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### Report to the Great Lakes Science Advisory Board: Biological Availability of Phosphorus

International Joint Commission. Expert Committee on Engineering and Technological Aspects  
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Report to the  
Great Lakes Science Advisory Board

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GLC 22222 166

**Biological Availability of Phosphorus**

[1981]



Report to the  
Great Lakes Science Advisory Board

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This report to the Science Advisory Board was prepared by the Engineering and Technological Aspects Expert Committee. Though the Board has reviewed and approved this report for publication, some of the specific conclusions and recommendations may not be supported by the Board.

## **Biological Availability of Phosphorus**

by the  
Expert Committee on Engineering and  
Technological Aspects of Great Lakes Water Quality

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DISCLAIMER

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## LIST OF SYMBOLS

AIP	-	Apatite Inorganic Phosphorus
NAIP	-	Non Apatite Inorganic Phosphorus
NaOH-IP	-	Sodium Hydroxide Extractable Inorganic Phosphorus
PIP	-	Particulate Inorganic Phosphorus
POP	-	Particulate Organic Phosphorus
PTP	-	Particulate Total Phosphorus
SRP	-	Soluble Reactive Phosphorus
STP	-	Soluble Total Phosphorus
SUP	-	Soluble Unreactive Phosphorus
TP	-	Total Phosphorus

LIST OF SYMBOLS

Agarose Inorganic Phosphorus	AIP	
Non Agarose Inorganic Phosphorus	NAIP	
Sodium Hydroxide Hydrolysis Inorganic Phosphorus	NaOH-IP	
.....		4
Particulate Inorganic Phosphorus	P1P	
.....		7
Particulate Organic Phosphorus	P2P	
.....		8
Particulate Total Phosphorus	P3P	
.....		11
Soluble Particulate Phosphorus	SP1P	
.....		15
Soluble Total Phosphorus	STP	
.....		15
Soluble Inorganic Phosphorus	SIP	
.....		15
Total Phosphorus	TP	

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## BIOLOGICAL AVAILABILITY OF PHOSPHORUS

### 1. INTRODUCTION

In September 1978 the Engineering and Technological Aspects (ETA) Committee expressed its concerns to the Great Lakes Science Advisory Board that efforts to control inputs of pollutants to the Great Lakes, such as heavy metals and, in particular, phosphorus, were not directed at biologically available forms, but rather at the total inputs of the pollutants. The Committee requested and received concurrence of the Board to investigate the concept of controlling biologically available forms of phosphorus. Two major activities took place in carrying out this task. ETA Committee members participated in a review of phosphorus availability presented at the IJC/Cornell University Conference on "Phosphorus Management Strategies for the Great Lakes". The major paper on phosphorus availability presented at the conference and published in the proceedings was prepared by Lee et al. (1). Secondly, a state-of-the-art report on "Biologically Available Phosphorus" (2) was developed by a subcommittee of the ETA Committee. This report was based primarily on information received at a meeting of experts convened by the Committee on December 8, 1978 in Chicago. Those who attended this meeting are listed on page 29 of this report.

Based on the above reports, and other relevant documents, the ETA Committee has prepared this summary report to answer the following questions with respect to phosphorus availability: 1) What forms of phosphorus are biologically available? 2) What analytical techniques are available to measure different forms of phosphorus and how do they compare with respect to their estimation of available phosphorus? 3) What are the differences in the proportion of biologically available phosphorus in total phosphorus inputs from various sources? and 4) What transformations in chemical forms of phosphorus take place in lakes and what effect do they have on considerations of phosphorus availability? The Committee reached several conclusions

based on its review of the question of phosphorus availability and in this summary report, discusses the implications for developing further strategies to control phosphorus inputs to the Great Lakes.

## 2. BIOLOGICALLY AVAILABLE FORMS OF PHOSPHORUS

The term "biologically available phosphorus" is not well defined, but has an implication that the phosphorus can be incorporated into living cells with reasonable speed. Generally, "availability" might be interpreted to mean that the phosphorus can become available for use during a single growing season.

Phosphorus is estimated to be eleventh in order of abundance among elements in igneous rocks on the earth's surface (3). Phosphorus occurs in all known minerals as orthophosphate, the fully ionized form of which is represented as  $PO_4^{-3}$ . One mineral family, the apatites, represent by far the major amount of phosphorus in the earth's crust. Important members of the apatite family are listed in Table 1. Although there is an almost unlimited supply of apatite phosphorus available in the earth's crust, these mineral forms, particularly the highly crystalline ones, are very insoluble and become available to organisms only slowly through physical or biological dissolution (4); hence, they are generally termed "non-biologically available". In a strict sense this is not true (5, 6, 7), but the rates of solution are sufficiently slow so that the presence of even large quantities of crystalline apatite minerals in lake sediments is not apt to contribute significantly to lake eutrophication.

Slowly with time, apatite and other insoluble phosphorus minerals can be brought into solution in forms which are readily available for the growth of algae and other aquatic life. The major inorganic forms of "biologically available phosphorus" existing naturally in aqueous systems are the soluble orthophosphates. Such orthophosphates are also a component of fertilizers and thus are commonly present in runoff from agricultural areas. They are also present in domestic sewage.

There are also many anthropogenic forms of phosphorus produced commercially from condensation of phosphates extracted from apatite minerals for use in detergents, for water treatment, etc. (3). These condensed forms are also generally soluble and upon hydrolysis, which occurs fairly readily through chemical or enzymatic activity in natural waters (8, 9, 10), yield soluble orthophosphates. Hence, the condensed phosphates (Table 1) are also considered to be biologically available.

