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A simplified procedure for evaluating phosphorus release from construction materials used in green infrastructure

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Abstract. The release of phosphorus from construction materials, including those used in environmental engineering facilities, is an underestimated problem. Improper or accidental selection of materials for systems such as filtration or retention structures may lead to surface water contamination with phosphorus. Therefore, it is recommended to test materials and select those with the lowest potential of phosphorus release in all constructions that come into contact with water and discharge excess water to receivers. The aim of this study was to adopt, refine, and test a method for analyzing phosphorus release from mineral materials of various types and origins. As a result of the research, a simplified procedure for testing materials was proposed, which can be applied in most environmental and chemical laboratories. The procedure developed in this work significantly reduces the consumption of chemicals and the amount of wastewater and waste generated in the material assessment. It can serve as an effective and simple tool for selecting materials for green infrastructure facilities, such as green roofs or rain gardens.

Introduction

Urban water bodies are subjected to substantial pollution from a variety of sources concentrated within relatively small areas. Due to hydrological alterations caused by human activity and climate change, water in urban environments is vulnerable to contamination (McGrane 2016, Miller and Hutchins 2017). Phosphorus pollution in surface waters is a major environmental concern, as it can trigger eutrophication and ecological instability. As nutrient levels rise, algal blooms proliferate, reducing light penetration and leading to diminished growth and die-offs of plants (Chislock et al. 2013). In addition to widely recognized sources of surface water pollution, such as industrial discharges, domestic and municipal sewage and stormwater runoff from urban areas (Müller et al. 2020), green infrastructure (GI) solutions, promoted as city climate change adaptation measures, are gaining importance. GI solutions, including green roofs or rain gardens, have demonstrated hydrological benefits such as runoff retention, delay, and infiltration (Bursztа-Adamiak 2012, Nawaz et al. 2015, Palla et al. 2010, Sharma and Malaviya 2021). However, comparatively less attention has been devoted to discharged water quality. Research conducted across various scientific institutions indicates that green roof runoff may be contaminated with phosphorus and heavy metals (Berndtsson et al. 2006; Cheng et al. 2022; Hachoumi et al. 2021; Karczmarczyk et al. 2018, 2020; Karczmarczyk and Kaminska 2020; Rowe 2011; Santos et al. 2022). Similar investigations into runoff from green roofs and rain gardens were also undertaken in our previous studies (Karczmarczyk et al. 2018 2020; Karczmarczyk and Kaminska 2020). The considerable variability in reported green roof runoff quality is primarily attributed to differences in design and maintenance practices. Czemiel Berndtsson identified key factors influencing green roof runoff quality, including the materials used in construction layers, substrate thickness, drainage type, vegetation selection, maintenance procedures, seasonal biomass uptake, precipitation dynamics, wind direction, local pollution sources, and physio-chemical properties of pollutants. Among these, substrate composition and the application of fertilizers exert the greatest influence on nutrient content in runoff (Czemiel Berndtsson 2010). Other GI solutions, such as constructed wetlands and roof wetlands, are usually regarded as systems that improve runoff quality by enhancing contact between stored rainwater and construction materials over extended periods (Gato-Trinidad et al. 2022). However, unlike filtration-based solutions, rainwater in such facilities stagnates with limited exchange, potentially accelerating quality degradation. Some studies nonetheless highlight the capacity of GI to purify rainwater, emphasizing that performance is highly dependent on the quality of construction materials (Liu et al. 2022).

