

Review

# Methods for Sample Collection, Storage, and Analysis of Freshwater Phosphorus

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Received: 17 July 2019; Accepted: 5 September 2019; Published: 11 September 2019



Abstract: Although phosphorus (P) is an essential nutrient for biological productivity, it can cause freshwater degradation when present at fairly low concentrations. Monitoring studies using continuous sampling is crucial for documenting P dynamics in freshwater ecosystems and to reduce the risk of eutrophication. Despite literature updates of developments of the analytical methods for measurement of P species in natural waters, there has been no comprehensive review addressing freshwater sample collection, sample preparation, and sample treatment to fractionate and characterize different forms of P. Therefore, this paper aims to elaborate the different techniques for freshwater sampling and to introduce alternative laboratory methods for sample preservation and P fractionation. The advantages and disadvantages of various sampling techniques, including the traditional manual and the recently developed automatic and passive methods, are presented to highlight the importance of collecting representative freshwater samples. Furthermore, we provide suggestions for sample pretreatment, including filtration, transportation, and storage steps to minimize microbial activity and to maximize the accuracy of measurement of various P fractions. Finally, the most common laboratory methods to measure dissolved and particulate as well as the organic and inorganic freshwater P fractions are efficiently provided. Using this guide, a comprehensive monitoring program of P dynamics in freshwater ecosystems can be developed and applied to improve water quality, particularly of P-rich freshwaters.

**Keywords:** phosphorus; freshwater; P fractionation; automatic and passive methods; sample pretreatment

# 1. Background

Although phosphorus (P) and nitrogen (N) are the main growth-limiting nutrients for algal blooms [1], debates are still ongoing in regard to the relative contribution of these nutrients to eutrophication of different aquatic ecosystems [2]. Natural eutrophication occurs through organic matter (OM) mineralization and oxygen depletion, whereas nutrient enrichment of water bodies by anthropogenic activities is the cause of cultural eutrophication [3,4]. Worldwide, cultural eutrophication is dominant due to continuous fertilization in excess of crop requirements, which is the main nonpoint



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source of P losses to natural waters [5,6]. Most attention has been paid to terrestrial P transport as the main cause of eutrophication [7–9]. Whilst terrestrial P is primarily known to discharge into the water bodies through surface runoff, subsurface leaching may also be important [6,10].

Phosphorus in aquatic environments exists in dissolved inorganic (orthophosphate), condensed or polyphosphate, and organically bound phosphate forms [11,12]. Orthophosphate, the dominant form of dissolved inorganic P, is the main bioavailable P form in aquatic ecosystems and is directly assimilated by bacteria and algae [13]. Nevertheless, it has been well documented that some organisms assimilate P from organic compounds after enzymatic hydrolysis [14,15]. Depending on pH, orthophosphate exists primarily in the oxidized forms of  $H_2PO_4^{-1}$  and  $HPO_4^{-2}$ . Kulaev et al. [16] categorized condensed phosphates into cyclophosphate, polyphosphate, and branched inorganic phosphates (or ultra-phosphate). Phosphate concentration, temperature, pH, presence of hydrolytic enzymes, and colloids and complexing cations may all contribute to degradation of condensed phosphate species [17]. Molecules with both carbon and phosphorus in their structure are referred as organic P forms and exist in nucleic acids, other nucleotides, inositol phosphates, phospholipids, and phosphonates in aquatic environments [18]. Dissolved organic P (DOP) makes a major contribution to total P in freshwaters [19], but extracellular microbial enzymes in soils can convert DOP to dissolved inorganic P through hydrolysis [20].

Because water quality depends on the bioavailable forms of nutrients, laboratory procedures to separate different P fractions are important [12]. Documentation of the dynamics of different P fractions can help to minimize the risks or to protect freshwater ecosystems from eutrophication. Furthermore, identification of sources discharging P into water bodies is also critical. Several analytical methods have been developed to characterize P forms in natural waters [12]. Most methods measure total P using the molybdenum blue method [21], which, in turn, requires first converting of all P forms into orthophosphate. Nevertheless, colorimetric methods may be unable to characterize different species of organic P and particulate inorganic P. To respond to these challenges, spectroscopy-based techniques, including inductively coupled plasma spectroscopy, X-ray absorption near edge structure (XANES) spectroscopy and solution- and solid-state <sup>31</sup>P nuclear magnetic resonance (NMR) methods have been developed and successfully used by several workers [22–24].

# 2. Perspectives

Previous reviews have briefly discussed sample collection and treatment, but they have emphasized the determination of P species in natural waters [12,25]. This work aims to: (1) summarize the pros and cons of different techniques for freshwater sample collection, (2) introduce the most commonly used methods for sample treatment and preservation, and (3) suggest the most analytically robust methods for freshwater P fractionation, including dissolved reactive P (DRP), particulate inorganic P (PIP), dissolved organic P (DOP), and particulate organic P (POP).

Using the methods described in this paper, we can improve understanding of P dynamics in freshwater ecosystems by promoting systematic and standardized approaches to sample collection and preservation for effective analysis of different P fractions. On this basis, environmental strategies can be undertaken to protect water resources, especially in P-rich waters. The steps involved in freshwater monitoring studies with respect to P fractionation are schematically shown in Figure 1.



Figure 1. Diagram of comprehensive freshwater monitoring steps for P.

# 3. Sampling

Sample collection is one of the main complexities in environmental freshwater monitoring. While traditional grab sampling procedures offer spot concentrations, recent techniques using automatic, continuous sample collection may improve the sample representativeness and accuracy of measurements. Sampling procedures must be selected by taking into account human, technical, and financial resources [26]. However, the research objective is also important. In addition to the method of sampling, attention should be paid to location, frequency/time-intervals, and depth of sampling. This section reviews the advantages and disadvantages of the most common sampling techniques for surface runoff, river, leachate, groundwater, lake, and wetland monitoring studies (Table 1).

