

Mechanism and Retention of Phosphorus in Sediment: A Review

Bijendra Kumar*¹ and Anshumali²

^{1,2}Department of Environmental Science and Engineering, Indian School of Mines, Dhanbad-826004, Jharkhand, India
E-mail: ¹bijendra2k8@gmail.com

Abstract—This paper gives a general overview of the nature and important mechanisms behind internal loading of phosphorus (P), which is a phenomenon appearing frequently in shallow, eutrophic lakes upon a reduction of the external loading. Lake water quality is therefore not improved as expected. The P release originates from a pool accumulated in the sediment when the external loading was high. In most lake sediments, P bound to redox-sensitive iron compounds or P fixed in more or less labile organic forms constitute major fractions form that are potentially mobile and eventually may be released to the lake water. The duration of the recovery period following P loading reduction depends on the loading history, but it may last for decades in lakes with a high sediment P accumulation. During the phase of recovery, both the duration and net P release rates from the sediment seem to decline progressively. However, an important prerequisite for achieving long-term benefits to water quality is a sufficient reduction of the external P loading.

Keywords: lake recovery, sediment, phosphorus release, phosphorus fractionation, restoration

1. INTRODUCTION

Nutrients, and in particular phosphorus (P) availability, have long been recognized as a factor of paramount importance for the water quality of lakes [1, 2, 3, 4, 5]. If P loading is excessive, phytoplankton is favored and this has significant negative implications for the overall water quality and biodiversity of the lake: the water becomes turbid, toxic algae may develop, submerged macrophytes disappear, fish stocks change toward less desirable species, and top down control by zooplankton on phytoplankton decreases. To reverse the eutrophication process, multiple measures have been introduced worldwide during the last 50 years with the aim to reduce the external loading of lakes, both at point sources by establishing sewage works and by reducing the nutrient loading from arable soils [6, 7, and 8]. Improved nutrient removal and catchment retention have also been achieved through the establishment of new wetlands or re-meandering of channelized streams [7, 9, and 10]. Although some lakes respond rapidly to changes in external P loading [11], lake recovery following a reduction of external loading is often delayed [12, 13, and 14]. Accumulated P in the sediment during the period of high loading equilibrates with the new and reduced loading and is released into the lake water [11,

12, 15, and 16]. This internal loading can be so significant that it prevents improvements in water quality and the lake may thus not meet the established water quality criteria [17, 18] despite a reduction of the P-loading to a level where improvements were expected. Originally, mainly stratified lakes, which develop an anoxic hypolimnion during summer, were believed to suffer from internal P loading due to the redox-dependent release of iron-bound P [19, 20, 21, 22, and 23]. In contrast, well-oxidized conditions throughout the water column and throughout the season in shallow lakes were believed to always establish an oxidized layer in the surface sediment that prevented P release. Later, numerous studies showed that sediments also release P if the overlying water is aerobic [22, 24, 25, 26] and that P released from the sediment of shallow lakes can constitute a substantial part of the total loading and sometimes even exceeds the external loading of P [16, 27, 28]. As a further difference to deep lakes, the sediment of shallow lakes may be in direct contact with the photic zone during the whole season that, together with a higher sediment surface per volume of water as water depth decreases, increases the importance of sediment–water interactions particularly in shallow lakes. The regular mixing regime in shallow lakes guarantees stable and near optimum conditions for primary production [29]. In this review we discuss the retention and release mechanisms of P in shallow, temperate lakes and illustrate it with results obtained from our own work in Danish, mainly shallow and eutrophic, lakes. In many of the lakes the external loading of P recently has been reduced but internal loading from the sediment constitutes a severe problem when trying to improve lake water quality.

2. RETENTION OF PHOSPHORUS

P enters the lake in either a particulate form, which can be directly deposited in the sediment, or as dissolved phosphate, which can be incorporated in organic matter by primary producers that eventually sink to the bottom in an organic form. Sedimentation may also occur via co precipitation with calcium carbonate [30, 31, 32, and 33] or the formation of and adsorption by iron-hydroxides [32, 34, 35, 36, and 37]. During early diagenesis, most of the sedimenting particulate P may be

redissolved [38]. The retention of P is lake specific. Lakes with a high flushing rate tend to have a lower relative P retention than lakes with a slower flushing rate. This relationship has been demonstrated through different simple, empirically established steady-state models of the Vollenweider type: $P_{\text{lake}} = LP / (z^*(\sigma + \rho w))$, relating in-lake P (P_{lake}) to specific loading (LP), sedimentary loss (σ), lake mean depth (z), and flushing rate (ρw) [39, 40]. Sedimentation rate can be estimated on the basis of observed empirical relationships with hydraulic retention time. As these models are based on systems in equilibrium, however, they cannot adequately describe the transient phase following a loading reduction before a new equilibrium is established. This is illustrated by the discrepancy often seen between measured and calculated annual P retention in eutrophic lakes in recovery [16, 41]. Attempts have been made to extend the Vollenweider models with simple models for P retention in lake sediment [28], or more or less complex dynamic models that attempt to describe the kinetics of the numerous physical, chemical, and biological processes determining sediment release [42, 43, 44, 45]. When above this ratio internal P loading may be prevented by keeping the surface sediment oxidized [46].

