Ref ID 88278

Glenn R. Phillips

Depression of Primary Productivity by Humic Matter in Lake and Reservoir Waters of the Boreal Forest Zone

TOGWELL A. JACKSON AND ROBERT E. HECKY

Department of the Environment and Department of Fisheries and Oceans, Freshwater Institute, Winnipeg, Man. R3T 2N6

JACKSON, T. A., AND R. E. HECKY. 1980. Depression of primary productivity by humic matter in lake and reservoir waters of the boreal forest zone. Can. J. Fish. Aquat. Sci. 37: 2300–2317.

Analysis of water from backwater and main-stem regions of three reservoirs and a natural lake belonging to major river systems in northern Manitoba (Canada) showed that primary productivity was inversely related to total "dissolved" (<0.45 μm) organic carbon and non-dialyzable dissolved iron, organic carbon, nitrogen, and H-bonded polymeric hydroxyl groups. The chemical data apparently represent allochthonous humic–FeOOH complexes with strong, covalent metal-ligand bonds. The results suggest that humic matter depressed primary productivity by making iron unavailable to phytoplankton, but not by attenuating light, lowering the pH, or sequestering phosphate (although the dissolved phosphorus appeared to be mostly in the form of humic-iron-phosphate complexes). Relatively stagnant backwater bays, where humic mater accumulates, were less productive than the more rapidly flushed, less humic main-stem waters. In addition, the reservoirs, which had been formed 6 mo, 3 yr, and 14 yr prior to the time of sampling, revealed short-term anomalies caused by impoundment. Evidently three distinct stages of geochemical and trophic development are represented, the sequence of stages being tentatively generalized as follows for reservoirs of this region: (1) soon after impoundment, rapid leaching of nutrients from submerged land causes a brief rise in productivity and aberrantly high levels of dissolved low molecular weight phosphorus and nitrogen in the backwaters; (2) subsequently, a "pulse" of soil humic matter released more gradually into the backwaters depresses productivity by fixation of minor elements such as iron, even if the dissolved phosphorus levels are high; (3) finally, a steady state is restored when this anomalous accumulation of humic matter is removed from the water column by sedimentation or flushing, allowing productivity to return to higher levels. But even under unperturbed natural conditions humic matter restricts the productivity of surface waters in this geographic region to a greater or lesser extent.

Key words: humic matter, organic matter, primary productivity, iron, lakes, reservoirs, nutrient availability, Canadian Shield, water quality, phytoplankton ecology

JACKSON, T. A., AND R. E. HECKY. 1980. Depression of primary productivity by humic matter in lake and reservoir waters of the boreal forest zone. Can. J. Fish. Aquat. Sci. 37: 2300–2317.

L'analyse de l'eau des régions de renvoi et de l'axe hydrographique de trois réservoirs et d'un lac naturel faisant partie de réseaux fluviaux majeurs du Manitoba septentrional (Canada) démontre que la productivité primaire est en relation inverse avec le carbone organique « disssous » (<0,45 μm) total, le fer, le carbone organique et l'azote dissous non dialysables, et avec les groupes hydroxyl polymériques à liaison hydrogène. Les données chimiques représentent apparemment des complexes humiques–FeOOH allochthones avec fortes liaisons covalentes fixatrices de métaux. Les résultats suggèrent que la matière humique abaisse la productivité primaire en rendant le fer hors de portée du phytoplancton, sans toutefois atténuer la lumière, abaisser le pH ou séquestrer les phosphates (bien que le phosphore dissous semble en grande partie sous forme de complexes humiques-fer-phosphates). Les baies relativement stagnantes de la région de renvoi, où s'accumule la matière humique, sont moins productrices que les eaux de l'axe principal, à vidange plus rapide et moins humiques. De plus, les réservoirs qui avaient été formés 6 mo, 3 ans et 14 ans avant l'échantillonnage montrent des anomalies à court terme causées par la retenue des eaux. Trois stades distincts de développement géochimique et trophique sont bien représentés, l'ordre de ces stades étant provisoirement généralisé comme suit pour les réservoirs de cette region : (1) peu après la retenue, le ruissellement rapide des nutriments du sol submergé entraîne une brève élévation de productivité et des niveaux anormalement élevés de phosphore et d'azote de faible poids moléculaire disssous dans les eaux de renvoi; (2) ensuite, une « pulsation » de matière humique du sol mise en liberté plus graduellement dans les eaux de renvoi abaisse la productivité par fixation d'éléments mineurs,

Hypothesis is: Humic matter from Warm Springs ponds may make metals temporarily unavailable to fish. Primary productivity is not depressed in the ponds because there is an excess of iron relative to humic matter available.

Printed in Canada (J5949)
Imprimé au Canada (J5949)

tels que le fer, même si les niveaux de phosphore dissous sont élevés; (3) finalement, l'équilibre se rétablit quand cette accumulation anormale de matière humique est enlevée de la colonne d'eau par sédimentation ou vidange, permettant à la productivité de retourner à des niveaux plus élevés. Mais, même dans des conditions naturelles non perturbées, la matière humique limite la productivité des eaux de surface dans cette région géographique à un degré plus ou moins grand.

Received January 29, 1980
Accepted August 1, 1980

Reçu le 29 janvier 1980
Accepté le 1 août 1980

CREATION of reservoirs by impoundment of river water causes marked changes in the physicochemical properties, trophic status, and biota of the water (Zhadin and Gerd 1961; Rzoska 1966; Campbell et al. 1975). There is usually an initial upsurge of biological production followed by a decline a few years later; finally, after several years, productivity may return to higher levels as long-term steady-state conditions are reestablished (Lapitsky 1968; Lowe-McConnell 1973). The initial increase in production is probably caused by release of soluble nutrients from inundated soil and vegetation (Zhadin and Gerd 1961; Lowe-McConnell 1973; Campbell et al. 1975; Ostrofsky and Duthie 1978). The subsequent "trophic depression phase" is not well understood, but possible reasons for it include (1) exhaustion of readily available nutrients, (2) fixation of nutrients in unavailable forms by humic matter and other binding agents leached or eroded into the water from submerged soil or peat, (3) attenuation of light by dispersed humic matter or soil particles, (4) lowering of the ambient pH by humic matter, and (5) release of toxic organics such as phenols into the water (Baranov 1961; Duthie and Ostrofsky 1974; Hecky and Harper 1974). Although allochthonous humic matter derived from soil occurs widely in unperturbed natural waters (Bordovskiy 1965) as well as reservoirs (Gjessing and Samdal 1968; Campbell et al. 1975) and is relatively abundant in cool, moist regions, flooding could increase the concentration, or alter the inherent character, of the humic component of the water.

Humic matter may play an important role in aquatic ecology, largely by affecting the bioavailability of nutrients and toxic substances. Although humic matter can promote the growth of algae, bacteria, and plants (Burk et al. 1932; D'yakonova 1962; Prakash and Rashid 1968; Nechutová and Tichý 1970; Vaughan 1974; Milanovich et al. 1975; de Haan 1976; Giesy 1976), it may also inhibit biological activity by fixation of trace metals or phosphate (Sakamoto 1971; Golterman 1973; Goodman and Cheshire 1973), by inhibition of enzymes (Butler and Ladd 1971), or by absorption of light or lowering of the ambient pH (Shapiro 1957). Humic complexes of iron and aluminum readily bind phosphates (Weir and Soper 1963; Lévesque and Schnitzer 1967; Lévesque 1969; Sinha 1971; Jackson and Schindler 1975). The ecological significance of this phenomenon is unknown, but the importance of phosphorus as a limiting nutrient in many inland waters (Vollenweider 1968; Schindler 1974, 1977) and the abundance and widespread occurrence of humic matter in natural waters and sediments (Bordovskiy 1965) suggest that the binding of phosphorus by humic matter could have an effect on primary production in lakes and reservoirs (Golterman 1973).

This report presents the results of a comparative study of humic matter, nutrients, and primary production in three reservoirs and one natural lake located in a cool, moist, forested region where humic matter is abundant. These bodies of water are situated in essentially the same geographic and environmental setting, but the reservoirs differ in the time elapsed since the water level was raised. Our purpose was (1) to test the hypothesis that fixation of phosphorus or other nutrients by dissolved or dispersed humic substances may limit primary productivity in lakes and reservoirs, and (2) to study anomalous effects due to impoundment.

Field Area, Materials, and Methods

SAMPLING LOCALITIES

The bodies of water investigated were the Notigi, Kettle, and Kelsey reservoirs, and Southern Indian Lake (together with two streams flowing into the lake) in northern Manitoba, Canada (Fig. 1; Table 1). The Rat River flows into

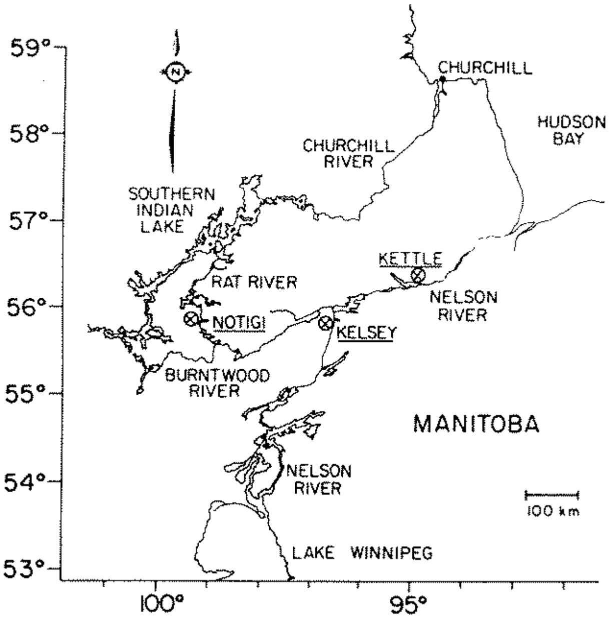

FIG. 1. The field area.

TABLE 1. List of water samples and sampling localities, with pH and conductivity data. ("n.d." means no data.)

Sample no.	Sampling locality	Backwater (BW) or main-stem (MS)	pH	Conductivity (μS/cm)	Comments
Not-1	Notigi Reservoir, east side	BW	7.50	119	Sampled 0.5 yr after impoundment.
Not-2	Notigi Reservoir, west side	MS	7.65	139	Sampled 0.5 yr after impoundment.
Ket-1	Kettle Reservoir	BW	8.00	280	Sampled 3 yr after impoundment.
Ket-2	Kettle Reservoir	MS	8.10	355	Sampled 3 yr after impoundment.
Kel-1	Kelsey Reservoir	BW	8.05	205	Sampled 14 yr after impoundment.
Kel-2	Kelsey Reservoir	MS	8.10	365	Sampled 14 yr after impoundment.
SIL-1	Stream entering South Bay, Southern Indian Lake	BW	7.40	n.d.	Sluggish, humus-rich brown water. Many rooted plants.
SIL-2	Mouth of stream entering South Bay, Southern Indian Lake	BW	7.55	n.d.	Humus-rich brown water. Many rooted plants.
SIL-3	South Bay, Southern Indian Lake	BW	8.55	171	Contained suspended clay and carbonate minerals eroded from glacial varve deposit on shore.
SIL-4	Center of South Bay, Southern Indian Lake	BW	8.20	155	
SIL-5	Stream entering Sand Hill Bay, Southern Indian Lake	BW	7.90	n.d.	Sluggish, humus-rich brown water.
SIL-6	Mouth of stream entering Sand Hill Bay, Southern Indian Lake	BW	8.10	n.d.	Many rooted plants.
SIL-7	Center of Sand Hill Bay, Southern Indian Lake	BW	8.00	116	
SIL-8	Northeast sector of Southern Indian Lake, near Missi Rapids	MS	8.15	99	

Notigi Reservoir, the Nelson River flows through the Kelsey and Kettle reservoirs (in that order), and the Churchill River flows through Southern Indian Lake. Originally, the Notigi, Kettle, and Kelsey reservoirs were natural lakes (Notigi Lake, Moose Lake, and Cauchon Lake, respectively), but they were enlarged by impoundment of river water to generate hydroelectric power. At the Kettle and Kelsey reservoirs, impoundment was completed, and full capacity reached, after a 2-yr transition period of rising water levels; stable water levels were reached 3 and 14 yr, respectively, prior to the time of sampling. At Notigi Reservoir, flooding had been going on for 6 mo prior to the time of sampling, and the water level was still rising. When the samples were collected, the waters of Southern Indian Lake had not been impounded at all, and so the lake was in a "baseline" condition.[1]

Each body of water investigated can be subdivided into (1) relatively stagnant "backwater" bays that are strongly influenced by local drainage and (in the case of the reservoirs) by recently inundated land, and (2) more rapidly flushed "main-stem" regions whose waters more nearly approximate the inflowing river water (Baxter 1977). To assess the effects of impoundment or local drainage, we sampled the main-stem and backwater zones of each water body separately, and observed the differences between them. Included in the backwater class were a pair of small, sluggish brown-water streams flowing into semi-isolated embayments of Southern Indian Lake. At Kettle Reservoir, paired observations of backwater and main-stem water had been made at different times of the year during 1972 and 1973 (~1–2 yr after impoundment) by Cleugh (1974) and by Hecky and Harper (1974), and relevant data from these studies are presented here.

