

## FORMATION OF ALEWIFE CONCRETIONS IN POLLUTED ONONDAGA LAKE

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### ABSTRACT

*The previously reported finding of alewife concretions along the shores of Onondaga Lake in Upstate New York prompted investigation of the field conditions necessary for their formation and laboratory simulation of these conditions to induce concretion formation. Onondaga Lake is shown to be calcium-polluted and continuously supersaturated with respect to  $\text{CaCO}_3$ . Anaerobic conditions exist in the hypolimnion in approximately eight months of every year.*

*In controlled laboratory experiments, formation of structure-retaining alewife concretions was successful under anaerobic conditions, and was enhanced by elevated calcium concentrations. Additional chemical analyses of fresh alewives, natural concretions and laboratory-formed concretions were performed.*

*A previously proposed mechanism for concretion formation is evaluated with respect to the presented results. The common occurrence of alewife concretions in Onondaga Lake is a manifestation of the unique polluted state of the ecosystem, combined with the invasion of the lipid-rich alewife.*

### INTRODUCTION

The alewife, *Alosa pseudoharengus*, is a lipid-rich marine fish that has become established in a number of Upstate New York lakes, including Onondaga Lake, Syracuse, NY. This fish inhabits the pelagic zones of invaded lakes, and often manifests its presence by high mortality. Carcasses of the dead alewives frequently wash ashore in great numbers in these systems. In contrast, in Onondaga Lake the dead alewives wash ashore as combustible, chalk-like concretions, which have

retained much of the fish's original external morphology. While similar concretions have been found on occasion on ocean shores (Wells & Erickson, 1933; Faber & Krejci-Graf, 1936), the common occurrence of the phenomenon at Onondaga Lake is unique. A number of researchers have studied this phenomenon, resulting in extensive characterisation of the concretions (Dence, 1956; Sondheimer *et al.*, 1966) and preliminary chemical mechanisms to explain their formation (Berner, 1968). In this paper we present:

- (1) further chemical data characterising the concretions of Onondaga Lake;
- (2) simulated laboratory conditions which resulted in the successful formation of alewife concretions from alewife carcasses; and
- (3) chemical data from Onondaga Lake that describe the unique polluted conditions which enhance concretion formation.

The concretions generally lack heads, tails and vertebral columns, but the ventral scutes, ribs, pelvic fins and some scales remain. The muscles have been replaced by a chalky substance. The chalky substance is a uniform pale yellow colour, which Dence (1956) has described as resembling candle wax in texture. The bone tissue and internal organs are missing. Table 1, which has been modified from Sondheimer *et al.* (1966), contrasts the elemental and gross fatty acid composition of normal alewife carcasses collected from Lake Ontario to the Onondaga Lake concretions.

TABLE 1<sup>a</sup>  
ELEMENTAL AND GROSS FATTY ACID COMPOSITION OF ALEWIFE CONCRETIONS (ONONDAGA LAKE) AND CARCASSES (LAKE ONTARIO)

<i>Alewife form</i>	C	H	N	Content %						Unsaturated fatty acid <sup>b</sup>	Saturated fatty acid <sup>b</sup>
				P	Ca	Mg	K	Cl	O		
Concretion	66.3	10.5	0.3	0.1	6.0	0.07	0.003	0	15.9	7.7	74.2
Carcass <sup>c</sup>	42.5	6.7	11.3	7.8	2.0	0.27	0.30	0	0	2.4	5.1

<sup>a</sup> Modified from Sondheimer *et al.* (1966).

<sup>b</sup> Percentage of total concretion or carcass weight.

<sup>c</sup> Heads, tails and viscera not analysed.

The low nitrogen and phosphorus content of the concretions reflects the small concentrations of proteinaceous material remaining. Clearly the concretions have become enriched with calcium and carbon. Additionally, great differences in fatty acid distribution are apparent. Concretions are comparatively enriched in saturated fatty acids. Myristic and palmitic acids make up 79% of the total fatty acids present in concretions, but only 35% in carcasses (Sondheimer *et al.*, 1966). Sondheimer *et al.* (1966) also found that the concretions have more low-molecular-weight components and fewer high-molecular-weight acids than do carcasses. Based on the total amount of fatty acids present on a per-fish basis, Sondheimer *et al.* (1966) estimated that the fatty acid content of the concretions is more than 30 times that of

the carcasses. In the light of this enrichment and carbon-13:carbon-12 ratios, it was suggested that most of the lipid material found in the concretions was deposited from external sources.

