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## ALKALINITY AND CHEMICAL OXYGEN DEMAND IN SOME FINNISH RIVERS DURING THE PERIODS 1911—1931 AND 1962—1979

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Water quality in the important Finnish rivers discharging into the Gulf of Bothnia was investigated by the Hydrographical Bureau over the years 1911—1931. Observations were made at monthly intervals at the river mouths. In the present report a comparison is made between this old data and more recent water quality data collected during the period 1962—1979 as part of a national survey of the quality of river waters carried out by the National Board of Waters. On the different quality variables, only alkalinity and COD are discussed in this context because the analysis methods used during the two data collection periods are directly comparable. Alkalinity was found to have decreased at all the sites investigated, the least change being observed in areas in which effluent or non-point loading has increased. From the point of view of the deleterious effects of acidity, the situation has reached a serious level in watercourse with an input from acidic sulphate lands. The least disturbing acidity levels were measured in the larger rivers of northern Finland, although even in these rivers the effects of acid rain are already discernable.

Material flows of COD have decreased in the larger rivers. Due to the effects of drainage, COD values have in most cases increased during the time of the spring flood, whereas in summer and in many rivers also in winter the COD of the waters has decreased during the twentieth century. Increase in COD has only occurred in watercourses in which loading has increased due to effluents or to the construction of reservoirs.

Index words: Alkalinity, COD, acidification, reservoirs, effects of drainage, trends

### 1. INTRODUCTION

The rivers flowing through Finnish territory into the Gulf of Bothnia have been subjected to considerable changes during the twentieth century. A considerable proportion of the basins of these watercourses has been drained, hydraulic construction works have been carried out and the level of loading has increased.

In many of the watercourses there are only a few lakes which can help to preserve the former balance of water quality.

Systematic monitoring of water quality in Finnish watercourses has been carried out since the beginning of the nineteen-sixties (Laaksonen and Malin 1980). Estimation of long-term changes is therefore made difficult by the lack of sufficient observational data.

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Another significant hindrance to comparison is the fact that many of the analysis methods have changed over the years. However, an interesting view of the history of watercourse quality variables is provided by the analysis data acquired between 1911 and 1931 by the Hydrographical Bureau in the important Finnish rivers discharging into the Gulf of Bothnia (Holmberg 1935). In the following, this data is compared with that compiled by the National Board of Waters in river observation sites during the period 1962–1979. The data compared are those of alkalinity and COD. They constitute a useful background to investigations of environmental acidification and to estimation of the changes in the humus concentration and organic loading of the watercourses.

## 2. MATERIALS AND METHODS

### 2.1 Observation sites

The basic data of the observation sites (Fig. 1) are presented in Table 1. The largest of the watercourses investigated is that of the River Kemijoki. The proportion of drained land in this watercourse is lower than in the other areas investigated. The two largest artificial reservoirs in Finland, Lokka and Porttipahta, were opened in the tributary streams of this river during the nineteen-sixties. By contrast, the watercourses of the rivers Iijoki and Oulujoki do not include any artificial reservoirs. In these rivers, regulation has been accomplished with the aid of natural lakes. The proportion of lakes of the total surface area of the watercourse is greater in the basin of the River Oulujoki than in any of the other watercourses investigated.

The watercourses of the rivers Siikajoki, Kalajoki, Lestijoki, Lapuanjoki and Kyrönjoki are rather small river networks containing only very few lakes. With the exception of the River Lestijoki, regulation has been accomplished with the aid of artificial reservoirs. In 1969 the third largest artificial reservoir in Finland, Uljua, was opened in the course of the River Siikajoki. The Hautaperä reservoir was constructed in the River Kalajoki in the beginning of the nineteen-seventies. The watercourses of the rivers Lapuanjoki and Ky-

rönjoki contain two and four reservoirs, respectively. Municipal loading effects are considerable in the River Kalajoki and in rivers to the south of it. Land utilization is intensive in the watercourses of the rivers Lapuanjoki, Kyrönjoki and Kokemäenjoki. Acid sulphate lands are found in the basins of the rivers Lapuanjoki and Kyrönjoki. Particularly in the River Kyrönjoki basin, the proportion of these acid lands of the total drainage area is particularly great (5.4 %, Erviö 1975). The lower reaches of the River Kokemäenjoki are loaded by effluents from the pulp and paper industry. The percentage of lakes of the total drainage basin area is second greatest in the River Kokemäenjoki basin, after the Oulujoki watercourse.

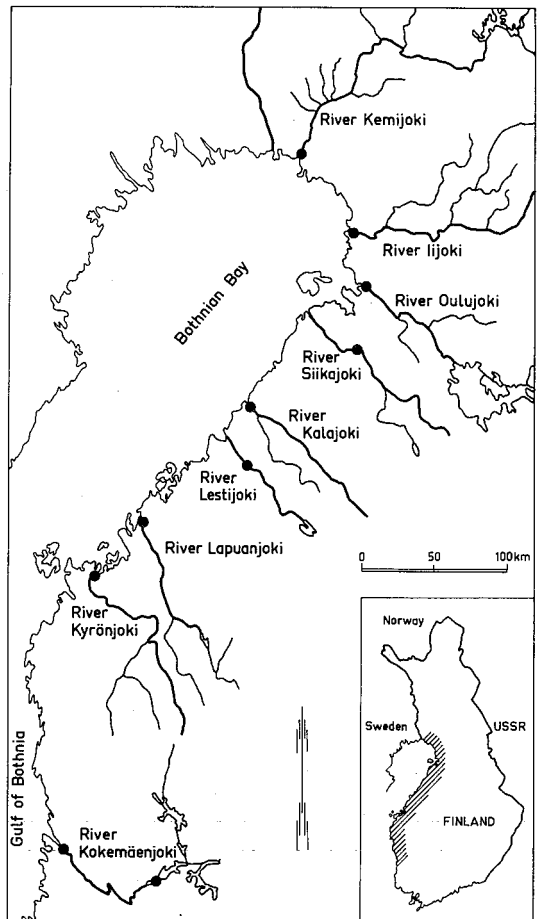


Fig. 1. Study area.

