



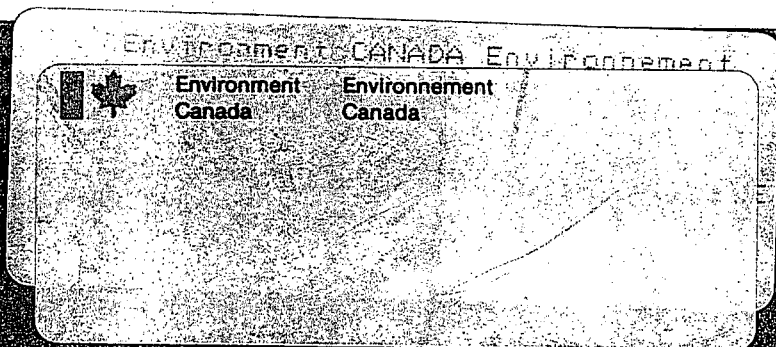
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DISTRIBUTION OF IRON-PHOSPHATE SPECIES  
IN ACID-STRESSED SOFT WATER LAKES

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**Inland Waters  
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DISTRIBUTION OF IRON-PHOSPHATE SPECIES  
IN ACID-STRESSED SOFT WATER LAKES

by

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## **ABSTRACT**

The objective of this work was to establish the distribution of iron-phosphate species in acid-stressed soft water lakes and to examine the mechanism of phosphate removal from the water column. Results of this work provide an approximate estimation of orthophosphate species present in the water in the free and complexed form.

Since the free orthophosphate species is utilized by phytoplankton and macrophytes preferentially, a useful information about the availability of this nutrient can be implied.

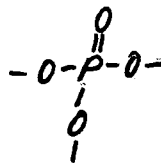
The primary productivity in most inland waters is more-less determined by their phosphorus content [1]. The role of phosphorus as limiting nutrient in the lake was convincingly demonstrated by Schindler's whole-lake experiments [1]. The objective of this paper is to examine inorganic reactions of phosphorus, which together with biochemical reactions control the dynamics and availability of this element in the lake [2]. Attention is given to complexation of iron by orthophosphates and to the adsorption of orthophosphates on solid surfaces in freshwaters with lower pH values.

Two pH values were chosen, for which the distribution of complexed species was determined. The higher pH, 6.5 is an average value for surface samples of 214 monitored Precambrian Shield Lakes, reported in OME report [3]. The lower value, 4.5, represents the pH of acidified lakes from the same geographic area and was reported for a number of softwater lakes. Another reason for choice of such relatively low value was the fact that the magnitude of iron-phosphate complexes increases with decreasing pH. At higher pH, phosphates are unable to compete with hydroxide ion and hydrolysis of iron takes place to a greater extent.

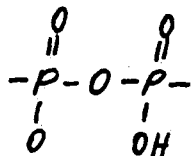
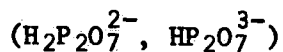
In order to establish the distribution of iron-phosphate complexes the simplified approach was taken. The presence of organic and inorganic ligands other than phosphates was not considered. Neither was the presence of cations other than iron taken into consideration. It has been established that cations such as  $\text{Ca}^{2+}$  have a competitive effect on  $\text{Fe}_{\text{III}}$  complex formation. If ligands other than phosphates are present in the system, the concentration of total dissolved iron will be higher than that estimated by the equation (1). To determine the distribution of all the species present in the system, all the involved equilibria have to be considered and a computer program REDEQL can be used.

Dissolved phosphorus is present in the water column in several forms:

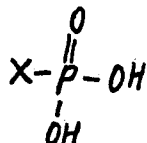
- 1) orthophosphates ( $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ )



- 2) inorganic condensed phosphates



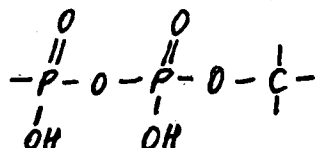
3) organic orthophosphates



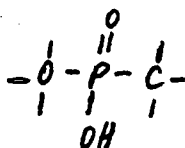
X = RO...sugar phosphates  
inositol phosphates  
phospholipids

