THE AFRICAN JOURNAL OF Tropical Hydrobiology and Fisheries

(Afr. J. Trop. Hydrobiol. Fish.)

Vol. 2 No. 2 1972

East African Literature Bureau
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REPRINTS

Authors will receive 60 reprints free of charge. Extra reprints may be procured on cost.

PUBLISHER

East African Literature Bureau, P.O. Box 30022, Nairobi, Kenya.

ISSUES

The Journal consists of one volume a year, consisting of two issues with approximately eighty pages each.

SUBSCRIPTION

Annual subscription within East Africa Sh. 35. Outside East Africa, East African Sh. 70, US $ 10.00

A REVIEW OF THE DISTRIBUTION OF ORGANIC COMPOUNDS IN FRESHWATER LAKES AND RIVERS

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The study of dissolved organic matter in natural lakes and rivers is of importance for a variety of reasons. The organic matter may serve in part or whole as an energy source for organisms living in the aquatic environment, or it may supply them with materials essential for their nutrition. It may regulate life in submerged environments by providing growth factors which stimulate the rate of growth, or toxic factors which may reduce or inhibit it. Organic matter may also affect aquatic ecosystems by interacting with inorganic matter, making nutrients such as trace elements available by processes such as solubilization, removing them by the formation of complexes, or affecting their function such as by oxidation/reduction phenomena. Organic matter may also affect the physical conditions of an aquatic environment by influencing phenomena related to water/gas or water/solid interfaces and by affecting membrane potentials. A knowledge of the composition and properties of the organic compounds in an ecosystem is, therefore, essential for a good understanding of the processes taking place within it.

When analysing dissolved organic matter, especially with regard to its role in aquatic ecosystems, two main fractions can primarily be distinguished. One of these is made up of relatively stable compounds which are little affected by biological processes and which exert mainly a physical influence on the environment. This fraction comprises the fulvic and humic matter of the organic material. The other fraction, which is usually smaller than the first one, is subject to a relatively large rate of turnover. It comprises substances which play an active part in the metabolic cycles of the ecosystem. Whereas, therefore, for the study of the more stable humus fraction it is often sufficient to analyse the properties of the material as it is present in the ecosystem at a certain time, for the metabolically more active fraction it is also important to study the actual rates of turnover of the components in the system. A complicating factor in the analysis of the functions of this more active fraction can be that the concentration at which many of its components are still biologically active are often well below the sensitivity of available analytical methods. Bacteria, for instance, with their permease transport system, are often able to utilize organic compounds well below a concentration which is detectable analytically. Algae, which lack such an enzyme system, make a much smaller use of the organic compounds in natural waters. To what extent multicellular organisms can make use of the dissolved organic matter in water is still an open question. Whereas phytoplankton is the major primary producer of organic matter in unpolluted natural waters, heterotrophic bacteria are usually the main consumers and decomposers. Under natural conditions a state of dynamic equilibrium exists between the processes of production, consumption and decomposition. A sudden rise in the productivity of phytoplankton will, therefore, usually result in an increase in bacterial growth, leading to a rise in the rate of decomposition of organic matter. Sometimes the quite appreciable amount of dissolved organic matter which one can observe in some natural waters is the result of conditions which are unfavourable to bacterial growth, and a build-up of organic material will then be the result.

THE OCCURRENCE OF TOTAL AND DISSOLVED ORGANIC MATTER IN LAKES AND RIVERS

According to WELCH (1952) the total dissolved solids in fresh waters range generally from 15 to 300 ppm.

KRYLOVA and SKOPINTSEV (1959) found that the organic matter content of large rivers in the USSR varied between 3.5-60 ppm, with the nitrogen content of the organic matter between 2.4-7.8% (average 4.7%) (DYSHKO and SKOPINTSEV 1959). In the lakes of the Moscow region the organic matter content varied between 3-25 ppm with the nitrogen content of the organic matter between 2.5-12.2% (average 5.5%).

In the Wisconsin lakes the organic matter was found to vary between 2.9-39.6 ppm with an average of 12.8 ppm (WELCH 1952). For L. Mendota (one of the Wisconsin lakes), BIRGE and JUDAY (1922) calculated an annual production of dry organic matter by plankton of approximately 1.2 kg/m^2. Another, although much less important source of organic matter is atmospheric precipitation. NEUMANN, FONSELIUS and WAHLMAN (1959) estimated that in Sweden atmospheric precipitation contributes annually approximately 3.5 g of organic matter per square metre.