Orthophosphates can also combine with different metal ions to form various insoluble minerals other than the apatites. In natural waters, the most common cations involved are iron, aluminum, and calcium (Table 1). Soluble orthophosphates can also become part of particulate materials through adsorption (3, 11). The solubilities of these non-dissolved phosphate containing materials varies widely, as does the biological availability of the phosphorus which they contain. Table 1 lists the solubilities of some of the more abundant materials containing phosphorus.

The biological availability of inorganic phosphate minerals depends not only upon the mineral itself but also upon its crystallinity. Most of the phosphate minerals occurring in the earth's surface are well-formed crystalline materials that have resulted from processes occurring over geological periods of time. However, many of the mineral precipitates that form during wastewater treatment or within a season in a lake are poorly crystalline. These "amorphous" forms are more soluble and more readily available to algae. Thus, in evaluating the ease or rapidity with which the phosphorus in sediments or particulate materials can become available, one must consider not only the kinds of minerals in which it is contained, but also their respective degrees of crystallinity.

Other important forms of phosphorus are organic in nature and are generally, but not always, products of biological processes. Organic phosphorus may be part of particulate materials within the structure of living or dead and decaying organisms. Organic phosphorus forms may also be dissolved in natural waters, perhaps resulting from excretion by either growing or decaying organisms. As with the inorganic forms, the biological

TABLE 1. INORGANIC AND ORGANIC FORMS OF PHOSPHORUS AND THEIR RELATIVE SOLUBILITIES

		Solubility
Biologically Available Inorganic Forms of Phosphorus		
Soluble Orthophosphates	$\text{H}_2\text{PO}_4^-$ , $\text{HPO}_4^{2-}$ , $\text{PO}_4^{3-}$	very soluble
Condensed Phosphates		
Pyrophosphate	$\text{H}_2\text{P}_2\text{O}_7^{-2}$ , $\text{HP}_2\text{O}_7^{-3}$ , $\text{P}_2\text{O}_7^{-4}$	6.70 g/100 cc at 25°C ( $\text{Na}_4\text{P}_2\text{O}_7$ )
Tripolyphosphate	$\text{H}_3\text{P}_3\text{O}_{10}^{-3}$ , $\text{HP}_3\text{O}_{10}^{-4}$ , $\text{P}_3\text{O}_{10}^{-5}$	20 g/100 cc at 25°C ( $\text{Na}_5\text{P}_3\text{O}_{10}$ )
Trimetaphosphate	$\text{HP}_3\text{O}_9^{-2}$ , $\text{P}_3\text{O}_9^{-3}$	very soluble ( $\text{NaPO}_3$ ) <sub>n</sub>
Biologically Unavailable Mineral Forms of Phosphorus		
Hydroxyapatite	$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	practically insoluble
Fluorapatite	$\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$	no information
Carbonate Fluorapatite	$\text{Ca}_{10}(\text{F},\text{OH})_2(\text{PO}_4,\text{CO}_3)_6$	no information
Phosphate Minerals with Varying Availability		
Brushite	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0.0316 g/100 cc at 25°C
Bobierite	$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	insoluble
Variscite, stringite	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ , $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	insoluble, very slightly soluble
Wavellite	$\text{Al}_3(\text{OH})_3(\text{PO}_4)_2$	practically insoluble
Clay-phosphate	$\text{Si}_2\text{O}_5\text{Al}_2(\text{OH})_4 \text{PO}_4$	no information
Organic Phosphates with Varying Availability		
Phosphates sorbed on amorphous aluminum and iron oxides		
Bacterial cell material	Inositol hexaphosphate	poor solubility (calcium magnesium salt)
Plankton material	Phospholipid	no information
Dissolved material	Phosphoprotein	no information
	Nucleic acids	no solubility information
	Polysaccharide phosphate	
	Phosphocreatine	very soluble ( $\text{C}_4\text{H}_{10}\text{N}_3\text{O}_5\text{P}$ )
	Glycerophosphate	soluble

availability of the various organic forms of phosphorus varies widely. Studies of phosphorus distributions in lakes indicate that the soluble organic phosphorus may amount to from 30 to 60 percent of the total dissolved phosphorus (12, 13, 14). Not much is known of the exact composition of the organic phosphorus compounds, nor of their relative availability to growth of aquatic organisms.

In summary, the actual amount of phosphorus which is available in an aquatic system to algae is a function of a complex set of physical, chemical, and biological processes (15). It is generally agreed that soluble inorganic forms of phosphorus including both the orthophosphates and condensed phosphates are readily available biologically. However, several studies have shown that in certain situations the availability of orthophosphates to algae may be reduced by low levels of trace metals in the water. On the other hand, the availability of dissolved organic forms is less certain. Some of the particulate inorganic and organic phosphorus forms are readily available and others are not. It is generally agreed that crystalline apatite minerals are among those not readily available. However, the availability of other particulate forms varies widely. In general non-crystalline forms are much more readily available than crystalline ones.

### 3. ANALYTICAL PROCEDURES FOR ESTIMATING BIOLOGICALLY AVAILABLE PHOSPHORUS

Since there are many different forms of phosphorus and their general availability varies widely, it is difficult, if not impossible, to develop analytical procedures to quantify directly each biologically available form which may be present. For this reason collective analytical tests have been sought that show good correlation between ease of solubilization under chemical conditions and relative availability to algae.

Both chemical procedures and bioassay techniques can be used to estimate the biologically available fraction of phosphorus in particular samples.

Chemical extractions are used to determine the amount of total phosphorus in a sample which can be converted to soluble phosphate under particular test conditions. Bioassay techniques are based on a determination of the amount of



growth a selected algal species exhibits on exposure to a particular form of phosphorus or the reduction of the nutrient content observed as a result of the growth. A summary of the various chemical and bioassay techniques and their limitations were presented by Lee et al. (1).