Type of Sample	Location of Sampling	Frequency of Sampling	Depth of Sampling	Sampling Techniques	Recommended Sampling Techniques
Surface Runoff	- Outflow of residential, industrial, and agricultural catchments - Channel outlet	Based on precipitation or irrigation intensity, time-interval of sampling could vary from seconds to hours	-	- Manual sampling - Automated sampler - Passive sampler - Flow-proportional sampling	- Automated sampler - Passive sampler
Leachate	- Point samples - Tile drains	Based on irrigation or precipitation regime	At different depths of soil profile, depending on research objectives	- Lysimeter - Passive sampler	- Zero-tension lysimeter - Passive sampler
Groundwater	- Point samples on uplands and alluvial settings - Springs	Depending on the purposes of groundwater monitoring studies varying from monthly to annually	Depth of phreatic zone or depth of perched water tables, depending on study goals	- Well - Piezometer - Passive sampler	- Well - Passive sampler
Rivers/Streams	- Upstream - Downstream - River mouth - Optimal location using mathematical models	Usually carried out on weekly, biweekly, monthly, or seasonal basis, depending on research objectives	Usually within top, middle, and bottom of each cross-section of the water column; also in the hyporheic zone; the depth may vary with sampling technique	- Manual sampling - Automated sampler - Piezometer - Passive sampler - Flow-proportional sampling	- Automated sampler - Passive sampler
Lakes/Ponds	- Inlets and outlets, where applicable - Multiple points within the water body	Usually carried out on weekly, biweekly, monthly, or seasonal basis, depending on research objectives	Depending on research objectives	- Manual sampling - Passive sampler	- Manual sampling - Passive sampler
Wetlands/ Estuaries	- Inlet - Outlet - Multiple points within the wetland	Usually carried out on weekly, biweekly, monthly, or seasonal basis, depending on research objectives	Depending on research objectives	- Manual sampling - Water column sampling - Flow-proportional sampling	- Water column sampling - Flow-proportional sampling

# **Table 1.** The most common sampling techniques to collect different aquatic samples.

#### 3.1. Leachate or Soil Solution

In this paper, we consider leachate water as equivalent to the soil solution. On that basis, soil solution refers to the interstitial water with its dissolved solutes, suspended particulate constituents, and dissolved gases [27]. Among environmental monitoring studies, subsurface P mobilization is one the most common, and it is sensitive to sample collection. Researchers have employed various sampling techniques to monitor P leaching in relation to land use, soil features, fertilization and irrigation schemes (Table 1). Often, one of the primary interests of land managers is to equip agricultural lands with tile drains. Although tile drains enhance crop productivity, they might cause degradation of surface and ground waters due to the discharges of nutrients and contaminants [28]. Tile drains can be instrumented with flow meters and water samplers. Therefore, flow-volume can be continuously monitored and flow-integrated drainage samples can be collected [29]. There are, however, questions regarding the accuracy of estimation of flow rate and representativeness of drainage water samples using tile drains in monitoring studies. This is due to the mixing of leachate water by tile drains from different parts of a landscape [30,31].

For lands not equipped with tile drains, other procedures can be used. Lysimeters are the most common method to monitor the subsurface flux of soil nutrients, including P. The literature has mentioned several dates for the first application of lysimeters to collect soil water [32–34]. Indeed, lysimeters have been used to monitor the rate, volume, and chemistry of soil solution or leachate water for over a century. Likewise, several types of lysimeters have been introduced by workers [27,35,36]. The present paper uses the terms "zero-tension" and "tension/suction cup" lysimeters as classified by Fares et al. [37], who have described components, materials, field installation, and mechanisms of lysimeters in detail. In general, collection of leachate water by a suction cup lysimeter is carried out by creating an artificially low pressure potential (suction) in the solution sampler, i.e., at a pressure potential slightly lower than the pressure potential of the soil (Figure 2) [27,37]. Hence, they are probably best to sample static soil water because it is sometimes a challenge to create the right pressure potential at the time water is moving in the soil. Furthermore, tension lysimeters are unable to efficiently capture water preferentially moving through the large and unsaturated pores (e.g., >1 mm diameter) [38]. Zero-tension lysimeters can be used to collect such mobile water under both saturated and unsaturated conditions (Figure 3) [38,39]. When using the tension lysimeters, one cannot use measured solute concentrations for flux calculations because the volume of soil the water is coming from is unknown. For these reasons, zero-tension lysimeters may be preferred to sample mobile soil water [38,39]. It is important to note that an initial cleaning of both suction and zero-tension instruments is required before their installation, particularly for P monitoring. Cleaning procedures often use distilled water along with acid solutions [35,40].

Both zero-tension and suction lysimeters are cost-effective and enable soil water collection from the same spot under the saturated/unsaturated condition at different depths. Nevertheless, their installation may disturb the soil moisture regime and soil hydrological regime [41,42]. Hence, it is recommended to install the lysimeter one year prior to sampling to let the surface of the solution sampler equilibrate with the surrounding soil [27]. Compared with zero-tension lysimeters, suction lysimeters generate higher bubbling pressure, facilitating the collection of soil water in drier months [35]. Zero-tension lysimeters allow one to measure both water volume and concentration, whereas suction lysimeters only allow measurement of the concentrations [40,43]. Since soil is a heterogeneous environment, particularly in terms of preferential flow pathways, these methods can give a rough estimation of distribution and flux of nutrients in soil solution. However, the longer soil water is stored in the sampler, the higher is the chance of P reaction with colloidal Fe and Al oxide minerals in the solution. Therefore, it is recommended to reduce the time of soil water storage in the solution sampler, and to immediately filter the sample following its collection, especially during wet seasons or after irrigation.