The field area is characterized by low topographic relief, spruce (*Picea mariana*)-dominated boreal forest, sub-Arctic climate, and podzolic soil. The region lies on the Precambrian Shield, but the bedrock is largely covered with calcareous glacial drift.

FIELD WORK

The water samples and field data were collected during September 10–13, 1974. Water samples were taken with a polyvinyl chloride (PVC) van Dorn bottle at a depth of 2 m and transferred to PVC bottles, or were collected by hand with polyethylene jugs. Temperature, conductivity, and light transmission profiles of the water column were made by means of a Whitney temperature-conductivity probe and a Martek horizontal-beam transmissometer with a 25 cm folded light path. Light transmission, expressed as percent transmittance(T), was converted to the beam attenuation coefficient (α) for a 1 m light path, using the equation $\alpha = \ln (T^{-4})$. A 25 cm black and white Secchi disc was used to determine attenuation of image-forming light, and the vertical extinction coefficient (k) of photo-

---

[1] Since completion of this research, Southern Indian Lake has been expanded by impoundment of the Churchill River.

synthetically active light was determined by measuring underwater irradiance and surface irradiance (in air) with a Lambda Instruments quantum meter and underwater quantum sensor.

LABORATORY WORK

Water samples were passed through ~1 μm glass fiber filters (Whatman GF/C) and then analyzed for major elements, including total dissolved phosphorus (TDP), total dissolved nitrogen (TDN), dissolved organic carbon (DOC), and iron (Fe), and for chlorophyll-*a* content, by the methods of Stainton et al. (1974). Color, which is often used as an indicator of humic matter (Christman and Ghassemi 1966) was measured with a Hellige Aquatestor. Maximum possible concentrations of dissolved inorganic phosphate-phosphorus (PO_4-P) were estimated by the $^{32}PO_4$ radiobioassay method described by Rigler (1966) and Levine and Schindler (1979), using unfiltered water. Primary productivity, defined as the rate at which inorganic carbon is transformed to particulate organic carbon by phytoplankton at optimum light intensity, was measured in a light-gradient incubator (Shearer 1976) using the ^{14}C liquid scintillation techniques described by Schindler (1966), Schindler et al. (1972), and Fee (1973). The results were expressed as mg $C \cdot m^{-3} \cdot h^{-1}$.

Water used for the study of dissolved or dispersed humic complexes was passed through 0.45-μm Millipore filters which had been pre-cleaned with 0.001 mol/L HCl and hot (90–100°C) deionized distilled water (DDW) and leached with 1 L of DDW at room temperature, and the pH of the filtrate was determined with a Corning-12 pH meter. A portion of each sample was then dialyzed in a Pope multiple dialyzer using cellulose dialysis tubing with a 4.8-nm pore diameter nominally capable of retaining substances of molecular weight $\geq$12 000. Known volumes of both the dialyzed and the undialyzed portions were freeze-dried in a Virtis freeze-dryer, and the nonvolatile residue was weighed. The freeze-dry residues of dialyzed and undialyzed water — defined as the "colloidal" (or "nondialyzable") and "total" dissolved solids, respectively — were analyzed by chemical and spectrophotometric techniques, and the data were calculated on the basis of unit volume of original water sample as well as unit weight of solid residue.

To determine the chemical composition of the freeze-dry residues, we redissolved weighed quantities of residue in DDW and made them up to a known volume, and the solutions were analyzed in duplicate or triplicate. Organic carbon (org. C) was determined with a Beckman-915 analyzer. Aliquots of the solutions were wet-ashed by ultraviolet photo-oxidation (Stainton et al. 1974), using 5 mL of sample solution + 20 mL of 0.33% H_2SO_4 + 10 drops of 30% H_2O_2, and were analyzed for phosphorus (P) by the molybdate method (Stainton et al. 1974), for iron (Fe) by the *o*-phenanthroline method (Sandell 1959) (or by atomic absorption if the sample was relatively Fe-rich), for aluminum (Al) by the aluminon method (Sandell 1959), for calcium (Ca) by means of a Perkin-Elmer-403 atomic absorption spectrophotometer, and for nitrogen (N) by the chloramine-T procedure (Banoub 1972).

Weighed portions of freeze-dry residue were dissolved in known volumes of 0.025 mol/L $Na_2B_4O_7$ buffer (pH 9.15) (giving concentrations of ~0.1–4.83 mg/mL) to maintain a constant ambient pH and ionic environment for all samples, and the ultraviolet (UV) and visible absorption spectra of the solutions were recorded with a Cary-14 spectrophotometer. Absorbance (A_λ) was then measured at selected wavelengths (λ), and the absorbance ratio A_{465nm}/A_{665nm} was used to determine the degree of "humic," as opposed to "fulvic," character of the humic matter (Schnitzer 1971; Chen et al. 1977). A_{465nm} and A_{665nm} represent a monotonic absorption band extending across the entire UV-visible range. Another parameter designated as A_{265nm} (peak) was used to represent the intensity of a discrete absorption peak superimposed on this otherwise featureless band (Jackson et al. 1980).

The light-absorption parameter A_{465nm} was used to estimate the relative abundance of humic matter in each sample (the humic content of the dissolved solids being represented by the A_{465nm} value for 1 mg of freeze-dry residue dissolved in 1 mL of borate buffer). A_{465nm} is widely used for semiquantitative determination of humic or fulvic acid in "solution" (Schnitzer 1971), but some caution is required in the interpretation of it, because (1) absorbance is a function of extinction coefficient as well as concentration, and (2) scattering of light by various dispersed colloids could contribute to the "absorbance" readings. The extinction coefficient varies with factors such as molecular size and structure, functional group content, and the nature and abundance of complexed substances.

The freeze-dry residues were further characterized by gel filtration, whereby components were separated approximately according to molecular size. Five-mL aliquots of the borate solutions were fractionated on a Pharmacia Sephadex G-25 column 25 cm in diameter using 0.025 mol/L $Na_2B_4O_7$ as the eluant, and 5-mL fractions were taken automatically every 3 min. The fractions were analyzed chemically and spectrophotometrically as outlined above.

Infrared (IR) absorption spectra of the freeze-dry residues of dialyzed water samples were recorded by means of a Perkin-Elmer-467 IR spectrophotometer employing KBr pellets. Dialyzed samples were used to minimize interference due to inorganic salts, even though some lower molecular weight humic matter may have been lost during dialysis. A portion (0.38–1.20 mg) of each sample was weighed out with a Cahn electrobalance, mixed with 400 mg of desiccated IR-grade KBr in a ball mill, and pressed into a pellet. KBr reference pellets were used to cancel out the spectrum of hygroscopic water in the KBr of the sample pellet. The absorbance values and frequencies (i.e. peak positions) of major IR absorption bands representing H-bonded "polymeric" hydroxyl (OH) and ionized carboxyl (COO^-) groups were measured. To verify the identity of the COO^- bands and to test the stability of carboxyl-metal bonding, portions of a selected backwater sample — sample SIL-2 (Table 1) — were treated with HCl solutions and then analyzed spectrophotometrically and chemically together with an untreated control. The purpose of acidification was to convert COO^- groups to COOH by displacement of metal ions. The acid treatment involved exposure to (1) 0.5 mol/L HCl at room temperature for about 16.5 h and (2) boiling 6 mol/L HCl for about 30 min; the control was dissolved in H_2O at room temperature. The HCl and control solutions were dialyzed and freeze-dried, and the IR spectra of the freeze-dry residues were recorded. The KBr pellets containing the samples, together with KBr blank pellets, were then analyzed for Fe, Al, and org. C.

Relationships between the various chemical, physical, and biological data were tested by regression analysis involving computation of regression lines, correlation coeffi-

TABLE 2. Primary productivity and average concentrations of total dissolved phosphorus and nitrogen and the maximum possible dissolved inorganic phosphate concentrations (determined by radiobioassay) in the lake and reservoir waters. For explanation of sample designations, see Table 1.[a] ("n.d." means no data.)

Sample	Primary productivity ($mgC \cdot m^{-3} \cdot h^{-1}$)	TDP	TDN	PO_4-P	% PO_4-P in TDP
		(μmol/L)			
Not-1 (BW)	13.1	1.23	42.1	0.039	3.2
Not-2 (MS)	n.d.	2.39	49.3	0.45	19
Ket-1 (BW)	8.6	5.10	42.8	0.0068	0.13
Ket-2 (MS)	15.8	1.32	27.8	0.087	6.6
Kel-1 (BW)	14.9	0.39	31.4	0.001	0.3
Kel-2 (MS)	15.1	0.42	28.6	0.0058	1.4
SIL-3 (BW)	3.9	0.42	21.4	n.d.	n.d.
SIL-4 (BW)	4.3	0.36	21.4	0.017	4.7
SIL-7 (BW)	3.1	n.d.	n.d.	n.d.	n.d.
SIL-8 (MS)	17.4	0.32	24.3	0.065	20

[a] "Not" = Notigi Reservoir; "Ket" = Kettle Reservoir; "Kel" = Kelsey Reservoir; "SIL" = Southern Indian Lake. "BW" and "MS" mean backwater and main-stem, respectively.

cients (r), and significance probabilities (P). A correlation is defined as "significant" if $P \leq 0.05$.

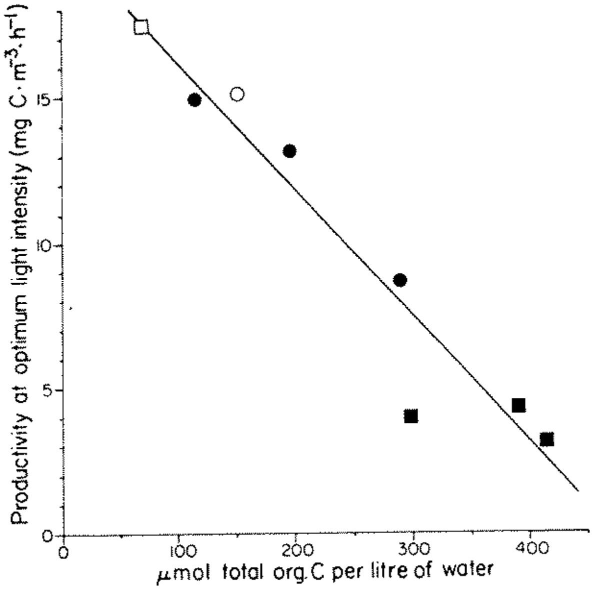

FIG. 2. Relationship between primary productivity and concentration of total dissolved organic carbon in the lake and reservoir waters ($r = -0.961$; $P < 0.001$). Explanation of symbols — reservoirs: backwater, ●; main stem, ○; Southern Indian Lake: backwater, ■; main stem: □.