The major concern with phosphorus inputs is with respect to differences in the soluble and particulate fractions.

The soluble total phosphorus (STP) portion is usually fractionated as:

- (i) SRP - soluble reactive phosphorus as measured by the molybdate method
- (ii) SUP - soluble unreactive phosphorus

As noted in Section 2, it is generally agreed that SRP is essentially all bioavailable and is rapidly assimilated by algae as orthophosphorus. However, there is some disagreement on the availability of other soluble phosphorus fractions. Lee et al. (1) question the extent of hydrolysis of soluble unreactive (SUP) and condensed phosphate under algal assay conditions but do not discuss direct incorporation, enzymatic modifications, photodegradation, or benthic decomposition.

The availability of particulate phosphorus is a much more controversial point. A summary of studies which have examined the bioavailability of particulate total phosphorus (PTP), using both chemical and biological techniques for urban runoff, sediments, and tributaries is shown in Table 2, and for atmospheric sources in Table 3. Figure 1 indicates the possible composition of PTP and attempts to show which species are extracted by the various extraction methods. For those soil and sediment particulates that have been examined (Table 2), the fraction of phosphorus which is extractable in NaOH would appear to be most highly correlated with biological growth. Furthermore, most researchers believe that sodium hydroxide extractable inorganic phosphorus (NaOH-IP) represents the maximum amount of PTP that is available. The minimum amount available is represented by the ion exchangeable portion. This means that for most particulate sources, the

FIGURE 1: POSSIBLE COMPONENTS OF PARTICULATE PHOSPHORUS AND THEIR RECEPTIVITY TO VARIOUS CHEMICAL EXTRACTION METHODS

TABLE 2: SUMMARY OF STUDIES OF AVAILABLE PARTICULATE PHOSPHORUS FROM DIFFUSE SOURCES (From Lee et al. (1))

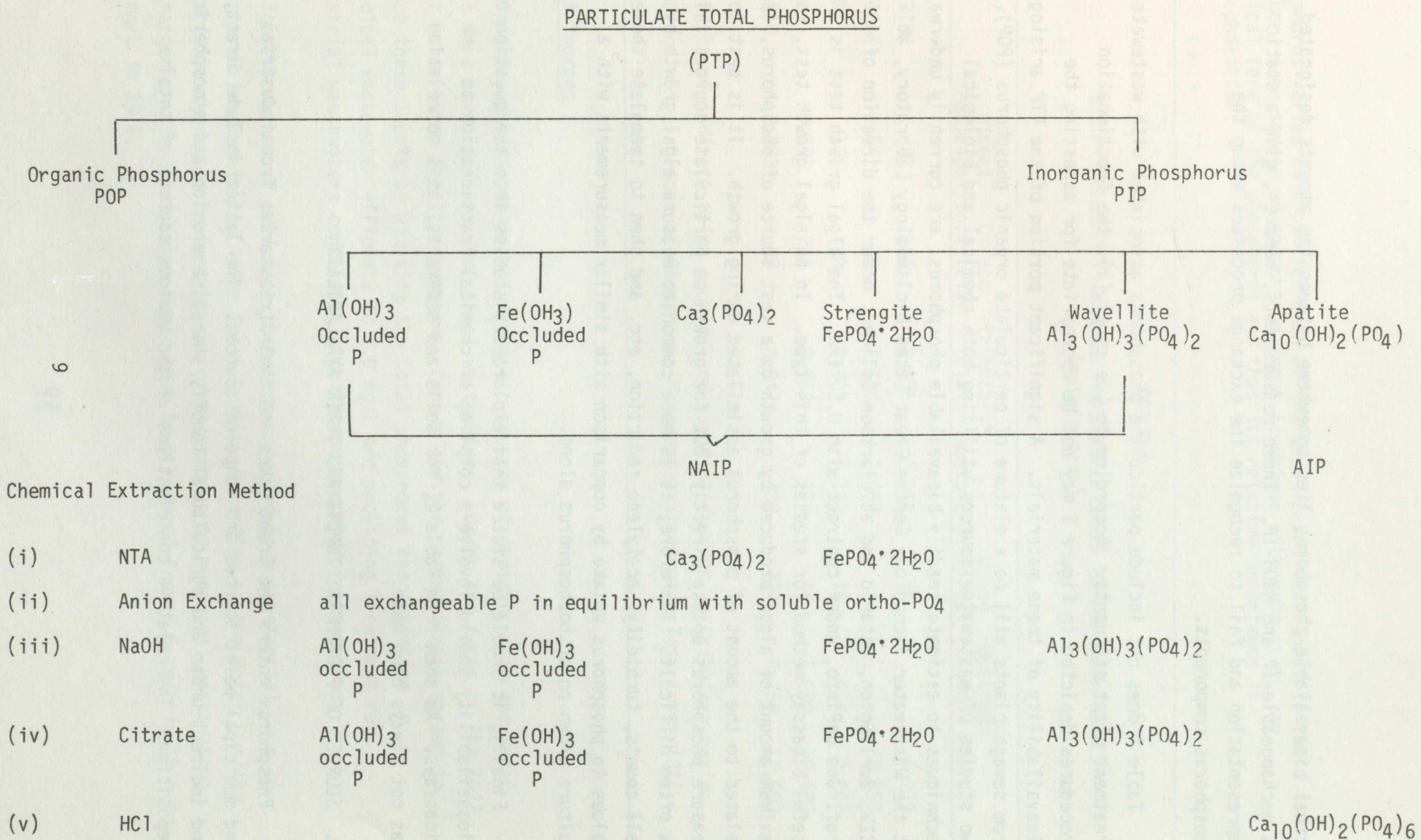
Particulate Source	Chemical Fraction Considered Available	Bioassay Technique	Bioavailability Correlation	Reference
Marine Sediments	NTA	<u>Scenedesmus</u>		Golterman (6)
Urban Runoff	NaOH or Anion Exchangeable	<u>Selenastrum</u>	Available P = SRP + 0.2 PTP	Cowen (17) Cowen & Lee (18)
Soils, Soil Runoff	NaOH	2 and 30-day assays with <u>Selenastrum</u>	66-94% of NaOH-PIP	Sagher, <u>et al.</u> (19)
Lake Sediment	NaOH	28-day assay with <u>Selenastrum</u>	74% of NaOH-IP	Sagher, <u>et al.</u> (19)
Soils	Aluminum Saturated-cation exchange			Huettl, <u>et al.</u> (20)
Lake Sediment	Exchangeable - IP	12-wks with macrophyte <u>M. spicatum</u>	13-17% of PTP	Li, <u>et al.</u> (21)
Bluff erosion, Lake sediments & Tributaries	NaOH	12-18 days with <u>Scenedesmus</u>	NaOH-IP	Williams, <u>et al.</u> (22)
Lake Erie Tributaries	NaOH + Citrate-Dithionite-Bicarbonate	Up to 143 days with indigenous algae	40% of NaOH-IP	Logan, <u>et al.</u> (23)
Great Lakes Tributary Sediments	NaOH		14-37% of PTP	Armstrong, <u>et al.</u> (24)
Great Lakes Shoreline Soils	HCl		43% of PTP	Monteith & Sonzogni (25)
Great Lakes Tributary Sediments	NAIP		20-40% of PTP	Thomas (26)

