The occurence and distribution of mercury in the sediments of the Petit Lac (western Lake Geneva)

The Occurrence and Distribution of Mercury in the Sediments of the Petit Lac (Western Lake Geneva)

By Jean-Pierre Vernet[1]) and Richard L. Thomas[2])

RÉSUMÉ

L'analyse des sédiments superficiels du Petit Lac (partie occidentale du Léman) donne des valeurs comprises dans l'intervalle de 24 à 1274 ppb avec une moyenne de 622 ppb. Moyenne qui correspond au triple de la teneur maximum due à l'apport de l'environnement naturel. La contamination du Léman est principalement due aux industries de la vallée du Rhône. Le mercure, associé à la fraction fine du sédiment, est transporté avec celle-ci dans le Grand Lac (partie orientale du Léman) puis dans le Petit Lac. Dans cette zone du Léman, les sédiments fins enrichis en mercure sont dispersés par les courants mais ils se déposent plus particulièrement dans trois petits sub-bassins. D'après les analyses de corrélation, le mercure est adsorbé d'une façon prédominante par les oxydes de fer hydratés et amorphes qui enveloppent les fines particules d'argiles.

ABSTRACT

Mercury analyses of surface sediments from the Petit Lac (western Lake Geneva) gave values ranging from 24 to 1274 ppb with a mean of 622 ppb representing an increase in concentration at least three times above natural levels. The contaminant mercury to Lake Geneva is derived from industrial sources in the upper Rhone River draining into the eastern part of the lake (Grand Lac) with subsequent transportation in association with fine sediments particles to the Petit Lac. In the Petit Lac the mercury enriched sediment is dispersed by current activity with sedimentation occurring predominantly in three deeper water sub-basins. From correlation analysis the mercury is believed to be adsorbed by amorphous, hydrated iron oxides with complexed phosphorus which occurs as a coating on individual clay mineral particles.

Introduction

Mercury determinations have been carried out on the surficial sediments of the Petit Lac of Lake Geneva as a part of a continuing programme on the geophysics, sedimentology and geochemistry of the lake (for example: Vernet and Parent 1970; Vernet and Horn 1971).

Vernet and Thomas (1972a) reported the mean mercury of the Petit Lac sediments relative to the upstream Rhone River and the Grand Lac (eastern basin of Lake Geneva). They concluded that the mercury was derived from the Rhone River and is specifically related to industrial effluent from three canal systems.

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A great deal of research work on the environmental impact of mercury in aqueous systems has been carried out over the last decade following the epidemic poisoning of inhabitants in Minimata, Japan, between 1953 and 1959 (IRUKYAMA 1966; "Minimata Disease" 1968) and in Niigata, Japan, in 1965 after eating locally contaminated fish and shellfish. The bulk of recent research work was carried out initially in Sweden (see LÖFROTH 1969) followed by on acceleration of activity in North America from 1969 to the present time. This work has been well reviewed by D'ITRI (1971). In both Sweden and North America surveys of mercury levels in fish revealed extensive contamination, potentially harmful to public health, which necessitated the closing of many water bodies to commercial fishing with associated restrictions on sport fishing. This resulted in considerable economic loss to individual fishermen and to local industries related to sport fishing and tourism.

Research work on the processes operating on the conversion of mercury compounds in the aquatic environment carried out in Sweden by JENSON and JERNALÖV (1967, 1968 and 1969), JERNALÖV (1968, 1969 and 1971) and in North America by WOOD (1972), WOOD et al. (1968) have elucidated the controlling mechanisms for the transfer of mercury to the aquatic food chain. These workers demonstrated the importance of bottom sediments as a reservoir of available mercury for conversion to soluble methylmercury compounds by sediment bacteria. The methylmercury is released from the sediment to the overlying waters where it is rapidly taken up by the food chain.

A knowledge of the concentrations of mercury in the bottom sediments of aqueous systems is thus extremely important in assessing the overall environmental impact of mercury contamination. Further, a knowledge of the mode of occurrence of mercury in the sediment will give some insight into mercury dispersal mechanisms and will give some information on the availability of the mercury for methylation processes. For example, it has been demonstrated by JERNALÖV (1969) that mercury is not available for methylation when in the sulphide form without a prior oxidation step. Yet mercury adsorbed or chelated by organic matter may be methylated even in the presence of free H_2S (JERNALÖV 1969, p. 71). For a more detailed discussion on sediment mercury the reader is referred to JONASSON (1970) and VERNET and THOMAS (1972b).