Wick lysimeters and passive capillary samplers require no external source of vacuum to extract the soil water [44,45]. In the former, wicks create suction on the overlying soil. The amount of tension is determined by the wick's characteristics in conjunction with the soil properties [37,46]. Similar

to zero-tension lysimeters, a passive capillary sampler collects both macropore and matrix flows, resulting in more representative soil water samples with higher volume [44]. Thus, a passive capillary sampler can estimate the flux of soil water and its solutes with higher accuracy, as shown by several studies [47,48].

A comprehensive monitoring study can incorporate multiple sampling techniques to overcome their individual shortcomings for estimation of mobile P concentrations and fluxes. For instance, leachate volume and P concentrations can be measured via tile drains, zero-tension lysimeters, and passive capillary samplers. Therefore, adopting multiple sampling methods can simultaneously provide information of P concentrations and fluxes at both macro scales (e.g., the entire catchment) and micro scales (e.g., site of sampling).



Figure 2. Components of suction cup lysimeter.



Figure 3. Components of zero-tension lysimeter (adapted from Thompson and Scharf [38]).

#### 3.2. Runoff

Surface runoff refers to overland flow, and it is typically sampled at the edge of a field. Surface runoff is perhaps among the most complicated freshwaters to sample when assessing the mass flux of nutrients. If runoff results from rainfall [49] or irrigation, then rainfall or irrigation intensity plays an important role in selecting the time-interval or frequency of sampling and consequently in monitoring temporal changes of runoff nutrient fluxes. In addition to the rainfall intensity, the gradient or the length of slope can impact the volume of runoff and its content of nutrients and contaminants [50,51]. The use of rainfall simulators and soil flumes allows concurrent assessment of the effects of rainfall intensity and slope gradient on runoff P transportation [52,53]. Soil flumes can be constructed for either indoor or outdoor experimental settings. Outdoors, this technique allows collection of runoff samples at the edges of a field, which, in turn, facilitates the measurement of runoff volumes. Furthermore, using a rainfall simulator allows one to evaluate the impacts of different rainfall intensities under controlled experimental conditions. Used together, rainfall simulators and flumes can demonstrate the impact of agricultural management on runoff P losses rather accurately, and the results can be extrapolated to various scales and shapes of existing landscapes. However, seasonal and monthly changes can also occur in runoff properties (volume, velocity, and P concentrations) in response to changes in precipitation and temperature. Therefore, using a heating apparatus in cold months is necessary to preserve runoff samples and samplers against freezing. In addition, to minimize microbial activities and P mineralization in warm months, it is important to use portable refrigerated samplers.

Although long-term data of annual intensity and distribution of precipitation may help to set a preliminary schedule for a runoff sampling scheme, accurate forecasting is difficult due to unpredictable weather conditions. To facilitate runoff monitoring, therefore, establishment of research stations equipped with sampling instruments and rainfall gauges adjacent to the important catchment outflows is necessary. However, scientific objectives and runoff characteristics (flow volume, turbidity, and concentrations of dissolved and particulate constituents) determine the sampling methods. Several approaches have been developed to collect composite runoff samples [54-56]; the most commonly used are listed in Table 1. Manual grab sampling is the simplest and the cheapest method of runoff collection. However, this method requires on-site, experienced technicians to fill and label the containers as well to filter and store the water samples. Technicians may encounter some dangers, particularly during heavy rains or electrical storms. Furthermore, a rain gauge and flow meter should also be installed at the sampling site to record the rainfall intensity and runoff volume, respectively. Since it is difficult to collect frequent grab samples, particularly during continuous flows, studies have found this method insufficient to obtain time-weighted average concentrations [57,58]. Automated samplers can ease these drawbacks by taking continuous composite samples with off-site recording of rainfall and runoff flow as well as the date and time of sample collection. Sample collection via automated samplers still leads to a storage period that may allow changes in water samples [59]. For example, delay in filtration may lead to reactions of dissolved inorganic P with colloidal Fe and Al minerals in the solution or mineralization of organic P. This issue may partly be reduced through adding acid solutions or microbial inhibitors into the bottles prior to sampling. In addition, an automated sampler is expensive, and the device may fail during sampling. This device needs an expert technician for installation, maintenance, and operation [60]. Although grab sampling may provide preliminary concentrations in base flow, the literature suggests that an automated sampler is the most common and successful technique for runoff monitoring [56,61,62].

To address the complexity of runoff characteristics more accurately, passive samplers have been employed. By definition, passively collected samples represent the net flux or diffusion of a substance or analyte between two media. An analyte diffuses according to its concentration gradient from where it has higher concentration to where it has lower concentration. Diffusion continues until equilibrium is established between the sampled and receiving media [63,64]. Unlike grab and automated sampling techniques, passive samplers do not require expensive equipment, cumbersome site occupations, or on-site technicians for continuous sampling. Several studies have introduced different types of

