

Tracing phosphorus sources and P-cycling by oxygen isotopes in phosphate; Lake Kinneret (Israel)

D. Markel
Y. Kolodny
B. Luz
A. Nishri

The Institute of Earth Sciences, The Hebrew University of
Jerusalem, Jerusalem 91904, Israel.

Israel Oceanographic Limnological Research, Kinneret Limnological Laboratory, PO Box 345, Tiberias 14102, Israel.

Introduction

Lake Kinneret (The Sea of Galilee, Fig. 1) is located in northern Israel, in the Dead Sea Rift Valley. Average lake area is 169 km² and average volume is 4.3 × 10⁹ m³. The major inflow into Lake Kinneret (LK.) is the Jordan River. In addition, there are several smaller streams which flow into the lake. The lake is stratified from May to December. The epilimnion is characterized by high pH and low P-PO₄ concentration, the hypolimnion by low pH and higher P-PO₄ concentration.

Inorganic dissolved phosphate is an important nutrient, limiting algal growth rate in lakes generally, and particularly in LK which is the major water reservoir of Israel (Berman, 1985; Serruya, 1971). Anthropogenic increase in the amount of a limiting nutrient in lake water can lead to eutrofication and damage to water quality. Phosphorus is drained into LK from several natural and anthropogenic sources: basalts of the Golan Heights, layers of phosphorite in the Senonian rocks of the Upper-Galilee, sewage,

fish ponds, fertilizers and industrial waste. The different isotopic composition of oxygen in phosphates is useful for distinguishing between these sources (Kolodny *et al.*, 1983).

The original inorganic phosphorus in LK is influenced by several sedimentary and diagenetic processes. Dominant among them is the massive precipitation of calcite in the epilimnion due to high Ca²⁺ concentration and high pH during the algal bloom (Serruya, 1971). Precipitation of a phosphate surface complex on calcite has been suggested, (Avnimelech 1983, Staudinger *et al.*, 1990), but never observed. Stoichiometric calculations suggested it could be either CCP - Ca₃(HCO₃)₃(PO₄) or DCP - CaHPO₄. Adsorption of phosphate on iron hydroxides was suggested as a mechanism of scavenging phosphate from the water column (Serruya, 1971).

We attempt here the use of the oxygen isotopic composition of phosphate ($\delta^{18}\text{O}$ of PO₄³⁻ shortened as δ_p) as a tracer of phosphate origin. The sharply different phosphate reservoirs are fingerprinted by specific δ_p values: basaltic apatite has a low δ_p (6 to 8‰), phosphate from sedimentary and anthropogenic sources is enriched in ¹⁸O (18 to 25, Kolodny *et al.* 1983). The crucial property of the oxygen-in-phosphate isotopic system is that whereas the oxygen is extremely resistant to isotopic exchange with water in normal inorganic reactions, it exchanges very rapidly during biological, enzyme catalyzed reactions. Hence changes in δ_p in lake sediments should serve as a monitor of increasing biological cycling of phosphate in the lake.

Methods

Box core samples, 8–10 cm long, were taken in three stations in LK (Fig. 1): A, G, and J. Grain size, phosphate concentration and carbonate were determined on sampled slices of the cores. $\delta^{18}\text{O}_p$, and the distribution of phosphate concentrations

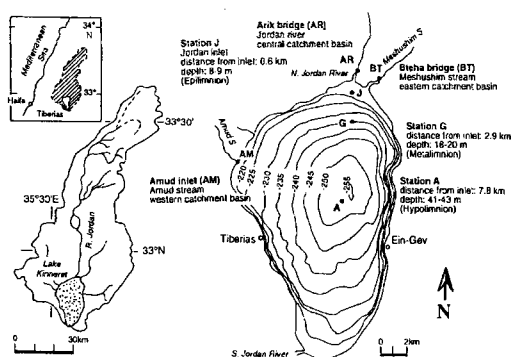


FIG. 1. Research area map; Lake Kinneret and its catchment basin; description of sampling stations (modified from Serruya, 1978).