The present study is directed towards defining the levels and distribution of mercury in the Petit Lac and towards achieving some understanding of its mode of occurrence.

The Petit Lac comprises the western basin of Lake Geneva separated from the eastern basin or Grand Lac by a low amplitude ridge trending northwest to southeast from Yvoire on the southern shore (Fig. 1). It is possible, though not yet established, that this ridge may form a sill separating sedimentation processes in the Petit Lac from the Grand Lac.

The bathymetry of the Petit Lac is given in Figure 1 and shows that this section of the lake is composed of four small sub-basins (A, B, C and D) separated by minor bathymetrical elevations. (For a detailed discussion and nomenclature of the morphology see FOREL 1892, p. 58.)

The Petit Lac as sampled here is approximately 27 km long with a maximum width of 4.7 km; the average depth is 41 m with a maximum depth of 78 m. The major input is directly from the Grand Lac with no significant river system and output is
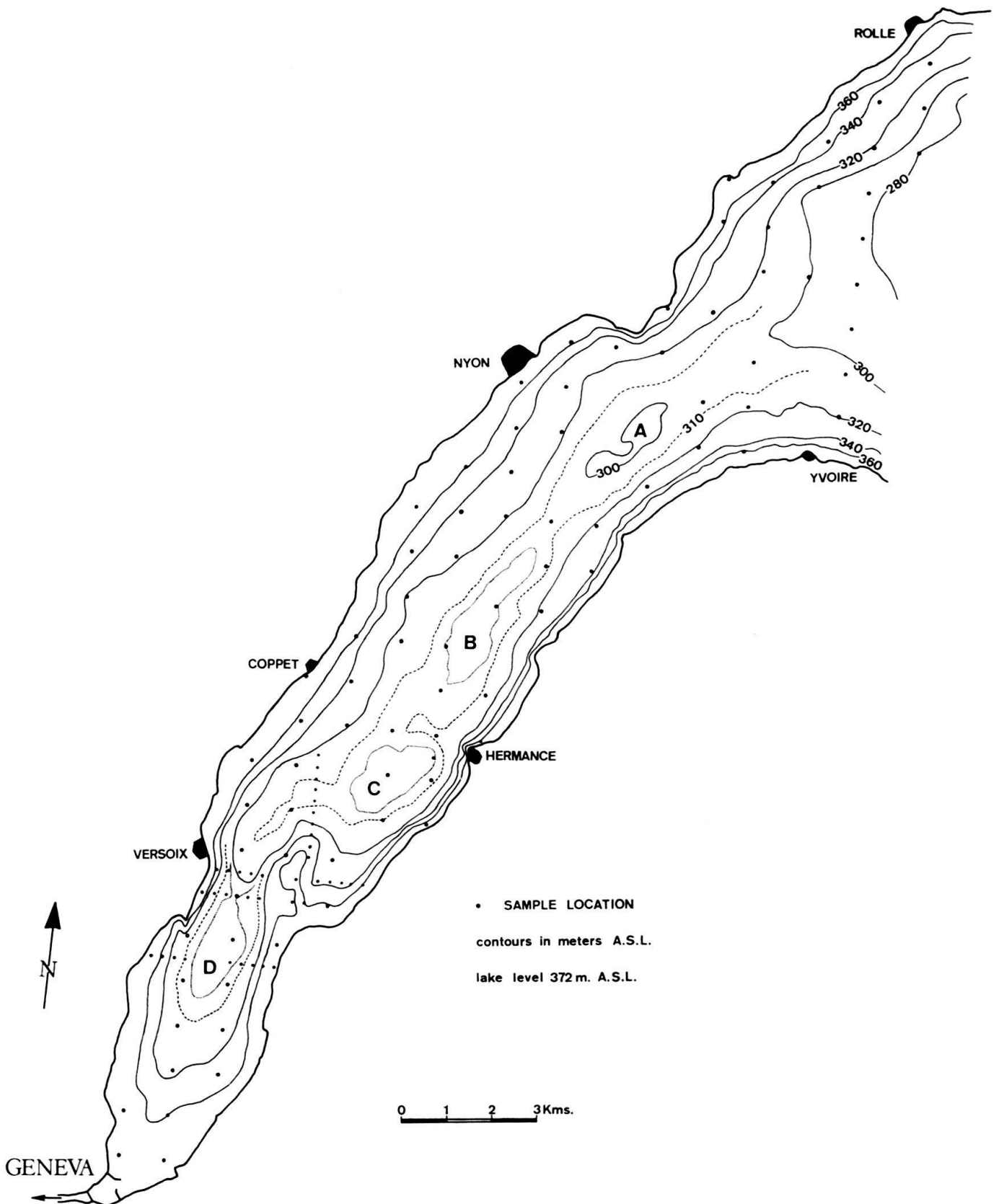
Fig. 1. Bathymetry of the Petit Lac with sampling locations.