Berner (1968) proposed a mechanism for the formation of calcium-fatty acid concretions with key processes that included bacterial decay, precipitation of calcium carbonate ( $\text{CaCO}_3$ ), and reaction of fatty acids with  $\text{CaCO}_3$  to form calcium salts of fatty acids. Calcium carbonate is thermodynamically unstable in the presence of excess free fatty acids, under the  $\text{CO}_2$  partial pressure conditions common to aquatic ecosystems, since equilibrium constants for the formation of calcium myristate ( $\text{R} = \text{C}_{13}\text{H}_{27}$ ), palmitate ( $\text{R} = \text{C}_{15}\text{H}_{31}$ ) and stearate ( $\text{R} = \text{C}_{17}\text{H}_{35}$ ) are  $5 \times 10^2$ ,  $7 \times 10^4$ , and  $3 \times 10^6$  atm respectively (Berner, 1968).



Perhaps the greatest uncertainty in the proposed mechanisms is the hypothesised precipitation of  $\text{CaCO}_3$  in the early phases of bacterial degradation by the elevation of pH through ammonia release (Berner, 1968; Berner, 1969).



This mode of  $\text{CaCO}_3$  formation is somewhat problematic since environments dominated by decay processes are generally acid-rich. Berner (1968) argues that micro-environment conditions at decay interfaces may allow the necessary localised high pH conditions. A number of investigators (Kitano & Hood, 1965; McCunn, 1972; Raiswell, 1976) have subsequently supported this bacterial decay mechanism for the diagenetic formation of calcite in sediments from unsaturated environments. Berner (1968) formed calcium salts of fatty acids from butterfish and smelt in sealed jars in 65–205 days, in both sea water and  $\text{CaCl}_2$  (0.125 M) media. X-ray diffraction analyses of these calcium soaps indicated that the fatty acids contain 14 to 18 carbon atoms. These X-ray patterns matched those of Onondaga Lake concretions (Berner, 1968). Structure-retaining concretions were not successfully formed in these experiments. Calcite or aragonite were not found in any of the jars, despite the fact that the solubility product(s) were exceeded, indicating that these mineral species

TABLE 2  
MORPHOMETRIC FEATURES OF ONONDAGA LAKE

<i>Feature</i>	<i>Value</i>
Drainage basin area, km <sup>2</sup>	600
Lake surface area, km <sup>2</sup>	11.7
Lake volume, m <sup>3</sup>	$1.4 \times 10^8$
Mean depth, m	12.0
Maximum depth, m	20.5
Shoreline length, km	17.9

were probably transition species in the overall transformation. Mabesoone & Tinoco (1973) found concretions of fish in limestone areas which contained fats, though in much lower concentrations than observed in Onondaga Lake concretions.

Onondaga Lake is located within metropolitan Syracuse, NY. Morphometric features of the lake are summarised in Table 2. It has been referred to as one of the most polluted lakes in the north-eastern region of the United States (Murphy, 1978). The lake has received the domestic effluents and much of the industrial waste from the metropolitan area during the last century of the region's development. Loadings of selected pollutants to the lake for a typical year, 1975, are presented in Table 3.

TABLE 3<sup>a</sup>  
TOTAL LOADINGS OF SELECTED MATERIALS TO ONONDAGA LAKE, 1975

<i>Material</i>	<i>Loading (kg day<sup>-1</sup>)</i>
Alkalinity	$2.7 \times 10^5$
BOD <sub>5</sub>	$3.4 \times 10^4$
Calcium	$5.0 \times 10^5$
Sodium	$4.1 \times 10^5$
Chloride	$1.5 \times 10^6$

<sup>a</sup> Modified from Onondaga County (1976).