NOTE: 3% OF PARTICULATE PHOSPHORUS IS ASSUMED TO BE AVAILABLE TO ALL METHODS

TABLE 3: SUMMARY OF STUDIES ON AVAILABLE PHOSPHORUS FROM ATMOSPHERIC SOURCES (From Lee et al. (1))

Sample Source	Chemical Fraction Considered Available	Bioassay Technique	Bioavailability Correlation	Reference
Wisc. Snow		18 days with <u>Selenastrum</u>	<25% of PTP + SRP	Cowen (17) Cowen & Lee (18)
Rain water	Exchangeable		38% of TP	Peters (27)
Precipitation			50% of TP	Murphy & Doskey (28)
Rainfall and Dry Fallout	SRP + Acid Extractable			Delumyea & Petel (29, 30)

FIGURE 1: POSSIBLE COMPONENTS OF PARTICULATE PHOSPHORUS AND THEIR SUSCEPTIBILITY TO VARIOUS CHEMICAL EXTRACTION METHODS



actual bioavailable phosphorus lies somewhere between the amounts designated as exchangeable-IP and NaOH-IP. These measurements, however, give a static representation and fail to recognize the exchange processes among the phosphorus components.

Table 2 does not include particulate phosphorus associated with wastewater treatment plant effluents. According to Lee et al.(1), the fractionation procedures depicted in Figure 1 may not be appropriate for assessing the bioavailability of these materials. A significant portion of the PTP arising from sewage plants will be a mixture of particulate organic phosphorus (POP). Two studies of wastewater sources utilizing both chemical and biological techniques to estimate readily bioavailable phosphorus, are currently underway at the Wastewater Technology Centre-Great Lakes Biolimnology Laboratory, at CCIW, Burlington, Ontario and at Clarkson College, under the direction of Prof. Joe DePinto, under contract with U.S. EPA. The algal growth test is a useful bioassay method for studies of this type. In an algal growth test, the maximum amount of algae produced by growth on a test source of phosphorus, is related to the amount of phosphorus assimilated during growth. It is best to measure phosphorus uptake directly, but for growth on particulate sources this is often difficult. Therefore, it is more common to measure algal growth by cell counts, turbidity, acetylene reduction, etc. and then to translate these values to phosphorus uptake by comparison with similar measurements with a culture grown on orthophosphorus alone.

Finally, it should be stated that exploratory studies into the question of bioavailability should involve a coupling of chemical fractionation to bioassays. As seen from Table 2, for soils and sediments, this correlation has not always been made.

#### 4. SOURCES OF PHOSPHORUS INPUTS AND THEIR AVAILABILITY

Phosphorus enters the Great Lakes and their tributaries from industrial and municipal point sources and nonpoint sources. The latter include direct and indirect urban and agricultural runoff, shoreline erosion and atmospheric deposition. The relative contributions of the various sources of total

phosphorus varies as shown for each of the Great Lakes watersheds in Table 4. Further, each source of phosphorus input is unique with respect to the chemical form of the phosphorus and thus its relative importance in eutrophication.

TABLE 4  
 "BEST" ESTIMATE\*\* OF 1976 PHOSPHORUS LOADS TO THE GREAT LAKES  
 (metric tons)

Lake	Direct Municipal	Direct Industrial	Tributary* Total	Atmosphere	Urban Direct	Upstream Load	Total
SUPERIOR	72	103	2,455	1,566	16	-	4,212
MICHIGAN	1,041	38	3,596	1,682	-	-	6,357
HURON	126	38	2,901	1,129	16	657	4,867
ERIE	6,292	275	9,960	774	44	1,080	18,425
ONTARIO	2,093	82	4,047	488	324	4,769	11,803

\*consists of indirect point sources and nonpoint sources in tributary basin.