directly to the Rhone River at Geneva situated at the southern extremity of the Petit Lac.

Methods

Samples were collected at 124 locations (Figure 1) using a clam type bottom sediment sampler. Sample positions were fixed by sextant angles to shore line features. The top 0.5 cm of sediment was sub-sampled for geochemical analysis, wet sieved with distilled water through a Tyler 80 mesh (175 μ) nylon screen and oven dried at 50 °C. Mercury analyses were carried out as previously described (VERNET and THOMAS 1972a). In addition to mercury total SiO_2, Al_2O_3, K_2O, Na_2O, MnO, total Fe as Fe_2O_3, CaO, MgO, S, P_2O_5 and TiO_2 were determined by X-ray fluorescence using a Philips P. W. 1220 C automatic spectrometer and organic carbon (Org. C) and inorganic carbon (Inorg. C) by Leco induction furnace carbon analyser and sulphurous acid digestion at room temperature (RITTENBERG et al. 1963; SHAW 1959).

Results and discussion

Distribution of mercury in the Petit Lac

Mercury concentrations in the surface sediments of the Petit Lac range from 24 to 1, 274 ppb with a mean of 622 ppb and a standard deviation of 321 ppb. The distribution of the mercury is given in Figure 2. In general the distribution shows a trend for increasing mercury concentrations in the deeper water regions with higher values occurring in association with sub-basins B, C and D as given in Figure 1. Lower values are seen to occur in sub-basin A which may be due to dilution by sediment derived by re-working from the ridge to the north. The distribution of the higher values in the northern part of the Petit Lac suggests that the input of sediment bound mercury from the Grand Lac is predominantly along the north-western shoreline past Nyon. Dispersal within the lake is subsequently controlled by current circulation and transportation energy with the fine particulate material and associated mercury sedimenting predominantly in the deeper water areas of the sub-basins.

On the basis of the mean mercury values (see above) and the mercury distribution (Figure 2) it is difficult to assess the degree of contamination of the sediments of the Petit Lac. VERNET and THOMAS (1972a) in a study of mercury in Swiss lakes assumed a high regional background level of 200 ppb. The background level of sediments in the upper Rhone River was calculated at 107 ppb (VERNET and THOMAS 1972a). On the basis of these two values it can be suggested that sediment mercury levels in the Petit Lac are presently 3 to 6 times above a natural level. The contaminated sediments are derived from the Grand Lac which constitutes the receiving waters for industrial mercury input from the Rhone River (VERNET and THOMAS 1972a).