For the Wisconsin lakes no definite relation could be established between the contents of organic and inorganic matter, although those lakes with the lowest contents in organic matter also had low contents of inorganic material (BIRGE and JUDAY 1927). The average amount of total organic matter of these lakes was 17 ppm. Of this 8-9% was in the form of plankton and 50.60% was in the form of soluble organic matter. Also in L. Baykal (USSR) it was found that the organic carbon of living material can constitute as much as 10% of the total organic carbon of suspended or dissolved material (VOTINTSEV 1961). In the water of some swampy lakes of the Estonian SSR, SIMM (1958) found that the dissolved organic matter constituted between 19-50% of the total organic matter of the lakes.

The conclusion can, therefore, be drawn that the amount of dissolved organic matter in lakes is several times larger than the organic matter contained in the plankton. BIRGE and JUDAY (1926a, 1926b) observed for the Wisconsin lakes that the dissolved carbohydrates form approximately 10x the amount of planktonic fats and the dissolved protein 3x that of the protein contained in the plankton. For the same lakes it was found that of the dissolved organic matter, carbohydrates constitute slightly over 80%, proteins about 15% and ether-extractable matter less than 1%. The mean C/N ratio was 12.7 (BIRGE and JUDAY 1934).

OHLE (1968) estimated that in some lakes 90% of the autochthonous primary products are already decomposed just beneath the euphotic zone. The breakdown of organic matter in lakes can, therefore, proceed at a very fast rate.

With respect to organic matter present in freshwater sediments, TAMAKI and HOSHIKAWA (1954-1955) found that the organic matter content of a pond mud generally decreased with the particle size of the sediment. VISSER (1964) made similar observations when investigating the decomposition of organic matter under submerged conditions in the presence of clay minerals.

According to WELTE (1959) there are practically no differences in the chemical characteristics of organic matter from fresh and marine waters.

Free amino acids

In temperate climates, DOMOGALLA, JUDAY and PETERSON (1925) observed a rise in the amino acid and protein content of lake waters in winter and a fall during the summer. They concluded from their analyses that the water at the bottom of a lake is richer in amino acids than that at the surface. OHLE (1968) reports a similar phenomenon.

For the actual amino acids and their concentration in natural waters see Table 1. It is shown that the following amino acids have so far been reported in natural waters: alanine, aspartic acid, cystine, glutamic acid, glycine, histidine, leucine, proline, serine, tryptophan, tyrosine and valine. Alanine, aspartic acid, glumatic acid and glycine seem to be the most commonly occurring amino acids.

In the large rivers of the USSR, DYSHKO

Table 1. The Occurrence of Free Amino Acids in Lake and River Waters

Concentration (ppm)	types described	location	reference
—	proline trypotophan	River Rhine	HOLLUTA *et al.* (1955)
0.05–0.23	total amino acids	English lakes	FOGG *et al.* (1955)
ʅ0.15–0.75	total amino acids	Wisconsin lakes	HUTCHINSON (1957)
ʅ 0.001	alanine	New Zealand lakes	BRIGGS (1962 a)
ʅ 0.001	aspartic acid		
ʅ 0.001	glutamic acid		
ʅ 0.001	glycine		
0.12–0.72	total amino acids	L. Zurich	SCHURMANN (1964)
—	always present: alanine aspartic acid glutamic acid glycine occasionally present: leucine serine valine	Japanese lakes, rivers, snow and rain	ISHIWATARI *et al.* (1965)
0.001–0.02	alanine aspartic acid glycine serine	lake waters	OHLE (1968)

and SKOPINTSEV (1959) found an organic nitrogen content of 0.15-2.14 ppm, whilst for lakes in the Moscow region, the organic nitrogen content varied from 0.16-1.70 ppm. ISHIWATARI, ITO and HANYA (1965) reported an average free amino acid-nitrogen content in Japanese waters of less than 1.3% of the total organic nitrogen content. This agrees with observations by IVLERA and DATSKO (1965) who showed a free amino acid-nitrogen content of the waters of Russian reservoirs of 0.4-1.2% of the total organic nitrogen content. Assuming an organic nitrogen content of the same order as that mentioned by DYSHKO and SKOPINTSEV (1959), this amounts to an average amino acid content of the order of 0.004-0.125 ppm.

Free amino acids in subsurface waters were reported by BYKOVA (1960).