X = RNH..phosphoramidates

4) organic condensed phosphates (ATP)

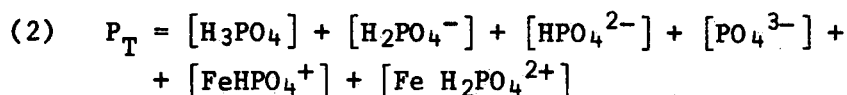
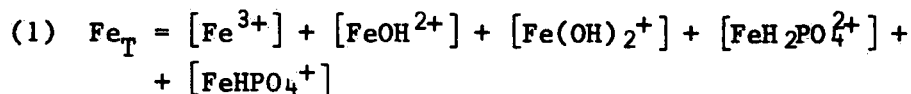


5) organic phosphonates (Aminophosphonic acids).

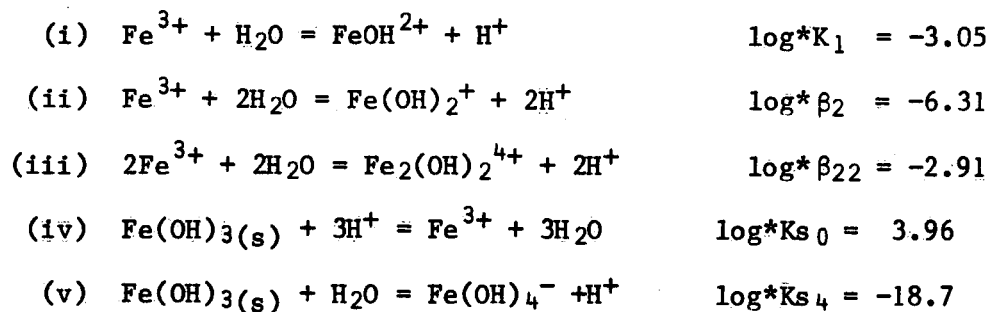


For the purpose of this study, average value for soluble phosphorus from [3], equal to  $1.5 \mu\text{g P/l} = 10^{-7.3} \text{M}$  was used. This value was rounded to  $10^{-8} \text{M}$  and considered as total orthophosphate concentration  $P_T$ , which is used in further calculations.

The following concentration conditions for Fe and P species must be fulfilled:



Assuming that the concentration of dissolved iron is controlled by the solubility of amorphous  $Fe(OH)_3(s)$ , at any given pH, concentration of different hydrolyzed iron species and free iron can be determined. The equilibria under consideration (at 25°C, I=0) are:



Equations (vi) to (x) are used to calculate the species distribution and the results are plotted in Fig. I.

$$(vi) \quad \log [FeOH^{2+}] = \log^*K_{s0} + \log K_1 + 2 \log [H^+] \\ \text{slope} + 2$$

$$(vii) \quad \log [Fe(OH)_2^+] = \log^*K_{s0} + \log^*\beta_2 + \log [H^+] \\ \text{slope} + 1$$

$$(viii) \quad \log [Fe_2(OH)_2^{4+}] = 2 \log^*K_{s0} + \log^*\beta_{22} + 4 \log [H^+]$$

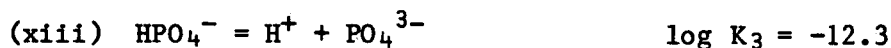
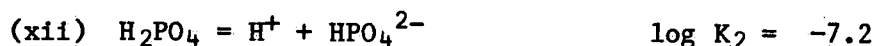
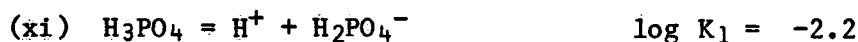
$$(ix) \log [Fe^{3+}] = \log *K_{s0} + 3 \log [H^+]$$

$$(x) \log [Fe(OH)_4^-] = \log *K_{s4} - \log [H^+]$$

(slopes of equations (viii) to (x): +4, +3, -1)

Similarly, at any given pH, concentration of orthophosphate species  $[H_3PO_4]$ ,  $[H_2PO_4^-]$ ,  $[HPO_4^{2-}]$ ,  $[PO_4^{3-}]$  can be determined. Both, graphical and numerical method of determination of orthophosphate species are presented here. The graphical method is illustrated in Fig. 2.

