

$b_0 = 0.577$) (11). The resulting structure function, normalized to unity for uncorrelated scattering, is shown in Fig. 2, compared with the experimental data of Wenzel *et al.* (12). The overall agreement is excellent. Even the small discrepancies can be understood; the overestimate of the oscillations in $S(k)$ for large k is due to the static nature of the model, whereas the displacement of the experimental points from the theoretical curve at low k could be due to experimental correction factors.

A striking feature of both the neutron and x-ray experimental results is the strong first peak at $k = 1.7 \text{ \AA}^{-1}$. It can be shown that the presence of this peak in the calculated results is due to an anisotropic layer structure which extends over a distance of at least the order of 15 \AA in the Polk-Boudreaux type of CRN model (13). It would thus appear that this type of relatively long-range order is present in typical samples of amorphous solid water. It should be emphasized that none of the peaks in $S(k)$ for $k < 8 \text{ \AA}^{-1}$ can be ascribed to intramolecular scattering, and that the structure observed and calculated for small k is determined by relatively long-range correlations.

In Fig. 3 we show the excess (above a smooth parabolic background) of the weighted radial distribution function (RDF) for a slightly modified version of the model. (Here the H_2O groupings were taken to have the same shape as gas-phase H_2O molecules.) This weighted RDF determines the neutron scattering $S(k)$ according to the relation:

$$S(k) = \int_0^{r_c} \Delta \text{RDF}(r) \frac{\sin kr}{kr} dr$$

where r_c is a cutoff distance taken as 20 \AA . The first few interatomic separations give rise to well-defined peaks labeled according to the pairs of atoms involved. The oscillatory behavior for large r with period $\sim 3.7 \text{ \AA}$ corresponds to the sharp peak in $S(k)$ at $k = 1.7 \text{ \AA}^{-1}$ discussed above.

In order to examine the sensitivity of our results to the properties of the Polk-Boudreaux model, we have constructed another random network which incorporates as much as possible large cages such as occur in the clathrate hydrates (2, 14). The near-neighbor coordinations in this model are essentially the same as those of the Polk-Boudreaux model, but there are differences in the longer-range correlations (distances greater than 10 \AA). We find that the

strong first peak is not reproduced by the cage model. We have also carried out calculations for a version of the Polk-Boudreaux model with one hydrogen for each bond, but placed without regard to the ice rules. This model also does not agree with experiment nearly as well as the original model.

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Enzymatic Characterization of Soluble Organic Phosphorus in Lake Water

Abstract. *Although the concentration of soluble organic phosphorus in lake water often exceeds that of orthophosphate severalfold, little is known of its composition. By using enzyme assays it was determined that up to 50 percent of the organic fraction is hydrolyzable by phytase. The enzymatically degradable material consists of both low and high molecular weight fractions.*

During periods of maximal algal growth the concentration of orthophosphate in natural waters approaches nondetectable levels. During such algal blooms organically bound phosphorus often constitutes 85 to 99 percent of the total soluble phosphorus (1). Nucleic acids (2) and nucleotides (3) have been identified as minor constituents of naturally occurring organic phosphorus; the preponderant portion, however, is undefined. Furthermore, the potential availability of organic phosphorus for algal growth is virtually unknown.

Because the ability of various organic phosphorus compounds to satisfy algal growth requirements depends on their susceptibility to enzymatic liberation of orthophosphate (4), we characterized naturally occurring soluble organic phosphorus by incubation with different enzymes and measurement of the orthophosphate released. Enzymes employed included (i) alkaline phosphatase, (ii) phosphodiesterase and alkaline phosphatase, incubated sequentially, and (iii) phytase (a nonspecific

phosphatase capable of hydrolyzing phytic acid). We determined that up to 50 percent of the soluble organic phosphorus is hydrolyzable by phytase, the hydrolysis kinetics of the degradable fraction being identical to that of myoinositol hexaphosphate.