Other nitrogenous compounds present in natural waters comprise hydroxylamine, which was found in a Japanese mountain lake (TANAKA 1953), purines, which were reported by PETERSON, FRED and DOMOGALLA (1925) in L. Mendota and by SHABAROVA (1950) in a lake mud, and urea present in filtered lake waters from several New Zealand lakes (BRIGGS 1962b).

With respect to free amino acids in freshwater sediments, SWAIN (1961) found that these are rare or absent in the deposits of some North American lakes.

From his observation that most of the amino acids present in lake sediments were also present in the same relative concentration in the seston, POVOLEDO (1959a) concluded that the chemical composition of the organic matter in lake sediments reflects that of the seston present in the supernatant waters.

In the sediments of one of the lakes in Northern Italy, POVOLEDO (1959a) found the presence of 2,2′-diaminopimelic acid. KAPELLER-ADLER and VERING (1931) reported traces of monomethylamine in freshwater seston, whilst SHOREY (1913) obtained indications of the presence of trimethylamine in a salt marsh deposit.

Peptides and proteins

For some English lakes, FOGG and WESTLAKE (1955) observed peptide-N concentrations of 0.016-0.043 ppm. This would amount to a peptide concentration of approximately 0.10-0.27 ppm. Much higher peptide-N contents were reported for some Wisconsin lakes by HUTCHINSON (1957). His figures would amount to a total peptide concentration of approximately 0.45-2.00 ppm.

KONSHIN (1939) showed for the sediments of lakes in the Moscow and Leningrad regions, in which the total nitrogen ranged from 1.07-3.63%, that only 1/3 to 1/2 of the freshwater nitrogen occurred in the form of proteinaceous compounds.

BRAGAGNOLO (1949) reported the presence of glutathione in natural water. VALLENTYNE (1954) found in the acid hydrolysates of dispersed organic matter of some North American lakes the following amino acids: aspartic acid, glutamic acid, alanine, leucine and/or isoleucine. SHABAROVA (1950) reported the presence of the following amino acids in freshwater sediments after hydrolysis: alanine, arginine, cystine, histidine, leucine, lysine and tryosine; whereas BLUMENALS and SWAIN (1956) showed that hydrolysates of various lake sediments, peats and humic acid constituents of peat contained the following amino acids: alanine, aspartic acid, glutamic acid, glycine, leucine and/or isoleucine, serine, threonine and valine. SWAIN in two later publications (1959, 1961) reported that amino acids with concentrations ranging from less than 2 ppm to more than 4,000 ppm (on a wet-weight basis) were obtained in acid hydrolysates of sediments from various North American lakes. He stated that freshly collected eutrophic lake deposits contain a variety of proteins, whereas humified lake deposits contain little or no proteins besides flutelins or sclero-proteins. Swain found that neutral peat deposits, well-humified organic lake sediments and deposits of brown-water dystrophic lakes favour the preservation of neutral and acidic amino acids in the approximate ratio of 6 : 1, whereas the basic amino acids are degraded in this environment.

Acid bogs and incompletely decomposed deposits were found to favour the preservation of some of the basic amino acids in addition to several neutral types. These environments are, on the whole, detrimental to the preservation of the acidic amino acids which are destroyed by decarboxylation. Lake sediments of low organic content generally yield small amounts of neutral amino acids with practically no or very few acidic or basic amino acids. The same is true for alkalitrophic lake deposits and for brown-water obligotrophic lake sediments.

Carbohydrates

Table 2 shows the distribution of free carbohydrates in lake and river water. From the analyses it appears that glucose, mannose, sucrose and xylose can usually be detected. Glucose is invariably present. According to BIRGE and JUDAY (1934) carbohydrates disappear less rapidly during decomposition than proteins. In contrast to amino acids, carbohydrates did not show any seasonal fluctuations in reservoir waters in the USSR (IVLEVA and DATSKO 1965), but in Oyster Pond (USA), WALSH (1966) found the lowest concentration of carbohydrates occurring during a period of plankton bloom. In Japanese lakes, SUGAWARA (1965) observed that the total carbohydrate content was highest in the epilimnion (0.73-1.26 ppm) during the summer stagnation. The ratios of the dissolved carbohydrates to the total carbohydrates were about 1/2, 2/3 and 1 in the epilimnion, thermocline and hypolimnion respectively.

