happojen dissosioitumistuotteen, orgaanisen anionin, laskemiseksi. Lisäksi selvitettiin järvien orgaanisen kokonaishiilen (TOC) pitoisuuksien riippuvuutta valuma-alueitekijöistä ja orgaanisen hiilen huuhtoutumiseen vaikuttavista tekijöistä. Happamoitumisprojektin (HAPRO) aikana syksyllä 1987 kerätty tilastolliseen otantaan perustuva koko maan kattava 978 järven aineisto oli suunniteltu siten, että orgaanisen happamuuden osuuden arviointi oli mahdollista epäsuorin menetelmin. Kyseisen aineiston lisäksi tässä julkaisussa esiteltävä tutkimus koostui lukuisista pienemmistä aineistoista, jotka painottuivat empiiriseen tutkimukseen sekä orgaanisen hiilen huuhtoutumisen selvittämiseen.

Koska järviaineisto valittiin kaksivaiheisella ryväotannalla, korkean TOC-pitoisuuden (12

mg l<sup>-1</sup>) ja väriluvun (100 mg l<sup>-1</sup> Pt) voidaan katsoa edustavan Suomen pienten järvien keskimääräisiä pitoisuuksia. Järvien mediaani pH oli 6,3 ja 93 %:ssa järvistä TOC-pitoisuudet olivat suurempia tai yhtä suuria kuin 5 mg l<sup>-1</sup>. Syksy näytteenottoajankohtana Etelä-Suomen sateisen ja kylmän kesän jälkeen saattaa jonkin verran korottaa korkeita TOC-pitoisuuksia, ja täten orgaanisen happamuuden osuutta. Hiilipitoisuudet olivat suurimmat Etelä- ja Keski-Suomen pienissä järvissä, joilla on suhteellisen suuri valuma-alue ja joiden valuma-alueesta suuri osa on soiden peitossa. Järven etelä-pohjois-sijainti ja soiden osuus valuma-alueella olivat tärkeimmät järvien TOC-pitoisuuksia selittäviä tekijöitä. Vaikka soiden osuus Pohjois-Suomessa oli keskimäärin suurempi kuin Etelä-Suomessa, TOC-pitoisuudet pohjoisessa olivat pieniä.

Humuksen happo-emäskäyttäytymisen selvittämiseksi luennut orgaaninen hiili fraktioitiin happamiin, emäksisiin ja neutraaleihin osiin XAD-8, kationinvaihto- ja anioninvaihtohartseja käyttäen. Keskimäärin 84 % orgaanisesta hiilestä koostui orgaanisista hapoista (hydrofobiset ja hydrofiiliset hapot). Täten valuma-alueilta huuhtoutuvalla humuksella on keskeinen merkitys Suomen järvien happamuuteen. Orgaanisten happojen huuhtoutumisen suovaltaisilta tai metsäisiltä valuma-alueilta arvioitiin olevan suurempi kuin vahvojen happojen laskeuma Etelä-Suomessa. Hydrologisilla tekijöillä oli tärkeä merkitys orgaanisen hiilen huuhtoutumiseen ja eri vuosien välinen vaihtelu huuhtoutumisessa oli suurta.

Orgaaniset hapot eristettiin ja niiden dissosioitumista pH:n funktiona selvitettiin happoemästitrauksella. Hydrofobisten ja hydrofiilisten happojen osuuksien ja titraustulosten avulla laskettu orgaanisten happojen kokonaispitoisuus (luonnonvesien pH-arvoissa) oli keskimäärin 9,7 µeq (mg DOC)<sup>-1</sup>, mikä tukee happamoitumistutkimuksissa yleisesti käytettyä arvoa 10 µeq (mg DOC)<sup>-1</sup> (Oliver et al. 1983). Hydrofobisten happojen keskimääräinen pK<sub>a</sub>-arvo oli 4,11 ja vahvempien hydrofiilisten happojen 3,82. Orgaanisten happojen keskimääräinen dissosioituminen kasvoi pH:n kasvaessa pH 4:n noin 48 %:sta pH 7:n noin 92 %:iin. Täten luonnonvesien pH-arvoissa orgaaniset hapot toimivat sekä luontaisina happamuuden lähteinä, mutta heikkoja orgaanisia happoja vastaavat anionit myös puskureina hapanta laskeumaa vastaan.