Table 1. Areas of the watercourses (F), lakes (L) and man-made lakes and mean discharges of the rivers in 1961—1975.

	F km <sup>2</sup>	L %	Man-made lakes km <sup>2</sup>	MQ m <sup>3</sup> s <sup>-1</sup>	MHQ m <sup>3</sup> s <sup>-1</sup>	MNQ m <sup>3</sup> s <sup>-1</sup>
Kokemäenjoki (Harjavalta)	26025	11,8	—	215	616	45
Kyrönjoki (Skatila)	4805	0,9	25	46	321	4,7
Lapuanjoki (Keppo)	3955	2,8	20	32	194	3,4
Lestijoki (Kannus)	1264	6,9	—	10	82	1,6
Kalajoki (Niskakoski)	3005	1,8	21	27	233	1,6
Siikajoki (Länkelä)	4395	1,5	39	41	388	4,5
Oulujoki (Merikoski)	22900	11,4	—	265	536	59
Iijoki (Raasakka)	14315	5,8	—	183	942	37
Kemijoki (Isohaara)	50900	2,9	638	553	3231	124

## 2.2 Data

Between the years 1911 and 1931 water samples were taken on the first day of every month. Sampling was in most cases less frequent during the period 1962—1979. The analysis data can be seen in Appendices 1 and 2. Of the many chemical analyses usually carried out from water samples, only alkalinity and COD are considered in the present work. Flow data are presented for the rivers Kemijoki, Iijoki and Oulujoki. The water quality data for the period 1911—1931 were collected by the Hydrographical Bureau (Holmberg 1935), while the data for 1962—1979 were obtained from the water quality register of the National Board of Waters. Discharge data were obtained from the Hydrological Bureau.

## 2.3 Methods

**Alkalinity:** Alkalinity was measured by HCl-titration. During the period 1911—1931 methyl orange was used as indicator. In 1962—1979 the titration was carried out using a mixed indicator in those samples of which the alkalinity value was below 0.1 mmol/l. In

samples exceeding this threshold value, methyl orange was used as indicator. Since 1972 the analysis has been carried out using a potentiometric method involving titration to pH values of 4.5 and 4.2. The results obtained by these methods are in most cases comparable. In the case of very low alkalinity values the methyl orange titration gives results which are too high.

**COD<sub>Mn</sub>:** This assay was carried out in both research periods by titrating with potassium permanganate solution after addition of sulphuric and oxalic acids and heating. Since 1972 the SCAN method has been used. The results obtained by the two methods are equivalent.

## 3. RESULTS

### 3.1 Discharges

Mean discharges are presented in Table 1. Changes in discharges in the larger rivers are shown in Fig. 2. In the River Oulujoki the discharge in summer was considerably greater in the nineteen-twenties than in the nineteen-seventies, whereas in winter an opposite chan-

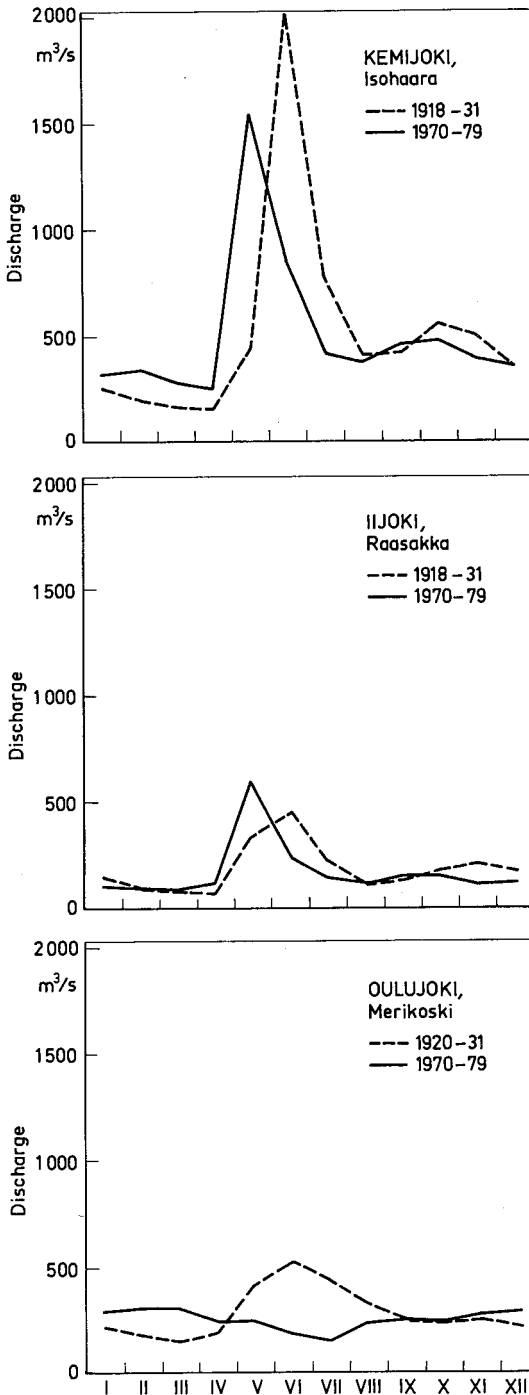


Fig. 2. Discharge of the rivers Oulujoki, Iijoki and Kemijoki during the 1920's and 1970's. Monthly means at the mouth of the rivers.

ge can be observed. In the rivers Kemijoki and Iijoki the maximum spring flood occurs nowadays earlier than in the nineteen-twenties. The mean flow rate in the River Iijoki in the nineteen-seventies was almost double that recorded fifty years earlier. In June, however, the situation was reversed. The mean annual discharge in the nineteen-twenties was in the rivers Oulujoki, Iijoki and Kemijoki 13 %, 6 % and 3 %, respectively, greater than in the nineteen-seventies.

