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Review

Determination of phosphorus in natural waters: A historical review



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HIGHLIGHTS

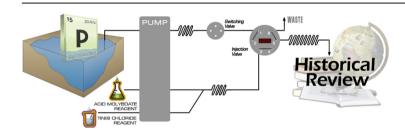
- Historical review of the determination of phosphorus in natural waters.
- Sampling and sample treatment procedures summarised.
- Analytical methods for dissolved reactive phosphorus discussed.
- Analytical methods for total and total dissolved phosphorus described.
- Phosphorus speciation considered.

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G R A P H I C A L A B S T R A C T



ABSTRACT

The aim of this paper is to introduce a virtual special issue that reviews the development of analytical approaches to the determination of phosphorus species in natural waters. The focus is on sampling and sample treatment, analytical methods and quality assurance of the data. The export of phosphorus from anthropogenic activities (from diffuse and point sources) can result in increased primary production and eutrophication, and potentially the seasonal development of toxic algal blooms, which can significantly impact on water quality. Therefore the quantification of phosphorus species in natural waters provides important baseline data for studying aquatic phosphorus biogeochemistry, assessing ecosystem health and monitoring compliance with legislation.

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1. Phosphorus biogeochemistry

Phosphorus (P) is an essential nutrient element that is used by all living organisms for growth and energy transport [1] and is often the limiting nutrient for primary production in terrestrial and aquatic ecosystems [2–4]. The terrestrial environment is a major P reservoir, with $8.4 \times 10^8 - 40 \times 10^8$ Tg in sediments, 96,000-200,000 Tg in soils (<60 cm deep) and 2600-3000 Tg in terrestrial biota [5]. In the aquatic environment the major reservoirs are the surface (0-300 m) ocean (2700 Tg), the deep (300-3000 m) ocean (87,000 Tg) and oceanic biota (50-140 Tg). The atmospheric environment is a relatively small reservoir (0.03 Tg) [5] but can be an important source for oligotrophic ecosystems [6]. The major P fluxes are between marine biota and ocean water, between soil biota and soil, from soil to the surface ocean and erosion/weathering of rocks. A schematic diagram of the aquatic phosphorus cycle, showing the major reservoirs and fluxes, is shown in Fig. 1.

The intensification of agriculture has resulted in a global demand for P of about 22 Tg y^{-1} from mined fossil phosphate resources [7], with minable reserves estimated at 10,000–20,000 Tg [5]. Current agricultural practices give rise to significant impacts on water quality due to P losses to water bodies, e.g. from agricultural

run-off [8], e.g. elevated levels of P can lead to eutrophication [3,9], harmful algal blooms, oxygen depletion and mortality of biota. Population growth and increasing industrialisation are also drivers of elevated P inputs to natural waters [10] from both diffuse and point (e.g. sewage treatment works) sources [11]. This has led to "cultural eutrophication", which is the accelerated anthropogenic enrichment of the environment with nutrients and the concomitant production of undesirable effects [12].

Dissolved inorganic P (DIP), in the form of orthophosphate, is easily utilised by primary producers and is therefore the major bioavailable form of P, but some dissolved organic P (DOP) species can also be utilised [13,14]. The fractionation and speciation of phosphorus are therefore important factors when considering the impact of the element on water quality. In natural waters phosphorus can be found in various "dissolved" forms (operationally defined as the fraction that passes through a 0.2 or 0.45 µm filter [15]), mostly as inorganic orthophosphates and condensed or polyphosphates, but also as organic phosphates (e.g. nucleic acids, proteins, phospholipids, phosphoamides, sugar phosphorus pesticides). "Particulate" P (defined as the fraction retained on a 0.2 or 0.45 µm filter [15]) can include clay and silt-associated organic and inorganic P, precipitates of authigenic origin and P-containing

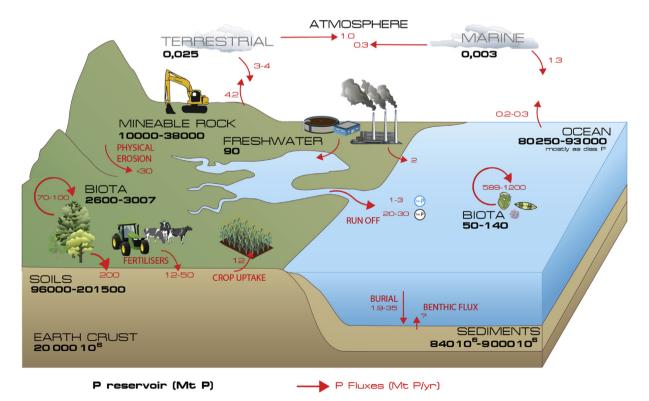


Fig. 1. A schematic diagram of the aquatic phosphorus cycle. Flux and reservoir data obtained from Refs. [5,121,150-158].

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