ell (Figure 4) (Eijkelkamp

passive samplers for runoff collection and analyses [64–66]. SorbiCell (Figure 4) (Eijkelkamp Soil and Water, Municipality of Alkmaar, the Netherlands) is one of the most common passive samplers for runoff monitoring studies due to its capability to collect both polar and non-polar compounds for periods as long as days to months. Furthermore, this device allows one to determine the water volume by releasing a tracer during the sampling period [46,67]. Therefore, it allows one to calculate the flux of solutes. Chemcatcher®(Figure 5a) (T. E Laboratories Ltd, Tullow, Co. Carlow, Ireland) is another type of passive sampler which can monitor nutrients or pollutants in water samples [68,69]. This device enables measurement of time-weighted average concentrations of multiple polar or non-polar compounds (including dissolved forms of P) over periods of weeks by housing multiple sorbent-receiving phases [69,70]. Nevertheless, Chemcatcher®cannot determine the water volume, and subsequently flow-weighted concentrations during the sampling period cannot be calculated. The diffusive gradient in thin-films (DGT) passive sampler (Figure 5b) [71] can also be used for in situ sampling of dissolved solutes in runoff [72,73]. The mechanism of the DGT sampler to remove the compound of interest in water samples is rather similar to that of the Chemcatcher®. This device consists of a filter membrane, a diffusive film of fixed thickness, and a binding gel housed by a plastic holder. A DGT sampler is unable to measure water volume to permit flow-weighted average concentrations of multiple polar or non-polar compounds. For more information about passive samplers, see Vrana et al. [64].

Although the passive samplers discussed in this section permit measurement of in situ concentrations, particularly for compounds with low concentrations [74], some drawbacks remain for using these techniques. First, passive samplers only collect dissolved compounds; hence, these methods are not useful for fractionation studies that include particulate forms, often an important concern for P studies [69]. Second, due to the low rate of sampling, longer periods are required to sample the target analyte, particularly at the fairly low concentrations normally found for P [75]. Third, identification of peak runoff concentrations is missed using passive samplers. This is a particular drawback for P studies, since surface runoff is usually considered to be a major contributor to freshwater P. Finally, these methods may have the highest exposure to solutes of interest during steady water flow, but they may lose the adsorbed P when there are sudden changes in water flow or intensive runoff.

Taking the above-mentioned sampling techniques and their shortcomings into account, an integrated passive sampler with multiple sorbent-receiving phases currently offers the best scheme for monitoring and sampling runoff transport of both polar and non-polar compounds that contain P. To determine the fluxes of P in both solute forms and suspended particulates, deployment of a flow meter at the sampling location is strongly recommended.



Figure 4. Components of a SorbiCell passive sampler.



**Figure 5.** Components of (**a**) Chemcatcher®and (**b**) diffusive gradient in thin-films passive samplers (adapted from Gong et al., [76]).

#### 3.3. Groundwater

Worldwide, groundwater resources are widely used for municipal, agricultural, and industrial purposes. Several methods are available for groundwater sample collection and quality assessment (Table 1). Wells are the simplest method to sample groundwater. The main complexities in well installation include site selection, drilling methods, and borehole construction, which, in turn, require experienced technicians, knowledge of local geological and hydrogeological conditions, and proper tools [77]. It is important to thoroughly clean the equipment prior to drilling. Furthermore, some information about temporal changes in groundwater level is required before well installation.

Depending on the monitoring scheme or frequency of sample collection, the groundwater in or adjacent to the wells should be immediately removed before sampling and samples must be filtered to minimize microbial mineralization of organic P in water that is exposed to air in the borehole. To provide context to the measurement of P forms and concentrations, it is important that total borehole depth, total depth of groundwater, and depth to the groundwater level are measured prior to sampling [77]. Borehole purging and low-flow sampling methods are the two main procedures to ensure the representativeness of groundwater samples. Even after purging the stagnant water from the borehole, repeated sampling is important to determine representative mean concentrations [46].

Groundwater samples may be collected by either pumping from the surface or by lowering collection vessels [78]. However, pumping groundwater can cause changes in the hydraulic flow field that, in turn, can change solute concentrations [79]. To overcome these shortcomings, passive samplers have recently been employed in groundwater monitoring studies [79–81]. As with surface water sampling, passive samplers have advantages over conventional methods in the groundwater context. Because passive sampling is driven by diffusion, it facilitates the collection of solutes in the water without pumping, but it also keeps the groundwater flow regime undisturbed [80]. In addition, groundwater passive sampling is time-integrated monitoring during which sampling can be extended

for long periods. Passive samplers do not need an on-site technician except for deployment and sample retrieval, and the number of measurements and costs of sample collection, preservation, and analyses are reduced [79,82]. Once solutes are trapped on the receiving phase, samplers can be transferred for long distances without changes in sample composition [80]. Drawbacks to deployment of passive samplers are similar to those noted earlier in this paper for other sampling contexts.

The sampling techniques presented here provide information about groundwater quality at the point of sampling. However, groundwater moves in heterogeneous environments. Therefore, flow-integrated sampling techniques may also be necessary to assess overall groundwater quality. In regions of karst bedrock, sampling of karst springs provides an important perspective on the representativeness of groundwater quality assessment from wells in the same way that sampling of tile drains provides understanding of the significance of soil leachates in agricultural settings. Integrated water quality indexes can be monitored in karst environments using grab and automated sampling [83], passive sampling [84], and in situ probes [85].

#### 3.4. Rivers and Streams

A river is a very dynamic ecosystem in terms of biological activities, concentrations of dissolved and particulate constituents, and temporal and spatial variations in water flow and temperature. Sampling location and time schedule are the two main components in river monitoring studies and should be chosen in relation to the dimensions of the river (surface area and depth) and temporal changes in water flow/temperature, respectively. The spatial concentrations of river constituents vary over short and long time intervals of sampling [86,87]. In addition, identification of optimal sampling locations to represent the distribution of nutrients along the whole river is preferred [88,89] compared to the traditional site selection at upstream, downstream, or river mouth locations [87]. Therefore, much attention has been paid to identify the optimal locations using mathematical models [90–92]. In addition, collection of representative and composite samples is also an important goal to consider.