With the exception of alkalinity, more than 80% of each material originates from pollution sources (Onondaga County, 1976). A chlor-alkali manufacturer contributes almost all the salts to the lake. In addition, the hypereutrophic state of the lake (Meyer & Effler, 1980) results in substantial autochthonous contributions of organic matter to the system. A selective summary of the water chemistry of the lake in 1975, related to the presented loadings, appears in Table 4, illustrating the

TABLE 4<sup>a</sup>  
SELECTED ONONDAGA LAKE CHEMISTRY PARAMETERS (SEASONAL AVERAGE), 1975

<i>Parameter</i>	<i>Epilimnion (mg litre<sup>-1</sup>)</i>	<i>Hypolimnion (mg litre<sup>-1</sup>)</i>
Alkalinity	182	216
BOD <sub>5</sub>	7.2	8.3
Calcium	346	426
Sodium	373	446
Chloride	1250	1500
Dissolved oxygen	7.0	2.2
Chlorophyll-a	0.059	0.011

<sup>a</sup> Modified from Onondaga County (1976).

polluted condition of the lake with respect to various ions, and organic matter. The  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Ca}^{++}$ , and  $\text{HCO}_3^-$  ions account for more than 90% of the lake's ionic strength (Murphy, 1978). These concentrations are subject to substantial seasonal and yearly variation, due to variations in lake flushing and manufacturing operations. The lower waters become anaerobic following the development of stratification (Onondaga County, 1976). Investigation of the recent sediments (Effler *et al.*, 1980) indicates that the industrial loading of calcium has induced extremely high sedimentation rates (5–9 cm/year) within the lake.

## METHODS

### *Laboratory simulations*

Laboratory simulations of concretion formation included reactions of fresh frozen alewives (averaging 2 g) from Lake Michigan with water samples from Onondaga Lake and Lake Ontario, and also Lake Ontario and distilled water with initial calcium concentrations adjusted to that of Onondaga Lake by the addition of  $\text{CaCl}_2$ . Duplicate 1 litre Erlenmeyer reaction vessels were prepared as indicated in Table 5. All vessels except I and J were closed to the air to produce anaerobic conditions. Frequent visual observations were made to denote morphological changes as they occurred.

TABLE 5  
LABORATORY EXPERIMENTS FOR SIMULATION OF CONCRETION  
FORMATION

<i>Experiment</i>	<i>Number of alewives</i>	<i>Solution</i>
A	1	Onondaga
B	1	Ontario
C	1	Ontario + $\text{Ca}^{++}$
D	10	Onondaga
E	10	Ontario
F	10	Ontario + $\text{Ca}^{++}$
G	1	Distilled water + $\text{Ca}^{++}$
H	10	Distilled water + $\text{Ca}^{++}$
I	1	Onondaga (aerobic)
J	10	Onondaga (aerobic)

The remains of the aerobic samples were removed and air-dried after 44 days and the anaerobic samples after 87 days. As the fish in experiments D, E and F showed considerable retention of structure, they were chosen for analysis, along with aerobic experiment J, and samples K (fresh alewife carcasses) and L (natural concretion from Onondaga Lake).

The analyses consisted of moisture content, protein content by % nitrogen ( $\times 6.25$ ), total neutral lipid content by ether extraction, fatty acid content by

extraction with a mixture of ether + 0.5N HCl, molecular weight of fatty acids by neutralisation equivalent titration, and IR spectrometry using KBr pellets.

Neutral lipids from the fresh alewife carcasses were saponified to release fatty acids from the glycerine structure. Some data were not obtainable because of the nature and amount of the recoverable portions of the samples.

#### *Ecosystem analysis*

The  $\text{CaCO}_3$  equilibrium conditions of Onondaga Lake were monitored from April 1978 through October 1978 by pH measurements and alkalinity and calcium analyses, which were performed immediately following sample collection. Analyses were performed according to the American Public Health Association (1975). Necessary auxiliary measurements included temperature and other major ion concentrations for ionic strength estimation. Samples were collected and analyses performed from 2–3 times per week. Samples were collected at a central deep water location at a depth of 15 m. This depth is located within the hypolimnion during stratification periods and is representative of the zones where alewife degradation occurs. Calcium carbonate equilibrium conditions were assessed by evaluation of the calcite saturation index (Plummer *et al.*, 1979). Appropriate temperature and ionic strength adjustments were included in all equilibrium calculations (Strumm & Morgan, 1970). Complexation/ion pair formation influences were ignored in the calculations, which results in significant overestimations of the index (by about 15%) for this ion-rich lake. Thus supersaturation with respect to calcite is indicated by index values greater than 1.15 (instead of 1.0). Equilibrium conditions with respect to other  $\text{CaCO}_3$  minerals have been ignored based on the high Ca/Mg ratio (Müller *et al.*, 1972) of the lake.

The vertical distribution of dissolved oxygen at 1 m intervals was also monitored at the same frequency as the carbonate species. Dissolved oxygen was measured with a calibrated YSI meter.