The equilibria under considerations at 25°C, I = 0 are:



$$\text{at pH} = pK_1 \quad [H_3PO_4] = [H_2PO_4^-] = P_T/2$$

$$\text{at pH} = pK_2 \quad [H_2PO_4^-] = [HPO_4^{2-}] = P_T/2$$

$$\text{at pH} = pK_3 \quad [HPO_4^{2-}] = [PO_4^{3-}] = P_T/2$$

$$\text{For pH} \ll pK_1 \quad [H_3PO_4] = \frac{P_T [H^+]}{K_1 + [H^+]} = P_T$$

slope  $H_3PO_4$  vs. pH is 0, since the value of  $K_1$  in denominator is much smaller than value of  $[H^+]$  and can therefore be neglected.

$$[H_2PO_4^-] = \frac{P_T K_1}{K_1 + [H^+]}$$



Similarly here the value  $K_1$  in denominator can be neglected and the slope of  $[H_2PO_4^-]$  vs. pH is + 1 ( $\log[H_2PO_4^-] = \log P_T + pH - pK_1$ ). Analogous calculations can be carried out in the interval  $pK_1 < pH < pK_2$ . In this interval the slope of  $H_3PO_4$  vs. pH is -1

$$[H_3PO_4] = \frac{P_T [H^+]}{K_1 + [H^+]}$$

since in this region  $[H^+]$  is much smaller than  $K_1$  and can therefore be neglected in the denominator. The slope of these species vs. pH is given by the equation:  $\log [H_3PO_4] = \log P_T - pH + pK_1$

$$[H_2PO_4^-] = P_T$$

$[HPO_4^{2-}]$  is determined from:

$$[HPO_4^{2-}] = \frac{P_T K_2}{K_2 + [H^+]} \text{ neglecting } K_2 \text{ in the denominator}$$

(since  $K_2 \ll [H^+]$ ) obtaining the equation:

$\log [HPO_4^{2-}] = \log P_T + pK_2 + pH$ . The slope of  $HPO_4^{2-}$  vs. pH is +1.

The concentration of the orthophosphate species in the remaining pH range can be derived in the same manner.

In the numerical method the following expressions were used to determine the distribution of orthophosphate species:

$$\begin{array}{ll} (4) \text{ [H}_3\text{PO}_4] = \alpha_0 P_T & (6) \text{ [HPO}_4^{2-}] = \alpha_2 P_T \\ (5) \text{ [H}_2\text{PO}_4^-] = \alpha_1 P_T & (7) \text{ [PO}_4^{3-}] = \alpha_3 P_T \end{array}$$

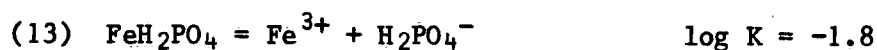
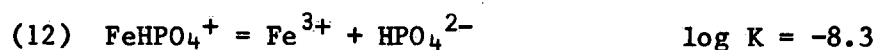
$\alpha_0$ ,  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  are ionization fractions given by the following equations:

$$\begin{array}{ll} (8) \alpha_0 = \frac{[\text{H}^+]^3}{[\text{H}^+]^3 + [\text{H}^+]^2 K_1 + [\text{H}^+] K_1 K_2 + K_1 K_2 K_3} \\ (9) \alpha_1 = \frac{[\text{H}^+]^2 K_1}{\text{Den.}} \\ (10) \alpha_2 = \frac{[\text{H}^+] K_1 K_2}{\text{Den.}} \\ (11) \alpha_3 = \frac{K_1 K_2 K_3}{\text{Den.}} \end{array}$$

The values of different ionization fractions with corresponding pH values are tabulated in Table (1). Concentration of orthophosphate species for few selected pH values at concentration  $P_T = 10^{-7.5} \text{ M}$  and  $P_T = 10^{-8} \text{ M}$  are presented in Table (2).