Table 2. The Occurrence of Free Carbohydrates in Lake and River Waters

Concentration (ppm)	types described	location	reference
0	—	L. Beloye (USSR)	GORYUNOVA (1954)
—	glucose sucrose	Eastern Ontario lakes	VALLENTYNE and WHITTAKER (1956)
0.00t	glucose sucrose	New Zealand lakes	BRIGGS (1962 a)
0.183–0.716	total sugars	natural waters (USSR)	SEMENOV *et al.* (1964)
—	glucose	L. Zürich	SCHURMANN (1964)
—	glucose mannose sucrose xylose	Minnesota lakes	ROGERS (1965)
—	glucose	L. Erken (Swedes)	WRIGHT *et al.* (1966)
1.3–2.9	total sugars	Oyster Pond (U.S.A.)	WALSH (1966)

ROGERS (1965) observed the following natural stability series for carbohydrates in the lacustrine environment of two Minnesota lakes:

fairly stable: xylose, glucose, rhamnose, arabinose
moderately stable: ribose, mannose
fairly unstable: galactose
very unstable: glucuronic acid

BYKOVA (1960) showed that subsurface waters could also contain carbohydrates.

Aldehydes up to a concentration of 0.11 ppm (in terms of formaldehyde equivalents) were found in the hypolimnion of the Japanese L. Kizaki (KAMATA 1966a).

In the sediments of lakes the origin of the free carbohydrates is presumably mainly from polysaccharide breakdown, although some of the sugars such as sucrose may have been derived directly from the sugars of living plants (WHITTAKER and VALLENTYNE 1957). Table 3 shows that the carbohydrates identified in lake and river sediments comprise arabinose, fructose, galactose, glucose, lactose, maltose, mannose, ribose, sucrose and xylose. The most commonly occurring is glucose, whereas galactose was also frequently found. WHITTAKER and VALLENTYNE (1957) observed that most of the carbohydrates in sediments will be absorbed on to the insoluble matter and will, therefore, not occur in the interstitial water of the mud. As in 5,000-9,000-year-old gyttja still 31-191 ppm of free glucose was found (Table 3) free sugars are not so quickly decomposed as is sometimes assumed. Ketoses are probably rather unstable in sediments (VALLENTYNE 1957b).

With regard to the presence of polysaccharides in lake and river waters, SEMENOV, IVLEVA and DATSKO (1964) stated that in natural waters of the USSR the reducing sugars of hydrolysates make up 0.517-1.740 ppm, this according to IVLEVA and DATSKO (1965) represents 1.8-5.5% of the total organic carbon.

GORYUNOVA (1954) found for L. Beloye that most of the organic matter in solution consisted of polysaccharides.

Polysaccharides from underground waters in Tokyo appeared to consist of arabinose, galactose, rhamnose and xylose (KOBAYASHI 1963).

Acid hydrolysis of the near-surface bottom sediments of two Minnesota lakes give rise to eight sugars, which in order of decreasing abundance were found to be: arabinose, xylose, galactose, glucuronic acid, glucose, rhamnose, mannose and ribose. These sugars varied in concentration from 100-19,100 ppm of dry sediment. Acid hydrolysis of the lower layers of the sediments produced xylose, glucose, arabinose, galactose, mannose and rhamnose (ROGERS 1965). In acid hydrolysates of gyttja, VALLENTYNE and BIDWELL (1956) observed the following sugars: fructose, glucose, galactose, xylose, ribose and arabinose.

Humic compounds

RYHANEN (1968) stated that the average content of humic substances in lakes and rivers is approximately 13 ppm. This fraction, which according to GJESSING (1967) has a molecular weight range between 700 and 20,000 consists of fulvic acids and of humic acids (OHLE 1933, THIEME 1936). In some swampy lakes of the Estonian SSR the percentage of the fulvic acid fraction was found to be between 42-76% of the total organic matter of the lakes (SIMM 1958). In the waters of some moorland areas of England, WILSON (1959) reported a fulvic acid content of between 2-30 ppm.

CHRISTMAN (1963, 1964) and CHRISTMAN and GHASSEMI (1966) described the fulvic acid fraction as to be made up of yellow aromatic polyhydroxy-methoxy-carboxylic acids with an equivalent weight of