Geochemistry of the mercury

In order to determine the manner in which the mercury is bound in the sediments of the Petit Lac the relationship of mercury to a number of other chemical parameters has been examined statistically by the use of a correlation matrix (CAMERON
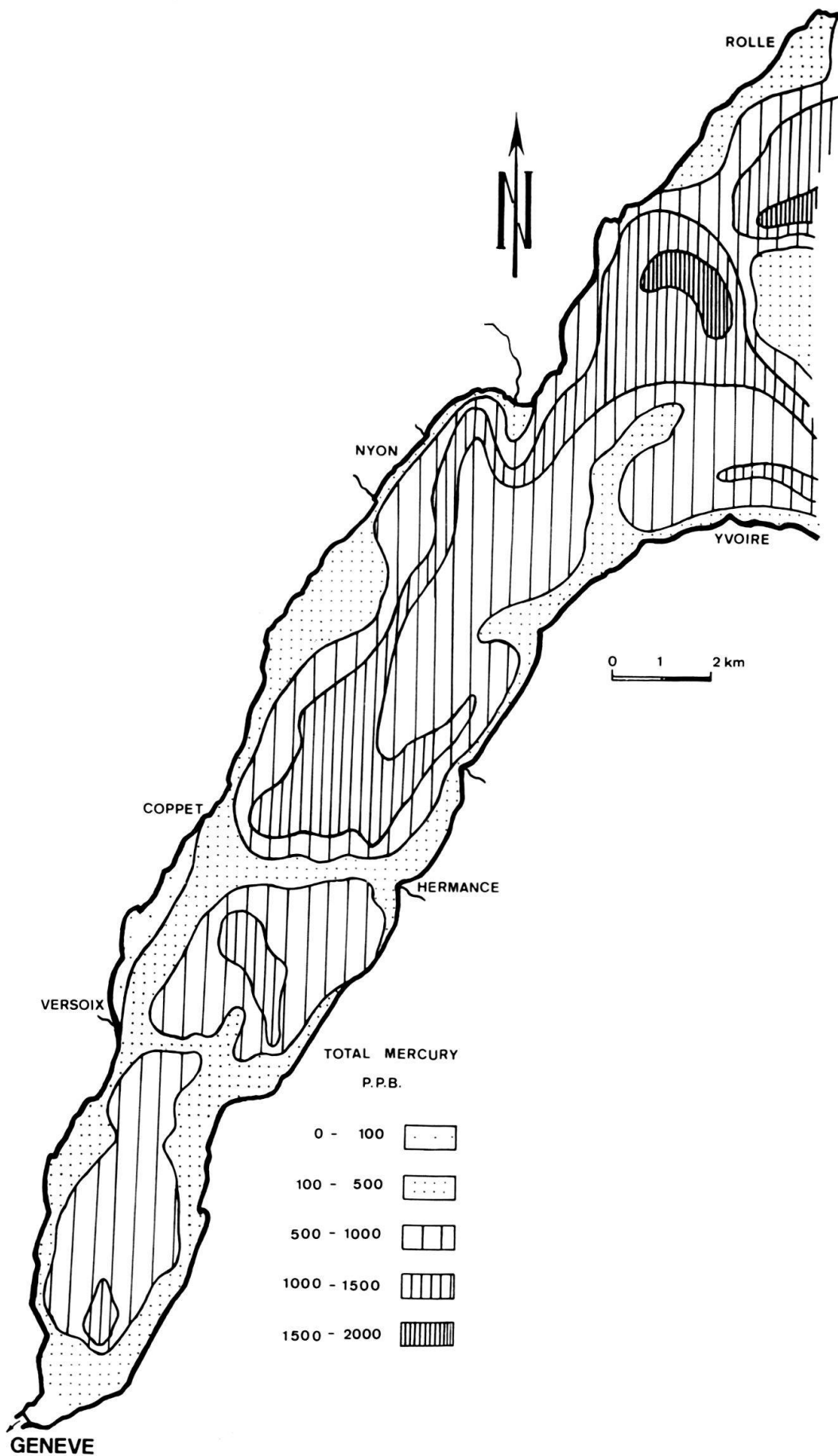
Fig. 2. Contour plan of mercury distribution in the surface sediments of the Petit Lac.

1968 and 1969). In addition to mercury the following variables have been utilized: Fe_2O_3, MgO, MnO, K_2O, S, Al_2O_3, CaO, P_2O_5 Org. C and Inorg. C. The correlation matrix based on 98 samples is given in Table 1. By examination of this matrix it can be seen that total mercury correlates at better than the 99 % confidence level to Fe_2O_3, MgO, MnO, K_2O, Al_2O_3 and P_2O_5. The degree of relationship of mercury to these variables may be given from the Table as follows, $Fe_2O_5 > P_2O_5 > Al_2O_3 > K_2O > MgO > MnO$, which suggests a possible primary relationship of mercury to iron with secondary relationships to the other variables.