Results and Discussion

GENERAL CHARACTERISTICS OF THE WATER

All water samples were weakly alkaline and had moderately high levels of dissolved salts (Table 1), reflecting the influence of calcareous glacial drift. The backwater regions had (1) generally higher concentrations of dissolved org. C and higher ratios of organic to inorganic dissolved solids (i.e. higher concentrations of org. C and N in their freeze-dry residues), (2) lower PO_4-P concentrations and lower PO_4-P:TDP ratios, and (3) lower levels of primary productivity than did the corresponding main-stem regions (Tables 2 and 3). Some of the backwaters — especially streams and mouths of streams — had a distinctly brownish coloration which may be ascribed to predominantly allochthonous humic matter. Presumably this humic matter had a greater tendency to accumulate in poorly flushed, semi-isolated bays than in main-stem waters. The systematic differences between backwater and main-stem environments imply that alteration of water properties in the backwater regions as a result of local drainage and low rates of water renewal has an adverse effect on primary production in both the lake and the reservoirs.

RELATIONSHIP BETWEEN PRIMARY PROCUCTIVITY AND WATER CHEMISTRY: THE IMPORTANCE OF ORGANIC MATTER AND IRON

In the light of current theories of eutrophication Vollenweider 1968; Schindler 1974, 1977), the depressed levels of primary productivity in backwater bays with respect to main-stem localities might seem at first sight to be readily explained by the low concentrations of dissolved PO_4-P in the backwater environments. Another seemingly plausible hypothesis is that organic matter in backwater regions depressed algal productivity by reducing the availability of light or by lowering the pH of the water. However, more detailed examination of our data (Tables 1–7) with the aid of regression analyses for testing the relationships between productivity and various physicochemical properties of the water (Table 8) failed to support these interpretations. We found that primary productivity was strongly correlated with organic matter and iron but not with phosphorus, light, or pH.

Primary productivity in both natural and impounded waters showed a highly significant *inverse* correlation with the total org. C concentration of the water (Fig. 2; Tables 2, 3, and 8) and significant, though weaker, inverse correlations with the Fe and org. C content of the colloidal dissolved solids and the colloidal Fe and N (but not the colloidal org. C) concentrations of the water (Fig. 3A and B; Tables 2, 3, and 8). In each plot shown in Fig. 2 and 3, the data for all the samples — lake as well as reservoir waters, and main-stem as well as backwater samples — cluster around the same trend line, indicating that the observed relationship prevails throughout the field area and is not restricted to a particular environment or locality. On the

TABLE 3. The average chemical composition of (A) dialyzed and undialyzed filtered water samples and (B) the dissolved solids isolated from these samples by freeze-drying, together with the yield of freeze-dry residue per unit volume of water. The data in Table 3A were computed from the data in Table 3B. For explanation of sample designations, see Table 1.[a] ("n.d." means no data.)

A	Undialyzed					Dialyzed				
Sample	P	Fe	Al (μmol/L)	org. C	N	P	Fe	Al (μmol/L)	org. C	N
Not-1 (BW)	0.381	0.270	0.292	196	14.5	0.132	0.231	0.550	158	8.22
Not-2 (MS)	0.114	0.638	5.64	117	5.29	0.0894	0.257	3.10	89.3	4.52
Ket-1 (BW)	0.733	0.445	19.0	289	15.2	0.242	0.338	3.47	214	12.8
Ket-2 (MS)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Kel-1 (BW)	0.104	0.167	4.59	114	4.62	0.187	0.0929	2.55	243	9.62
Kel-2 (MS)	0.140	0.224	13.0	152	7.26	0.0414	0.0642	3.53	53.4	3.70
SIL-1 (BW)	0.403	2.83	15.5	710	22.6	0.326	2.26	1.64	337	13.6
SIL-2 (BW)	0.403	2.77	11.8	698	21.2	0.343	1.60	1.21	377	15.8
SIL-3 (BW)	0.118	0.371	7.73	298	7.40	0.212	0.687	3.92	239	17.3
SIL-4 (BW)	0.128	0.123	2.62	390	8.89	0.0408	0.145	1.34	99.7	9.16
SIL-5 (BW)	0.334	1.21	11.0	329	19.7	0.193	0.950	2.05	408	16.1
SIL-6 (BW)	0.433	1.39	15.7	721	21.8	0.185	0.969	5.37	373	21.4
SIL-7 (BW)	0.111	0.559	4.06	416	18.6	0.182	0.509	4.24	276	12.2
SIL-8 (MS)	0.0702	0.149	4.38	69.5	2.50	0.553	0.0843	1.39	41.7	4.82

B	Undialyzed						Dialyzed					
Sample	Freeze-dry residue (mg/L)	P	Fe	Al (μmol/g)	org. C	N	Freeze-dry residue (mg/L)	P	Fe	Al (μmol/g)	org. C	N
Not-1 (BW)	40.0	9.52	6.76	7.31	4895	363	11	11.7	20.5	50.0	14 100	731
Not-2 (MS)	49.88	2.29	12.8	113	2350	106	6.0	14.9	42.9	517	14 900	754
Ket-1 (BW)	135.8	5.40	3.28	140	2130	112	16.6	14.6	20.4	209	12 900	768
Ket-2 (MS)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Kel-1 (BW)	86.8	1.20	1.92	52.9	1317	53.2	19.6	9.54	4.75	130	12 400	491
Kel-2 (MS)	205.7	0.679	1.09	63.3	737	35.3	7.1	5.85	9.06	497	7 535	523
SIL-1 (BW)	131.2	3.07	21.6	118	5410	172	21.8	15.0	104	75.3	15 500	625
SIL-2 (BW)	131.4	3.07	21.1	89.8	5310	161	24.5	14.0	65.4	49.5	15 400	643
SIL-3 (BW)	104.5	1.13	3.55	74.0	2850	70.8	17.8	11.9	38.6	220	13 400	969
SIL-4 (BW)	81.56	1.57	1.51	32.1	4780	109	7.38	5.53	19.6	182	13 500	1240
SIL-5 (BW)	112.8	2.96	10.7	97.6	2920	175	25.0	7.70	38.0	82.1	16 300	644
SIL-6 (BW)	135.3	3.20	10.3	116	5330	161	24.2	7.66	40.0	222	15 400	885
SIL-7 (BW)	71.8	1.53	7.79	56.5	5800	259	19.0	9.56	26.8	223	14 500	643
SIL-8 (MS)	36.8	1.91	4.05	119	1890	68	6.6	8.40	12.8	211	6 340	732

[a] "Not" = Notigi Reservoir; "Ket" = Kettle Reservoir; "Kel" = Kelsey Reservoir; "SIL" = Southern Indian Lake (or influent stream). "BW" and "MS" mean backwater and main-stem, respectively.

other hand, productivity failed to correlate significantly with total or colloidal dissolved P, PO_4-P, total dissolved N, Fe, or Al, colloidal dissolved Al, or pH, or with any of the light attenuation parameters (k, α, and Secchi disc value) (Tables 1–4, and 8). It would seem, then, that the photosynthetic activities of phytoplankton in the bodies of water investigated are depressed in the presence of relatively high concentrations of dissolved organic matter and high molecular weight nitrogenous organic-Fe complexes or colloidal hydrated ferric oxide (FeOOH) peptized by adsorbed organic matter; but this phenomenon evidently cannot be ascribed to the scavenging of phosphate by these ferric complexes nor to absorption or scattering of light or excessive lowering of the pH of the water (which is well buffered in any case). Before proposing an hypothesis to explain these results, let us examine in greater detail the nature of the organic matter and iron and their relationship with primary productivity.

THE NATURE OF THE ORGANIC-IRON COMPLEXES IN RELATION TO THE MECHANISM OF TROPHIC DEPRESSION

The preponderance of humic components in the dissolved organic matter — The organic matter dissolved or dispersed in the lake, reservoir, and stream water appeared to consist chiefly of humic substances, as indicated by the UV-visible and IR absorption spectra (Fig. 4A and B), the Sephadex data (Fig. 5), and

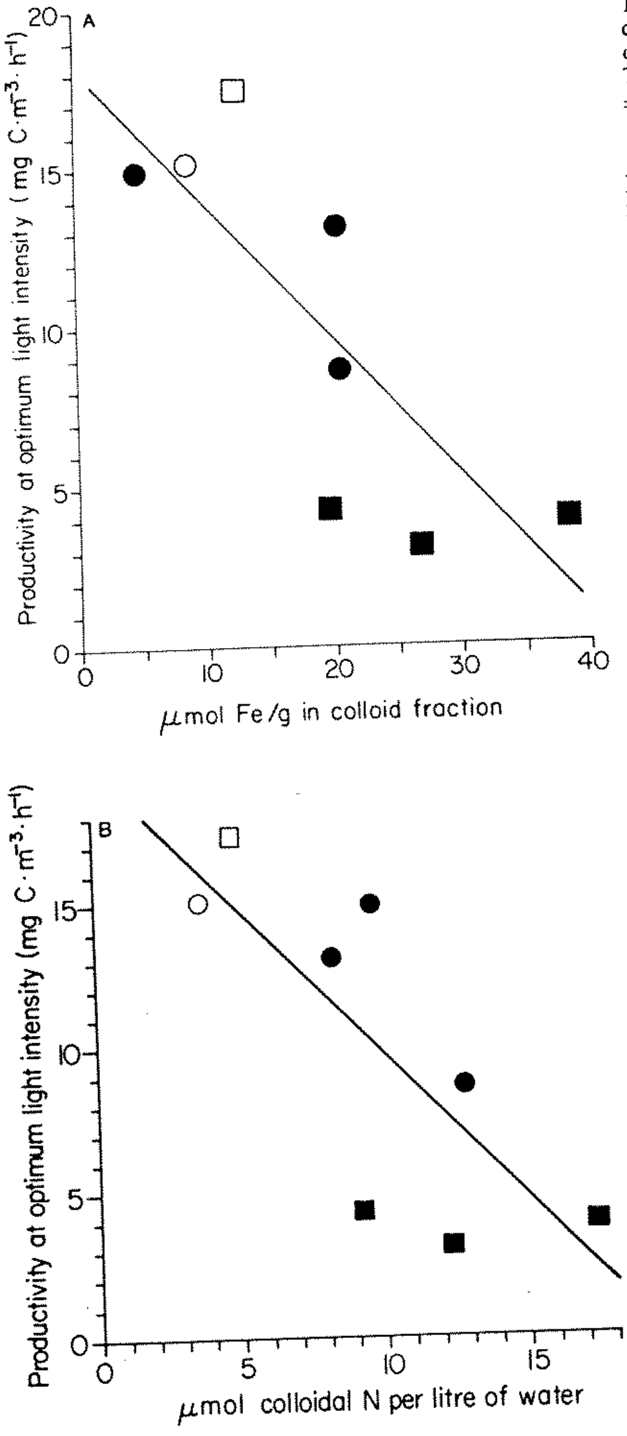

FIG. 3. Relationship between primary productivity and (A) concentration of iron in freeze-dried colloidal dissolved solids ($r = -0.793$; $P < 0.02$, >0.01) and (B) concentration of colloidal dissolved nitrogen in the water ($r = -0.768$; $P < 0.02$, >0.01). Explanation of symbols — reservoirs: backwater, ●; main stem, ○; Southern Indian Lake: backwater, ■; main stem, □.