It should be noticed that  $[\text{PO}_4^{3-}]$  values are not presented here, since at the pH range of most natural freshwaters, the

concentration of  $[\text{PO}_4^{3-}]$  is negligible. For this reason, the term  $[\text{PO}_4^{3-}]$  in equation (2) can be neglected. Using values from Table (2) and values of  $[\text{Fe}^{3+}]$  estimated from Figure (1), the concentration of iron phosphate species at any particulate pH can be calculated from the following equilibrium conditions:



$$\text{where } K = \frac{[\text{Fe}^{3+}][\text{HPO}_4^{2-}]}{[\text{FeHPO}_4^+]} \quad (14)$$

$$K = \frac{[\text{Fe}^{3+}][\text{H}_2\text{PO}_4^-]}{[\text{FeH}_2\text{PO}_4^{2+}]} \quad (15)$$

The concentrations of hydrated iron species as well as iron-phosphate species, calculated for  $P_T = 10^{-8} \text{M}$ , using equations (14) and (15) are given in Table (3).

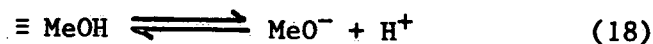
The obtained results indicate that magnitude of complexing among phosphate species decreases with decreasing of ionic charge. This is in agreement with findings of Kester and Pytkowicz [4,5].

It is also obvious that the extent of complexation of various forms of phosphorus and iron depends on the pH and on the relative concentration of both elements in the water.

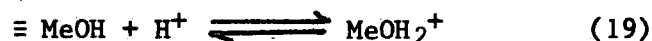
Removal of phosphorus in natural waters takes place by precipitation and by sorption onto electrically charged surfaces of solids. It was estimated that under aerobic conditions, the rate of phosphorus removal to the lake sediments is between 25% - 50% of the input load [1]. Sorption of phosphates is an important factor in controlling the concentration of phosphorus in the water column. It takes place on the surfaces of clays, freshly precipitated hydrated iron and aluminum oxides, which are suspended in the water and gradually settle to the bottom. At the pH conditions of natural waters under consideration most iron and aluminum hydroxides have positively charged surfaces on which negatively charged phosphate species get adsorbed. The development of the pH dependent surface charge of Al or Fe oxides may be visualized as surface hydrolysis of the metal. This reaction produces hydroxylated surface, which is schematically represented in Figure (3).

The surface MeOH group can develop a charge by:

(a) amphoteric dissociation (equivalent to desorption of  $H^+$ )



or by (b) hydrolysis (equivalent to adsorption of  $H^+$ ) [6]



On the surfaces of metal oxides, competition exists for available coordinating sites between protons and the metal ions. The adsorption of cations leads to release of protons from the surface, while adsorption of anions leads to release of  $OH^-$ . The sorption of protonated ligands may be accompanied by deprotonation of the ligand at the surface and with the shift of isoelectric point to lower pH values. Adsorption of  $H_2PO_4^-$  is a good example of ligand deprotonation:



The relation between coordination in solution and coordination at oxide surfaces indicates that a positive correlation exists between the stability of complexes in solution and the stability of complexes at the surfaces.

Following generalization, concerning the adsorption of anions on hydrated metal oxides can be applied, according to Balistieri and Murray [7], to the adsorption of phosphates on hydrated iron oxides:

1. There is a narrow range of pH, where adsorption increases from near 0% to 100%. This pH range is called the adsorption edge.
2. Adsorption of anions, in this case, orthophosphates, is inversely related to the pH, and is accompanied by the uptake of protons or release of  $\text{OH}^-$  ions.
3. The surface sites of oxides can be thought of as ligands and adsorption of ions can be imagined as formation of complexes. The significant difference is the formation of pH dependent electrical double layer at the oxide solution interface, which can significantly effect the adsorption process.

In summary, although the complex formation involving phosphate and iron effects the distribution of iron more significantly at the lower pH than at the higher pH, the concentration of iron-phosphate complexes is very low. The  $\text{Fe}(\text{OH})_2^+$  species remains the largest portion of soluble iron, even at this relatively low pH values.

The negatively charged phosphate species are removed from the soluble phase by sorption on positively charged surfaces of iron and aluminum oxides and on the surfaces of clay minerals. The process

of sorption is favored by decreasing of the pH values. Ligands other than phosphates compete for available coordinating surface sites and changes in their concentration effect the quantities of adsorbed phosphates.