### 3.2 Alkalinity

Monthly means of alkalinity during the two periods of investigation are presented in Fig. 3 and seasonal means in Appendix 1. In all the sites investigated the mean annual alkalinity values were lower in 1962—1979 than in 1911—1931. The difference was smallest in the Rivers Kalajoki and Kokemäenjoki. In the Rivers Kyrönjoki and Lapuanjoki alkalinity values had decreased to a very low level by the period 1962—1979. The difference between the two investigation periods was almost equal at all times of year in the River Oulujoki, whereas in the rivers Siikajoki, Kalajoki and Kemijoki the greatest reduction in alkalinity occurred in winter and during the spring flood.

### 3.3 Chemical oxygen deman ( $COD_{Mn}$ )

Monthly means of COD are presented in Fig. 4 and the seasonal means in Appendix 2. The annual mean value of COD increased considerably in the rivers Kokemäenjoki and Lestijoki, if the figures for the years 1913—1931 and 1962—1979 are compared. Reduction in COD values between the two periods of investigation occurred in the rivers Oulujoki, Iijoki and Kemijoki. In the rivers Siikajoki and Kemijoki the winter COD value increased, and an increase in COD was also observed in all the rivers during the spring flood season. Summer COD values decreased in most cases between the two research periods. The materials flow of COD in the three largest rivers is presented in Fig. 5. The annual materials flow

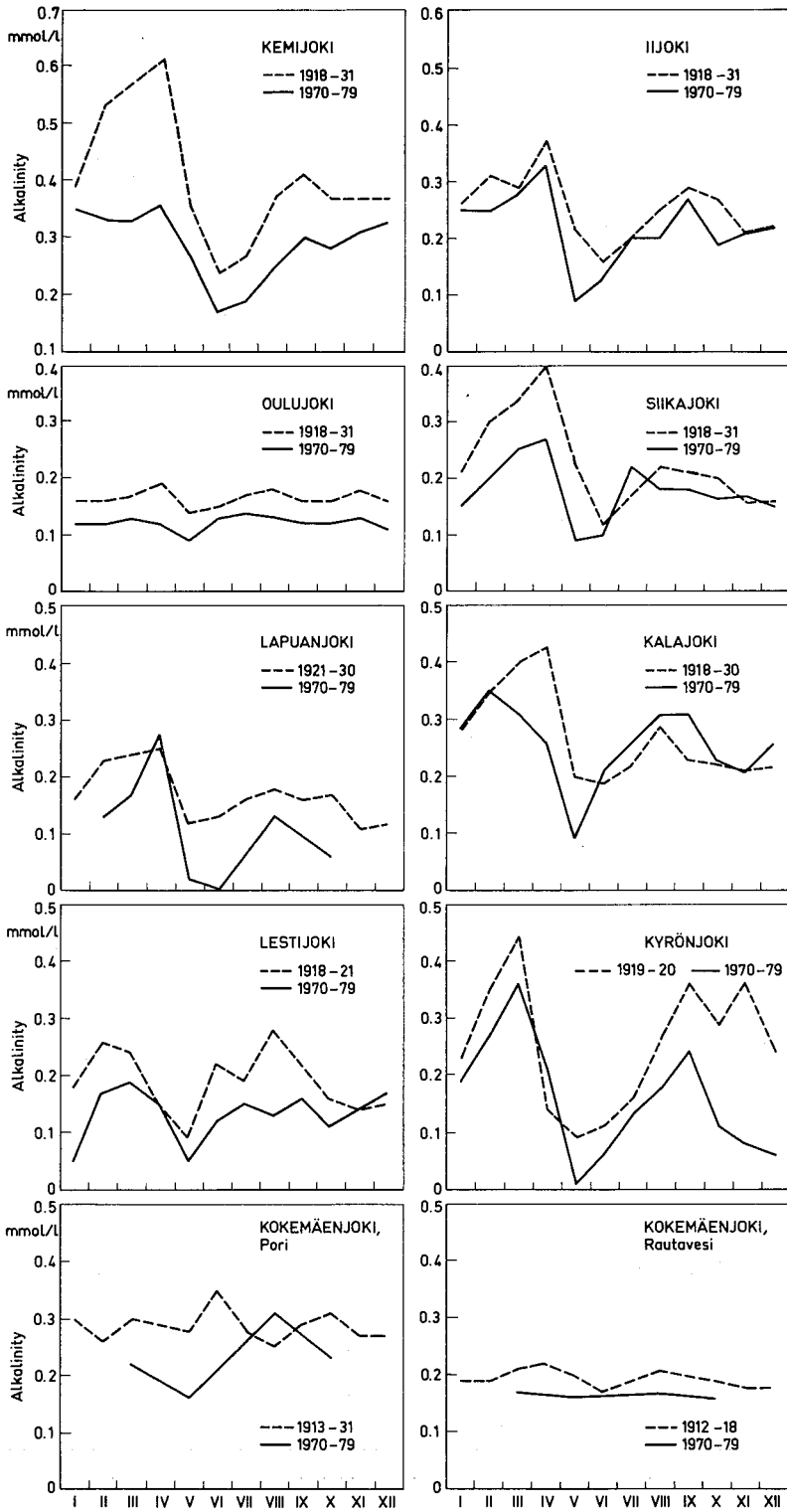


Fig. 3. Monthly means of the alkalinity values in the river water in the years 1913–1931 and 1971–1979.