## RESULTS

#### *Laboratory simulations*

Visual observations of laboratory experiments simulating concretion formation showed major decomposition occurring in aerobic samples I and J within two days. Fish in distilled water experiments G and H began breaking apart within three days, as did several individual fish in experiments A–F. Some structure-retaining samples occurred in each A–F experiment, but the best results were obtained from D, E and F, which contained 10 fish/litre of water. Of the samples that retained the structure of the fish, the following general observations were made. The head portion became detached within 7 days. Within 16 days, the tail portion had become detached,

the body cavity had erupted to release gases, and a yellowing of the carcass had occurred. By 28 days, yellow–orange globular materials had appeared, and by 40 days, white growth around the opened ventral cavity was observed.

After removal at 87 days, followed by air-drying, dissection of structure-retaining samples D, E and F showed D and F to be almost entirely composed of a dry, white, chalk-like substance similar to that found in natural concretions. Sample E contained some of that substance, but there was much more oily, fleshy material, bones and skin present.

Selected chemical analyses of laboratory samples, fresh alewife carcasses, and natural Onondaga Lake concretions are shown in Table 6. The laboratory-formed

TABLE 6  
SELECTED CHEMICAL ANALYSES OF LABORATORY<sup>a</sup>, FISH AND CONCRETION SAMPLES

Parameter	D Onondaga	E Ontario	F Ontario + Ca	J Aerobic	K Carcass	L Concretion
<i>Water conditions</i>						
Calcium (mg litre <sup>-1</sup> )	900	39	900	900	N/A	N/A
Initial pH	7.3	6.4	7.3	7.3	N/A	N/A
Final pH	5.5	5.5	5.9	6.7	N/A	N/A
<i>Sample content</i>						
Moisture (%) <sup>b</sup>	0.58	1.28	1.09	—	71.95	0.59
Nitrogen (%) <sup>c</sup>	0.75	2.22	1.42	2.05	7.99	0.62
Protein (%) <sup>c</sup>	4.72	13.84	8.91	12.81	49.62	3.88
Neutral lipids (%) <sup>c</sup>	7.86	26.72	7.37	6.73	30.84	10.26
Fatty acids (%) <sup>c</sup>	32.12	18.90	36.68	—	—	33.29
MW of acids (g)	261.0	267.6	270.3	—	299.3	259.1

<sup>a</sup> Conditions described in Table 5.

<sup>b</sup> Whole sample basis.

<sup>c</sup> Dry weight basis.

N/A = not applicable.

concretions from experiment D, which used Onondaga Lake water, show striking similarities to the natural concretions. Experiment F samples, Lake Ontario with calcium added, also show formation of the calcium salts of fatty acids, as do the Lake Ontario, experiment E samples. However, more proteinaceous material is present in these samples.

The infrared spectra of chalk-like concretion materials obtained from experiments D and F are nearly superimposable on the IR spectrum of the natural concretion (Fig. 1). The most readily identifiable absorption bands are the asymmetrical C=O stretch of the carboxylate anion at 1570 cm<sup>-1</sup> and the C—H stretch at 2900 cm<sup>-1</sup>. Both are consistent with a calcium salt of a long chain fatty acid. Other bands are difficult to identify positively due to shifts and overlaps (Silverstein *et al.*, 1974).

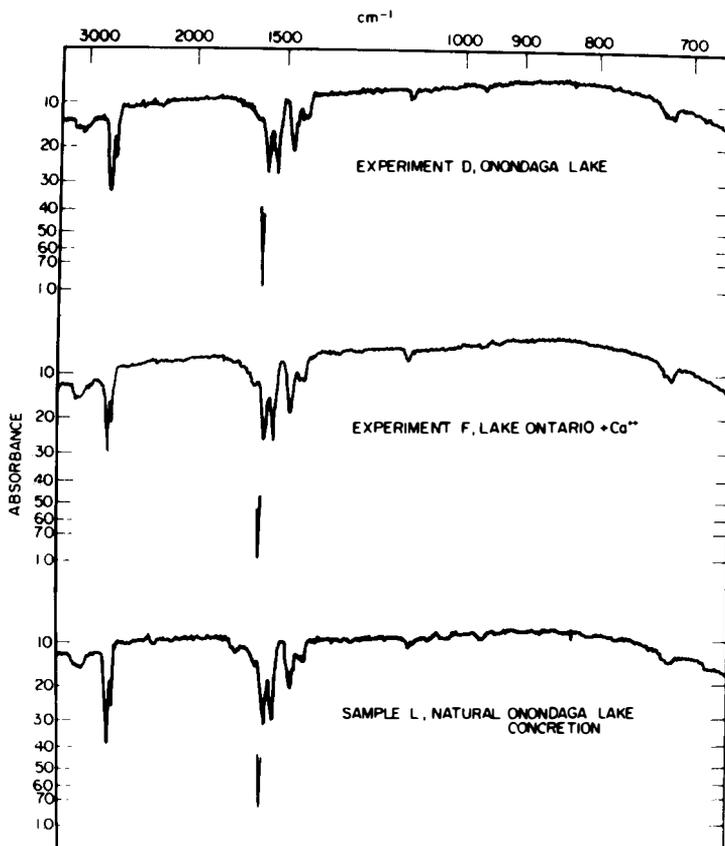
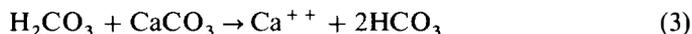