Table 3. The Occurrence of Free Carbohydrates in Freshwater Sediments

Concentration (ppm)	types described	location	reference
—	pentoses	river and lake Seston near Moscow	SKOPINTSEV (1948)
total: 24–72 (dry sedt)	main sugar: glucose (> 50%) other sugars: galactose arabinose xylose ribose	North American lakes	VALLENTYNE (1954)
—	main sugars: glucose galactose others: xylose ribose aribinose uncommon: sucrose fructose	lake muds (Connecticut)	VALLENTYNE and BIDWELL (1956)
—	fructose glucose maltose sucrose	freshwater seston	WHITTAKER *et al.* (1957)
31–191 (dry sedt)	glucose	sediment, Bethany Bog (Connecticut)	VALLENTYNE and BIDWELL (1956)
—	fructose galactose glucose sucrose xylose and /or arabinose	Italian lake deposits	POVOLEDO (1959 a)
—	galactose glucose lactose maltose sucrose xylose	Minnesota lake deposits	ROGERS (1965)

89-113 and containing di-substituted phenyl rings. SHAPIRO (1956), however, has claimed that the coloured fraction of the fulvic acids is without an aromatic structure. He identified the main colouring material of the fulvic acid fraction as organic carboxylic hydroxy acids with a molecular weight of between 200-400 (SHAPIRO 1958, 1963, 1964).

Humic acids were found to occur in the above-mentioned Estonian lakes at concentrations of 4-13% of that of the total organic matter (SIMM 1958), whereas CHRISTMAN (1963) reported for North American waters a combined humic acid and hymatomelanic acid concentration of less than 10% of the organic matter present. IVLEVA and DATSKO (1965) found in some Russian water reservoirs a humic-C concentration of 0.7-3.4% of the total organic-C. Whereas aromatic groups were indicated in humic acids by LAMAR and GOERLITZ (1964) besides olefinic, hydroxy and carboxylic groups, KARAVAEV and BUDYAK (1960), as well as ISHIWATARI, KOSAKA and HANYA (1966) reported that humic substances from lake sediments show no aromatic character. On oxidation of humic matter these authors obtained malonic, succinic, glutaric, adipic and some long-chain acids but practically no phthalic acid. Neither did IR spectra show aromatic or $-C{=}C-$ or $-C-H$ bonds. The apparent stability of humic substances of lakes and rivers according to RYHANEN (1968) is mainly due to a lack of appropriate nutrients such as N or P. An increase in the levels of these will often result in a rapid microbial breakdown of humus.

Above a certain concentration humic acids can be toxic to several types of zooplankton (CZECZUGA 1957).

Phenolic compounds

Phenolic compounds such as phenols, phenolcarboxylic acids and phenolglucosides which have been found to occur in natural waters, originate mainly from the decomposition of organic matter. They can exert a preservative and antiseptic action to the environment.

KAPLIN and FESENKO (1965) found phenols at a concentration of 3.4-36.4 μ g/l in rivers and ponds of the Northern Caucasus, whilst KAPLIN, MATVEEV and FESENKO (1965) detected phenols varying in concentration from 2.1-64.2 μ g/l in samples from rivers, a glacier and a glacier lake in the Caucasus. Some natural waters in the Krasnoyarskiy region (USSR) were found to contain 4.1 μ g/1 of phenol (DIYUK and KIRICHUCK, 1963). SHAPIRO (1951) reported phenolic compounds at a concentration of 200-400 μ g/l in springs at the Truskavets health resort. They comprised: guaiacol, thymol, carvacrol, cresol, xylenol and α-naphthol. Alkali and alkaline earth naphthenates have been found in natural waters which have been in contact with petroleum (MULIKOVSKAYA 1956).

Phenolic compounds often occur in polluted waters. In the riven Rhine they were found to make up approximately 5.3% of the organic matter present in the river (HOLLUTA and TALSKY, 1955). Compounds that could be identified were: resorcinol, phloroglucinol, guaiacol, phenol, salicylalcohol, chlorophenols, hydroxytoluenes, thymol, hydroxybenzoic acids, gallic acid, protocatechuic acid, hydroxyhippuric acid and naphthols. HOAK (1962) reported in some waters minute quantities of phenol, m-cresol and 3,5-dimethylphenol.

Lipids, fatty acids and other organic acids

According to BIRGE and JUDAY (1926a, 1926b, 1934) the concentration of ether-extractable fats in some North American lakes was approximately 4% of the dissolved organic matter. WELCH (1952) reported a concentration of these lipids in the lake waters of 0.2-0.8 ppm.

The distribution of the lower fatty acids in lakes and rivers has been tabulated in Tables 4 and 5. It is shown that in the waters formic acid, acetic acid, propionic acid, butyric acid and valeric acid have been detected, with acetic acid as the most commonly occurring component.