The composition of the clays from the sediments of the Petit Lac has been given as Illite 50 percent, chlorite 30 percent, kaolinite 10 percent and montmorillonite and/or mixed layer clay 10 percent (VERNET and PARENT 1970). From the correlation data given in the Table this composition is reflected in the relationships between Al_2O_3 and K_2O ($r = 0.903$) in illite and Al_2O_3 and MgO ($r = 0.895$) in chlorite. The high degree of relationship between total iron as Fe_2O_3 and Al_2O_3 shown in Figure 3 indicates that the bulk of the iron is held uniformly by the clay minerals though the relationships of iron to MgO and K_2O (Table) suggests that some of the iron may be bound in the chlorite lattice.

WILLIAMS et al. (1971) in studies on sediments from Wisconsin lakes demonstrated a relationship between total iron and phosphorus with a correlation coefficient of 0.828, almost identical to that observed in the present study (Table). They further demonstrated (1,116) that the bulk of the total phosphorus was oxalate extractable (92–100 %) whereas an average of 69 % of the total iron was extractable by the same
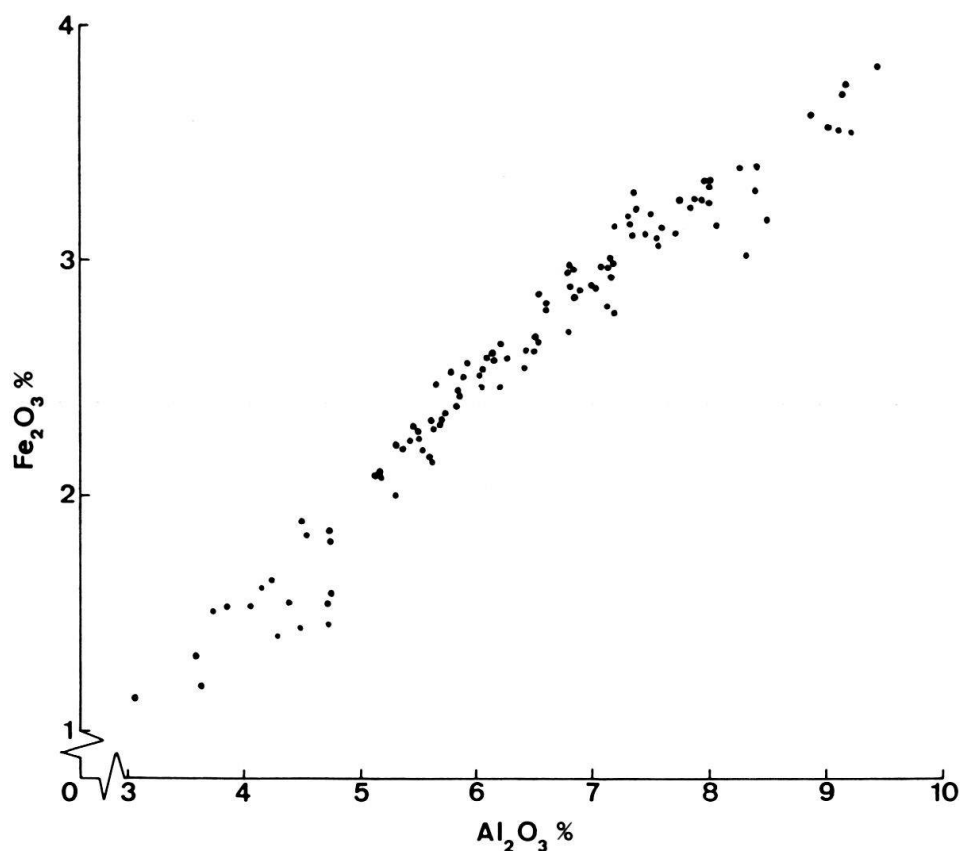

Fig. 3. Graph showing the relationship of total iron as Fe_2O_3 to Al_2O_3.