\*\*Source: Final Report of Phosphorus Management Strategies Task Force (31)  
 November

### Point Sources

In the past, the major anthropogenic sources of phosphorus to the Great Lakes were municipal and industrial wastewaters. Under the terms of the 1972 Great Lakes Water Quality Agreement, Canada and the United States agreed to reduce these inputs by limiting the total phosphorus concentration in municipal wastewater effluents to 1.0 mg/L and providing treatment for industrial wastewaters containing significant amounts of phosphorus.

These programs of pollution abatement have led to a substantial drop in phosphorus loading to the lower Great Lakes. According to the Water Quality Board (32), aggregate concentrations of phosphorus in municipal wastewaters discharged in the Great Lakes basin have been reduced from 2.6 mg/L in 1975 to 1.8 mg/L in 1978.

Phosphorus in wastewater is normally present as organic phosphorus, inorganic condensed phosphates, and orthophosphates (33). Most of the organic phosphorus is particulate in nature and includes bacterial cells. Inorganic condensed phosphates from synthetic detergents, together with orthophosphate from urine, microbial degradation of organic phosphates or hydrolysis of condensed phosphates comprise the major dissolved fraction.

The increase in the inorganic condensed phosphorus fraction in municipal wastewaters which accompanied the introduction of synthetic detergents has since been reduced by legislative limitations imposed on phosphorus content of detergent formulations. Subsequent to the adoption of legislative limitations, decreases in the phosphorus content of domestic wastewaters were reported to be as high as 50 to 60% where the industrial contribution is low; Lee et al. (1). Other observations following legislative limitations have shown reductions in effluent phosphorus content as high as 67% (34). In areas of the U.S. without legislative controls, there have been voluntary decreases in the phosphorus content of detergent formulations; and it is estimated that a complete phosphorus ban would now produce only a 30 to 35% reduction in the phosphorus content of municipal wastewaters in these areas (35). However, since detergent phosphorus is both highly soluble and bioavailable, reductions in the phosphorus content of detergents to 2.2 to 0.5% by weight may slow eutrophication more than merely lowering the total phosphorus in municipal wastewater by a third. This reduction probably has most significance in reducing phosphorus inputs from individual treatment systems or where phosphorus removal is not required under the Great Lakes Water Quality Agreement.

It is generally believed that the major fraction of wastewater phosphorus is available. Lee et al. (1) have questioned whether upon hydrolysis of the condensed phosphate in wastewater, all the phosphate becomes available as orthophosphate and hypothesize that up to 50% may be converted to non-available forms. At primary and secondary wastewater treatment plants practicing chemical precipitation to meet the 1 mg/L total phosphorus requirement, most of the residual phosphorus is present as mixtures of organic and particulate iron, aluminum, or calcium hydroxides. The metal hydroxides

could be unavailable for direct algal growth. Residual soluble phosphorus generally is less than 0.3 mg/L. Lee et al. (1) indicated that phosphorus associated with iron and aluminum will be included in non apatite inorganic phosphorus (NAIP) determined by hydroxide extraction. In a previous study by Lee (35), it was concluded that phosphorus incorporated into hydrous oxide flocs is not readily returned to the water column over extended periods of time and is thus considered unavailable. On the other hand, Dorich and Nelson (34) found, in their investigation of the portions of soluble and sediment bound phosphorus in drainage from agricultural watersheds in the Maumee River basin, that phosphates loosely sorbed on amorphous aluminum and iron oxide complexes supplied the highest proportion of phosphorus assimilated by algae. For systems using iron for phosphorus removal, release of orthophosphate may occur under reducing conditions in anoxic hypolimnia. Further long and short term availability studies are required to determine the biological availability of the residual phosphorus in municipal wastewaters following treatment by the three widely practiced chemical precipitation processes.

#### Nonpoint sources

With the implementation of point source phosphorus control programs attention has focused on the contribution of nonpoint sources. The major nonpoint sources for phosphorus in the Great Lakes Basin have been identified by the IJC's International Reference Group on Great Lakes Pollution from Land Use Activities (PLUARG) (37); as:

1. urban runoff;
2. agricultural runoff;
3. shoreline erosion; and
4. atmospheric deposition.

Urban runoff samples collected during 12 events at Madison, Wisconsin from residential, commercial and urban construction land areas were examined for phosphorus content and bioavailability by Cowen and Lee (38). A further study by the same authors was reported for two urban-residential areas in the Genesee River basin. From algal assays of the samples they concluded that



NaOH and anion exchange resin extraction techniques gave the best estimates of available particulate phosphorus . At Madison, mean values of the extractable phosphorus were between 22 and 27% of particulate total phosphorus (PTP) while for the Genesee study base extractables averaged between 18 and 30%. Cowen and Lee (38) concluded that an upper bound for available phosphorus in urban runoff could be obtained from

$$\text{Available P} = \text{SRP} + 0.3 \text{ PTP}$$

Subsequently, Lee et al. (1) modified the estimate to account for factors affecting availability in receiving waters. They suggested that the ultimate availability can be estimated, based on soluble reactive phosphorus (SRP) and PTP, as follows:

$$\text{Available P} = \text{SRP} + 0.2 \text{ PTP}$$

The general applicability of this relationship needs further investigation and verification.

In its Final Report (37) to the IJC, PLUARG identified intensive agricultural operations as a major nonpoint source of phosphorus. The most important land related factors are soil type, land use, and materials usage. As can be seen from Table 5, unit area loads vary from less than 0.1 kilograms/hectare/year for land with mostly forest to over 1.5 kilograms/hectare-year from land with extensive row crops on fine textured soils.