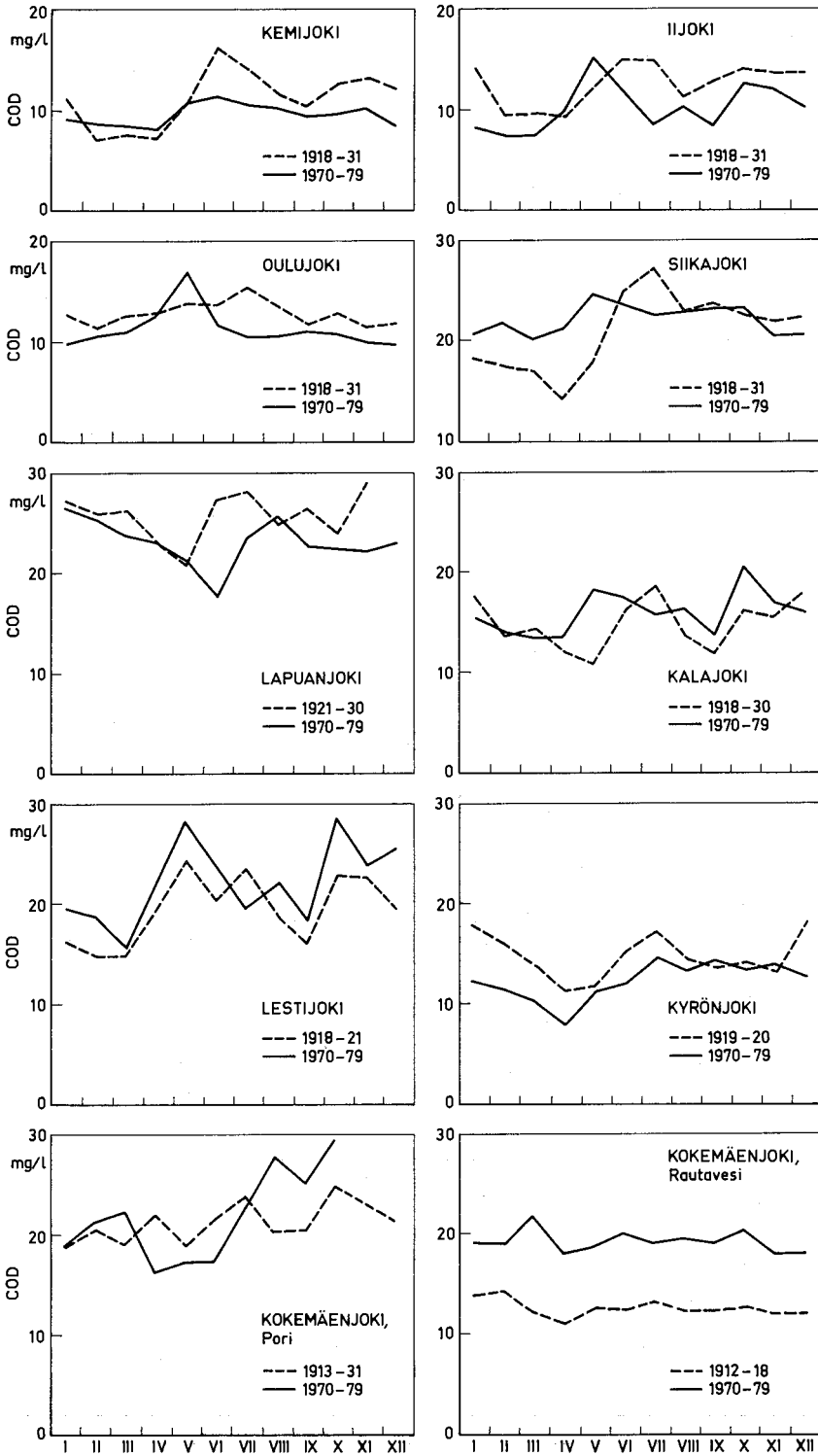


Fig. 4. Monthly means of the  $COD_{Mn}$  values in the river water in the years 1913-1931 and 1971-1979.



in the nineteen-twenties was 22 % greater than in the nineteen-seventies in all the rivers investigated.

Changes which have occurred in the annual distribution of material flow are connected with changes in flow rates. In the nineteen-seventies, the materials flow in the River Oulujoki in July-August was less than one third of the corresponding value during the nineteen-twenties, whereas in February-March it was almost double the value recorded during the earlier period of investigation. The winter material flows of COD also increased considerably between the two observation periods in the rivers Iijoki and Kemijoki. Moreover, the spring maximum was recorded earlier in the more recent data than in that from 1911—1931.

## 4. DISCUSSION

### 4.1 Discharges

River discharges have been affected over the passage of time by drainage of cultivated and forested lands as well as by water regulation, reservoir construction, lake level reduction, embankment construction, etc. At the present time the most important influencing factors are regulation and forest drainage (Hyvärinen and Vehviläinen 1981).