	Fe_2O_3	MgO	MnO	K_2O	Na_2O	S	Al_2O_3	CaO	P_2O_5	Org. C.	Inorg. C.
MgO	.912										
MnO	.847	.745									
K_2O	.867	.704	.772								
Na_2O	.233	.313	.302	.262							
S	.247	.204	.193	.074	-.034						
Al_2O_3	.980	.895	.850	.903	.263	.179					
CaO	-.181	-.112	-.303	-.424	-.102	.010	-.317				
P_2O_5	.824	.731	.712	.787	.191	.216	.787	-.318			
Org. C.	.281	.390	.129	-.013	.041	.304	.197	.192	.266		
Inorg. C.	-.246	-.284	-.365	-.323	-.394	.038	-.348	.756	-.290	-.076	
Hg	.643	.538	.483	.606	.039	.194	.608	-.068	.609	.200	.037

Table 1: Correlation matrix based on 98 samples.

technique. The relationship between the extractable P and Fe was shown to have a correlation coefficient of 0.979 which, as they concluded, indicated the presence of a short-range order, hydrated iron oxide-inorganic phosphorus complex. The similarity in the characteristics of the sediments of the Petit Lac to those described by WILLIAMS et al. (1971) suggests that the active iron is in an amorphous hydrated oxide directly associated with the clay minerals and probably occurring as a coating on the individual clay micelles (CARROLL 1958). The surface area of such a coating is directly related to the clay particle size and hence both total iron and adsorbed or complexed ions will increase as sediment particles fine outwards into the deeper water regions of the sub-basins of the lake.

The relationship of mercury to total iron as Fe_2O_3 is given in Figure 4. The diagram shows the scatter related to the correlation coefficient of 0.643 (Table) and is a reflection of the variable adsorption of mercury by the hydrated iron oxides and to the partition of the iron between these iron oxides and a chlorite lattice held component. The degree of correlation might be significantly improved by relating the mercury to an oxalate extractable iron fraction.

In the sediments of the Petit Lac the mercury is thus believed to be held predominantly by the iron oxides which is indicated by a primary relationship between mercury and total iron. This mode of occurrence has been discussed by JONASSON (1971). Since the iron oxides occur as a coating on the clay mineral particles then a secondary relationship exists between the mercury and the clays. This is reflected in
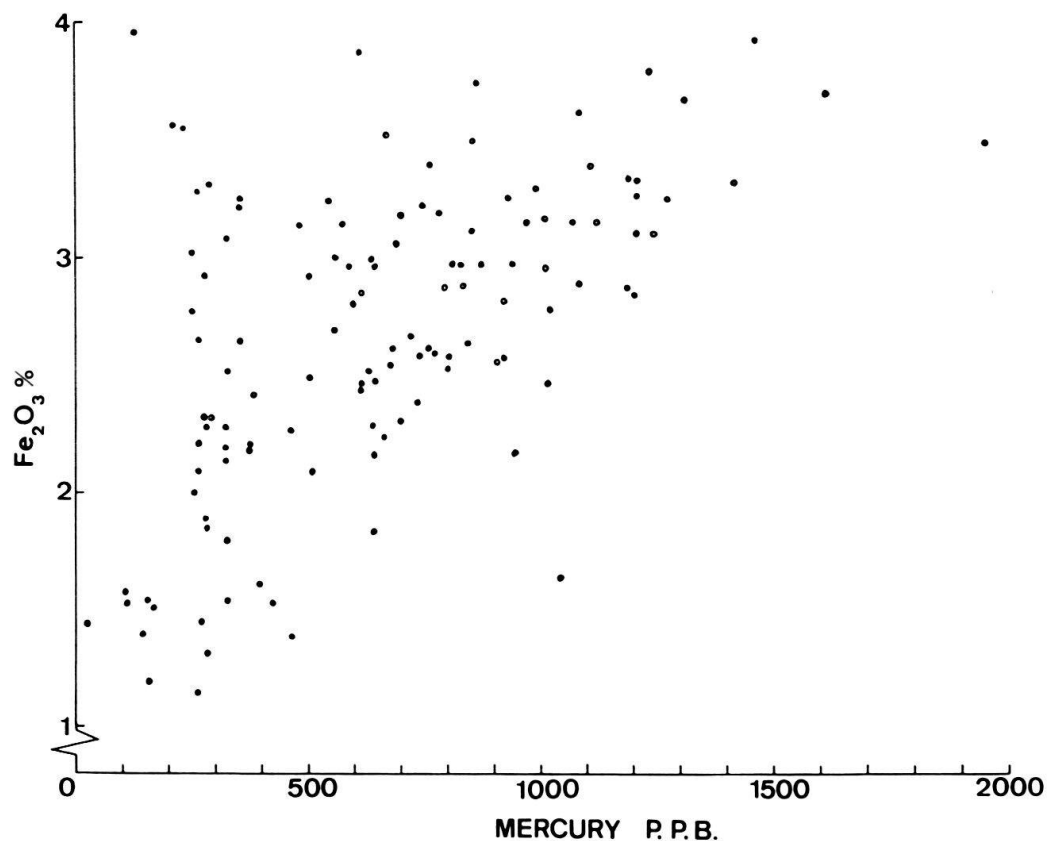
Fig. 4. Graph showing the relationship of total mercury to total iron as Fe_2O_3.