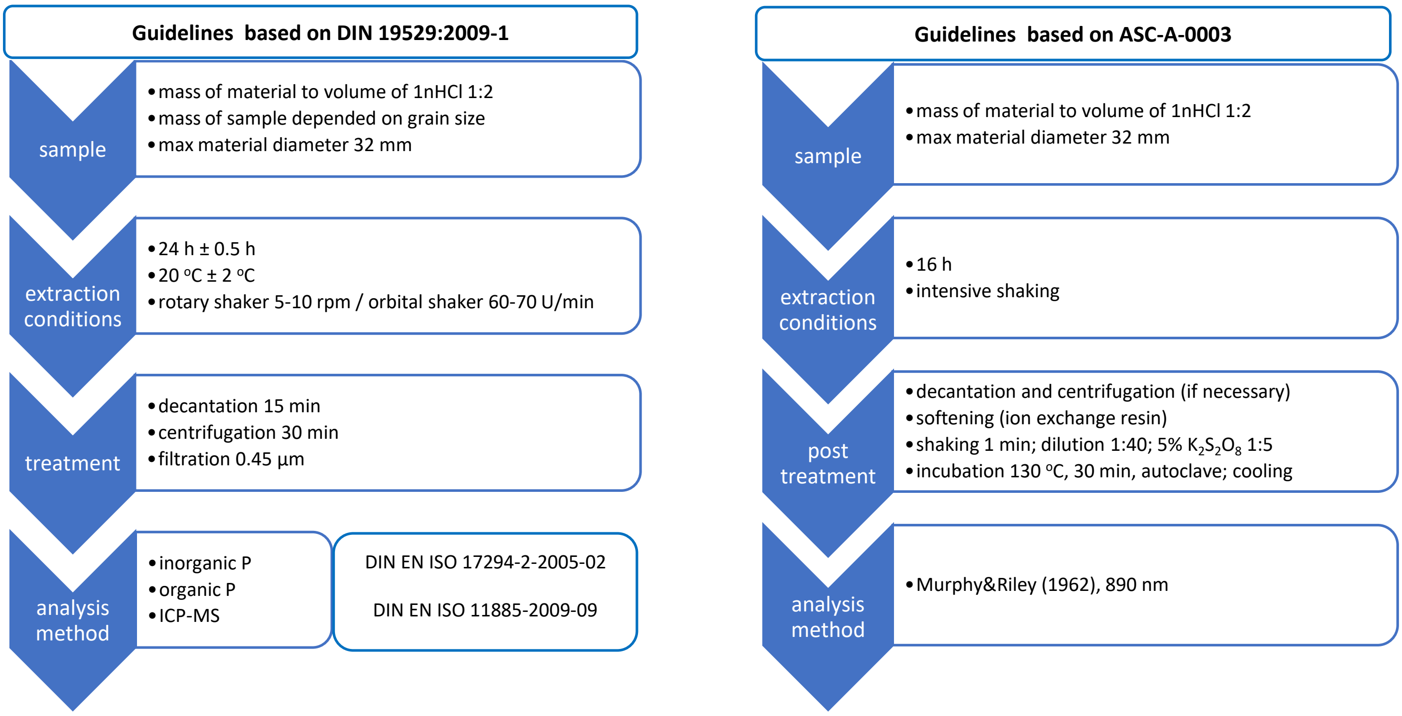

Figure 1. Procedures for testing of materials used in the construction of swimming ponds (ASC-A-0003 2012; DIN 19529:2009-01 2009)

There is scientific evidence showing that construction materials can contribute to the release of phosphorus, making it crucial to assess their suitability for use in systems that are sensitive to phosphorus pollution (Karczmarczyk et al. 2020). Swimming ponds (natural swimming pools) are an example of facilities where phosphorus concentrations is kept at a level 0.01 mg/L to ensure their proper ecological functioning (Walczak et al. 2023). In natural swimming pools, the water treatment avoids the use of chemical methods and is based on the phenomenon of water self-purification and the rhizofiltration capacity of repository macrophytes in the regeneration zone, as well as on typical physical filtering processes (e.g., straining, sedimentation, or flotation). In several European countries, standards governing the construction and operation of natural swimming pools (Fachempfehlung... 2017; FLL 2013; Standardy ... 2014) provide detailed guidelines regarding both facility design and the quality of water for filling up and use. Recommendations for the selection of construction materials in swimming ponds are based on established norms (ASC-A-0003 2012; DIN 19529:2009-01 2009), which also formed the foundation for the development of a more universal and simplified methodology proposed in this study.

The need to simplify currently used methods can be justified by the increasing number of GI solutions being developed as cities adapt to climate change. The universality of these solutions, combined with the increased phosphorus contamination of waters discharged from them (Berndtsson et al. 2006; Cheng et al. 2022; Czemiel Berndtsson 2010; Hachoumi et al. 2021; Karczmarczyk et al. 2018 2020) poses a risk of heightened phosphorus pollution in urban receivers and, consequently, an increase in the contribution of cities to the total phosphorus load discharged into rivers and seas. At the same time, there is growing interest in retaining and collecting rainwater, in which qualitative aspects are also very important (Murat-Błażejewska and Błażejewski 2020). In addition, climate change, even in the temperate zones, is expected to cause water shortages, which will further exacerbate water quality issues in the future.

Therefore, the selection of low P-emission materials for the construction of GI facilities, and the development of tools to support such selection, is crucial. The aim of this study was to adopt, refine, and test a method for assessing the phosphorus release potential (PRP) of mineral materials of various types and origins, which, in contact with water, may act as potential phosphorus sources. The method is universal and suitable for evaluating mineral materials used in P-sensitive water systems in most environmental laboratories, supporting both resource efficiency and environmental protection.