TABLE 4. Vertical extinction coefficient (k), beam attenuation coefficient (α), Secchi disc reading, and chlorophyll-a content of the water. For explanation of sample designations, see Table 1.[a]

Sample	k	α	Secchi disc (m)	Chlorophyll-a (μg/L)
Not-1 (BW)	1.33	1.9	2.4	4.2
Not-2 (MS)	1.15	2.3	1.7	1.4
Ket-1 (BW)	1.05	2.0	2.1	6.0
Ket-2 (MS)	0.96	6.9	0.8	6.7
Kel-1 (BW)	0.92	3.3	1.8	4.7
Kel-2 (MS)	n.d.	7.0	0.8	5.0
SIL-3 (BW)	1.3	6.9	0.7	1.9
SIL-4 (BW)	0.60	1.5	1.6	1.7
SIL-7 (BW)	1.0	1.6	1.9	2.3
SIL-8 (MS)	0.69	1.5	2.6	4.7

[a] "Not" = Notigi Reservoir; "Ket" = Kettle Reservoir; "Kel" = Kelsey Reservoir; "SIL" = Southern Indian Lake. "BW" and "MS" mean backwater and main-stem, respectively

the brownish coloration of the dissolved solids. The spectra of all samples are similar to the spectra of humic matter extracted from soil and lake mud (Schnitzer 1965, 1971; Stevenson and Goh 1971) and are almost identical to each other qualitatively. The total and colloidal org. C and Fe correlated significantly with light absorption at 465 nm (Table 9), lending credibility to the conclusion that much of the organic matter consisted of humic substances associated with Fe. The brownish color of the streams draining the field area (Table 1) suggests that at least a major part of this humic matter was leached or eroded from local soils. The A_{465nm}/A_{665nm} ratios of the samples were relatively high (≥ 6.0) (Table 5), showing that most of the humic matter belonged to the "fulvic acid" category (Schnitzer 1971; Chen et al. 1977), as is generally the case with humic substances dissolved in natural waters (Black and Christman 1963; Ghassemi and Christman 1968; Reuter and Perdue 1972).

Gel filtration — Gel filtration provided additional evidence that the organic matter was predominantly humic. Thus, the Sephadex elution patterns, as illustrated in Fig. 5, revealed that the dissolved organic matter strongly absorbed UV-visible radiation, was concentrated in the higher molecular size fractions (near the "void" volume), and accounts for the UV-visible spectra of the water. In the example shown (representing local stream water draining into Southern Indian Lake), most of the dissolved P was associated with the two highest molecular weight Fe fractions, and probably represented phosphates bound to FeOOH and Fe^{3+} complexed with humic matter; but no free ortho-PO_4 was detected. The Sephadex data suggest that the colloidal fractions of the dissolved solids are composed primarily of humic matter complexed with inorganic species such as FeOOH and Fe^{3+}.

Infrared spectra — The IR spectra of the colloidal dissolved solids (Fig. 4B; Table 6) yielded additional information on the nature of the humic-iron complexes and their role in the limitation of primary productivity. The spectra demonstrate that the major functional groups of the "dissolved" colloids were H-bonded "polymeric" hydroxyl (OH) groups, whose stretching vibrations are represented by the band at 3300–3400 cm^{-1}, and ionized carboxyl (COO^-) groups, whose antisymmetric and symmetric stretching frequencies are represented by the bands at approximately 1600 cm^{-1} and 1400 cm^{-1}, respectively (Bellamy 1958). The band at 1600 cm^{-1}, however, may be due to aromatic C=C and H-bonded or conjugated carbonyl groups as well as COO^- groups (Schnitzer 1971; Stevenson and Goh 1971). In all of the samples examined, undissociated carboxyl (COOH) groups are relatively unimportant, as demonstrated by the fact that the COOH band at about 1700 cm^{-1} is only a small shoulder on the flank of the 1600 cm^{-1} band. Thus, the humic substances in their native state are mainly in the form of complexes or salts.

Strong binding of Fe and Al oxides by humic COO^- groups — Acid treatments caused small but measurable increases in the intensity of the COOH band with respect to the two COO^- bands, the effect being more pronounced, as expected, for hot 6 mol/L HCl than for cold 0.5 mol/L HCl (Table 7; Fig. 4C). These results tend to confirm our assignment of the 1600 cm^{-1} and 1400 cm^{-1} bands to COO^- groups, but the effect of acidification was much less pronounced than might be anticipated, suggesting that most of the carboxyl–metal bonds were exceedingly strong and predominantly covalent. Chemical analysis furnished additional support for this conclusion. The concentrations of org. C, Fe, and Al in the nondialyzable fraction *increased* with increasingly rigorous acid treatment (Table 7), presumably owing to accumulation of acid-resistant organic complexes of Fe and Al accompanied by loss of the more hydrolyzable or acid-soluble constituents such as the unidentified substances (possibly compounds with ether linkages, like polysaccharides) which yielded the C-O and =C-O absorption bands at 1000–1100 cm^{-1} and approximately 1250 cm^{-1}, respectively (Fig. 4C) (Stevenson and Goh 1971). It would seem that the nondialyzable Fe and Al were largely in the form of extremely stable, refractory high molecular weight humic complexes in which carboxyl

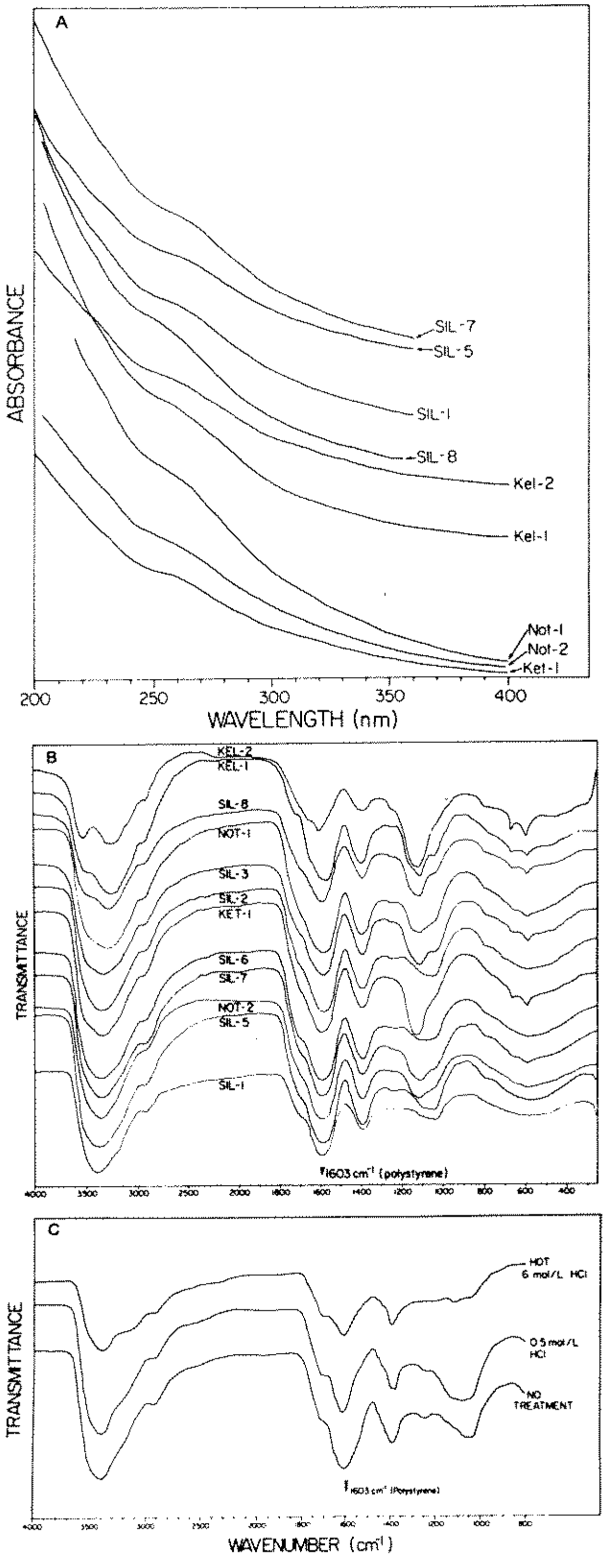

FIG. 4. Absorption spectra of dissolved substances. For explanation of sample designations, see Table 1. ("Not" = Notigi; "Ket" = Kettle; "Kel" = Kelsey; "SIL" = Southern Indian Lake [or influent stream].) A, Ultraviolet spectra of sodium borate solutions of total dissolved solids isolated from undialyzed water samples by freeze-drying; B, Infrared spectra of colloidal dissolved solids isolated from dialyzed water samples by freeze-drying; C, Infrared spectra of acid-treated colloidal dissolved solids, and untreated control, from Southern Indian Lake backwater sample SIL-2.

TABLE 5. Data from visible absorption spectra obtained by analysis of sodium borate solutions of dissolved solids isolated from dialyzed and undialyzed filtered water samples by freeze-drying. "$A_{465nm} \cdot mg^{-1} \cdot mL^{-1}$" represents 1 mg of freeze-dry residue redissolved in 1 mL of borate buffer; "A_{465nm}/L" represents concentration in the water sample. For explanation of sample designations, see Table 1.[a] ("n.d." means no data.)

Sample	Undialyzed			Dialyzed		
	$A_{465nm} \cdot mg^{-1} \cdot mL^{-1}$	A_{465nm}/L	$\frac{A_{465nm}}{A_{665nm}}$	$A_{465nm} \cdot mg^{-1} \cdot mL^{-1}$	A_{465nm}/L	$\frac{A_{465nm}}{A_{665nm}}$
Not-1 (BW)	0.0910	3.64	14.8	0.324	3.65	11.6
Not-2 (MS)	0.0901	4.49	14.5	0.354	2.12	12.3
Ket-1 (BW)	0.0395	5.36	12.0	0.186	3.08	13.4
Ket-2 (MS)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Kel-1 (BW)	0.0351	3.05	35.8	0.169	3.31	13.6
Kel-2 (MS)	0.00632	1.30	61.0	0.127	0.900	4.07
SIL-1 (BW)	0.0804	10.6	10.7	0.319	6.94	12.5
SIL-2 (BW)	0.0710	9.33	14.0	0.323	7.91	12.0
SIL-3 (BW)	0.0184	1.92	7.51	0.119	2.12	15.8
SIL-4 (BW)	0.0112	0.914	6.03	0.122	0.901	7.09
SIL-5 (BW)	0.0941	10.6	15.0	0.363	9.08	12.1
SIL-6 (BW)	0.0969	13.1	14.3	0.388	9.40	12.9
SIL-7 (BW)	0.0587	4.21	15.4	0.315	5.99	13.4
SIL-8 (MS)	0.0276	1.01	14.5	0.157	1.03	14.7

[a] "Not" = Notigi Reservoir; "Ket" = Kettle Reservoir; "Kel" = Kelsey Reservoir; "SIL" = Southern Indian Lake (or influent stream). "BW" and "MS" mean backwater and main-stem, respectively.

groups played a major metal-binding role (Křibek et al. 1977). Metals bound in this ~~summer~~ manner could well be unavailable to organisms.

Assignment of the two COO⁻ bands to humic matter is consistent with the observation that the band intensities correlate significantly with A_{465nm} and org. C (Table 10). The intensity of the OH band, however, is more weakly correlated with A_{465nm} and org. C, suggesting that the OH groups belong to inorganic as well as organic constituents of the nondialyzable solutes. In contrast, nondialyzable Fe is much more strongly correlated with OH than with antisymmetric or symmetric COO⁻ band intensity (Table 10). A reasonable interpretation of our data would be that the Fe and the OH groups were largely in the form of colloidal FeOOH particles firmly bound to "protective" organic coatings composed predominantly of humic matter. The results of acid treatment (Fig. 4C) suggest that these organic

TABLE 6. Data from infrared absorption spectra for "colloidal" dissolved solids isolated from dialyzed filtered water by freeze-drying. For explanation of sample designations, see Table 1.[a] "Antisym." and "sym." refer to antisymmetric and symmetric stretching vibrations, respectively. ("n.d." means no data.)