In freshwater sediments much larger concentrations of the lower fatty acids have been found to be present than in the waters. So far formic acid, acetic acid, propionic acid and butyric acid have been detected,

Table 4. The Occurrence of Dissolved Lower Fatty Acids in Lake and River Waters

Concentration (ppm)	types described	location	reference
0.1–2.0	total fatty acids	River Volga	KOLOSOVA *et al.* (1957)
—	formic acid acetic acid	natural waters	MÜLLER *et al.* (1958)
—	acetic acid	L. Maggiore (130m)	POVOLEDO (1959 c)
—	formic acid acetic acid	New Zealand lakes	BRIGGS (1962 a)
—	formic acid acetic acid propionic acid butyric acid	River Tama (Japan)	KOBAYASHI *et al.* (1962)
—	formic acid acetic acid propionic acid butyric acid valeric acid	—	HOAK (1962)
6.7	acetic acid propionic acid	natural waters (Krasnoyarskiy region—USSR)	DIYUK *et al.* (1963)
—	butyric acid valeric acid	river water	LAMAR *et al.* (1963)
0.044–0.058 (meq/L)	volatile acids	mineral waters (Borzhomi—USSR)	ERISTAVI *et al.* (1965)
0.00–0.03 0.00–0.10	formic acid acetic acid	Japanese lakes (0–25m)	KAMATA (1966 b)

Table 5. The Occurrence of Lower Fatty Acids in Freshwater Sediments

Concentration %	types detected	location	reference
—	formic acid acetic acid butyric acid	lake sediments	KUZNETZOV (1934, a, 1934 b) KUZNETZOV *et al.* (1935)
0.00–0.36 (dry sedt)	formic acid	lake sediments	SPERANSKAYA (1935)
0.04–2.30 (dry sedt)	acetic acid		
0.00–0.73 (dry sedt)	butyric acid		
—	formic acid acetic acid butyric acid	lake sediments	VALLENTYNE (1957 b)
—	main acid: acetic acid other acids: formic acid propionic acid butyric acid	Japanese lakes	MIYOSHI *et al.* (1962)

with acetic acid again as the main component. MIYOSHI, SHIRAI and KADOTA (1962) found that the concentration of these acids fell with the depth from which the sediment was obtained.

The presence of high-molecular weight fatty acids in fresh waters has been reported by BRAUS, MIDDLETON and WALTON (1951) and by GORYUNOVA (1952, 1954). The latter author reported for L. Glubokoye (USSR) that the bulk of the 96 ppm of organic matter which was present, consisted of high-molecular weight fatty acids and colloidal complexes. GORYUNOVA (1954) also reported the presence of high-molecular weight fatty acids in L. Beloye (USSR).

The occurrence of other organic acids in lake and river waters is shown in Table 6. The acids so far detected comprise: citric acid, glycollic acid, lactic acid, malic acid, oxalacetic acid, pyruvic acid and succinic acid, with lactic acid as the most commonly occurring component.

Table 6. The Occurrence of Organic Aeids in Lake and River Waters

Concentration (ppm)	types detected	location	reference
1.3–3.2	total organic acids	spring waters (Truskavets-USSR)	SHAPIRO (1951)
——	lactic acid	——	MÜLLER *et al.* (1958)
——	citric acid lactic acid malic acid	River Tama (Japan)	KOBAYASHI *et al.* (1962)
——	oxalacetic acid pyruvic acid	New Zealand lakes	BRIGGS (1962 b)
——	lactic acid malic acid pyruvic acid succinic acid	——	LAMAR *et al.* (1963)
——	glycollic acid	——	FOGG *et al.* (1964)
1.2–7.2	total organic acids	surface and sub-surface waters (S. Yakutia-USSR)	BYKOVA *et al.* (1964)
0.4–0.6 (meq/L)	total organic acids	mineral waters (Borzhomi-USSR)	ERISTAVI *et al.* (1965)
0.00–0.05	lactic acid	Japanese lake	KAMATA (1966 b)
——	amino benzoic acid benzoic acid gallic acid hydroxy benzoic acid hydroxy hippuric acid phthalic acid (trace) protocatechuic acid	River Rhine (polluted)	HOLLUTA *et al.* (1955)

In some Japanese lake sediments, MIYOSHI SHIRAI and KADOTA (1962) reported the presence of lactic acid, whereas POVOLEDO (1959a, 1959b) detected the following keto acids in deposits of some North Italian lakes: pyruvic acid, glyoxylic acid, oxalacetic acid and 2-oxoglutaric acid.