#### **ACKNOWLEDGEMENTS**

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7. Balistieri, L.S., T.W. Murray. *Geochim. Cosmochim. Acta*, 46, 1253-1265, (1982).

Table (1). Ionization fractions as a function of pH for orthophosphate system.

pH	$\alpha_0$	$\alpha_1$	$\alpha_2$	$\alpha_3$
2	0.631335	0.38686		
2.2	0.49999	0.49999		
2.4	0.386859	0.63130		
3.0	0.136799	0.863146		
3.5	0.047717	0.95029	0.0001899	
4.0	0.01559	0.98378	0.0006207	
4.5	0.004976	0.99304	0.0019813	
5.0	0.001572	0.992167	0.006260	
5.5	0.00049114	0.97995	0.195623	
6.0	0.0001490	0.940508	0.0593420	
6.5	$5.4 \times 10^{-4}$	0.863145	0.1367994	$1.722 \times 10^{-7}$
7.0	$9.717 \times 10^{-6}$	0.613129	0.386856	
7.2	$5.0 \times 10^{-6}$	0.49999	0.49999	
7.5	$1.67 \times 10^{-6}$	0.333856	0.666131	
8.0	$2.168 \times 10^{-7}$	0.1368009	0.863155	
8.5	$2.39 \times 10^{-8}$	0.0477195	0.952129	0.0001509
		0.155939	0.9839129	0.0004931
		0.004979	0.993446	0.001574
		0.001574	0.993446	0.004979
		0.000493	0.983912	0.0155939
		0.0001509	0.952129	0.0477196
			0.8631557	0.1368009
			0.666132	0.3338570
			0.49999	0.49999
			0.38686	0.6131356

Table (2). Concentration of phosphate species for  $P_T = 10^{-7.5} \text{ M}$  and  $P_T = 10^{-8} \text{ M}$ .

$[H^+]$	$P_T = 10^{-7.5} \text{ M}$			$P_T = 10^{-8} \text{ M}$		
	$[H_3PO_4]$	$[H_2PO_4^-]$	$[HPO_4^{2-}]$	$[H_3PO_4]$	$[H_2PO_4^-]$	$[HPO_4^{2-}]$
$10^{-4.5}$	$10^{-9.81}$	$10^{-7.50}$	$10^{-10.20}$	$10^{-10.30}$	$10^{-8.00}$	$10^{-10.70}$
$10^{-6.5}$	$10^{-11.77}$	$10^{-7.56}$	$10^{-8.43}$	$10^{-11.26}$	$10^{-8.06}$	$10^{-8.86}$
$10^{-7}$	$10^{-12.51}$	$10^{-7.71}$	$10^{-7.91}$	$10^{-13.01}$	$10^{-8.21}$	$10^{-8.41}$
$10^{-8.5}$	$10^{-15.12}$	$10^{-8.82}$	$10^{-7.52}$	$10^{-15.62}$	$10^{-9.32}$	$10^{-8.02}$

Table (3). Concentration of different iron complexes.

pH	$[Fe^{3+}]$ from Fig. I	$[FeOH^{2+}]$ from Fig. I	$[Fe(OH)_2^+]$ from Fig. I	$[FeHPO_4^+]$ calculated	$[FeH_2PO_4^{2+}]$ calculated
4.5	$10^{-9.5}$	$10^{-7.8}$	$10^{-6.9}$	$10^{-11.9}$	$10^{-15.7}$
6.5	$10^{-15.2}$	$10^{-11.5}$	$10^{-8.9}$	$10^{-15.76}$	$10^{-21.46}$



Figure 1. Solubility of amorphous  $\text{Fe}(\text{OH})_3$  as a function of hydrogen in concentration.