Fig. 1. IR spectra of concretions formed in the laboratory (top and centre) and collected from Onondaga Lake (bottom).

### *Ecosystem analysis*

Figure 2(a)–(c) summarises the temporal distributions of pH, alkalinity and calcium at 15 m for the monitoring period of 1978. The pH remains above 7.0, the alkalinity rises to a maximum of  $4.4 \times 10^{-3}$  moles litre $^{-1}$ , and calcium never drops below  $1.0 \times 10^{-2}$  moles litre $^{-1}$ . Based on alkalinity and pH measurements, the partial pressure of  $\text{CO}_2$  ( $P_{\text{CO}_2}$ ) ranges from  $10^{-2.81}$  to  $10^{-1.20}$  atm., indicating a major enrichment with  $\text{CO}_2$  (atmospheric  $P_{\text{CO}_2}$  of approximately  $10^{-3.5}$  atm.). This enrichment occurs progressively during stratification. These aggressive  $\text{CO}_2$  conditions (exceeding atmospheric equilibrium concentrations) may solubilise portions of available  $\text{CaCO}_3$  precipitates according to



contributing to the observed increase in calcium with time. This phenomenon is

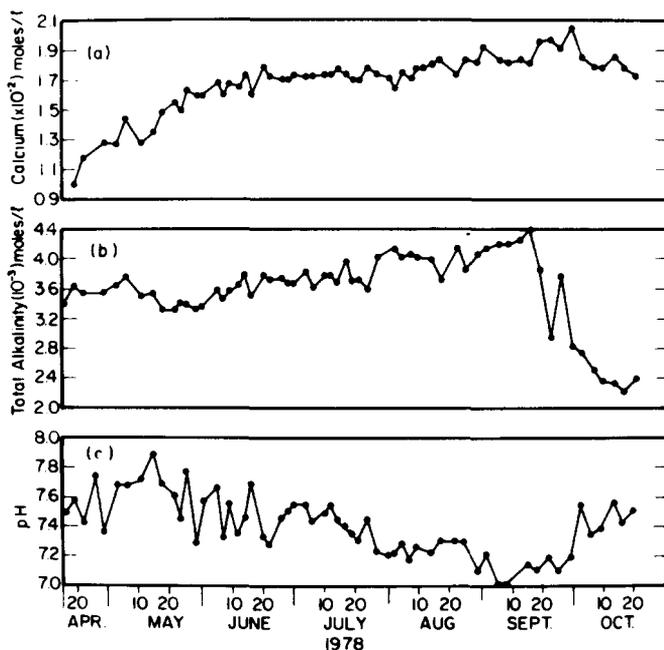


Fig. 2. Temporal distribution of carbonate chemistry parameters from Onondaga Lake, at 15 m, 1978; (a) pH, (b) alkalinity and (c)  $\text{Ca}^{++}$  concentration.