Results of studying the relative bioavailability of phosphorus in extensive samples of Great Lakes waters and tributaries have been reported by Armstrong et al. (39) and PLUARG (37). Both used the NaOH-extractable phosphorus to estimate the non-apatite inorganic phosphorus (NAIP). Mean distribution of phosphorus species from the PLUARG study conducted in the Lake Ontario, Erie and Huron basins are given in Table 6. A consistency of percentage composition particularly for the NAIP fraction was noted between monitored streams and lakes. For the streams the coefficient of variation ( $s/\bar{x}$ ) of the apatite (18%) was significantly lower than either the NAIP (50%)

TABLE 5: ANNUAL UNIT AREA LOADS OF TOTAL PHOSPHORUS BY LAND USE AND LAND FORM IN CANADA

	Annual Unit Area Loading of (kg/ha-yr) Phosphorus by Land Form Types						
	Fine-textured soils		Medium-textured Soils		Coarse-textured Soils		Miscellaneous
	Level	Sloping	Level	Sloping	Level	Sloping	
Greater than 50% rowcrops; low animal density*	1.5	-	0.7	-	0.2-	-	(sand on clay) 0.9
Greater than 50% rowcrops; medium animal density**	-	-	-	-	0.2	-	-
25-50% rowcrops; medium animal density	0.6	4.7	0.2	0.3	0.1	0.2	-
25-50% rowcrops; high animal density***	0.7	0.8	0.3	0.4	0.2	0.2	(sand on clay) 0.7
Less than 25% rowcrops; medium animal density	0.3	0.4	0.1	0.1	0.1	0.1	(sand on clay) 0.4
Less than 25% rowcrops; high animal density	0.4	0.5	0.1	0.2	0.1	0.1	-
Greater than 60% forest	0.2	0.2	0.1	0.1	0.1	0.1	(shield) 0.1

\* Less than 0.1 animals/km<sup>2</sup>

\*\* Greater than 0.1 and less than or equal to 0.3 animals/km<sup>2</sup>

\*\*\* Greater than 0.3 animals/km<sup>2</sup>

kg/ha-yr - kilograms per hectare per year

Multiply kg/ha-yr by the factor 1.12 to convert to pounds per acre per year (lb/ac/yr)

Source: Ref. (40)

or the organic phosphorus (59%). It was concluded that this represented a reflection of the texture and soils of the individual watersheds. Both the NAIP and Organophosphorus showed more variation reflecting both stream productivity and adjoining land usage. These values are in general agreement with those reported by Armstrong et al. (24), but higher in NAIP or base extracted particulate phosphorus when compared with the range of 13 to 18% reported by Cowen and Lee (18) for non-urban Genesee River watersheds. Analyses of 36 tributaries in the U.S. Lake Erie Basin by Logan (39) and Logan et al. (23) indicated the NaOH extractable was 30 to 40% of the total inorganic phosphorus or 6 to 15% of the particulate fraction.

Published data indicate relatively low percentages of particulate phosphorus in sedimentary material either from erosion of shore line bluff or lake bottom sediments are available for algal growth. In samples from 22 locations, Williams et al. (22) showed that with two exceptions, apatite phosphorus averaged 51% of total particulate while NAIP averaged 31%. The two typical exceptions had high particulate total phosphorus. They concluded that the percentage of available phosphorus in geologic materials is highly variable. In unweathered samples or samples of low total particulate phosphorus, the available phosphorus in NAIP tended to be low.

TABLE 6:  
PARTICULATE PHOSPHORUS DISTRIBUTION

	Apatite %	NAIP %	Organic %
Streams	28.1	33.4	38.5
Lake Ontario	24.5	31.6	43.9
Lake Erie	29.8	37.4	32.8
Lake Huron	43.4	23.1	33.5
Source: Ref. No. (37)			

Thomas and Haras (41) estimated that, on the basis of Canadian data, the contributions of total phosphorus from shoreline erosion to Lakes Huron and Ontario are low with maximum values of 9.3 and 6.2% respectively. Conversely, the loading to Lake Erie is estimated at 35.2%. The available or NAIP loadings were estimated to be 4.0, 1.1 and 5.0% for Lakes Huron, Ontario, and Erie, respectively. This indicates that phosphorus eroded bluff material is generally not available for algal growth as concluded by PLUARG (37). The corresponding U.S. study by Monteith and Sonzogni (25) indicated that 25% of the total phosphorus loading could result from shoreline erosion.

A number of investigators have attempted to assess the atmospheric contributions of phosphorus to water bodies. As indicated in Table 4, this input is a substantial portion of total phosphorus loads especially for Lakes Superior, Michigan and Huron. A further quantity of phosphorus is deposited on land and could migrate into the Lakes.

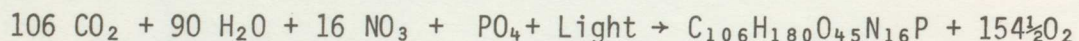
Delumyea and Petel (29, 30) found highly variable soluble phosphorus concentrations ranging from 1 to 36  $\mu\text{g/L}$  during 21 event samples on the Lake Huron shoreline. Analyses of integrated wet samples, leached at pH 2 in  $\text{H}_2\text{SO}_4$ , were also highly variable ranging from a 10  $\mu\text{g/L}$  up to 700  $\mu\text{g/L}$ . This probably exceeds the available fraction. Murphy (42) reported 34  $\mu\text{g/L}$  of total phosphorus in rainfall in urban Chicago. Soluble orthophosphate comprised approximately 35%. A further survey around Lake Michigan by Murphy and Doskey (28), indicated a weighted average in 188 samples from six locations varied from 16 to 36  $\mu\text{g/L}$  total phosphorus. Soluble orthophosphate ranged from 30 to 50%. Snow samples had total phosphorus content of 7 to 58  $\mu\text{g/L}$ . They estimated possibly 50% of the total phosphorus may ultimately be available.