Sample	Frequency (cm^{-1})			Absorbance per mg of sample		
	OH	Antisym. COO^-	Sym. COO^-	OH	Antisym. COO^-	Sym. COO^-
Not-1 (BW)	3329	1594	1408	0.675	0.785	0.534
Not-2 (MS)	3370	1604	1404	0.676	0.740	0.492
Ket-1 (BW)	3362	1604	1405	0.793	0.755	0.457
Ket-2 (MS)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Kel-1 (BW)	3299	1584	1409	n.d.	0.666	0.484
Kel-2 (MS)	3289	1626	1409	n.d.	0.325	0.209
SIL-1 (BW)	3409	1609	1404	1.32	0.961	0.566
SIL-2 (BW)	3359	1599	1409	0.784	0.811	0.508
SIL-3 (BW)	3349	1599	1407	0.606	0.631	0.434
SIL-4 (BW)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SIL-5 (BW)	3389	1598	1407	0.842	0.800	0.538
SIL-6 (BW)	3369	1600	1409	0.802	0.881	0.671
SIL-7 (BW)	3369	1609	1409	0.692	0.713	0.469
SIL-8 (MS)	3309	1612	1402	0.668	0.623	0.396

[a] "Not" = Notigi Reservoir; "Ket" = Kettle Reservoir; "Kel" = Kelsey Reservoir; "SIL" = Southern Indian Lake (or influent stream). "BW" and "MS" mean backwater and main-stem, respectively.

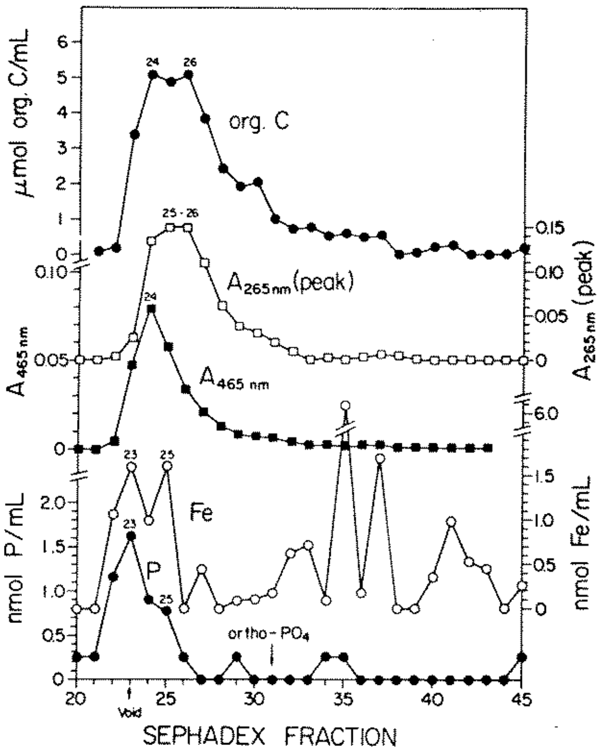

FIG. 5. Distribution of organic carbon, iron, phosphorus, and spectral properties in Sephadex G-25 fractions of borate solution of total dissolved solids from the stream entering Sand Hill Bay of Southern Indian Lake (sample SIL-5). Numbers on peaks refer to corresponding Sephadex fractions.

layers were fixed to the FeOOH surfaces largely by -COO-Fe bonds.

Relevance of complexed FeOOH to primary productivity — Primary productivity showed a significant inverse correlation with the frequency of the 3300–3400 cm^{-1} IR band for OH groups (Fig. 6; Tables 2, 6, and 8). This relationship holds true for all four bodies of water and for both the main-stem and the backwater zones. However, productivity was not significantly related to the frequencies of the COO$^-$ bands, although productivity in *backwater* regions did tend to correlate inversely with the 1600 cm^{-1} band frequency (Tables 2 and 6). The frequency of the OH band also correlates strongly with the Fe content of the non-dialyzable material, and significantly though more weakly with the concentrations of org. C and A_{465nm} units (Fig. 7; Tables 3, 6, and 10). Al, however, gave no significant correlation (Tables 3 and 10). These observations probably indicate that the OH groups of the FeOOH give a higher band frequency than do the

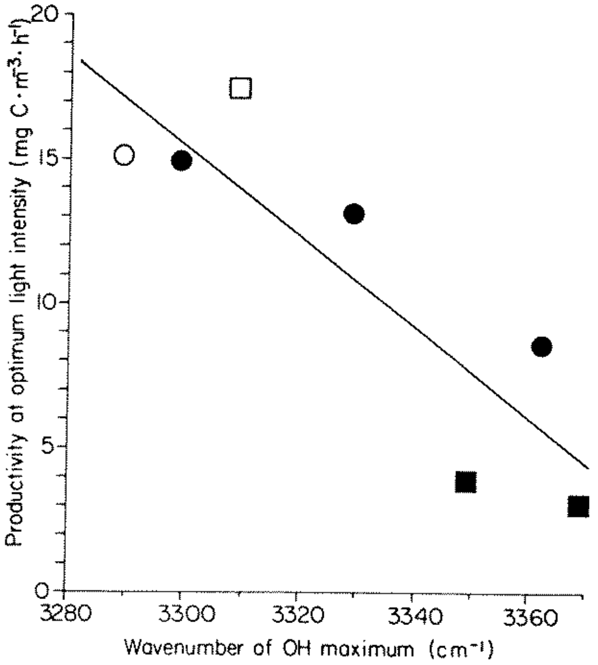

FIG. 6. Relationship between primary productivity and frequency (position) of infrared absorption band for stretching vibration of H-bonded "polymeric" OH groups in colloidal dissolved solids isolated from dialyzed water samples by freeze-drying ($r = -0.873$; $P < 0.02$, >0.01). Explanation of symbols — reservoirs: backwater, ●; main stem, ○; Southern Indian Lake: backwater, ■; main stem, □.

TABLE 7. Chemical and infrared-absorption data for acid-treated and untreated "colloidal" dissolved solids from Southern Indian Lake backwater sample SIL-2 (see Table 1). The treated subsamples and untreated control were dialyzed and freeze-dried before being analyzed. ("n.d." means not detected.)

	Absorbance ratio					
Reagent used	COOH / OH	COOH / Antisym. COO$^-$	COOH / Sym. COO$^-$	org. C (μmol/g)	Fe (μmol/g)	Al (μmol/g)
H_2O	0.358	0.424	0.656	34 700	n.d.	570
0.5 mol/L HCl	0.361	0.517	0.774	33 300	920	1600
Hot 6 mol/L HCl	0.547	0.649	0.792	105 000	1850	2100

TABLE 8. Correlation matrix showing relationship between primary productivity and various physicochemical parameters of the water and dissolved solids in backwater and main-stem regions of the reservoirs and Southern Indian Lake. "n.s." means not significant.[a] "Antisym." and "sym." refer to antisymmetric and symmetric stretching vibrations, respectively. Other abbreviations are explained in sections on field work and laboratory work.

Chemical and physical properties of the water			Correlation with productivity	
Type of property or phenomenon measured (and units used)	Treatment of water sample	Parameter or constituent tested	*r*	*P*
Elemental composition of water (μmol/L)	Undialyzed	org. C	−0.961	<0.001
		Fe	−0.580	n.s.
		P	−0.0442	n.s.
		TDP	−0.157	n.s.
		PO_4-P	0.459	n.s.
		N	−0.555	n.s.
		TDN	0.210	n.s.
		Al	0.0105	n.s.
	Dialyzed	org. C	0.0663	n.s.
		Fe	−0.761	<0.05; >0.02
		P	−0.371	n.s.
		N	−0.768	<0.02; >0.01
		Al	−0.436	n.s.
Elemental composition of freeze-dried dissolved solids (μmol/g)	Undialyzed	org. C	−0.653	<0.1; >0.05
		Fe	−0.247	n.s.
		P	0.143	n.s.
		N	−0.210	n.s.
		Al	0.136	n.s.
	Dialyzed	org. C	−0.732	<0.05; >0.02
		Fe	−0.793	<0.02; >0.01
		P	−0.155	n.s.
		N	−0.611	n.s.
		Al	0.114	n.s.
Infrared band frequency (cm^{-1})	Dialyzed	OH	−0.873	<0.02; >0.01
		COO^- (antisym.)	0.0828	n.s.
		COO^- (sym.)	−0.275	n.s.
		COO^- (antisym.) minus COO^- (sym.)	0.130	n.s.
Visible and infrared light absorption (absorbance units/L in water)	Undialyzed	$A_{465\mathrm{nm}}$	−0.213	n.s.
	Dialyzed	$A_{465\mathrm{nm}}$	−0.351	n.s.
		OH	−0.873	<0.1; >0.05
		COO^- (antisym.)	−0.662	n.s.
		COO^- (sym.)	−0.624	n.s.
Visible and infrared light absorption (absorbance units/mg in freeze-dried dissolved solids)	Undialyzed	$A_{465\mathrm{nm}}$	0.0353	n.s.
	Dialyzed	$A_{465\mathrm{nm}}$	−0.0857	n.s.
		OH	0.0805	n.s.
		COO^- (antisym.)	−0.340	n.s.
		COO^- (sym.)	−0.325	n.s.
Light scattering and extinction	Unfiltered	*k*	−0.141	n.s.
		α	0.188	n.s.
		Secchi disc	0.142	n.s.
Hydrogen ion concentration	Undialyzed	pH	−0.373	n.s.

[a] The *P*-value of each "insignificant" correlation in this table is >0.1. Numerical *P*-values are given only if they are "significant" (<0.05) or of doubtful significance (<0.1; >0.05).

phenolic and alcoholic OH groups of the humic substances, thus causing the composite OH band of the sample material to shift to higher frequencies with an increase in the concentration of FeOOH relative to humic matter. Therefore, we postulate that the OH band frequency indirectly measures the FeOOH concentration of the colloidal material, and that FeOOH concentration, in turn, plays a key role in limiting primary productivity. The strong correlation between Fe concentration and OH band intensity (Table 10) lends

TABLE 9. Correlation matrix relating A_{465nm} to organic carbon and iron in dialyzed and undialyzed filtered water and in total and "colloidal" (undialyzable) freeze-dried dissolved solids (see Table 3). ("n.d." means not determined.)

			Undialyzed				Dialyzed			
			org. C		Fe		org. C		Fe	
			r	P	r	P	r	P	r	P
A_{465nm}	Based on composition of water	Undialyzed	0.772	<0.01; >0.001	0.795	<0.01; >0.001	0.852	<0.001	0.770	<0.01; >0.001
		Dialyzed	n.d.	n.d.	n.d.	n.d.	0.933	<0.001	0.820	<0.001
	Based on composition of dissolved solids	Undialyzed	0.582	<0.05; >0.02	0.870	<0.001	n.d.	n.d.	n.d.	n.d.
		Dialyzed	n.d.	n.d.	n.d.	n.d.	0.700	<0.01; >0.001	0.519	<0.1; >0.05

credence to this interpretation, although another theoretically possible explanation is that the complexing of Fe^{3+} ions by humic matter shifted the IR maximum for phenolic OH groups to higher frequencies by an inductive effect (Bellamy 1958; Nakamoto 1970).

Proposed mechanism of trophic depression — In summary, it would seem that the lake and reservoir waters are less productive at higher concentrations of "dissolved" organic matter, most of which consists of humic substances. The observed effect, which may well be widespread and important in surface waters of northern Manitoba and other regions of the boreal forest zone, is related to the accumulation of Fe in the colloidal component of the dissolved material. This colloidal Fe is probably in the form of FeOOH which has been complexed and peptized by epitaxial films of nitrogenous humic matter. The research data failed, however, to substantiate the hypothesis that the humic–iron complexes depressed primary productivity by re-

TABLE 10. Correlation matrix relating infrared spectral parameters to concentrations of organic carbon, iron, and "humic matter" (as measured by absorption of light at 465 nm) in dialyzed water samples. "n.s." means not significant.[a] "Antisym." and "sym." refer to antisymmetric and symmetric stretching vibrations, respectively. The chemical and IR- and visible-absorption data employed represent concentration in the water (on a volume basis) as well as concentration in the freeze-dried dissolved solids (on a weight basis).