typical of temperate hardwater lakes (Hutchinson, 1957; Wetzel, 1975). Pollution also contributed to this seasonal enrichment in Onondaga Lake due to the extremely high calcium loading to the lake. The calcium loading often continues at a nearly constant rate during the reduced hydraulic flushing period of summer stratification. Figure 3 presents the temporal calcite equilibrium conditions at 15 m, indicating continual supersaturation throughout the monitoring period. Thus, the pollution-based enrichment of calcium (which originates mostly from the chlor-alkali manufacturer) within the lower waters more than compensates for the high  $\text{CO}_2$  concentrations that also develop. The degree of supersaturation is even greater in the upper waters (personal observations). This continuous supersaturation with respect to calcite throughout the water column of a stratified lake may be rather unique to Onondaga Lake. In other lakes, including hardwater systems, undersaturation with respect to calcite occurs in the hypolimnion during much of the stratification period due to elevated  $\text{CO}_2$  (reduced pH) levels (Hutchinson, 1957; Wetzel, 1975). Particle analysis, with a scanning electron microscope equipped with computerised dispersive X-ray diffraction (X-ray fluorescence) analysis, and with standard X-ray diffraction on particles collected from the hypolimnion and the surface sediments, depicts an abundance of calcite particles at these depths and within the sediments.

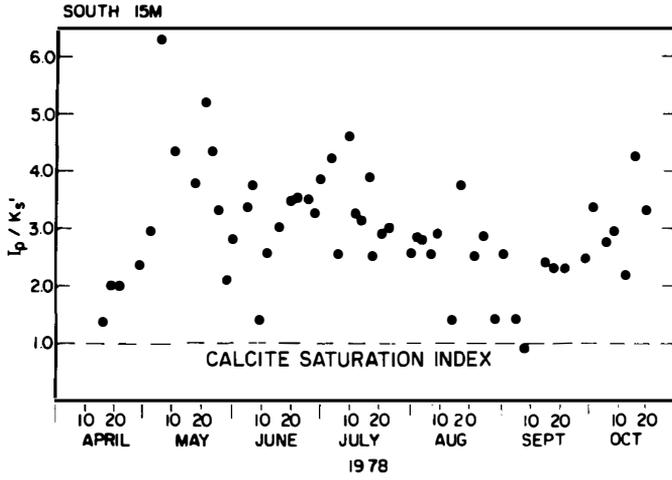


Fig. 3. Temporal calcite equilibrium conditions in Onondaga Lake, at 15m, during 1978.

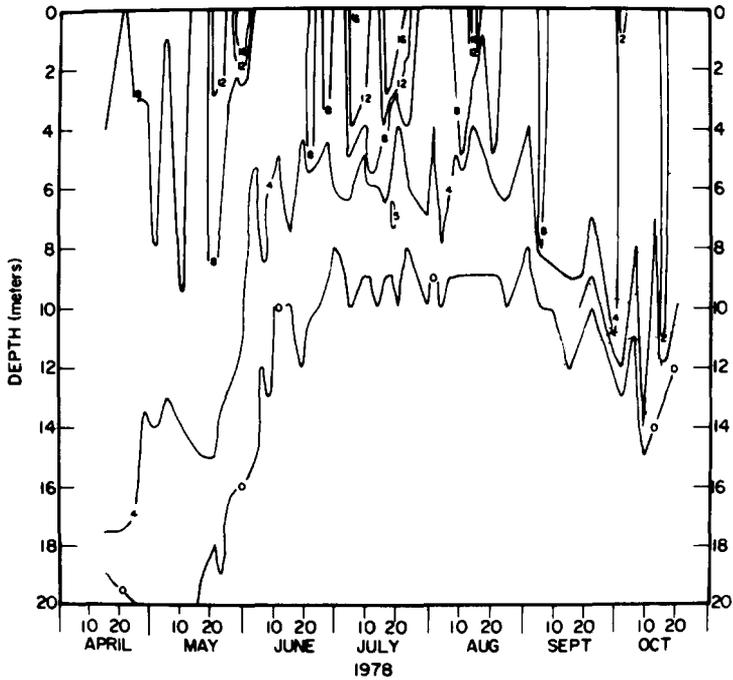


Fig. 4. Dissolved oxygen (mg litre<sup>-1</sup>) isopleths (partial) for Onondaga Lake, during 1978.

A partial dissolved oxygen isopleth plot for 1978 is shown in Fig. 4. Anaerobic conditions occurred within the hypolimnion by 15 April 1979, only several days after the establishment of stratification. These conditions prevailed until autumn turnover (late October). Hypolimnic anaerobic conditions also typically occur during the latter periods of winter stratification. Subject to small yearly variations due to meteorological (most importantly wind (Hutchinson, 1957; Wetzel, 1975)) conditions, the lower waters of Onondaga Lake are anaerobic for approximately eight months of every year (Onondaga County, 1976).