A survey of the principal sources of emissions in the U.S. bordering the Great Lakes would indicate that orthophosphate (or  $\text{P}_2\text{O}_5$ ) would predominate in precipitation (43). Major orthophosphate emissions reported were 4600 metric tons from handling and spreading of fertilizer, 2800 metric tons from the iron and steel industry and 3900 metric tons from combustion of coal.

## 5. IN-LAKE TRANSFORMATIONS

As described in Sections 2 and 4, phosphates become available to the aquatic biological community in the Great Lakes through erosion, air transport, and the activities of man.

Biological systems require several elements at a rate to satisfy their nutritional demands, which for algae has been expressed by Golterman (44) as:



In addition to phosphorus other nutrients such as carbon and nitrogen are required for growth. The maximum biomass which can result is a function of, among other things, the essential nutrient which is available in the least amount relative to the need. Assuming phosphorus is the limiting nutrient for aquatic organisms in a lake, then one has to consider not only the availability of the various forms of phosphorus but also the selection, cycling and utilization of these various forms by the biological community. As the different biological species frequently have different strategies to meet their nutritional demands, the situation becomes quite complex. These complexities have resulted in experimental "evidence" which conflict and numerous debates about which forms of phosphorus are available and which are not.

The different phosphate components of the phosphorus cycle are recognized by analytical procedures and can be grouped as follows:

- I - Inorganic orthophosphate:  $\text{PO}_4 - \text{P} (= \text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-} + \text{PO}_4^{3-})$
- II - Hydrolysable phosphate: Dissolved polyphosphate +  
Dissolved organic phosphate
- III - Total dissolved phosphate: I + II
- IV - Particulate phosphate: Part P
- V - Sum of III + IV = Total P = (Part phosphate +  
Total dissolved phosphate)

It is essential to note that the above chemical components are as perceived by their chemistry, and does not represent the interpretation of the chemical environment by the algae. With this caveat in mind, the phosphate cycle in lakes can be presented as in Figure 2.

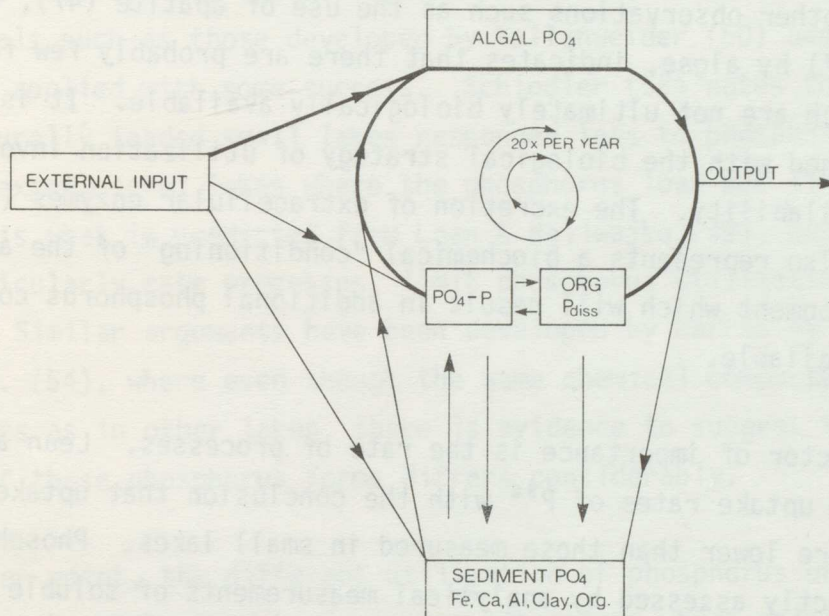


Figure 2: Schematic representation of the phosphate cycle. The indicated turnover of 20 times per year may vary between 10 and 40. (Source: reference (44))

Within this cycle, two interactive processes can be identified. The first is a metabolic process, represented by two phases:

- (1)  $PO_4-P$  water  $\xrightarrow{\text{Primary Production}}$  Cell  $PO_4$   $\xrightarrow{\text{Mineralization}}$   $PO_4-P$  water & Org P
- (2) Org P  $\xrightarrow{\text{Heterotrophy}}$  Cell  $PO_4$   $\xrightarrow{\text{Mineralization}}$   $PO_4 - P$  water & Org P

The second cycle is an "external" phosphate cycle represented by:

- (3)  $PO_4 - P$  water  $\longrightarrow$  sediment  $\longrightarrow$   $PO_4 - P$  water & Org P

Clays are cation exchangers capable of adsorbing large amounts of phosphates. Golterman (6) reviewed the mechanisms of phosphate adsorption, and Olsen (45, 46) illustrated that the exchange of phosphate is a rapid process that directly reflects uptake rates by algae. This information combined with other observations such as the use of apatite (47), and the use of  $\text{FePO}_4$  (48, 7) by algae, indicates that there are probably few forms of phosphorus which are not ultimately biologically available. It is the rate process, combined with the biological strategy of utilization involved, which determines availability. The excretion of extracellular enzymes (alkaline phosphatase) also represents a biochemical "conditioning" of the aquatic chemical environment which will result in additional phosphorus components becoming bioavailable.

Another factor of importance is the rate of processes. Lean and Nalewajko (49) described uptake rates of  $\text{P}^{32}$  with the conclusion that uptake rates in large lakes were lower than those measured in small lakes. Phosphorus demand cannot be directly assessed by analytical measurements of soluble reactive, soluble unreactive, and particulate phosphorus which provide a static representation of the phosphorus pools. Lean's observations with natural communities suggest that analytical measurements cannot be used to distinguish areas of high or low phosphorus demands. Attempts to define biologically available phosphorus by growth cultures (22, 23) may also be of limited value because rate processes will be altered by the culture conditions.