Suomen järvien suuri hiilipitoisuus ja suuret

orgaanisten happojen pitoisuudet laskevat järvien pH-arvoa ja puskurikykyä. Jokaisen hiilimiligramman arvioitiin alentavan Granin alkaliniteettä  $5 \mu\text{eq l}^{-1}$ . Siirtyminen alemmalle pH tasolle merkitsee bikarbonaattipuskurikyvyn pienenevästä, minkä vuoksi humusjärviä voidaan kemiallisesti pitää kirkkaita järviä herkempinä happamalle laskeumalle. Happaman laskeuman aiheuttamat biologiset seurannaisvaikutukset ovat kuitenkin humusjärvissä yleensä vähemmän haitallisia kirkkaisiin järviin verrattuna, koska humuksen voimakas kompleksimuodostuskyky vähentää esim. alumiinin myrkyllisimpien epäorgaanisten muotojen pitoisuutta. Humuksen aiheuttaman puskurivaikutuksen vuoksi happaman laskeuman aiheuttamat pH-muutokset ovat humusjärvissä hitaampia kuin kirkkaissa järvissä. Orgaanisten anionien aiheuttama keskimääräinen puskurikapasiteetti Granin alkaliniteetissa oli  $1,6 \mu\text{eq (mg TOC)}^{-1}$ . Orgaanisen anionin puskurivaikutus 978 järven aineistossa oli keskimäärin noin 16 % verrattuna orgaanisten happojen aiheuttamaan happamuuteen.

Suomen järvien happamuus määräytyy pitkälti kunkin alueen herkyyden, happaman laskeuman ja valuma-alueelta huuhtoutuvien orgaanisten happojen perusteella. Minorogeenisen ja orgaanisen happamuuden osuuksia voidaan tarkastella vertailemalla ei-merellisen sulfaatin ja valuma-alueelta peräisin olevan orgaanisen anionin pitoisuuksia järvissä. Orgaanisen hiilen fraktiointitulosten ja eristettyjen orgaanisten happojen titraustulosten perusteella kehitettiin malli orgaanisen anionin arvioimiseksi pH:n ja DOC:n avulla. Järvikartoitusaineistoa käytettiin verrattaessa tätä kokeellisiin mittauksiin perustuvaa mallia kahteen Pohjois-Amerikan ja Pohjois-Euroopan happamoitumistutkimuksissa yleisimmin käytettyyn orgaanisen happamuuden arviointimenetelmään, 1) ionitasapainoihin ja 2) Oliverin ym. (1983) malliin. Orgaaninen anioni arvioituna millä tahansa kolmesta menetelmästä (mediaani  $96-114 \mu\text{eq l}^{-1}$  käytetystä menetelmästä riippuen) on sulfaattia (mediaani  $71 \mu\text{eq l}^{-1}$ ) tärkeämpi anioni Suomen järvissä. Happamia humusjärviä on herkillä alueilla koko maassa, ja orgaanisen happamuuden dominoimia järviä esiintyi runsaasti etenkin Keski-Suomen suovaltaisilla alueilla. Happamissa järvissä orgaaninen anioni oli selvästi dominoiva anioni. Verrattuna muissa maissa tehtyihin tutkimuksiin orgaanisten happojen merkitys Suomen järvien happamuuteen on suuri.

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This article summarizes the following papers, which are referred to in the text by their Roman numerals:

- I Kortelainen, P., Mannio, J. & Mäkinen, I. 1986. Strong and weak acids in lake waters – a methodological study. *Aqua Fennica*, vol. 16, no. 2, p. 221-229.
- II Kortelainen, P. & Mannio, J. 1988. Natural and anthropogenic acidity sources for Finnish lakes. *Water, Air, and Soil Pollution*, 42, p. 341-352.
- III Kortelainen, P., Mannio, J., Forsius, M., Kämäri, J. & Verta, M. 1989. Finnish lake survey: The role of organic and anthropogenic acidity. *Water, Air, and Soil Pollution*, 46, p. 235-249.
- IV Kortelainen, P. & Mannio, J. 1990. Organic acidity in Finnish lakes. In: Kauppi, P., Anttila, P. & Kenttämies, K. (eds.). *Acidification in Finland*. Berlin, Springer-Verlag. P. 849-863.
- V Kämäri, J., Forsius, M., Kortelainen, P., Mannio, J. & Verta, M. 1991. Finnish lake survey: Present status of acidification. *Ambio*, vol. 20, no. 1, p. 23-27.
- VI Kortelainen, P. & Saukkonen, S. 1992. Leaching of organic carbon and nitrogen from peatland-dominated catchments. *Suo*, vol. 43, no. 4-5, p. 221-225.
- VII Kortelainen, P. 1993. Content of total organic carbon in Finnish lakes and its relationship to catchment characteristics. *Canadian Journal of Fisheries and Aquatic Sciences*, vol. 50, no. 7, p. 1477-1483.