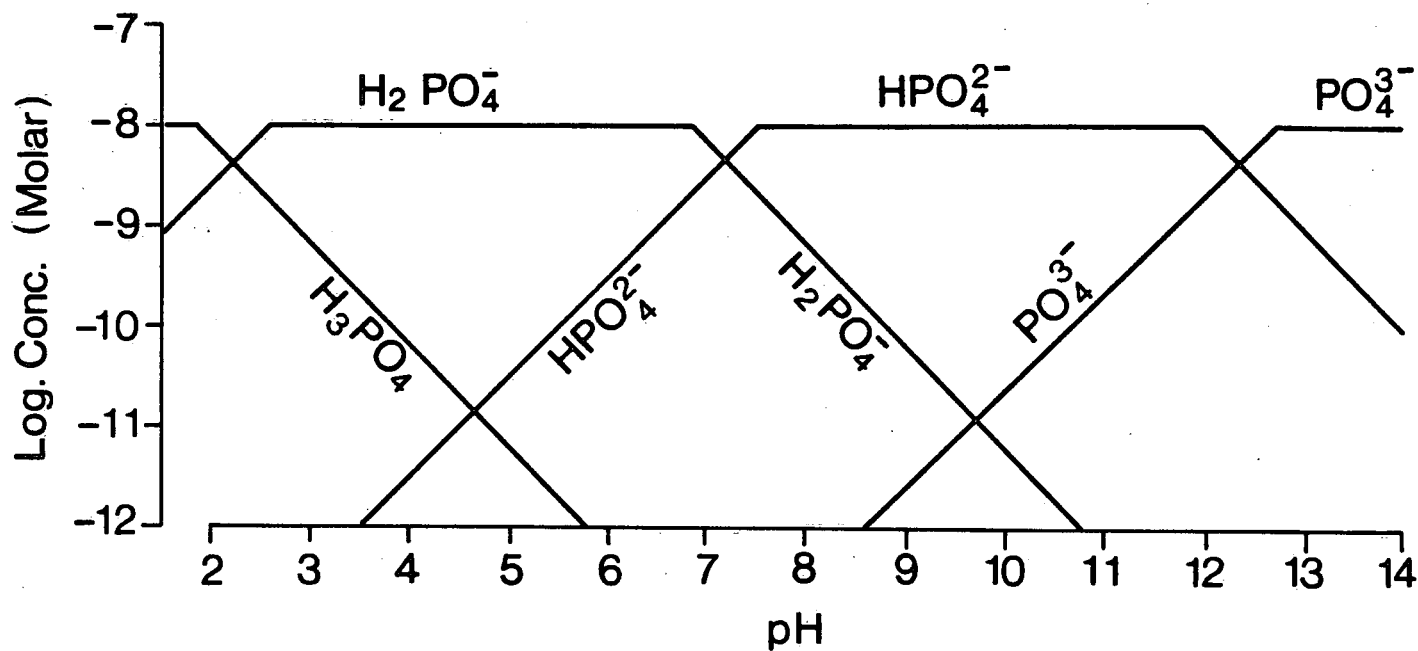


Figure 2. Distribution of phosphate species in aqueous system (total phosphate concentration in the water  $P_t = 10^{-8} \text{ M}$ ).

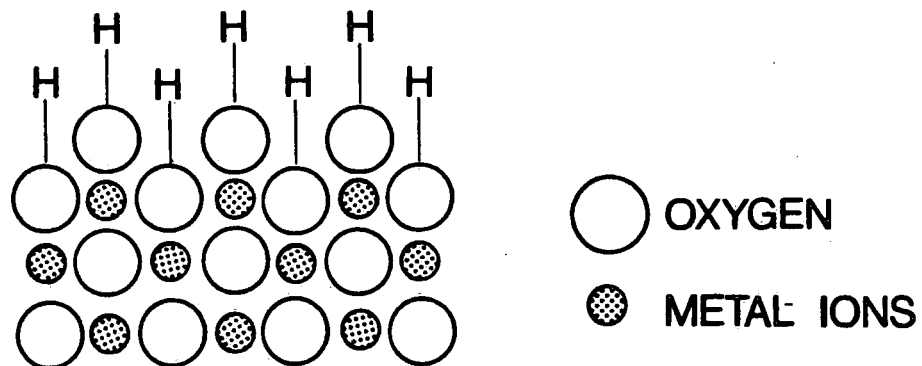


Figure 3. Schematic representation of the surface layer of a metal oxide (after Stumm and Morgan).



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