Hydrocarbons and sterols

Hydrocarbons in a concentration between 2.0-4.4 ppm were found to be present in springwater at the Truskavets health resort (USSR) by SHAPIRO (1951). Traces of hydrocarbons in subsurface waters have been reported by BYKOVA (1960). Polycyclic hydrocarbons, many of which carcinogenic, were found in polluted waters by BORNEFF and FISHER (1962a, 1962b, 1963). Compounds comprised: fluoranthene; pyrene; 11,12-benzofluoranthene; 1,12-benzoperylene; 3,4-benzopyrene; 3,4-benzofluoranthene; 10,11-benzofluoranthene; 1,2-benzanthracene; chrysene; 1,12-benzoperylene and indeno (1,2,3-cd) pyrene.

In lake deposits in Minnesota, SWAIN (1956) detected a total amount of hydrocarbons of 890-3,600 ppm.

It is not our intention to review here the many reports on hydrocarbons in environments near geological oil formations.

Estrogenic substance have been reported by BRAGAGNOLO (1949) and BRARAGNOLO and SANESI (1950) in several mineral waters, particularly those used for therapeutical purposes. TRASK and WU (1930) were the first to report the presence of phytosterol and cholesterol in freshwater deposits. Sterols were also detected in freshwater sediments by SCHWENDIGER and ERDMAN (1964). They could find no correlation between the sterol content of the environment and the depth of burial of the sediment.

Substances with estrogenic activity were found in the mud of several Grecian Springs by LOUROS, TERZIS, PAVLATOU and EVANGELOPOULOS (1958). Phenol steroids were present in concentrations of 75-250 μ g/kg mud, whereas estrogens were present in the range of 10-80 μ g/kg mud. Estrogenic substances have also been reported in the muds of Czechoslovakian baths (KILIAN 1937), in muds of Roumania (RAINER and VLADUTIN 1938), in therapeutic muds of Lettland (KRASTINS 1939) and in mud of the spa Tuheljske Toplice (KRSNIK, TOCMIC and SUPEK 1944).

Pigments

Table 7 shows that a great many pigments have been found to be present in freshwater seston and sediments. The compounds so far detected comprise: antherozanthin, α-carotene, β-carotene, diatoxanthin, echinenone(?), flavacin, flavorhodin, fucoxanthin, glycemerin, leprotene, lutein, myxoxanthin, myxoxanthophyll, petaloxanthin, rhodopurpurin, rhodoviolascin, sulacatoxanthin(?), torulene, xanthophyll and zeaxanthin. The average total concentration of the carotenoids and the xanthophylls in sediments seems to be of the order of 30 ppm.

MURAVEISKY and CHERTOK (1938) found for L. Biserovo (USSR) that in the sediment xanthophylls (0.26% per dry weight) predominated over carotenes (0.17%), whereas SCHWENDIGER and ERDMAN (1963) stated that all xanthophyll to carotene ratios of both freshwater and marine sediments have been found to be within the range of 1.3-3.6.

According to BELCHER and FOGG (1964) the ratio of chlorophyllic degradation products absorbing at 667 m μ to ephiphasic matter, mainly β-carotene with an absorption at 450 m μ, can be used as an inverse index of the fertility of a lake at the time of the formation of the sediment.

Flavinoid pigments like chlorophylls may

Table 7. The Occurrence of Pigments in Freshwater Sediments

Concentration (ppm)	types detected	location	reference
——	carotenoids	lake sediments	TRASK *et al.* (1930)
——	carotene chlorophyll xanthophylls	Swedish gyttja	BAUDISCH *et al.* (1934) BAUDISCH (1938)
——	carotene	Swedish gyttja	KLIMOV *et al.* (1937)
——	β-carotene chlorophyll 4 xanthophylls	organic detritus	BEATTY (1941)
1.5–33.3 (dry sedt)	carotene	medicinal mud (Ukraine-USSR)	SAVINOV *et al.* (1950)
9–57 (wet sedt)	unsaponifiable pigments		
up to 30	carotenoids	lake sediments (Ural-USSR)	TITOV (1950)
——	3 chlorophyll degradation products	Canadian lake sediment (11,000 yrs old)	VALLENYNE (1955)
27.8 (β-carot. equivalents)	carotenes: α-carotene β-carotene echinenone (?)	L. Searles sediment (20,000 yrs old)	VALLENTYNE (1957 a)
23.0 (β-carot. equivalents)	xanthophylls.		
——	5 chlorophyll derivatives 3 yellow pigments: fucoxanthol, luteol or related compounds red pigments (including a carotenoid)	Interglacial gyttja-Denmark (100,000 yrs old)	ANDERSEN *et al.* (1955)
——	rhodoviolascin	L. Nakuru (Kenya)	KARRER *et al.* (1940)
——	β-carotene, flavacin, lutein, myxoxanthin, myxoxathophyll, sulcatoxanthin (?)	seston	VALLENTYNE (1957 b)
——	antheroxanthin, β-carotene, β-carotene, diatoxanthin, flavorhodin, fucoxanthin, glycymerin, leprotene, myxoxanthin, petaloxanthin, rhodopurpurin, rhodoviolascin, torulene, xanthophyll, zeaxanthin	lake sediments, marshes, peats	VALLENTYNE (1957 b)
10–50 (wet sedt)	flavinoid pigments	lake sediments	SWAIN *et al.* (1964)