Materials and Methods

Phosphorus is an element that needs to be limited in P-sensitive water systems. Therefore, it is essential to consider the amount of phosphorus introduced by materials used in system construction. While water extracts of materials do not provide such information, phosphorus extracted using hydrochloric acid allows for the assessment of a material's for use in applications such as swimming ponds and natural pools (ASC-A-0003 2012; DIN 19529:2009-01 2009). According to ASC, the hydrochloric acid extraction method can be compared to accelerated weathering, as it registers the phosphates likely to dissolve in an aquatic environment during the first few years (ASC-A-0003 2012). However, this method does not determine the total phosphorus content of the material, which may be significantly higher. A schematic overview of testing procedures used so far for swimming pond construction materials is shown in Figure 1 (ASC-A-0003 2012; DIN 19529:2009-01 2009). These procedures, however, have several important limitations, including restrictions on the maximum diameter of the test material, the need for large sample masses, high volumes of reagents, and requirements for specialized laboratory equipment.

Careful selection of GI components is critical to both the quality of effluent rainwater and the maintenance costs of GI systems. Materials used in various GI applications can be classified into three groups: (i) construction materials (e.g., concrete, wood, plastic, etc.), (ii) filling or filtration materials (e.g., aggregates, substrates, etc.), and (iii) decorative materials (e.g., rocks, stones, gravels, etc.). Aggregates and substrate components used in these structures may originate from either natural or anthropogenic sources. Quantitative phosphorus release from 14 substrates and 29 substrate components of diverse origins has been the subject of previous research (Karczmarczyk et al. 2020). The present work focuses on refining and simplifying testing methods so that they can be used for a wide range of applications in standard environmental laboratories. To this end, a set of assumptions was adopted in line with the principles of sustainable development and circular economy criteria, in particular those aimed at reducing resource consumption, minimizing waste generation, and reducing environmental impact. In essence, the use of tested materials, reagents, chemicals, and clean water, as well as the generation of waste materials and wastewater, should be minimized. These assumptions address not only environmental considerations but also significantly reduce the costs and time of analysis.

Tested materials and used procedures.

The observations and recommendations presented in this paper are based on many years of tests conducted on aggregates of various origins. Most of the results discussed were obtained using quartzite with a particle size of 2-8 mm. However, findings concerning the effects of rinsing, grinding, mixing, and repeated testing on phosphorus release come from experiments involving nearly 50 different materials. Quartzite in the 2-8 mm fraction was used to determine the optimal material mass-to-extractant volume ratio, assess dilution validity, and evaluate contact time. This material was selected based on preliminary tests, with selection criteria including PRP results and high material homogeneity, as indicated by the low variability among replicates. Tests were carried out on quartzite samples weighing 1, 2, 5, 10 20, 30, 50, and 100 g, with material mass-to-1n HCl volume ratios of 1:2, 1:5, 1:10, 1:20, 1:30 and 1:50. However, due to technical constraints and the objective of minimizing chemical use and waste generation, certain combinations of masses and volumes within this range were excluded. The final set of masses and ratios used in the analyses is presented in Table 1.

Following the guidelines of ASC-A-0003 (2012) and DIN 19529:2009-01 (2009), as well as the modification proposed by Sýkora (2015), phosphorus release was analyzed at three extraction times: 1, 16, and 24 h. Phosphorus determination in the extracts after 1 and 16 hours was carried out according to the 1:40 dilution procedure recommended by DIN 19529:2009-01 (2009). For the 24-hour extraction, the influence of dilution on the phosphorus release potential was also assessed due to the larger extract volume obtained. Phosphorus concentrations in the extracts were measured using the ammonium molybdate method on a FIAstar 5000 analyzer, with detection ranges of 0.005 to 1 mgP-PO$_4$/L and 0.1 to 5 mgP-PO$_4$/L. The amount of extracted phosphorus (A), expressed per dry weight of material [mg/kg], was calculated using the following formula (FLL 2013):

$$A = \frac{C*V}{m} \qquad \text{(eq. 1)}$$

where: V – volume of eluent used [L]; m – dry mass of the sample [kg]; C- concentration of phosphorus in the eluate [mg/L].