The major part of the lake regulation constructions in Finland were accomplished in the nineteen-fifties and — sixties. Spring flood water is held in the lakes and released during autumn and winter. Regulation has no appreciable effect on long-term changes in flow rate, although its effect on summer and winter flow values is considerable (Hyvärinen and Vehviläinen 1981). Intensive forest drainage was commenced in the latter part of the nineteen-sixties. Forest drainage has a considerable effect on the volume of runoff water (Mustonen and Seuna 1971), increasing the rate of flow of water to the watercourse. According to Seuna (1981), draining of a river basin increases the annual runoff and the spring flood runoff, with the result that evaporation is decreased and water conductivity increased. Minimum runoff values are also increased. Hyvärinen and Vehviläinen (1981) reported that forest drainage had caused an

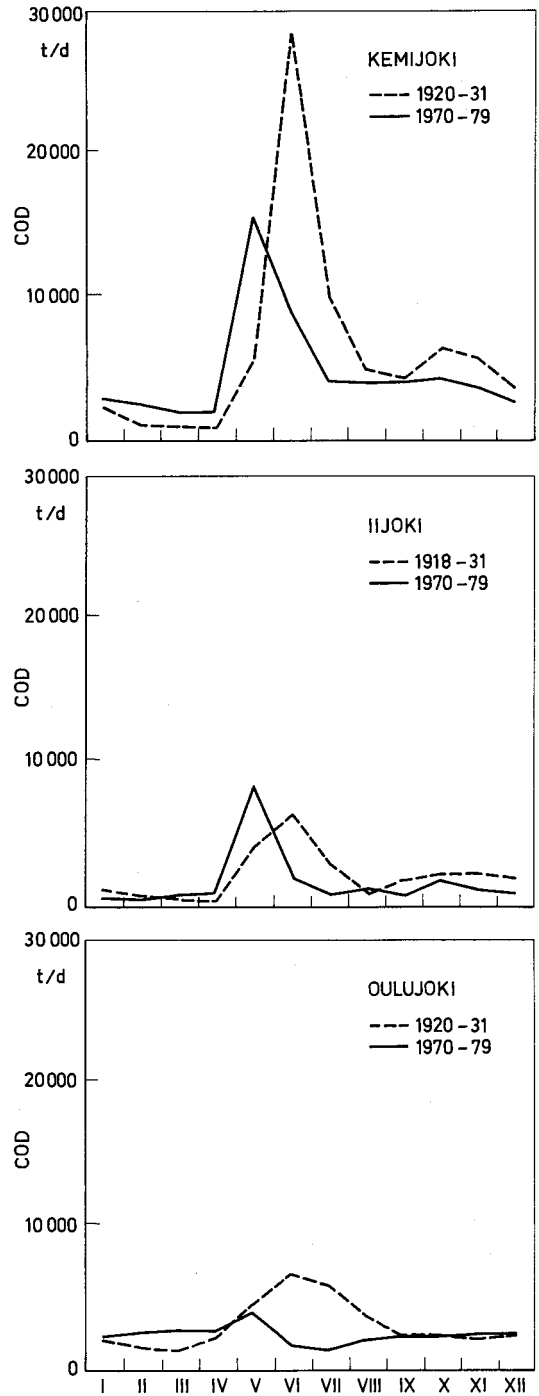


Fig. 5. Material flows of the  $COD_{Mn}$  in the rivers Oulujoki, Iijoki and Kemijoki. Monthly means during the 1920's and 1970's.

increase in maximum spring runoff values over wide areas of swamplands in central and northern Finland. However, in a study of Ostrobothnian rivers (Turunen 1980) no definite indications of increase in flow rates as a result of forest drainage were observed.

The effect of regulation on changes in annual mean discharges can clearly be seen in the River Oulujoki (Fig. 2). The summer discharge is considerably reduced and the winter discharge increased. The effect of regulation on discharges can also readily be observed as an increase in winter discharge and decrease in summer flow discharge in the River Kymijoki. In the River Iijoki the degree of regulation is lower than in the rivers described above and the changes due to regulation are less obvious. In the rivers Iijoki and Kemijoki the spring flood came earlier in the season during the nineteen- twenties than during the nineteen-seventies: the mean May discharge increased considerably in these observed changes are in all probability drainage and also embankment construction undertaken as an aid to log floating. The mean annual flow rate was lower in the large rivers in the nineteen-seventies than in the nineteen-twenties. The observed differences are correlated with the extent of drainage. In the long flow rate observation series of Hyvärinen and Vehviläinen (1981), the variation recorded is in the main due to climatic variation, particularly that of rainfall, in Finland during the period of the investigation. When comparing ten-year periods, the flow rate changes due to these factors may be considerable.

## 4.2 Alkalinity

Alkalinity provides a measure of the buffering capacity of waters in the watercourse. The value of this variable may vary considerably e.g. according to the nature of the soil layer. Increase in the hydrogen ion concentration of the water is usually evidenced first as a reduction in alkalinity and only later as acidification of the water. According to Kenttämies (1979), no statistically significant reduction in pH can be observed in the waters of unpolluted Finnish lakes. However, reduction in alkalinity values have been demonstrated between the periods 1962—1964 and 1975—1977. This decrease in alkalinity is attributable to the effect of acid

rain. According to Henriksen (1979), appreciable acidification has occurred in Norway when the hydrogen ion concentrations of rain has exceeded 20—25 mmol/l (pH 4.7—4.6). Järvinen (1982) reported that the pH of rainwater in the area of the present investigation exceeded the above value only in the River Kemijoki watercourse during the period 1971—1977. The significance of acid rain as an acidification agent of watercourses is only marginal in areas which include acid sulphate lands. The maximum sulphur levels reaching Finland with acid rain are about 30 kg/ha annually (Järvinen 1982), whereas amounts as high as ten times this values may be leached from acid sulphate lands (Yli-Halla and Ala-saarela 1983). The sulphur reaching watercourses by the latter mechanism is mainly in the form of sulphates of iron and aluminium, which are particularly active as agents of acidification.