Worldwide, sample collection using manual techniques and automated samplers are the two main sampling methods in river monitoring studies (Table 1). The commonly used method of grab sampling at a single location or at a few locations to represent cross-sectional mean concentration has been shown not to produce temporally or spatially representative concentrations [86,93]. This is due to the inability of fixed-interval grab sampling to capture variations in the flux of nutrients or contaminants [61]. Although it requires more human resources, collection and integration of multiple cross-sectional samples give rise to cross-sectional mean concentrations with higher accuracy [93]. If financial and technical resources allow, automated samplers can be considered, especially for sampling highly turbid discharges caused by heavy rain [94]. However, one should keep in mind that sample collection using automated samplers may delay water filtration, as mentioned earlier in this section. Passive samplers, as discussed in Section 3.2, have recently been used for river monitoring studies [94–96]. As noted earlier, despite their low cost and ease of operation, passive samplers have shortcomings, particularly for highly fluctuating waters such as rivers and streams.

Although most studies of rivers have focused on surface waters, the hyporheic zone has also been monitored for P dynamics [97–99]. The hyporheic zone consists of the water-saturated sediments immediately below the stream or adjacent to the streambank where there is typically a mixture of surface water and groundwater. Biochemical reactions in the hyporheic zone influence the biogeochemistry of the stream or river ecosystem [100]. Due to its inaccessibility and fragility, sampling water in the hyporheic zone can be complicated. Pore water in the sediment might drain out or become mixed with the river water during sample collection. An appropriate sampling technique should not destroy the sediment structure in this zone. One simple method uses a cylindrical core to collect sediments. Although this method is limited in depth and unable to collect very coarse sediments (>10 cm), in situ core freezing using liquid nitrogen helps to capture both fine sediments and pore water [101–104]. However, freezing is costly and difficult to manage in a field situation [105]. Alternatively, pump sampling using installed standpipe wells is a practical, cost-effective alternative for collection of water

samples from this zone (Figure 6) [101]. Piezometers have also been used to sample water in the hyporheic zone and to monitor P dynamics [99,106]. For more details of hyporheic zone sampling, see Biddulph [107].



Figure 6. Pump sampling of hyporheic zone (adapted from Biddulph [107]).

As suggested, a multi-point horizontal and vertical grab sample collection either to estimate cross-sectional mean concentrations or to calculate temporal and spatial nutrient discharge may offer a comprehensive scheme for river monitoring studies. An integrative passive sampler with multiple sorbent phases to receive both polar and non-polar compounds is usually cost-effective to efficiently monitor P transport in rivers. However, automated samplers are recommended during flooding when stream discharges can fluctuate greatly.

# 3.5. Lakes and Ponds

Like rivers, lakes are very complex environments. Therefore, several parameters should be taken into consideration to collect representative samples. Research objectives should be clearly defined, and optimum sampling locations should be chosen accordingly. Furthermore, it is important to estimate the required frequency of sampling, as well as human and technical costs. It has also been shown that the depth and time of sampling influence the determination of total P concentrations in lakes [108]. Vertical variations in TP concentrations can be due to stratified algae and sediments that release phosphate [109]. Furthermore, water temperature can have a major impact on concentrations and distributions of different P forms.

Several protocols have been practiced for lake sampling. Manual grab sampling is the most common technique in lake monitoring studies, providing a snapshot of P concentrations. Although grab sampling cannot accurately estimate the average P concentrations due to the dynamic spatial and temporal changes in lake P status, it can give preliminary information of various P fractions, as mentioned earlier. Composite or integrated sample collection methods can also be chosen according to the monitoring objectives. These methods are categorized as depth-, area-, and time-integrated, combining a series of samples taken at predetermined depth intervals, at a single depth interval but at spatially distributed locations, and at regular time intervals, respectively. Such integrated sample collection methods can produce greater accuracy in the reported average concentrations, but they require on-site personnel and accessible sampling stations. Furthermore, frequent sampling needs immediate filtration, preservation, and transportation to minimize changes in P fractions caused by microbial activity or reaction of freely dissolved P with suspended particles. Alternatively, passive sampling may be valuable in lacustrine studies due to its capability to determine time-weighted average concentrations of contaminants in the lake environment [110]. Using passive samplers, the

spatial and temporal changes in contaminant concentrations, including P, can be monitored with higher accuracy over a longer period of time without need for intensive sample collection and preservation. As noted earlier, however, passive samplers are unsuitable for P fractionation studies. In general, better estimations of temporal and spatial changes in lake P concentrations require monitoring studies that merge both grab and passive samplings protocols.

# 3.6. Wetlands and Estuaries

The literature includes several definitions for wetlands. The most widely used definition identifies wetlands as the transitional lands between terrestrial and aquatic ecosystems where the water table is usually at or near the surface or where the land surface is covered by shallow water and oxygen-free processes prevail [111]. Wetlands primarily support hydrophytes at least periodically, have an undrained hydric soil in their substrate, and are typically covered by shallow water for some period each year. Wetlands may be classified as marshes, swamps, bogs, fens, and peatlands [111]. Wetlands may also be divided according to their substrate into mineral and organic types. Marshes and swamps are of the former type, and bogs and fens belong to the latter type [112].

Similar to other aquatic environments discussed above, clarification of research objectives and an appropriate sampling plan and equipment are required to facilitate wetland management efficiently. When developing the sampling scheme for studies of P or other nutrients, attention should be paid to the biophysical and vegetation characteristics of the wetland as well as to the water regime. Furthermore, variations might occur in the concentrations of different P fractions due to the dynamic nature of the wetland ecosystem, such as seasonal changes in water level, vegetation, anthropogenic activity, and microbial activity. A comprehensive sampling plan should be able to overcome these complexities, providing time-average concentrations of solutes in the water.