			A_{465nm}		org. C		Fe	
			r	P	r	P	r	P
Based on composition of dissolved solids	IR band position (frequency)	COO^- (antisym.)	−0.255	n.s.	−0.565	<0.1; >0.05	0.0422	n.s.
		COO^- (sym.)	0.124	n.s.	0.317	n.s.	−0.216	n.s.
		OH	0.694	<0.02; >0.01	0.802	<0.01; >0.001	0.881	<0.001
	IR band intensity (absorbance)	COO^- (antisym.)	0.742	<0.01; >0.001	0.784	<0.01; >0.001	0.692	<0.02; >0.01
		COO^- (sym.)	0.768	<0.01; >0.001	0.789	<0.01; >0.001	0.544	<0.1; >0.05
		OH	0.400	n.s.	0.381	n.s.	0.831	<0.01; >0.001
Based on composition of water	IR band intensity (absorbance)	COO^- (antisym.)	0.924	<0.001	0.978	<0.001	0.814	<0.01; >0.001
		COO^- (sym.)	0.931	<0.001	0.970	<0.001	0.788	<0.01; >0.001
		OH	0.862	<0.01; >0.001	0.942	<0.001	0.906	<0.001

[a] The P-value of each "insignificant" correlation in this table is >0.1. Numerical P-values are given only if they are "significant" (<0.05) or of doubtful significance (<0.1; >0.05).

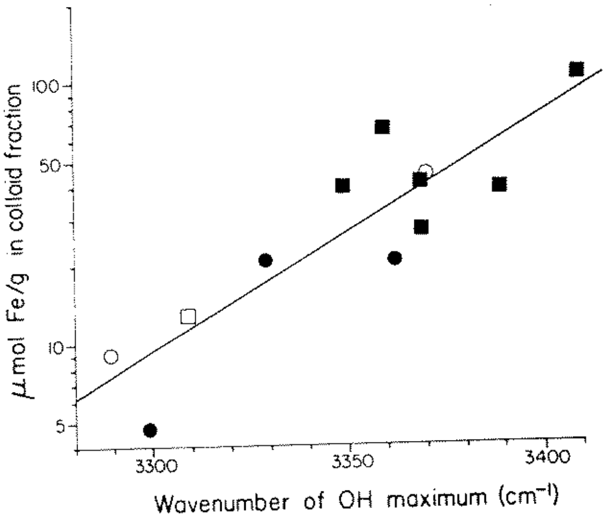

FIG. 7. Relationship between iron and OH groups in colloidal dissolved solids isolated from dialyzed water samples by freeze-drying ($r = 0.881$; $P < 0.001$). Explanation of symbols — reservoirs: backwater, ●; main stem, ○; Southern Indian Lake: backwater, ■; main stem, □.

ducing the availability of phosphate or light or by lowering the pH of the water. What, then, can account for the observed results?

Perhaps the most likely explanation for the apparent depression of primary productivity in the presence of colloidal humic-Fe complexes is that the humic matter renders the Fe and other micronutrients which it sequesters unavailable to phytoplankton. Sakamoto (1971), in a study of other Canadian Shield lakes, reached the same conclusion, and a comparable situation is thought to exist in the case of plants growing on peaty soils (Goodman and Cheshire 1973). Similarly, Giesy (1976) reported that humic acid reduced the availability of Fe to Fe-starved *Scenedesmus* cultures (although the net effect of the humic acid was to stimulate growth of the algae). Possibly Fe fixation by humic matter is responsible for widespread limitation of productivity in the relatively humus-rich waters of the boreal forest zone. Our tentative conclusions do not necessarily conflict with the work of Burk et al. (1932) and D'yakonova (1962), who claimed that humic substances enhance the bio-availability of Fe, thereby stimulating the growth of microorganisms and plants. Whether humic substances stimulate or depress biological activity probably depends on their nature (e.g. average molecular weight) and abundance. Metals bound to the less soluble, higher molecular weight humic substances of soil are thought to be relatively unavailable to plants (Stevenson and Ardakani 1972), and the same principle may well apply to algae. In the present case, possible reasons for inhibition of the biological uptake of metals in the less productive waters include the following: (1) strong, essentially covalent bonding of nutrient metals by humic substances, which thereby interfere with the complexing of these metals by biochemical "carrier" molecules; (2) inability of higher molecular weight humic-metal complexes to pass through cell membranes of algae; (3) steric factors preventing contact between sequestered metals and algal cells or carrier molecules; and (4) scavenging of micronutrients by the FeOOH associated with the humic matter. The greater the concentration of dissolved organic matter, the more efficient the sequestering process.

Nevertheless, our data also suggest that fixation of Fe and other minor metals by humic matter or humic–FeOOH complexes only partially accounts for the unfavorable ecological effect of the organic matter. Primary productivity is more significantly correlated with total dissolved org. C than with any of the parameters associated with colloidal humic–Fe complexes, and is not significantly correlated with $A_{465\mathrm{nm}}$, which supposedly represents the humic component of the organic matter (Table 8). Although the weak correlation between productivity and $A_{465\mathrm{nm}}$ may merely reflect the limitations and ambiguity of the $A_{465\mathrm{nm}}$ parameter (see section on LABORATORY WORK), our data are consistent with the possibility that nonhumic organic compounds as well as humic matter played a significant role in limiting primary productivity. For instance, toxic compounds such as phenols could have accumulated along with humic matter in the backwater regions. More research is needed to establish the mechanisms of the trophic depression and their relative importance, but the data presented here serve to identify some likely possibilities which merit further study.

SHORT-TERM CHEMICAL ANOMALIES CAUSED BY IMPOUNDMENT, AND THEIR ECOLOGICAL EFFECTS

Analysis of dissolved solids showed that the undialyzed backwater samples from 0.5-yr-old Notigi Reservoir and 3-yr-old Kettle Reservoir had marked chemical anomalies with respect to the rest of the water samples (including samples from lake as well as reservoir stations) (Fig. 8 and 9; Table 3). In contrast, neither the backwater sample from 14-yr-old Kelsey Reservoir nor the main-stem reservoir samples showed such aberrations, demonstrating that the aberrations are short-term effects caused by inundation following impoundment.

Total soluble P in the "normal" samples (all samples except the two aberrant ones) is strongly correlated with $A_{465\mathrm{nm}}$ (representing soluble humic matter) and with total soluble Fe, but the Notigi and Kettle backwaters had abnormally high concentrations of P in proportion to $A_{465\mathrm{nm}}$ and Fe (Fig. 8A–C). Similarly, total soluble N is correlated with total soluble org. C, but the Notigi backwater had an abnormally high N content (Fig. 8D). In each of these plots, all the "normal" samples cluster about a single regression line,

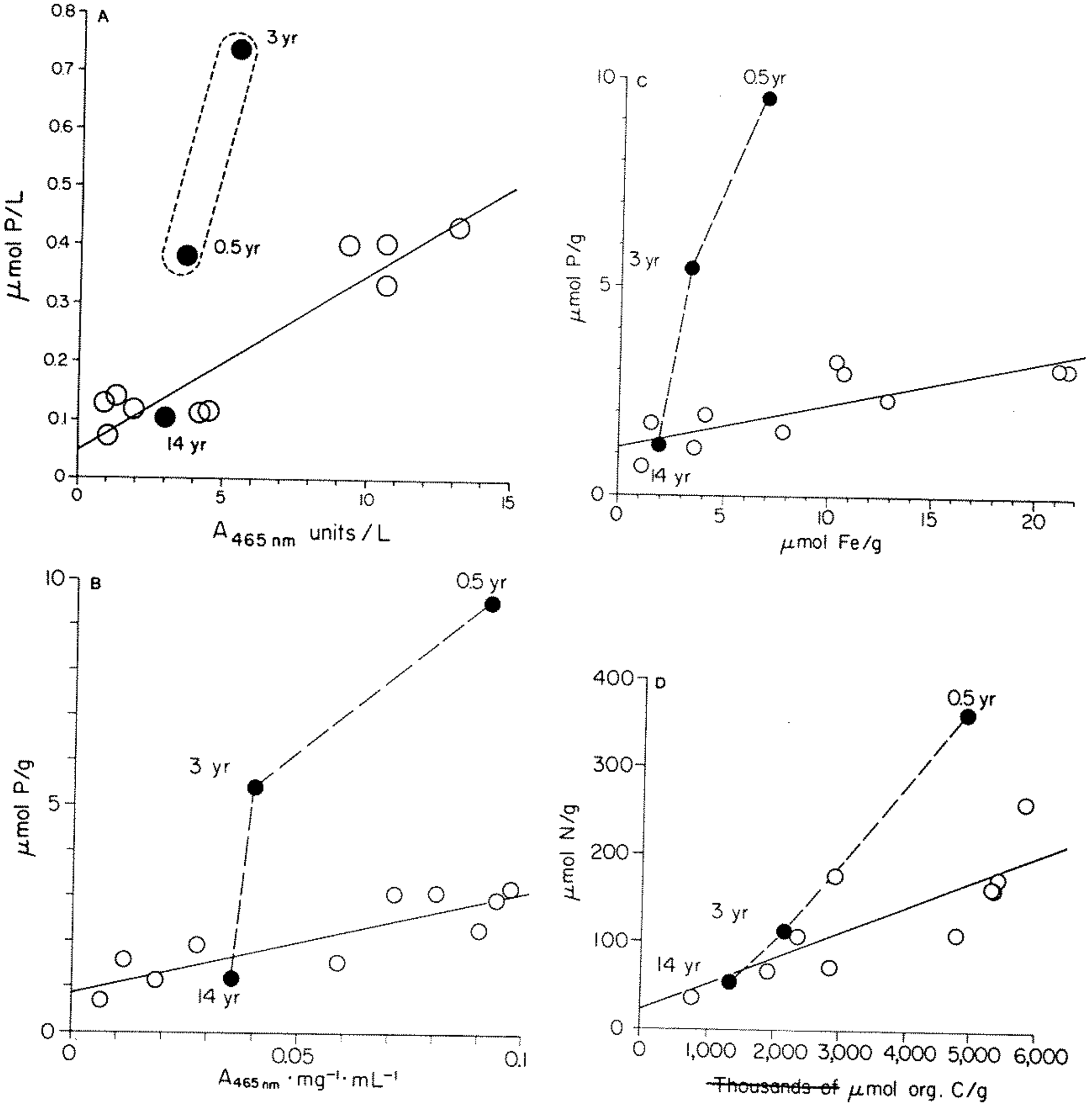

FIG. 8. Relationships between different chemical and spectral properties in the lake, stream, and reservoir waters. A, Total dissolved phosphorus content of water plotted against "humic" content as estimated by absorption of light at 465 nm (for all samples except the 0.5- and 3-yr reservoir backwaters, $r = 0.941$; $P < 0.001$); B, Phosphorus content of total dissolved solids (isolated from undialyzed water by freeze-drying) plotted against "humic" content (estimated by absorption of light at 465 nm) (for all samples except the 0.5- and 3-yr reservoir backwaters, $r = 0.867$; $P < 0.001$); C, Phosphorus content of total dissolved solids plotted against iron content (for all samples except the 0.5- and 3-yr reservoir backwaters, $r = 0.833$; $P < 0.01$, >0.001); D, Nitrogen content of total dissolved solids plotted against organic carbon content (for all samples except the 0.5-yr reservoir backwater, $r = 0.820$; $P < 0.01$, >0.001). NOTE: "A_{465nm}" values represent 1 mg of freeze-dried dissolved solids redissolved in 1 mL of borate buffer. Explanation of symbols — reservoir backwater, ●; all other samples, ○. "Ages" of reservoir backwaters refer to time elapsed since onset of impoundment.