In this sense, bioassay work must be viewed with great trepidation. At the December 8 meeting, Harris (2) cautioned about extrapolation of bioassay results to "in lake" phosphorus availability. Even in situ work, however, has its problems. Fitzgerald (2) noted that alkaline phosphatase activity measured in situ could depict the nutritional status of the biological community. High alkaline phosphatase levels were indicative of algae with high phosphorus demands. Only a portion of the algal community, however, will use this extracellular enzyme strategy. Mucilaginous algae create their own surface to trap particulates, others extend fibrils, and still others are capable of ingestion of particulate or heterotrophic uptake of organic phosphorus, and therefore, do not depend on extracellular phosphatase. This

diversity in strategies of obtaining phosphorus means the question of available phosphorus is complex and not well resolved by simple chemical measurements or bioassays.

Phosphorus availability and utilization do follow the central tendency theorem. Models such as those developed by Vollenweider (50) and Dillon (51) are generally applied with some success. Schindler (52) notes that the Great Lakes and naturally loaded small lakes responded less to phosphorus loading than smaller experimental lakes where the phosphorus load was almost entirely  $\text{PO}_4\text{-P}$ . This is what is predicted from Lean & Naliwajko (49); other factors, particularly rate processes, limit phosphorus utilization in the Great Lakes. Similar arguments have been developed by Harris *et al.* (53) and Haffner *et al.* (54), where even though the same chemical compartments exist in the Great Lakes as in other lakes, there is evidence to suggest that utilization of these phosphorus forms differs considerably.

This latter point, the different utilization of phosphorus under different conditions, can be emphasized by reviewing situations which exist in two other lakes.

Lake Kinneret in Israel, receives about grams of phosphate per square meter per year  $1.0 \text{ g PO}_4\text{-P m}^{-2}\text{yr}^{-1}$  compared with a loading of  $0.98 \text{ g PO}_4\text{-P m}^{-2}\text{yr}^{-1}$  to Lake Erie, and yet is classified as oligotrophic. (55,56) It is postulated that excessive eutrophication does not occur because the major phosphorus inputs are transported directly to the hypolimnion, and the phosphorus is strongly bound within the clay structure.

Great Slave Lake in the Northwest Territories, receives about  $3 \text{ g PO}_4\text{-P m}^{-2}\text{yr}^{-1}$  is also oligotrophic primarily because the phosphorus transported by clay is unavailable (57).

These represent two examples where natural inputs of phosphorus are such that the biological community cannot respond to them. It can generally be concluded that phosphorus from natural sources is less available than that introduced by man's activities.



The availability of phosphorus associated with clay particles is not simple. Braidech et al. (58) observed that algae in Lake Erie obtained nutrients directly from the sediment. Lin and Blum (59) noted that nearshore algae in Lake Michigan did not utilize insoluble polyphosphate or organic phosphates, but the offshore algae were capable of hydrolyzing polyphosphates. Also, bio-recycling of phosphorus by fish, zooplankton, and zoo benthos may affect bioavailability and very little is known of their role in this complex problem.

Thus, the relationships among phosphorus loading, phosphorus forms, and biological productivity are complex. Some readily available forms may become complexed or adsorbed onto particulate matter within the lake, settle to the bottom, and through these physical and chemical processes become less available. Other less readily available forms may be transported to a biologically active zone and chemically or biologically be converted slowly to useable forms. Once taken up by algae, the phosphorus may be used over and over many times, before either leaving the lake or settling to the bottom as refractory organic or poorly available inorganic particulates. Nevertheless, given equal inputs of readily available and poorly available forms of phosphorus, the readily available forms have greater potential for stimulation of algal growth and production of high concentrations of algal mass. For this reason, it would be useful in a phosphorus management strategy to distinguish between forms of phosphorus entering a lake which are readily available and those which are not.

## 6. CONCLUSIONS

1. Phosphorus exists in many other forms in an aquatic environment, some of which may, under certain conditions, become available to the biological community. Soluble inorganic forms of phosphorus are readily available for biological growth. The rate and opportunity for various forms, especially particulate phosphorus, to become biologically available varies widely. For all practical purposes apatite phosphorus can be considered to be unavailable.

2. Chemical and bioassay techniques are available to estimate the biologically available fraction of total phosphorus contained in a sample. Although there is only a limited amount of data available on direct comparisons between estimates provided by the different techniques, they do not appear to differ significantly.
3. None of the existing chemical or bioassay techniques can provide a meaningful assessment of what fraction of phosphorus is available, on a whole lake, long-term scale. A considerably higher level of research activity is required in this area if accurate methods are to be developed.
4. The relative bioavailability of phosphorus associated with the particulate matter in effluents from wastewater treatment plants using the addition of aluminum or iron salts to achieve 1.0 mg/L P is currently under investigation. The results of these investigations could have a bearing on the choice of chemical to be used to achieve the 1.0 mg/L total phosphorus objective if the long term bioavailability of the residual phosphorus in the effluent is significantly different depending upon the chemical used.
5. Continued research is required to provide a better understanding of the relationships between algal production-nutrient limitation in the Great Lakes. These programs should be designed to determine the impact of further reductions in external controllable phosphorus loadings on the Great Lakes eutrophication. In the meantime, however, assessments of the relative bioavailability of phosphorus as estimated by currently available techniques should be used to assign priorities for the control of various point and nonpoint sources of phosphorus inputs where unit costs for control are comparable.
6. In view of the significant costs associated with the implementation of more restrictive phosphorus control measures for point sources, i.e., requiring 0.5 mg/L total phosphorus or less in the effluents from municipal wastewater treatment plants, and the uncertainty associated with commensurate social benefits, further restrictions should await resolution of the bioavailability question.

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