In general, sampling takes place at the inlet and outlet of a wetland to determine the mass balance of nutrients or pollutant of interest. Such sampling can indicate whether the wetland acts as a sink or source. For instance, wetlands receiving urban and agricultural storm waters have been shown to remove significant amounts of N and P [113]. In the case of water sampling within a wetland, sampling sites should be chosen across the wetland to ensure the reliability of mean concentrations of P.

Grab sampling is the simplest approach for wetland monitoring studies. In this case, water samples can often be collected approximately 5–10 cm below the water surface using a long-handled dipper [114]. As mentioned earlier, there are challenges to grab sampling. For instance, this method is time-consuming, and it requires on-site human resources. Routine weekly or monthly wetland sample collection using these methods may not provide time-average concentrations, particularly for dynamic wetland waterways [115]. Wetlands with significant water depth are preferably sampled throughout the water column. Depending on the depth of the water, sampling may be conducted using a telescopic dipper or a bailer [116]. Since both chemical (e.g., P) and physical (e.g., temperature) properties of the water column can vary within a wetland with the time of sampling, vegetation, and water depth, selection of suitable sampling locations and depths is a prerequisite. A suitable water column has a minimum 15 cm of standing water in the sampling site. Furthermore, the water sample should be collected at the middle of the water body to avoid atypical results near the inlet or the outlet. Flow-proportional sampling has also been used as an alternative technique to collect composite wetland water samples [117,118]. This approach uses datalogger-controlled pumps to sample water proportional to the corresponding flow rates at both inlets and outlets of wetlands, resulting in volume-weighted composite samples. The use of passive samplers (e.g., SorbiCell, Chemcatcher®, or DGT samplers) in wetland monitoring studies might improve the representativeness of both time- and volume-weighted average P concentrations.

#### 4. Future Perspectives of Freshwater Sampling Techniques

Despite the significant improvement in freshwater P monitoring studies, there are still shortcomings for investigating P dynamics using the current traditional and passive sampling techniques. Overall,

these techniques are rather time consuming and expensive, and they can provide only a snapshot of P concentrations. However, some of these drawbacks might be partly addressed by the development of in situ sensors that allow on-site continuous monitoring and measurements, eliminating the time of sample transportation to the lab [119–122]. Furthermore, in situ spectrophotometer sensors have been used to simultaneously and continuously differentiate dissolved and particulate P fractions through measuring light absorbance at multiple wavelengths in the UV-visible spectrum [122]. Hence, due to their long-term deployment and continuous operation, in situ sensors may be viable alternatives to periodic sampling for measurement of freshwater P concentrations and fluxes [120,122]. However, these techniques may suffer from lower sensitivity and reproducibility for P measurements than the standard, laboratory-based molybdenum blue method [120]. Methods using stable isotope tracers can also measure the concentrations and identify the sources of some soluble or biologically available phosphate fractions in water bodies. Quantification of stable oxygen (O) isotopes (<sup>16</sup>O and <sup>18</sup>O) in dissolved inorganic phosphate (PO<sub>4</sub>) ions has been successfully applied to distinguish between P sources from agricultural runoff and rural sewage [123], to identify the sources of sediment-bound phosphate [124,125], to distinguish the sources of river water P [126] and lake water P [127], and to quantify DRP fluxes and elucidate flow pathways controlling DRP transport to tile drains [128,129]. Both in situ sensors and stable isotope tracers are freshwater analysis techniques that may improve measurements of both P concentrations and fluxes and assessment of freshwater P dynamics.

#### 5. Sample Treatment and Storage

Procedures to preserve water samples through reduction of microbial activities are classified as storage techniques [130]. Although immediate analysis is recommended after water sample collection to minimize microbial activity and to prevent the short-term changes in P fractions, possible failures of sampling or experimental equipment and the distance between the sampling location and laboratory emphasize the importance of sample storage. The literature summarizes several methods to preserve water samples [12,25,131]. Here, we note the significance for water sample preservation and storage in terms of the time of filtration, choice of filter pore size, and cleaning procedures for sample containers, which, in turn, impact the measured concentration of different P fractions.

Before any water sampling for P measurement, it is essential to wash the bottles with ultrapure water, soaked in 10% HCl overnight, and then rinsed again with ultrapure water [132]. For dissolved constituents in natural waters, it is recommended to use polycarbonate or cellulose acetate membrane filters [133]. Although the usual definition of soluble components in natural waters is based on filtration at 0.45  $\mu$ m, filtration through 0.2  $\mu$ m filters is recommended to remove the majority of bacteria and plankton that could influence dissolved P concentrations during the time of storage [134]. Previous studies have shown that freezing the samples is not the best treatment due to the possibility of phosphate and calcite co-precipitation [135]. Storage at 4 °C in the darkness prior to the analysis has, therefore, been recommended [136–138], together with chloroform addition to reduce biological activity. Since the use of chloroform is discouraged due to its toxicological risks, storage at 4 °C after acidification with H<sub>2</sub>SO<sub>4</sub> is preferable. It is also recommended that stored samples (4 °C) should be analyzed within 48 h of sample collection [139,140]. However, acidification with 0.2 M sulfuric acid can also sufficiently minimize biological activity during the storage of water samples.