TABLE 11. Average chlorophyll-*a* content of water in northwest sector (main-stem region) of Notigi Reservoir for days 154–267 of the years 1973–76. The 1973 value was recorded prior to the time (t_o) when impoundment was commenced.

Year	Chlorophyll-*a* (μg/L)
1973	5.4
- - - - - - - - - - - - - - -	- - - - - - - - - - - - - - t_o
1974	8.1
1975	12
1976	13

which evidently represents the norm for the surface waters of the field area.

Among the three reservoir backwaters, the quantity of P or N per unit weight of total dissolved solids decrease in the order Notigi > Kettle > Kelsey (i.e. younger > older) (Fig. 8B–D), suggesting that in the study area impoundment causes an initial upsurge in the proportions of P and N to other dissolved constituents (probably owing to rapid leaching from flooded land) followed by a progressive decline leading to a return to normal background levels several years after impoundment. The excess nutrients initially released into the water were at least partly available for algal growth, as indicated by data from Notigi Reservoir showing an increase in the mean summer chlorophyll content of the water after the onset of impoundment (Table 11) (also see Campbell et al. 1975; Ostrofsky and Duthie 1978).

On the other hand, the Kettle backwater had a larger quantity of dissolved P per unit volume of water than any other sample, and the proportions of P and N in the backwater to P and N in the associated main-stem water were higher for Kettle Reservoir than for the other three bodies of water (Table 2; Fig. 8A). Moreover, the Kettle backwater had the smallest proportion of ortho-PO_4 to total dissolved P, indicating that the anomalously high P levels are attributable to forms of P other than free ortho-PO_4. In spite of being enriched in dissolved P, the Kettle backwater had a lower level of primary productivity than the other reservoir waters (Table 2), suggesting that it is in the "trophic depression" phase. We initially postulated that this trophic depression had arisen because most of the dissolved P was fixed in biologically unavailable forms such as humic-Fe-phosphate complexes (Hecky and Harper 1974; Jackson and Hecky 1977). Although fixation of P by humic-metal complexes is not ruled out by our data and may well occur in the lake and reservoir waters (Fig. 5, 8B–C), the evidence presented in this report favors the interpretation that the available forms of P in the Kettle backwater were not being fully utilized by the phytoplankton owing to a deficiency in trace metals (e.g. Fe) caused by the sequestering of these metals by humic matter.

Another noteworthy observation is that the Kettle backwater had an anomalous Al:Fe ratio with respect to the other water samples. Whereas the other samples gave a highly significant positive correlation between the Al:Fe ratios of the colloidal and total dissolved solids, the Kettle backwater was aberrant because its total Al content, but not its colloidal Al content, was anomalously high (Fig. 9; Table 3). Thus, the Kettle backwater presumably had an abnormally high concentration of low molecular weight (dialyzable) dissolved Al. Considering that Al(III), like Fe(III), has a strong affinity for phosphate (Larsen 1959; Lévesque and Schnitzer 1967; Schnitzer 1969; Sinha 1971), there could be a direct cause-and-effect relationship between the exceptionally high levels of dissolved Al and P in the Kettle backwater.

We have presented a limited set of data suggesting the appearance of temporary perturbations in the geochemistry and productivity of impounded waters within 3 yr following impoundment. Our observations, though based on single water samples, are consistent with physicochemical and primary-production data for multiple paired water samples collected at the backwater and main-stem stations of Kettle Reservoir in different seasons during the period 1972–73 (Cleugh 1974; Hecky and Harper 1974), indicating that our results are not fortuitous (Table 12). According to

TABLE 12. Physical, chemical, and biological-production data for paired water samples collected from the backwater and main-stem stations of Kettle Reservoir during the period 1972–74. Data for 1972–73 were taken from Cleugh (1974) and Hecky and Harper (1974). ("n.d." means no data.)

Station	Date(s)	No. of observations	Chlorophyll-*a* (mg/m³)	TDP	TDN	DOC (μmol/L)	Fe	P/org. C	Color (Pt units)	pH	Primary productivity (mgC·m⁻³·h⁻¹)	*k*	α	Secchi disc(m)
Backwater	June–Oct. 1972	5	2.3	2.1	38.6	90.76	0.0034	0.023	n.d.	7.6	n.d.	n.d.	n.d.	1.8
	March 1973	1	1.0	1.9	29.7	87.01	0.0079	0.022	50	7.3	n.d.	n.d.	n.d.	n.d.
	June–Oct. 1973	4	3.2	2.4	39.3	80.5	0.0032	0.030	n.d.	7.6	n.d.	n.d.	n.d.	2.2
	Sept. 1973	1	3.0	2.7	45.6	100.0	0.0056	0.027	n.d.	7.7	5.0	1.80	n.d.	1.8
	Sept. 1974	1	6.0	5.10	42.8	n.d.	0.001	—	n.d.	7.5	8.6	1.05	2.0	2.1
Main stem	June–Oct. 1972	5	6.0	0.74	28.3	58.2	0.0029	0.013	n.d.	8.2	n.d.	n.d.	n.d.	0.5
	March 1973	1	3.1	0.90	24.1	74.8	0.0020	0.012	15	7.9	n.d.	n.d.	n.d.	n.d.
	June–Oct. 1973	4	2.4	0.58	24.0	48.0	0.001	0.012	n.d.	8.3	n.d.	n.d.	n.d.	0.8
	Sept. 1973	1	2.7	0.58	23.1	69.5	0.0030	0.0083	n.d.	8.4	12	1.3	n.d.	0.8
	Sept. 1974	1	6.7	1.3	27.8	n.d.	0.002	—	n.d.	8.1	15	0.96	6.9	0.8

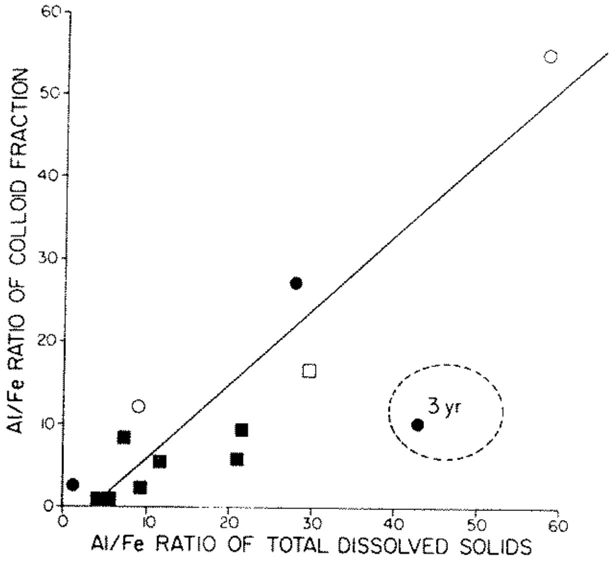

FIG. 9. Relationship between aluminum:iron ratio of colloidal fraction of dissolved solids and aluminum:iron ratio of total dissolved solids (for all samples except the 3-yr reservoir backwater, $r = 0.928$; $P < 0.001$). Explanation of symbols — reservoirs: backwater, ●; main stem, ○; Southern Indian Lake: backwater, ■; main stem, □.

these data, concentrations of dissolved P and N were much higher in the backwater region than in the main-stem region, but primary productivity was much lower, and algal standing crops (as measured by chlorophyll concentration) were either less abundant or virtually the same (within experimental and sampling error). The backwater zone had considerably higher concentrations of dissolved org. C, more intense coloration, a generally higher Fe content, a higher P:org. C ratio, and lower pH values. These observations are at least consistent with the hypothesis that the backwater region was enriched in humic substances which depressed algal productivity. The differences in productivity between the backwater and main-stem stations cannot be attributed to differences in physical factors such as thermal stratification, depth of water, and light penetration. No significant thermal stratification was detected at either station, and light penetration was similar at both stations (or more favorable at the backwater station). Furthermore, the water was shallower at the backwater site (7–8 m) than at the main-stem site (16–22 m); on the basis of critical depth alone (Sverdrup 1953), productivity should have been higher at the backwater station, whereas the reverse was true.

Among the water samples as a whole, not including the aberrant ones from the Notigi and Kettle backwater stations, dissolved P was more strongly correlated with $A_{465\text{nm}}$ than with any other chemical parameter. Thus, the degree of association between total P and total Fe, Al, org. C, and $A_{465\text{nm}}$ decreased in the order $A_{465\text{nm}}$ > Fe > org. C > Al (Table 13). We tentatively infer that most of the dissolved P in the surface waters of the field area is normally in the form of humic-iron-phosphate complexes. The Sephadex elution patterns (Fig. 5) support this interpretation. Similarly, most of the dissolved N is probably in the form of organic compounds. On the other hand, the excess P and N released into the younger reservoir backwaters following impoundment are probably not in the same form as the P and N of the "normal" surface waters, as suggested by the abnormally high concentrations of P and N relative to other chemical parameters (Fig. 8). Dialysis obliterated the distinction between "normal" waters and "abnormal" (Notigi and Kettle) waters (Table 3), suggesting that the excess P and N initially released into the impounded backwaters had relatively low molecular weights. This may account for their apparent availability to phytoplankton (Table 11).

According to our interpretation, impoundment initially causes rapid leaching of available nutrients, including P and N, from inundated soil and vegetation, thereby stimulating an upsurge in primary production

TABLE 13. Correlation matrix relating total dissolved phosphorus to total dissolved iron, aluminum, organic carbon, and "humic matter" (represented by absorption of light at 465 nm) in the water samples, excluding those from the Notigi and Kettle backwater stations. "n.s." means not significant.[a] The analytical data employed represent concentration in the water (on a volume basis) as well as concentration in the freeze-dried dissolved solids (on a weight basis).

		$A_{465\text{nm}}$		Fe		org. C		Al	
		r	P	r	P	r	P	r	P
P	Based on composition of water	0.941	<0.001	0.878	<0.001	0.863	<0.001	0.838	<0.01; >0.001
	Based on composition of dissolved solids	0.867	<0.001	0.833	<0.01; >0.001	0.435	n.s.	−0.104	n.s.

[a] The P-value of each "insignificant" correlation in this table is >0.1. Numerical P-values are given only if they are "significant."

and algal biomass. Humic substances released more slowly into the water subsequently bring about a progressive decline in productivity by sequestering Fe and other trace metals, thus preventing the algae from taking full advantage of the available P and N. This interpretation is consistent with the observation that Kettle Reservoir displayed an anomalously low level of productivity despite the presence of supposedly available low molecular weight forms of P leached from flooded land. Toxic effects of other dissolved organics and the binding of phosphate by humic complexes of Fe and Al could conceivably contribute to the ensuing environmental deterioration. Accumulation of humic matter in the water is made possible by the fact that humic substances are generally very resistant to biodegradation. The "trophic depression phase" is inaugurated when the adverse effect of the humic matter exceeds the beneficial effect of the available nutrients. The trophic depression phase probably comes to an end when the "pulse" of foreign humic matter is dissipated by processes such as sedimentation and flushing. But even under natural, unperturbed conditions, the productivity of surface waters in the field area is limited to a greater or lesser extent by dispersed humic matter.

Acknowledgments

The research was funded by the Government of Canada. In the field we were assisted by C. Anema and K. Burridge. Sample preparation and chemical and UV-visible spectrophotometric analyses involved in the study of humic substances were done by R. N. Woychuk. IR spectrophotometry was the work of T. A. Jackson. Determination of TDP and chlorophyll was performed by the analytical chemistry unit of the Freshwater Institute, and C. Anema assisted in the preparation of samples. S. Guildford performed the primary productivity measurements, and S. Levine did the radiobioassays for PO_4-P. We thank Drs P. Healey, D. Povoledo, and F. Rigler for critical comments on the manuscript.