In most of the areas investigated in the present work, alkalinity was found to have decreased between the nineteen-twenties and nineteen-sixties. Further slight decrease to the nineteen-seventies can also be detected in an examination of the mean annual values presented in Appendix 1.

Alkalinity has decreased less in the River Kokemäenjoki than in several rivers situated further north. This apparent contradiction is explained by the compensating effect of increased municipal and non-point loading in the River Kokemäenjoki. Due to the buffering capacity of lakes, the alkalinity does not reach very low levels in spring. In the rivers Kyrönjoki and Lapuanjoki the alkalinity of water has decreased appreciably in all months except April (fig. 3). Due to the effects of sulphate lands, alkalinity has reached very low levels in May-June and also in autumn: the river water is almost totally devoid of buffering capacity. The situation in winter is improved by regulation, as a result of which acidic runoff waters are more efficiently diluted in the watercourse than at the beginning of the century. Acidification of river water as a result of floods or heavy rain has caused several cases of fish deaths in the River Kyrönjoki. The situation was better at the beginning of the century, although cases of fish death after sudden clarification of river water were reported as early as in the nineteenth century (Vasabladet 29.10.1896). Draining of the sulphate lands has increased watercourse acidification (Man-ninen 1972).

In the rivers Lestijoki, Kalajoki and Siikajoki the alkalinity is lowest in May. The spring value of alkalinity in these rivers decreased considerably between the two investigation periods described in this work. Winter values also decreased, except that an increase in alkalinity during the open water season was recorded in the River Kalajoki as a result of increased loading.

In the Rivers Oulujoki, Iijoki and Kemijoki alkalinity decreased rather regularly between the periods 1918—1931 and 1970—1979 (Fig. 3). In the River Oulujoki seasonal variations are smoothed by the large number of lakes in the watercourse. Although the level of alkalinity in the River Kemijoki has decreased, the present level is still appreciably higher than in the other rivers.

### 4.3 Chemical oxygen demand (COD<sub>Mn</sub>)

COD is an indicator of the amount of oxidizable organic material in water. In Finnish watercourses COD is correlated most closely with the effects of the humus content and organic loading of the water. COD is positively correlated with the percentage of swamps in the drainage basin and negatively with the areal percentage of lakes (Laaksonen 1970). Reservoirs increase the COD value of water in late winter (Heinonen 1979, Kenttämies 1980), whereas forest drainage has been found slightly to decrease the concentration of organic substances in the water (Korpijaakko and Pheaney 1976, Kenttämies 1981). Laaksonen (1975) did not observe an increase in the concentration of organic compounds in rivers of central and northern Finland during the period 1962—1973 although the area of drained forest doubled during the nineteen-sixties. According to Kenttämies (1981), suspended organic material is both more common and more harmful in the waters of drained areas than dissolved organic material. In the absence of sedimentation basins, the leaching sediment has in some cases caused marked decrease in water quality.

Comparing the investigation periods 1911—1931 and 1962—1979, it can be seen that the mean value of COD has increased in those rivers loaded by effluents or other sources. In the large rivers of northern Finland both COD values and material flows have cle-

arly decreased. This effect can hardly be explained by forest drainage alone. In general, COD values have increased during the time of the spring flood but decreased at all other times. The spring increase is due to drainage operations, as a result of which the leaching of organic materials during the spring flood has increased.

The COD values of the River Kokemäenjoki increased between the periods 1913—1931 and 1960—1970 as a result of the growth of the pulp and paper industry. Some improvement was however recorded during the nineteen-seventies.

In the rivers Kyrönjoki and Lapuanjoki COD values decreased at all times of year with the exception of spring flood. Slight increase was observed in the rivers Lestijoki, Kalajoki and Siikajoki. In the rivers Lestijoki and Kalajoki the increase was mainly during the spring flood and in the summer season, indicating an increase in organic loading. In the River Siikajoki the winter COD values have increased considerably as a result of the Uljua reservoir.

A regular decrease in COD values occurred in the River Oulujoki, with the exception of the flood season. Draining in the lower reaches of the watercourse has caused an increase in the leaching of organic material. A similar change can be discerned in the River Iijoki. In the basin of the River Kemijoki drainage operations have been less extensive and the flood season COD level did not increase between the investigations of 1918—1931 and 1962—1979. The effect of the large reservoirs constructed in the tributary streams of River Kemijoki can be seen as an increase in the winter COD values (Nenonen 1978).

## LOPPUTIIVISTELMÄ

Hydrografinen toimisto on tehnyt veden laadun seurantatutkimusta tärkeimmissä Pohjanlahteen laskevista joista v. 1911—1931. Havainnot on tehty jokien suualueilla kerran kuukaudessa. Vanhoja tutkimustuloksia verrataan vesihallituksen hankkimaan tietouteen vastaavilta paikoilta v. 1962—1979. Tässä yhteydessä tarkastellaan alkaliniteettia ja COD-

arvoja, jotka ovat vanhassa ja uudessa aineistossa vertailukelpoisia.