3. FORMS OF PHOSPHORUS IN THE SEDIMENT

Fixation of P in the sediment depends on the transport of soluble phosphate between solid components, adsorption-desorption mechanisms, chemisorption, and biological assimilation [47]. Chemisorption is the chemical fixation of soluble compounds that are subsequently unaffected by changes in solute concentrations, whereas adsorption is a physical fixation of soluble compounds on surfaces in constant equilibrium with solute concentrations. Ad- and chemisorption processes often depend on both pH and the redox potential and are therefore influenced by the bacterial metabolism. Fractionation schemes using different methods of chemical sequential extractions have been widely used in order to describe the many different forms in which P can be found in the sediment [48, 49, 50, and 51]. The inorganic forms are often bound to iron, aluminum and calcium compounds or to clay minerals [22, 52]. The organic P occurs in more or less labile forms or in a refractory form that is not released during mineralization and constitutes a fraction permanently buried in the sediment. It can be debated which type of sediment P the different fractionations actually measure [53, 54], but fractionation schemes usually yield operationally defined fractions [53]. The reason for fractionating and studying P forms in the sediment is usually to allow a more precise description of the potentials for P release from the sediment and to predict its future influence on lake water concentrations [55, 56]. Particularly loosely sorbed organic and inorganic fractions as well as the iron-bound and redox-sensitive sorption of P are considered potentially mobile, which may contribute to an internal release [22, 57, 58, 59, 60, and 61]. Total P release rates have been found to be

closely correlated to the iron-bound P components in the sediment [62]. Due to inadequate knowledge of the mechanisms behind internal loading in shallow lakes [63, 64], however, it has been difficult thus far to establish general relationships between simple lake or sediment characteristics, including different sediment P forms and the intensity and duration of internal loading. Such knowledge may provide information on the overall and long-term conditions for P sorption expected to prevail in the sediment, whereas knowledge of static P binding gives only limited insight into the changes of P forms released under dynamic conditions.

4. RELEASE MECHANISMS

The exchange of P between water and sediment is influenced by many factors. These include biological (e.g., bacterial activity, mineralization processes, and bioturbation), chemical (e.g., redox conditions, pH, iron ratio, nitrate availability), and physical factors (e.g., resuspension and sediment mixing) [22, 25, 28, 64, 65, 66, 67, 68]. Overall, the net release of P observed from sediment is the difference between the downward flux caused mainly by sedimentation of particles continuously produced in the water column (algae, detritus) and the upward flux and gross release of P driven by the decomposition of organic matter and the P gradients and transport mechanisms established in the sediment. Laboratory experiments often demonstrate high release rates compared to in situ or mass balance calculations because the downward flux via sedimentation is excluded. The significance of gross release vs. net release can be observed in lakes during periods with clear water and low sedimentation rates. The interstitial water of the sediment that normally contains less than 1% of the sediment's total P pool is important for the P transport between sediment and water. Interstitial phosphate constitutes the direct link to the water phase above and the solid-liquid phase boundary between water and sediment [22, 69]. An upward transport of P is created via a diffusion-mediated concentration gradient, normally appearing just below the sediment surface. Bioturbation from benthic invertebrates or through gas bubbles produced in deeper sediment layers during the microbial decomposition of organic matter may significantly enhance the process [63, 70, 71, and 72]. Benthic invertebrates can also have a negative effect on P release by supplying oxic water into the sediment and increasing the depth of the oxidized layer [22]. Wind-induced resuspension may significantly affect the sediment P release, particularly in shallow lakes. In very shallow lakes, resuspension events increase, more or less continuously, the contact between sediment and water [73, 74], and particulate nutrients settling to the bottom are most probably resuspended several times before long-term burial [75]. In some lakes, year-to-year variation in internal P loading has been shown to be largely controlled by wind mixing [76]. Potentially, resuspension of sediment can both reduce and increase the sediment P release because the overall process depends on the actual equilibrium conditions between sediment and water [67, 75, and 77].

Submerged macrophytes, which particularly in shallow lakes may become abundant and the plant-filled volume consequently high, may also influence the P cycle both negatively and positively. Oxygen released from the roots can increase the redox-sensitive P sorption to iron compounds [78, 79] and high abundance of macrophytes may diminish the resuspension rate and decrease P release from the sediment [80, 81]. Increased P release may be recorded in dense macrophyte beds and beneath macrophyte canopies due to low oxygen concentrations [82, 83].

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