#### 6. Phosphorus Fractionation and Determination

To understand and predict the fate of P in freshwaters and related sediments, it is often useful to distinguish the forms of P that are present in a water sample. As noted earlier, water samples are normally passed through a 0.45- or 0.2- $\mu$ m cellulose acetate membrane filter as soon after collection as possible. This approach reflects the most commonly used empirical distinction between dissolved and particulate P fractions, and it is the approach we will elaborate here. It is important to note however, that freshwater P fractions associated with particulates can also be studied over a larger range of particle size [141,142]. Thus, P fractions could be classified as dissolved ( $\leq 0.001 \mu$ m), colloidal (0.001–1)

 $\mu$ m), supra-colloidal (1–100  $\mu$ m) and settleable (>100  $\mu$ m). For example, Jarvie et al. [143] studied a river in the United Kingdom that had been affected by industrial discharges and reported that 87% of the organic P present in was in a colloidal form (defined as > 1 kDa and < 0.45  $\mu$ m).

Overall, the analysis of P fractions can proceed on both the complete sample and the dissolved subsample. P associated with particulate, suspended materials may be assessed by the difference in concentrations of the complete and dissolved samples or by analysis of the suspended material on the filter, as described below. In addition to distinguishing between dissolved and suspended or particulate forms of P, organic and inorganic forms may also be of interest. In this section, we summarize methods established to make such distinctions. A more detailed treatment of these analyses has been presented in *Standard Methods for the Examination of Water and Wastewater* [144].

Most methods for phosphorus determination are based on the spectrophotometric detection of a coloured phosphomolybdate complex [12]. For example, the colorimetric malachite green method measures P through formation of a complex of the aromatic amine, malachite green, with phosphorus and molybdate [145]. The molybdate-blue method is the most widely used colorimetric method to determine P [21]. Several reductants can be used to reduce Mo in the complex [146]. Ascorbic acid is the most widely used, and antimony is used to catalyze the reduction of Mo by ascorbic acid. When the Mo in the complex is reduced, the P-molybdate complex turns blue. The absorbance is measured with a spectrophotometer at 880 nm. Colour development in this method is independent of temperature, but the method can be time-consuming and laborious [12]. Furthermore, it may generate significant chemical waste as some reagents are not stable at room temperature for more than 24 hours [147].

# 6.1. Dissolved Reactive P (DRP)

The dissolved forms of P in freshwater samples are typically of major importance. While the molybdate blue method is targeted at orthophosphate species, the acidic conditions of the molybdate-containing reagent may lead to hydrolysis of small amounts of labile polyphosphates. In some circumstances, depending on temperature and concentration ranges, dissolved silica may interfere in the determination of P by molybdate-based methods [148]. Therefore, the term dissolved reactive P (DRP) is a general term for any forms of dissolved P that is determined in the molybdate colorimetric procedure. Of all DRP components, orthophosphate is the most readily bioavailable form of P to aquatic plants, and thus it is often considered the most critical P fraction contributing to accelerated eutrophication of surface waters [149]. Normally, DRP is considered an adequate proxy for such environmentally significant, bioavailable orthophosphate P.

# 6.2. Total Dissolved Reactive P (TDRP)

Total dissolved reactive P (TDRP) includes both inorganic orthophosphate ions and Acid-Hydrolyzable P (AHP), which generally consists of polyphosphates such as hexametaphosphate  $((PO_3)_6^{-3})$ , tripolyphosphate  $(P_3O_{10}^{-5})$ , and pyrophosphate  $(P_2O_7^{-4})$ . Some organic P may also be hydrolyzed in this step. The acid-hydrolyzable forms of P are converted into molybdate-reactive P by boiling with a solution of concentrated sulfuric acid and nitric acid. Then, the concentration of total dissolved reactive P forms is measured using a colorimetric P-molybdate method, and the AHP (largely polyphosphate species) is determined by difference between TDRP and DRP.

# 6.3. Total Dissolved Phosphorus (TDP)

Dissolved P also includes organic forms of P, and organic P species contain P-O-P and C-O-P bonds that need to be broken before colorimetric determinations of P [21]. Total dissolved P (TDP) refers to both inorganic and organic species and is determined after oxidative digestion of the filtered water sample. Several methods have been developed to digest water samples using, for example, acid persulfate (0.4 M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) [150], alkaline persulfate (0.185 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> + 0.375 M NaOH + 0.485 M H<sub>3</sub>BO<sub>3</sub>) [151], and alkaline/acid persulfate (0.15 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> + 0.15 M NaOH) [152]. (For additional digestion methods, see Maher and Woo [131] and Huang and Zhang [153]). Acid persulfate was the

most reliable and accurate digestion method to determine TDP in leachate waters collected from 10 different UK soils [154]. In a more recent study, acid persulfate, alkaline/acid persulfate, and alkaline persulfate methods had total P recoveries of 96.6, 76.1, and 24.5%, respectively, for fresh surface water samples when P was determined by inductively coupled plasma spectrometry (ICP) instead of by colorimetric analysis [22]. However, some drawbacks remain in relation to the determination of released orthophosphate. For example, intermediate products of persulfate may slow color development in the molybdenum blue method, particularly in the acid persulfate procedure [155]. Furthermore, determination of P by the molybdate blue method requires adjustment of acid or alkaline persulfate digests to a neutral pH to accelerate color development. These considerations suggest that ICP determinations of TDP may be advantageous where total P concentrations are high enough to exceed method detection limits.