## DISCUSSION

### *Formation of concretions*

The data presented in Table 6 indicate that laboratory-formed concretions in Onondaga Lake water are similar to naturally occurring Onondaga Lake concretions. Moisture content, protein content, lipid and fatty acid content and molecular weights of fatty acids present correspond quite closely. Laboratory-formed concretions in Lake Ontario water with calcium added also correspond to natural concretion composition, with some minor differences that may indicate that the conversion process is not complete. The IR spectra (Fig. 1) of both laboratory-formed concretions are superimposable on that of the natural concretion, providing striking evidence that the three dry, white, chalk-like substances are very similar.

The molecular weights of the fatty acids (Table 6) were close to that of palmitic acid (256.4 g), indicating that the majority of the acids are palmitic as found by Sondheimer *et al.* (1966). There were differences in natural concretion composition between this study and the work of Sondheimer *et al.*, particularly in the total percentage of fatty acids. The concretions used by Sondheimer *et al.* for analysis were collected at a different time, and may have been subject to greater crumbling and loss of bones, fins and scales, or may have been more selectively sorted.

Fish remains in experiment E, Lake Ontario water, showed only partial conversion to the characteristic concretion previously described. It therefore appears that elevated calcium concentrations are responsible for enhancing concretion formation. The fact that some conversion to calcium soaps occurred in experiment E despite the lack of high calcium concentrations lends credence to Berner's (1968) theory of a micro-environment for such 'jar-type' experiments. However, rapid deposition of calcium-fatty acids which results in structure-retaining concretions may be greatly enhanced if supersaturated  $\text{CaCO}_3$  conditions exist, and the microenvironment process is not required.

In addition to the implied importance of calcium levels (and the presence of  $\text{CaCO}_3$ ) anaerobic conditions are apparently required for the successful formation of concretions. Rapid break-up of all fish carcasses in the aerobic experiments precluded any structure-retaining reactions that may have been associated with

anaerobic decay in the other experiments. The importance of anaerobic conditions has not previously been noted.

#### *Critical Onondaga Lake conditions*

The conditions within Onondaga Lake appear to meet the unique requirements for concretion formation implied by the laboratory simulations. First, the hypolimnion of the lake is rich in calcium (and calcite) throughout the year. The formation of  $\text{CaCO}_3$  has been noted as critical in the formations of concretions of calcium salts of fatty acids (Berner, 1968, 1969). The predominance of anaerobic conditions within the lake's hypolimnion provides the second critical condition necessary for concretion formation. Additionally, the start of the anaerobic period in late spring appears to be well timed for the phenomenon, since it precedes the high mortality period commonly observed for the alewife in fresh waters (Dence, 1956).

#### *Mechanism of formation*

The findings of this study allow some evaluation of the mechanisms proposed by Berner (1968) for concretion formation, particularly as it applies to the prevalent occurrence of the phenomenon in Onondaga Lake. Berner's (1968) mechanisms cannot be discounted for the formation of calcium salts of fatty acids in 'jar-type' laboratory simulations, since similar results, even for low calcium systems (E), were obtained in these experiments. The observed enhancement of the transformation at high calcium levels (and calcite supersaturation) (D and F) is not inconsistent with his mechanism, and indicates the importance of the formation of  $\text{CaCO}_3$ . Certainly a number of systems have anaerobic lower layers with substantial calcium concentrations (greater than E). It is, of course, most uncommon that these same systems would be supersaturated with  $\text{CaCO}_3$ , as assessed through bulk solution analysis. What cannot be assessed by ecosystem analysis is the presence of the necessary micro-environment of high pH invoked by Berner (1968), which would apparently make this phenomenon relatively common. The obvious question is: why is the formation of alewife or other fish concretions not a more commonly observed phenomenon? The combined requirements of the existence and duration of high pH micro-environments at interfaces of decaying carcasses appears unlikely since even isolated hypolimnic layers undergo a significant degree of mixing (Wetzel, 1975). These unlikely micro-environment requirements for precipitation of  $\text{CaCO}_3$  need not be invoked in the case of Onondaga Lake since the hypolimnion apparently remains rich in  $\text{CaCO}_3$  throughout the extensive anaerobic period of the year. We propose that the continued availability of unstable  $\text{CaCO}_3$  enhances the formation of calcium-fatty acids and the retention of structure in the concretions of Onondaga Lake. Thus, the unusual and common occurrence of alewife concretions in Onondaga Lake is a manifestation of the unique polluted state of the ecosystem, combined with the invasion of the lipid-rich alewife.

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