Two small lakes of mesotrophic and highly eutrophic nutrient enrichment status (5) were studied between March 1973 and April 1974. Four-liter samples were obtained from the upper 1 m and were immediately passed through membrane filters and subjected to cation exchange. Because the soluble organic phosphorus content seldom exceeded $40 \mu\text{g}$ of PO_4 per liter we concentrated samples by partial freezing (6). After concentration by a factor of 10 to 12, recovery of soluble phosphorus routinely exceeded 80 percent.

The enzymes employed included commercial preparations (Sigma) of alkaline phosphatase and phosphodiesterase, and a phytase which we extracted and purified from wheat bran (7). They were added (at 0.04 to 0.06 mg of protein per milliliter) to con-

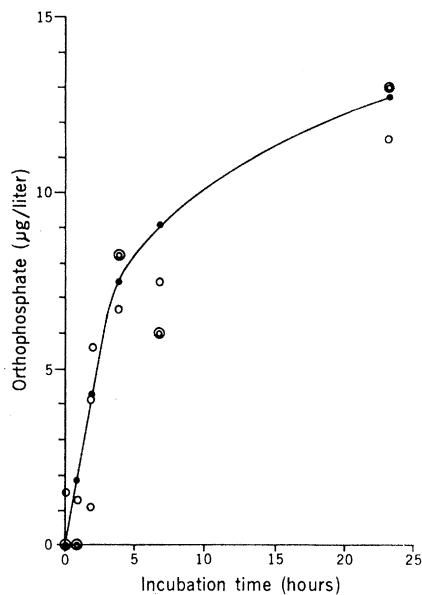


Fig. 1. Kinetics of hydrolysis of naturally occurring phytase substrate and of myoinositol hexaphosphate. (Open circles) Increase in orthophosphate concentration in freeze-concentrated lake water sample (10 September 1973) during incubation with phytase. (Filled circles and curve) Increase in orthophosphate concentration in a sample spiked with myoinositol hexaphosphate (0.5 mg of PO_4 per liter). Values for the myoinositol hexaphosphate hydrolysis curve were divided by 30.7 to normalize the curve to the data points of naturally occurring substrate. Incubation mixtures consisted of 60.0 ml of concentrated lake water; 20.0 ml of 0.2M acetate buffer, pH 5.0; and 3.2 ml of phytase prepared from wheat bran (0.6 mg of protein per milliliter) and were held at 33°C. Quadruplicate 3.0-ml portions were removed at intervals, enzyme activity was halted by addition of 0.3 ml of 25 percent trichloroacetic acid, and portions were stored at 5°C until they were analyzed for orthophosphate.

concentrated lake water samples; each sample was buffered with tris(hydroxymethyl)aminomethane or acetic acid-acetate to the pH maximum of the enzyme employed in the assay. Quadruplicate 3.0-ml portions were removed at zero time and enzyme activity was halted with trichloroacetic acid; additional portions were removed after overnight incubation at 33°C. Spontaneous hydrolysis and enzyme degradation were measured simultaneously in controls. Orthophosphate in each portion was determined colorimetrically (8).

Although added amounts ("spikes") (0.5 mg of PO_4 per liter) of 12 organic phosphorus esters and of pyrophosphate and tripolyphosphate salts were hydrolyzed completely by alkaline phosphatase, no orthophosphate was

released in any of ten concentrated lake water samples. Similarly, no increase in orthophosphate concentration was observed after sequential incubation of samples with phosphodiesterase and alkaline phosphatase, although orthophosphate release from added DNA and RNA was complete within the incubation period.

In contrast to samples incubated with alkaline phosphatase and phosphodiesterase plus phosphatase, samples incubated with phytase invariably released significant quantities of orthophosphate. To further characterize the phytase-hydrolyzable material, portions were removed from a concentrated lake water incubation mixture. The kinetics of hydrolysis within a 24-hour incubation period was identical to the breakdown kinetics of myoinositol hexaphosphate (Fig. 1). The distinctive hydrolysis pattern, consisting of rapid liberation of half the orthophosphate organically bound followed by much slower release of the remainder (9), was not characteristic of any other organic phosphorus compound tested.