the correlation of mercury to Al_2O_3, K_2O and MgO. The degree of relationship Al_2O_3 > K_2O > MgO is interpreted firstly as a relationship to the total clay minerals indicated by Al_2O_3 and followed by K_2O and MgO as a reflection of the predominant clay minerals illite and chlorite.

The relationship of mercury to P_2O_5 and to a lesser degree to MnO are again secondary relationship due to the association of iron to phosphorus and iron to manganese (WILLIAMS et al. 1971). Poor correlations are seen between mercury and sulphur and Org. C (Table) which may well be indicative of oxidizing conditions at the sediment water interface in the Petit Lac and is a very different situation to that observed in Lake Ontario where the mercury is predominantly adsorbed or complexed by the organic matter with subsidiary sulphide (THOMAS 1972). This difference may additionally be accentuated by the different sub-sampling techniques in the studies. In the Petit Lac only the top 0.5 cm has been utilized compared to 3.0 cm in Lake Ontario. The Petit Lac samples are thus predominantly of the surficial oxidized microzone whereas samples from Lake Ontario constitute the microzone and the underlying sediment which is often strongly reducing (KEMP and LEWIS 1968; THOMAS et al. 1972). This would certainly account for the lack of a relationship of mercury to sulphur in the Petit Lac, though the lack of a relationship with organic matter can only be explained by a lack of uptake of mercury by the plankton in the lake waters or by rapid mineralization of the organic matter under strongly oxidizing conditions. This can only be resolved by future detailed investigation of the mercury content and partition in the suspended solids of the lake.

Conclusions

Total mercury concentrations in the topmost 5 mm of sediment in the Petit Lac range from 24 to 1, 274 ppb with a mean of 622 ppb and a standard deviation of 321 ppb. The mercury is derived from the Grand Lac to the east in association with fine sediment particles. The transportation of the mercury into the Petit Lac occurs predominantly along the northwestern shoreline with dispersion and dilution into the lake being controlled by water circulation and transport energy. This results in the accumulation of the finer particles and consequently higher levels of mercury in the deeper water regions of the bathymetric sub-basins of the lake. Highest values occur in the three southernmost sub-basins, designated B, C and D with lower values in the northern sub-basin A due to dilution by the input of uncontaminated sediment eroded from the ridge sub-dividing the Petit Lac from the Grand Lac to the east.

The degree of contamination when related to the mean level of mercury observed in the lake is estimated as being 3 to 6 times above natural background levels. Industrial effluent to the Rhone River and the Grand Lac is believed to be the prime cause of the increased concentrations.

Total mercury correlates with total Fe_2O_3, P_2O_5, Al_2O_3, K_2O, MgO and MnO. This is interpreted as indicating a primary relationship of mercury to an inorganic iron-phosphate complex probably in the form of hydrated iron oxide with adsorbed mercury. This iron oxide is associated with the clay minerals of the sediment and occurs as a coating on individual clay micelles leading to secondary statistical correlations of mercury to Al_2O_3, K_2O and MgO representing the predominantly illite and chlorite clay content of the sediments.

Acknowledgment

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