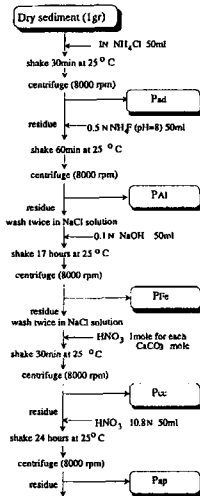


FIG. 2. Flow chart diagram of sequential extraction of various phosphorus forms in sediment.

in different fractions of the sediments were measured. A sequence of solvent extractions adopted from Chang and Jackson (1957) and Yamada and Kayama (1987) (Fig. 2) were used for separating the different chemical forms of phosphate in the sediment. The purpose of sequential extraction was to separate adsorbed phosphate (P_{ad}), from phosphate linked to iron and aluminium (P_{Fe} , P_{Al} respectively), P associated with carbonate (P_{cc}) and apatitic phosphate (P_{ap}), which may be either detrital or authigenic.

Results and discussion

Sequential extracts of phosphate show that the major fraction of phosphorus in L.K. sediments is linked to calcium (P_{cc}), either as apatite (P_{ap}) or as a surface complex on calcite crystals. A minor fraction is adsorbed on clays and iron hydroxides. No iron-phosphate or aluminum-phosphate minerals were detected.

The results of analyses of δ_p in sediments from Lake Kinneret and its catchment basin are summarized in Fig. 3. The most striking feature of this figure is the significant difference between the δ_p of the sediment size fractions. In the clay samples δ_p was heavier than +15‰, in silts between +12 and +15‰ and in sand lighter than +12‰. In addition, δ_p of clay increased from +15.7‰ at the Jordan inlet to +17.7‰ at station J. There was a slight decrease in δ_p from station G (+17.5‰) to station A (+16.8‰).

Approximately 70% of the particulate inorganic phosphate entering L.K. is from a basaltic

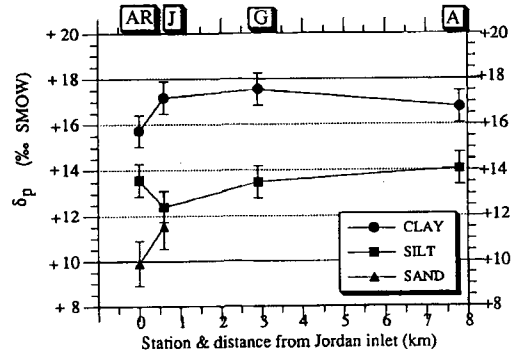


FIG. 3. Average δ_p of Lake Kinneret and Jordan River sediments. The average was calculated from the results of different depths at a single station and same size fraction.

source ($\delta^{18}O_p \approx 6\%$). This includes the detrital sand fraction (probably fluor-apatite,) most of which sinks to the bottom immediately upon entering the lake and is thus mechanically removed from the cycle. Only 40% of the phosphate in the silt and clay fractions is derived from a basaltic source; the rest is of sedimentary and anthropogenic origin ($\delta^{18}O_p \approx 18$ to 25‰). Isotopic mass balance shows that authigenic apatite is precipitated in L.K., mostly at the Jordan delta, due to high pH and intermediate dissolved phosphate concentration. This apatite, possibly hydroxy-apatite, reaches the deep part of the lake and dissolves at relatively low pH (~ 7.5) mainly during the stratification period (April–November). A phosphate surface complex on calcite crystals, $Ca_3(HCO_3)_3(PO_4)$ (CCP), or $CaHPO_4$ (DCP), is precipitated in the L.K. catchment basin and contributes one quarter of the particulate phosphate entering the lake from the Jordan. A large part of this complex is removed at the Jordan delta at relatively high pH, but it is re-precipitated on calcite surfaces in the deep part of the lake. The phosphorus which is released from dissolution of authigenic apatite in the deep part of the lake and from the dissolution of the phosphate surface complex are both internal sources of bio-available inorganic phosphate.

References

- Avnimelech, Y. (1983) *Limnol. Oceanogr.*, **28**: 640–5.
 Berman, T. (1985) *Andis*, Rome, Italy, p. 240–8.
 Chang, S. C. and M. L. Jackson (1957) *Soil. Sci.*, **84**, 133–44.
 Kolodny, Y., B. Luz, and O. Navon (1983) *Earth Planet. Sci. Lett.*, **64**, 398–404.
 Serruya, C., (1971) *Limnol. Oceanogr.*, **10**, 167–72.