BANOUB, M. W. 1972. A method for the determination of particulate organic nitrogen in natural waters. Int. J. Environ. Anal. Chem. 2: 107–112.

BARANOV, I. V. 1961. Biohydrochemical classification of the reservoirs in the European U.S.S.R. *In* P. V. Tyurin [ed.] The storage lakes of the U.S.S.R. and their importance for fishery. Izv. Gos. Nauchno-Issled. Inst. Ozer. Rech. Rybn. Khoz. 50: 139–183.

BAXTER, R. M. 1977. The environmental effects of dams and impoundments. Annu. Rev. Ecol. Syst. 8: 255–283.

BELLAMY, L. J. 1958. The infra-red spectra of complex molecules. Methuen, London; John Wiley and Sons, New York, NY. 425 p.

BLACK, A. P., AND R. F. CHRISTMAN. 1963. Chemical characteristics of fulvic acids. J. Am. Water Works Assoc. 55: 897–912.

BORDOVSKIY, O. K. 1965. Accumulation and transformation of organic substances in marine sediments. Mar. Geol. 3: 1–114.

BURK, D., H. LINEWEAVER, AND C. K. HORNER. 1932. Iron in relation to the stimulation of growth by humic acid. Soil Sci. 33: 413–454.

BUTLER, J. J. A., AND J. N. LADD. 1971. Importance of the molecular weight of humic and fulvic acids in determining their effects on protease activity. Soil Biol. Biochem. 3: 249–257.

CAMPBELL, P. G., B. BOBEE, A. CAILLE, M. J. DEMALSY, P. DEMALSY, J. L. SASSEVILLE, AND S. A. VISSER. 1975. Pre-impoundment site preparation: a study of the effects of topsoil stripping on reservoir water quality. Verh. Int. Ver. Limnol. 19: 1768–1777.

CHEN, Y., N. SENESI, AND M. SCHNITZER. 1977. Information provided on humic substances by E_4/E_6 ratios. Soil Sci. Soc. Am. Proc. 41: 352–358.

CHRISTMAN, R. F., AND M. GHASSEMI. 1966. Chemical nature of organic color in water. J. Am. Water Works Assoc. 58: 723–741.

CLEUGH, T. R. 1974. Hydrographic survey of lakes on the lower Churchill and Rat-Burntwood Rivers and reservoirs and lakes on the Nelson River. Lake Winnipeg, Churchill, and Nelson Rivers Study Board, Canada–Manitoba 1971–'75 Technical Report Appendix 5, vol. 2, Report E, 230 p. Published jointly by governments of Canada and Manitoba.

DE HAAN, H. 1976. Evidence for the induction of catechol-1,2-oxygenase by fulvic acid. Plant Soil 45: 129–136.

DUTHIE, H. C., AND M. L. OSTROFSKY. 1974. Plankton, chemistry, and physics of lakes in the Churchill Falls region of Labrador. J. Fish. Res. Board Can. 31: 1105–1117.

D'YAKONOVA, K. A. 1962. Iron-humus complexes and their role in plant nutrition. Sov. Soil Sci. (no. 7): 692–698 (English transl.).

FEE, F. J. 1973. Modelling primary production in water bodies: a numerical approach that allows vertical inhomogeneities. J. Fish. Res. Board Can. 30: 1469–1473.

GHASSEMI, M., AND R. F. CHRISTMAN. 1968. Properties of the yellow organic acids of natural waters. Limnol. Oceanogr. 13: 583–597.

GIESY, P. J. JR. 1976. Stimulation of growth in *Scenedesmus obliquus* (Chlorophyceae) by humic acids under iron limited conditions. J. Phycol. 12: 172–179.

GJESSING, E. T., AND J. E. SAMDAL. 1968. Humic substances in water and the effect of impoundment. J. Am. Water Works Assoc. 60: 451–454.

GOLTERMAN, H. L. 1973. Natural phosphate sources in relation to phosphate budgets: a contribution to the understanding of eutrophication. Water Res. 7: 3–17.

GOODMAN, B. A., AND M. V. CHESHIRE. 1973. Electron paramagnetic resonance evidence that copper is complexed in humic acid by the nitrogen of porphyrin groups. Nature (New Biol.) 244: 158–159.

HECKY, R. E., AND R. J. HARPER. 1974. Phytoplankton and primary productivity of the lower Churchill lakes, the Rat-Burntwood lakes, and the Nelson River lakes and reservoirs. Lake Winnipeg, Churchill, and Nelson Rivers Study Board, Canada–Manitoba 1971–'75 Technical Report Appendix 5, vol. 2, Report F (39 p.). Published jointly by governments of Canada and Manitoba.

JACKSON, T. A., AND R. E. HECKY. 1977. Geochemical and biological effects resulting from creation of man-made lakes, and their variation through time (abstract). Third Int. Symp. Environ. Biogeochem. (Wolfenbüttel, West Germany, March 27–April 2, 1977): Abstracts, p. 65–66.

JACKSON, T. A., G. KIPPHUT, R. H. HESSLEIN, AND D. W. SCHINDLER. 1980. Experimental study of trace metal chemistry in soft-water lakes at different pH levels. Can. J. Fish. Aquat. Sci. 37: 387–402.

Jackson, T. A., and D. W. Schindler. 1975. The biogeochemistry of phosphorus in an experimental lake environment: evidence for the formation of humic-metal phosphate complexes. Verh. Int. Ver. Limnol. 19: 211–221.

Kribek, B., J. Kaigl, and V. Oruzinsky. 1977. Characteristics of di- and trivalent metal-humic acid complexes on the basis of their molecular-weight distribution. Chem. Geol. 19: 73–81.

Lapitsky, I. I. 1968. Development of fisheries and the ways of raising fish productivity of big reservoirs. Food & Agricultural Organization (FAO), Rome, TA no. 2547, p. 124–134.

Larsen, J. E., G. F. Warren, and R. Langston. 1959. Effect of iron, aluminum, and humic acid on phosphorus fixation by organic soils. Soil Sci. Soc. Am. Proc. 23: 438–440.

Lévesque, M. 1969. Characterization of model and soil organic matter metal-phosphate complexes. Can. J. Soil Sci. 49: 365–373.

Lévesque, M., and M. Schnitzer. 1967. Organo-metallic interactions in soils: 6. Preparation and properties of fulvic acid-metal phosphates. Soil Sci. 103: 183–190.

Levine, S. N., and D. W. Schindler. 1980. Radiochemical analysis of orthophosphate concentrations and seasonal changes in the flux of orthophosphate to seston in two Canadian Shield lakes. Can. J. Fish. Aquat. Sci. 37: 479–487.

Lowe-McConnell, R. H. 1973. Reservoirs in relation to man — fisheries. *In* W. C. Ackermann, G. F. White, and E. B. Worthington [ed.] and J. L. Ivens [assoc. ed.] Man-made lakes: their problems and environmental effects. Geophys. Monogr. 17, Am. Geophys. Union, Washington, D.C., p. 641–654.

Milanovich, F. P., D. W. Wilson, and Y. Yeh. 1975. Detoxifying effect of yellow substance on *E. coli* in media containing copper. Nature 253: 460–461.

Nakamoto, K. 1970. Infrared spectra of inorganic and coordination compounds. Wiley-Interscience, New York, Toronto, London, Sydney. 338 p.

Nechutová, H., and V. Tichy. 1970. Effect of humus substances on the production and the quality of the biomass of *Scenedesmus quadricauda*. Arch. Hydrobiol., Suppl. 39, Algological Studies 2/3: 26–37.

Ostrofsky, M. L., and H. C. Duthie. 1978. An approach to modelling productivity in reservoirs. Verh. Int. Ver. Limnol. 20: 1562–1567.

Prakash, A., and M. A. Rashid. 1968. Influence of humic substances on the growth of marine phytoplankton: dinoflagellates. Limnol. Oceanogr. 13: 598–606.

Reuter, J. H., and E. M. Perdue. 1972. Chemical characterization of dissolved organic matter and its influence on the chemistry of river water. Report no. ERC-0372, Georgia Inst. Technol. (Atlanta), 33 p.

Rigler, F. 1966. Radiobiological analysis of inorganic phosphorus in lake water. Verh. Int. Ver. Limnol. 16: 465–470.

Rzoska, J. 1966. The biology of reservoirs in the U.S.S.R., p. 149–154. *In* R. H. Lowe-McConnell [ed.] Man-made lakes. Academic Press, London and New York.

Sakamoto, M. 1971. Chemical factors involved in the control of phytoplankton production in the Experimental Lakes Area, Northwestern Ontario. J. Fish. Res. Board Can. 28: 203–213.

Sandell, E. B. 1959. Colorimetric determination of traces of metals (vol. 3 of B. L. Clarke, P. J. Elving, and I. M. Kolthoff [ed.] Chemical analysis). Wiley-Interscience, New York, NY. 1032 p.

Schindler, D. W. 1966. A liquid scintillation method for measuring carbon-14 uptake in photosynthesis. Nature 211: 844–845.

1974. Eutrophication and recovery in experimental lakes: implications for lake management. Science 184: 897–899.

1977. Evolution of phosphorus limitation in lakes. Science 195: 260–262.

Schindler, D. W., R. V. Schmidt, and R. A. Reid. 1972. Acidification and bubbling as an alternative to filtration in determining phytoplankton production by the ^{14}C method. J. Fish. Res. Board Can. 29: 1627–1631.

Schnitzer, M. 1965. The application of infrared spectroscopy to investigations on soil humic compounds. Can. Spectrosc. 10: 121–127.

1969. Reactions between fulvic acid, a soil humic compound and inorganic soil constituents. Soil Sci. Soc. Am. Proc. 33: 75–81.

Schnitzer, M. 1971. Characterization of humic constituents by spectroscopy, p. 60–94. *In* A. D. McLaren and J. J. Skujins [ed.] Soil biochemistry, vol. 2, Marcel Dekker, New York, NY.

Shapiro, J. 1957. Chemical and biological studies on the yellow organic acids of lake water. Limnol. Oceanogr. 11: 161–179.

Shearer, J. 1976. Construction and operation of a portable incubator for phytoplankton primary production studies. Fish. Mar. Serv. Tech. Rep. 638: 22 p.

Sinha, M. K. 1971. Organo-metallic phosphates. Plant Soil 35: 471–493.

Stainton, M. P., M. J. Capel, and F. A. J. Armstrong. 1974. The chemical analysis of fresh water. Can. Dep. Environ. Misc. Spec. Publ. 25: 119 p.

Stevenson, F. J. and M. S. Ardakani. 1972. Organic matter reactions involving micronutrients in soils. *In* J. J. Mortvedt, P. M. Giordano, W. L. Lindsay, R. C. Dinauer, V. S. Clark, and P. Eith [ed.] Micronutrients in agriculture. Soil Sci. Soc. Am. (Madison, Wisconsin), p. 79–114.

Stevenson, F. J., and K. M. Goh. 1971. Infrared spectra of humic acids and related substances. Geochim. Cosmochim. Acta 35: 471–483.

Sverdrup, H. U. 1953. On conditions for the vernal blooming of phytoplankton. J. Cons. Int. Explor. Mer 18: 287–295.

Vaughan, D. 1974. A possible mechanism for humic acid action on cell elongation in root segments of *Pisum sativum* under aseptic conditions. Soil Biol. Biochem. 6: 241–247.

Vollenweider, R. A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication. Organization for Economic Co-operation and Development, DAS/CSI/68.27: 61 p.

Weir, C. C., and R. J. Soper. 1963. Interaction of phosphates with ferric organic complexes. Can. J. Soil Sci. 43: 393–399.

Zhadin, V. I., and S. V. Gerd. 1961. Fauna and flora of the rivers, lakes, and reservoirs of the U.S.S.R. (English transl.). Israel Program for Scientific Translations, Jerusalem (1963). 626 p.