Enzyme incubations were necessarily limited to 24 hours to minimize adsorption of phosphorus on the container walls during the assay. However, only 60 to 70 percent of an added myoinositol hexaphosphate spike was hydrolyzed during the incubation period. To extrapolate the amount of organic phosphorus ultimately hydrolyzable by phytase, the amount of orthophosphate liberated from concentrated lake water during the phytase incubation was divided by the fractional extent of hydrolysis of the myoinositol hexaphosphate spike incubated concurrently. Concentrations of phytase-hydrolyzable organic phosphorus were similar in highly eutrophic Frain's Lake (3.5 to 12.4 μg of PO_4 per liter) and less eutrophic Third Sister Lake (4.9 to 10.0 μg of PO_4 per liter). In Third Sister Lake the concentration of phytase-hydrolyzable material was found not to vary throughout the epilimnion and upper hypolimnion.

The percentage of soluble organic phosphorus hydrolyzable by phytase in five samples from Frain's Lake is shown in Fig. 2. There was a rapid decrease during early spring followed by an approach to an apparent steady state throughout late summer.

To determine whether the phytase-hydrolyzable matter was phytic acid, we applied concentrated lake water to a Bio-Gel P-60 molecular gel column

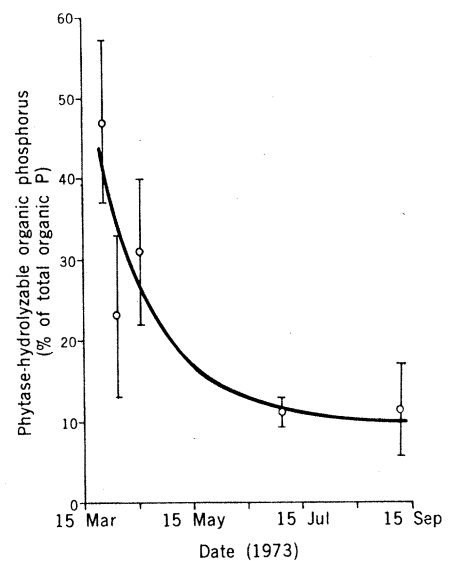


Fig. 2. Percentage of soluble organic phosphorus hydrolyzable by phytase in surface water from Frain's Lake during March to September 1973. Vertical bars indicate standard deviations. Concentrations of phytase-hydrolyzable organic phosphorus were extrapolated (see text).

(2.5 by 30 cm) and incubated the two organic phosphorus fractions with phytase. The fraction eluted last corresponded to the elution position of myoinositol hexaphosphate. About 50 percent of the phytase-hydrolyzable material present, however, appeared in the higher molecular weight fraction.

These results substantiate earlier observations (10) that virtually no phosphatase-hydrolyzable compounds are dissolved in natural waters; such compounds are probably rapidly degraded. The lack of a detectable phosphodiesterase-hydrolyzable fraction suggests that any nucleic acids present are sterically protected from attack by snake venom phosphodiesterase, which requires a free terminal 3'-hydroxyl group to initiate cleavage (11).

The phytase-hydrolyzable material appears to be composed of both low and high molecular weight fractions. The low molecular weight component may consist of inositol polyphosphates, which constitute a significant fraction of sedimentary organic phosphorus (12). The high molecular weight fraction may be composed of inositol phosphates bound to proteins and lipids (13) or to fulvic acid (14), all of which have been postulated to exist in soils.

We have used incubation with phytase to characterize up to 50 percent of soluble organic phosphorus. We believe that the detection and quantifica-

tion of specific substrates by enzymes—a procedure well known to biochemists for many years—may prove extremely useful in the analysis of other trace components of biological origin in natural waters.

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5. Highly eutrophic Frain's Lake is located in southeastern Michigan in Washtenaw County about 6½ km east of Ann Arbor. The lake is approximately 8 ha in area and has no inlet or outlet; maximum depth is 9 m. Drainage from septic tanks, which border the western end, and runoff from agricultural land provide an influx of nutrients which produces massive algal blooms during the early summer. Third Sister Lake is a 4-ha lake approximately 3 km west of Ann Arbor.