#### 6.4. Total Particulate P (TPP)

Total particulate P (TPP) is comprised of particulate inorganic P (PIP) and particulate organic P (POP). Despite the importance of TPP in freshwater samples, few methods have been developed to measure this fraction accurately. One alternative is to treat the unfiltered, complete sample using the same digestion methods developed for total dissolved P. Then, P in suspended sediment (particulate P) can be determined by difference between the corresponding fractions. Zhang [156] argued that such TP measurement methods suffer from low recovery of particulate P (PP), and he also mentioned that the widespread use of wet persulfate digestion method has resulted in many underestimated TP measurements. High-temperature ignition or digestion with strong acid [157] has been widely employed by several workers to measure TPP in natural water samples [158,159]. This method was originally developed to determine TP in sediments through high-temperature combustion (550 °C) and extraction with 1 N hydrochloric acid or digestion by sulfuric acid - potassium persulfate at 135 °C [157]. Unfortunately, high-temperature, strong-acid hydrolysis might lead to overestimation of particulate inorganic P (PIP) or underestimation of particulate organic P (POP) through extraction of acid-labile organic P compounds [160,161].

Despite some adaptations of this method, little attention has been paid to the collected particles on the filter [161]. To overcome these shortcomings, a reliable high-temperature combustion method to measure total particulate P in the collected particles on the filter (0.45- or  $0.2-\mu m$ ) should be followed in practice. Among the available methods, the one developed by Solórzano and Sharp [162], a modification of the method of Stockner and Armstrong [163], is the most cited. The modification includes hydrolysis of condensed phosphates in the final mixture using strong acid and heating particularly for low salinity freshwater samples. Labry et al. [161] found this method as the most appropriate one to measure TPP, and others have also used it [164–166]. After the high-temperature digestion of collected particles, the orthophosphate species produced can be measured by colorimetric malachite green or blue colored P-molybdate methods.

#### 6.5. Calculations

Here, we have summarized the most common approaches to calculate different P fractions in freshwater samples from analyses of subsamples of a single water sample. To use the colorimetric molybdate methods, all P compounds should be converted completely into DRP forms by hydrolysis or oxidation treatments. DRP forms are reacted with molybdate to form a coloured complex.

Figure 7 outlines the calculations using the values of dissolved reactive P (DRP), total dissolved reactive P (TDRP), total dissolved P (TDP), and total particulate P (TPP). First, the concentration of each of these fractions of P in freshwater samples is calculated using Equation (1):

$$P_{\text{Con}}\left(\frac{\text{mg}}{\text{L}}\right) = P_{\text{Con}} \text{ in solution } (\text{mg/L}) \times \left(\frac{\text{Total diluted volume } (\text{mL})}{\text{Original sample volume } (\text{mL})}\right)$$
(1)



**Figure 7.** Determination of various organic and inorganic P fractions in freshwater samples (Adapted from Worsfold et al. [12]).

Then PIP, DOP, and POP are calculated as {TDRP – DRP}, {TDP – DRP}, and {TPP – (TDRP – DRP)}, respectively (Figure 7).

Although the analytical methods presented above allow for measurements of organic and inorganic P fractions in freshwater samples with high reproducibility, the need for higher selectivity and lower limits of detection of various organic and inorganic P species may call for using advanced techniques. Worsfold et al. [12] have recently reviewed such methods and have identified the improved techniques as functional speciation. In brief, some organic P species can be differentiated by their reactions with different phosphatase enzymes, and inorganic species may be more finely separated by using ion chromatography or coupling ion chromatography with inductively coupled plasma spectroscopy. Other advanced methods include the in-line photo-oxidation technique developed by Tue-Ngeun et al. [167] to distinguish inorganic and organic P forms using flow-injection analysis. Metal-bound P species (e.g., P adsorbed to or precipitated with Fe oxides, Al oxides, CaCO<sub>3</sub>, or hydroxyapatite) in particulates still cannot be distinguished using the chemical P fractionation methods outlined in this paper. Although these forms are not directly bioavailable, changes in pH and anoxic condition can release P from the particulates or from sediments and cause freshwater degradation [168,169]. Therefore, sequential extractions, using complexing agents (NH<sub>4</sub>F), alkaline (e.g., NaOH) solutions, and acid (e.g., HCl) solutions, may be used to assess metal-bound P species in particulate fractions collected during the initial filtration step. This procedure is similar to the Hedley P fractionation scheme used in soil P investigations [170,171].

# 7. Conclusions

We have attempted to update the most common techniques for sample collection and preparation with respect to freshwater phosphorus (P) fractionation and analysis. This review may help environmentalists to select an appropriate sampling technique for continuous freshwater sample collection in accordance with their research objectives as well as human, technical, and financial resources. Furthermore, one can practically preserve and treat the collected samples to improve the accuracy of P measurements. Finally, we have identified the most rigorous analytical methods to measure different freshwater P fractions with high reproducibility. Methods to minimize sample contamination and secondary chemical reactions while collecting and treating the samples have been presented. The analytical methods described depend on conversion of all P forms into orthophosphate and detection of Malachite green or blue coloured P-molybdate complex by visible spectrophotometry. Nevertheless, to better understand P dynamics in freshwater ecosystems and to recognize the relative contribution of different P species to eutrophication, the sensitivity of some P measurements should be increased, particularly for organic P species. Hence, attention must still be paid to develop low cost and simple techniques for functional detection of P species with high accuracy and quality assurance.

Author Contributions: Investigation, Y.K.K.; B.J.A.; B.H.; and W.H.; Writing—original draft preparation, Y.K.K. and B.J.A.; Writing—review and editing, B.H.; W.H.; A.H.K.; H.G.; and M.L.T.; Supervision, H.G. and M.L.T.

**Funding:** This research was funded by the National Key R&D Program of China (2016YFD0200107 and 2016YFD0300801); the National Natural Science Foundation of China (41877099 and 31328020); and the Science and Technology Major Project of Anhui Province (18030701188).

Conflicts of Interest: The authors declare no conflict of interest.

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