Alkaliniteetti on laskenut kaikissa havaintopaikoissa; vähiten kohteissa, joissa kuormitus on lisääntynyt. Veden happamoitumisen kannalta tilanne on mennyt vaikeimmaksi Etelä-Pohjanmaan joissa, joiden valuma-alueella on happamia sulfaattimaita. Kyrönjoessa ja Lapuanjoessa oli vuosisadan alussa vielä tulvien aikana puskurikapasiteettia; nykyisin alkaliniteettia ei kevättulvan aikana ole lainkaan. Tilanteeseen vaikuttavat kuivatustoiminta ja happamat sateet. Myös muissa joissa alkaliniteetti on sadeveden happamoitumisen seurauksena laskenut ennen muuta kevättulvan aikana. Selvä tason lasku on havaittavissa myös Pohjois-Suomen suurissa joissa. Jokiveden happamoitumisen kannalta alkaliniteetti on pohjoisessa selvästi turvallisemmalla tasolla kuin Etelä-Suomessa.

COD:n ainevirtaama on laskenut suurissa joissa. Ojituksen vaikutuksesta COD-arvot ovat useimmissa joissa nousseet kevättulvan aikana. COD-arvot ovat laskeneet kesäaikana ja useissa joissa myös talvella; nousua on tapahtunut vain kohteissa, joissa kuormitus on selvästi lisääntynyt jätevesien tai tekoaltaiden johdosta.

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Appendix 1. Alkalinity of river waters (mmol/l) by season during the periods 1913—1931, 1962—1970 and 1971—1979. Means ( $\bar{x}$ ), variations (s) and numbers of observations (n).

River	Year	I—XII			I—III			IV			V			VI—VIII			IX—XII		
		$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n
Kokemäenjoki Pori	13—31	0,28	0,14	208	0,28	0,18	51	0,29	0,28	15	0,24	0,06	17	0,28	0,19	51	0,28	0,09	74
	62—70	0,22	0,07	73	0,24	0,04	17	0,17	0,03	2	0,23	0,13	14	0,23	0,05	23	0,23	0,07	17
	71—79	0,23	0,12	42	0,22	0,04	11	—	—	—	0,16	0,03	10	0,31	0,21	11	0,06	0,23	10
Kokemäenjoki Harjavalta	13—31	0,21	0,07	204	0,22	0,12	51	0,22	0,06	17	0,19	0,03	16	0,21	0,03	53	0,22	0,04	67
	62—70	0,17	0,03	34	0,17	0,03	8	—	—	—	0,18	0,05	8	0,17	0,02	9	0,18	0,02	9
	71—79	0,16	0,02	30	0,17	0,02	10	—	—	—	0,16	0,02	10	0,17	0,02	10	—	—	—
Kyrönjoki	19—20	0,25	0,14	24	0,12	0,03	6	0,07	0,01	2	0,35	0,01	2	0,77	0,02	6	0,14	0,04	8
	62—70	0,18	0,16	141	0,34	0,14	29	0,23	0,23	14	0,01	0,02	21	0,19	0,11	39	0,13	0,13	38
	71—79	0,15	0,16	173	0,29	0,15	37	0,21	0,23	17	0,01	0,02	25	0,13	0,10	42	0,11	0,69	52
Lapuanjoki	21—31	0,17	0,09	128	0,21	0,11	33	0,25	0,10	10	0,12	0,06	10	0,15	0,07	32	0,14	0,07	43
	62—70	0,18	0,17	72	0,32	0,23	19	0,12	0,06	6	0,08	0,06	7	0,15	0,09	18	0,14	0,14	22
	71—79	0,09	0,09	42	0,17	0,08	11	—	—	—	0,02	0,02	11	0,04	0,13	7	—	—	—
Lestijoki	19—21	0,19	0,08	36	0,23	0,07	8	0,16	0,04	3	0,09	0,04	3	0,23	0,08	9	0,17	0,06	13
	62—70	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	71—79	0,13	0,06	38	0,17	0,07	9	0,15	0,10	4	0,05	0,04	6	0,14	0,03	10	0,14	0,04	9
Kalajoki	18—31	0,27	0,11	130	0,34	0,10	35	0,43	0,13	11	0,20	0,08	11	0,23	0,07	36	0,21	0,07	37
	62—70	0,28	0,13	75	0,43	0,11	19	0,24	0,12	4	0,16	0,06	9	0,27	0,08	18	0,23	0,11	25
	71—79	0,25	0,11	91	0,31	0,09	23	0,26	0,12	6	0,09	0,03	11	0,27	0,09	21	0,25	0,09	30
Siikajoki	18—31	0,23	0,19	154	0,28	0,09	37	0,40	0,08	12	0,18	0,10	11	0,16	0,06	39	0,18	0,08	55
	62—70	0,18	0,13	39	0,34	0,12	8	—	—	—	0,09	0,03	8	0,20	0,09	9	0,13	0,10	14
	71—79	0,16	0,09	114	0,21	0,07	21	0,27	0,11	8	0,08	0,05	36	0,17	0,08	19	0,16	0,06	30
Oulujoki	18—31	0,16	0,05	154	0,16	0,04	37	0,18	0,08	12	0,14	0,03	10	0,16	0,05	39	0,16	0,04	56
	62—70	0,11	0,03	138	0,09	0,05	7	—	—	—	0,11	0,02	7	0,16	0,07	7	0,11	0,05	9
	71—79	0,12	0,03	95	0,12	0,02	22	0,12	0,02	3	0,09	0,03	11	0,13	0,04	29	0,12	0,02	31
Iijoki	18—31	0,25	0,11	152	0,28	0,08	34	0,37	0,07	12	0,22	0,12	13	0,20	0,06	39	0,24	0,13	53
	62—70	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	71—79	0,16	0,09	86	0,27	0,04	11	0,03	0	2	0,09	0,06	38	0,17	0,05	20	0,21	0,06	15
Kemijoki	18—31	0,41	0,26	152	0,50	0,12	35	0,60	0,11	12	0,35	0,17	13	0,29	0,08	38	0,43	0,38	54
	62—70	0,32	0,09	31	0,40	0,06	7	—	—	—	0,30	0,11	8	0,32	0,08	8	0,28	0,08	8
	71—79	0,28	0,06	68	0,33	0,03	18	0,36	0,02	4	0,25	0,08	10	0,22	0,05	16	0,30	0,04	20

Appendix 2. COD of river waters (mg O<sub>2</sub>/l) by season during the periods 1913—1931, 1962—1970 and 1971—1979. Means ( $\bar{x}$ ), variations (s) and numbers of observations (n).