Because it is deeper and is surrounded by forest, considerably less eutrophication has occurred, and the algal blooms experienced are less massive than those at Frain's Lake. The two typify many of the lakes found throughout southern Michigan.

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the rainfall is from cumulus clouds; and (iii) transports of heat by the winds are particularly weak and inefficient at counteracting temperature changes due to albedo changes. This mechanism offers a possible explanation for past changes in the climate of the Sahara (3), and, in particular, for droughts in the Sahel (the southern region of the Sahara), where the process could be initiated by overgrazing.

Otterman (4) has also drawn attention to the possible effects on rainfall of changes in the albedo due to overgrazing. He presents data showing actual albedo and temperature changes in the Sinai-Negev region and conjectures that similar changes on a far larger scale have occurred in the Sahel. His argument is that an increase in the albedo causes cooling of the ground and the development of a "thermal depression," the reverse of the "equivalent mountain" of Malkus and Stern (5), so that the air has to descend. The equivalent mountain effect of surface heating is essentially a gravity-wave phenomenon and applies only to small-scale heating. It might be relevant to the Sinai-Negev region, but in our opinion it is not applicable to the Sahel or to other large regions. Contrary to Otterman's assertion in his report, it is not in accordance with Charney's approach to the dynamics of subsidence in desert climates. In Charney's analysis an increase in the albedo in a large region causes enhanced sinking and drying only to the extent that the temperature departs further from radiative-convective equilibrium, and this departure depends on the efficiency of a frictionally controlled circulation which reduces the horizontal temperature gradients that would be established by radiation alone. However, both mechanisms fail to take into account the dynamical effect of the release of latent heat in precipitation and both ignore the effects of the global circulation. For example, they do not take into account the interaction of the desert circulation in the Sahara with the monsoon circulation to the south.

In order to assess the plausibility of Charney's mechanism, we need to calculate its effect together with the effect of all other mechanisms which operate simultaneously, and see if the net effect is appreciable. In the past decade computer models of the general circulation of the atmosphere have been developed which implicitly or explicitly include most atmospheric processes,

Drought in the Sahara: A Biogeophysical Feedback Mechanism

Abstract. Two integrations of a global general circulation model, differing only in the prescribed surface albedo in the Sahara, show that an increase in albedo resulting from a decrease in plant cover causes a decrease in rainfall. Thus any tendency for plant cover to decrease would be reinforced by a decrease in rainfall, and could initiate or perpetuate a drought.

In the Royal Meteorological Society's Symons Memorial Lecture for 1974 Charney (1) discussed a biogeophysical feedback mechanism which tends to produce changes in rainfall and plant cover. This mechanism operates because of the dependence of the surface albedo on plant cover. Ground covered by plants has an albedo in the range 10 to 25 percent, whereas ground with no vegetation frequently has a higher albedo, as high as 35 to 45 percent in the case of dry, light, sandy soil (2). Thus a decrease in plant cover may be accompanied by an increase in the surface albedo. This would lead to a decrease in the net incoming radiation and an increase in the radiative cooling of the air. As a consequence, the air would sink to maintain thermal equilibrium by adiabatic compression, and cumulus convection and its associated rainfall would be suppressed.

The lower rainfall would in turn have an adverse effect on plants and tend to enhance the original decrease in plant cover. This positive feedback will be particularly important in regions such as the Sahara where (i) large-scale subsidence already occurs; (ii) most of

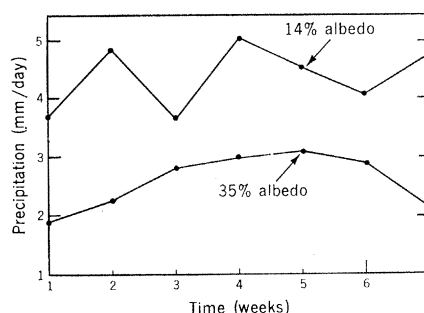


Fig. 1. Weekly mean rainfall rates in the Sahara during the 7 weeks of the experiments.