also be preserved in lake muds for thousands of years. According to SWAIN and VENTERIS (1964) the level of concentration of flavinoid pigments in lake sediments can be used as an indication of the level of biological activity of the environment.

Vitamins and toxins

Several vitamins have been detected in aquatic environments. Table 8 lists the vitamins in the waters, whereas in Table 9 the vitamins are shown which have so far been detected in freshwater sediments.

Vitamin B_{12} may be an important ecological factor as many algae are known to have a B_{12} requirement. The concentration of the vitamin was found for a Japanese lake to increase with depth (KASHIWADA, KAKIMOTO and KAWAGOE 1957-1958). It was also found that the concentration was largest in the early morning and decreased after sunrise (KASIWADA, KAKIMOTO, KANAZAWA, KUROKI and NOZAWA 1959). EMANUILOV, NACHEV, VELCHEVA and DAOV (1962) reported for Bulgarian lake sediments a rise in the vitamin B_{12} content towards the autumn.

Several unidentified toxins have been reported in aquatic environment (LUCAS 1947, DENFFER 1948, LEFEVRE and NISBET 1948, LUCAS 1949, LEFEVRE, JAKOB and NISBET 1952, RICE 1954, RYTHER 1954). Some of these are toxic products produced by freshwater algae. Phytoplankton such as *Anabaena*, *Aphanizomenon*, *Chlorella*, *Coelosphaerium*, *Gleatrichia*, *Microcystis*, *Nitzschia*, *Nodularia*, *Oscillatoria*, *Pandorina*, *Protosiphon*, *Prymnesium*, *Stichococcus*, and *Thalassiosira* can produce compounds that are either toxic to other species of algae or to bacteria, zooplankton, mice, guinea pigs, fish, chickens, ducks, geese, turkeys, rabbits, cats, dogs, pigs, sheep, cattle and horses (FLINT and MORELAND 1946, PRESCOTT 1948, LOUW 1950, OLSON 1951, LEFEVRE, JAKOB and NISBET 1952, INGRAM and PRESCOTT 1954, RICE 1954, RYTHER 1954, HUGHES, GORHAM and ZEHNDER 1955, SAUNDERS 1957).

Table 8. The Occurrence of Vitamins in Lake and River Waters

concentration (μg/L)	types detected	location	reference
0.03–1.2	thiamin (vit.B_1)	North American inland lakes	HUTCHINSON (1943)
0.15–0.89	niacin (nicotinic acid)	North American inland lakes	HUTCHINSON (1943) HUTCHINSON *et al.* (1946)
0.003–0.004	biotin	North American inland lakes	HUTCHINSON (1943) HUTCHINSON *et al.* (1946)
0.1–2	vitamin B_{12}	lake waters	ROBBINS *et al.* (1950)
0–0.063	vitamin B_{12}	L. Ikeda (Japan)	KASHIWADA *et al.* (1957–1958)
0–0.260	folic acid	river waters (Japan)	KASHIWADA *et al.* (1962)
0.024–0.104	folic acid	L. Ikeda (Japan)	KASHIWADA *et al.* (1962)

Table 9. The Occurrence of Vitamins in Freshwater Sediments

concentration (ppm)	types detected	location	reference
35 (dry weight)	thiamin (vit. B_1)	lake seston	HUTCHINSON (1943)
2.3–3.1 (dry sedt)	thiamin (vit. B_1)	mud	HUTCHINSON (1943)
33	niacin (nicotinic acid)	lake seston	HUTCHINSON *et al.* (1946)

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