River	Year	I—XII			I—III			IV			V			VI—VIII			IX—XII		
		$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n	$\bar{x}$	s	n
Kokemäenjoki Pori	13—31	21,2	10,8	208	19,5	7,8	47	22,0	11,8	16	19,0	6,9	18	21,9	12,3	55	22,3	12,0	72
	62—70	32,8	15,9	121	37,7	16,6	24	40,0	26,9	2	26,5	12,2	25	32,4	17,7	38	34,0	14,4	32
	71—79	22,7	14,6	71	21,2	4,9	20	16,0	1,7	3	17,1	1,4	12	17,5	20,4	21	26,4	19,5	15
Kokemäenjoki Harjavalta	14—31	16,7	4,1	202	16,4	4,3	50	16,5	4,2	16	15,5	3,6	16	16,1	3,9	53	15,7	4,0	67
	60—70	22,6	2,8	35	25,0	1,5	8	—	—	—	20,0	1,7	9	22,1	2,7	9	23,2	3,0	9
	71—79	19,9	3,2	41	21,1	3,8	11	18,0	—	1	18,6	2,4	8	19,5	2,8	10	19,8	2,9	11
Kyrönjoki	19—20	29,4	8,7	24	31,7	5,0	6	22,5	8,2	2	23,5	4,7	2	31,4	5,8	6	29,5	12,8	8
	62—70	29,8	35,8	149	35,6	7,0	37	20,0	4,7	9	25,9	9,1	19	28,8	10,1	38	29,4	9,3	46
	71—79	25,4	6,0	239	23,2	4,1	52	18,7	4,3	21	23,2	4,1	26	27,9	6,8	64	27,5	5,1	75
Lapuanjoki	21—31	26,0	6,8	125	26,6	5,8	32	23,7	6,9	10	21,6	3,7	10	26,6	7,9	33	27,2	6,6	40
	62—70	23,6	5,3	96	26,0	3,1	27	22,3	4,3	7	22,6	2,3	9	20,9	6,0	26	24,5	6,1	27
	71—79	25,4	21,9	86	24,8	4,3	20	23,0	4,1	9	21,2	3,8	16	23,8	5,5	21	22,2	4,3	20
Lestijoki	19—21	19,5	6,4	37	15,4	2,3	9	19,1	6,0	3	24,1	5,4	3	20,8	8,7	9	20,4	6,2	13
	62—70	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	71—79	22,6	6,7	62	17,9	5,1	14	22,0	6,6	4	28,3	3,3	7	21,9	6,2	15	24,6	7,2	21
Kalajoki	18—31	25,0	6,6	131	26,1	5,4	31	22,2	5,9	11	20,5	4,2	11	26,2	6,5	36	25,6	7,3	42
	62—70	24,3	6,3	93	24,6	5,4	25	21,0	4,8	6	25,0	1,6	10	22,4	5,3	23	26,0	8,4	29
	71—79	25,2	4,7	119	23,7	6,1	31	23,6	3,9	12	28,1	3,1	12	26,5	6,4	29	25,4	4,3	35
Siikajoki	18—31	21,1	6,2	149	17,5	4,2	33	14,6	4,1	12	18,1	4,6	12	25,2	6,0	39	22,8	5,2	53
	62—70	20,7	6,9	43	14,5	3,4	10	—	—	—	24,9	2,7	8	22,5	7,3	11	21,2	7,5	14
	71—79	22,6	4,6	170	20,7	3,4	34	21,3	3,3	18	24,8	3,9	39	23,1	5,3	38	22,1	5,1	40
Oulujoki	18—31	13,0	3,2	151	12,4	2,9	36	12,8	4,2	12	14,0	2,8	12	14,4	3,5	39	12,1	2,6	52
	62—70	13,2	2,0	32	12,6	1,8	7	—	—	—	15,7	1,6	7	12,3	1,6	9	12,4	1,0	9
	71—79	11,3	2,8	128	10,6	2,4	31	12,6	2,9	7	17,1	2,8	12	11,0	1,9	37	10,6	1,7	41
Iijoki	18—31	12,7	4,4	146	11,0	5,1	33	9,3	4,3	12	12,2	4,4	12	13,7	3,7	39	13,6	3,9	50
	62—70	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	71—79	12,1	3,8	113	7,6	1,8	15	10,0	3,5	7	15,7	3,8	43	10,5	2,8	28	11,4	3,3	20
Kemijoki	18—31	11,8	6,0	143	8,7	3,6	31	7,3	2,9	12	10,6	6,3	12	14,4	4,4	37	11,7	4,2	51
	62—70	9,0	2,3	33	6,3	0,8	8	—	—	—	9,4	1,9	8	9,8	1,8	9	10,2	2,3	8
	71—79	9,7	2,4	86	8,7	1,3	23	8,0	1,1	5	10,9	3,3	9	10,7	2,4	22	9,6	2,7	27