In order to compare the phosphorus release potential results obtained using the modified method with those derived from the method proposed by Upmeier (2014), 250 g of quartzite was extracted with 1n HCl at a mass-to-volume ratio of 1:2 in triplicate. After 24-hour contact period, the extract was decanted, centrifuged, and filtered, followed by phosphorus determination using the recommended 1:40 dilution. The

Table 1. Volume of 1n HCl used for the assessment of optimal mass to volume ratio and influence of contact time (repetitions not included)

		mass of sample [g]							
		1	**2**	**5**	**10**	**20**	**30**	**50**	**100**
mass to volume ratio m:V [g:mL]	**01:02**	2	4	10	20	40	60	100	200
	01:05	5	10	25	50	100	150	250	
	01:10	10	20	50	100	200			
	01:20	20	40	100	200				
	01:30	30	60	150					
	01:50	50	100	250					

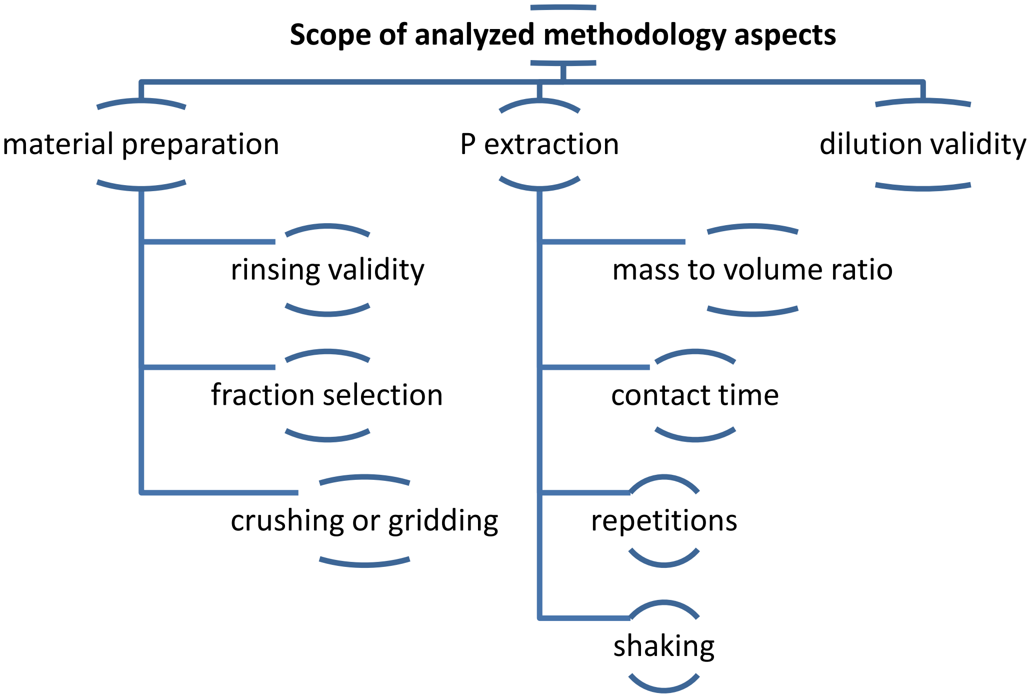

Figure 2. The scope of methodology aspects covered by the study

scope of the methodological aspects included in this study is presented in Figure 2.

The results obtained were subjected to statistical analysis in order to determine correlation between selected parameters, standard deviations, and statistically significant differences between data series. All analyzes were performed using Statistica, ver. 13.3.

Results

Preparation of the material: rinsing validity.

Certain materials, such as gravels, may carry attached impurities. Tests have shown that this is a common occurrence in stones and gravels, which are often used as decorative and filtration components in GI. An important question, therefore, is whether such materials should be rinsed prior to testing. Assuming that the objective of the test is to assess the risk of phosphorus introduced into the water along with the material, it is reasonable to consider the practical conditions of use. If it can be ensured that the material will be rinsed prior to use, it should likewise be rinsed prior to testing. Otherwise, if rinsing is not guaranteed during application, testing should reflect those real-use conditions. In unspecified cases, it is advisable to perform tests in two variants to decide whether rinsing is necessary and should be recommended before application. Washing processes remove fine clay and silt particles from coarser sand and gravel fractions (Hamisi et al. 2019). Inorganic phosphorus concentrations in sand, silt, and clay fractions, based on 77 samples, were reported as 316, 567, and 1237 mg/kg, respectively, while total phosphorus (organic and inorganic) reached 397, 898, and 2024 mg/kg, respectively (Spohn 2020). The effects of rinsing on phosphorus extracted from gravel in this study is shown in Figure 3.

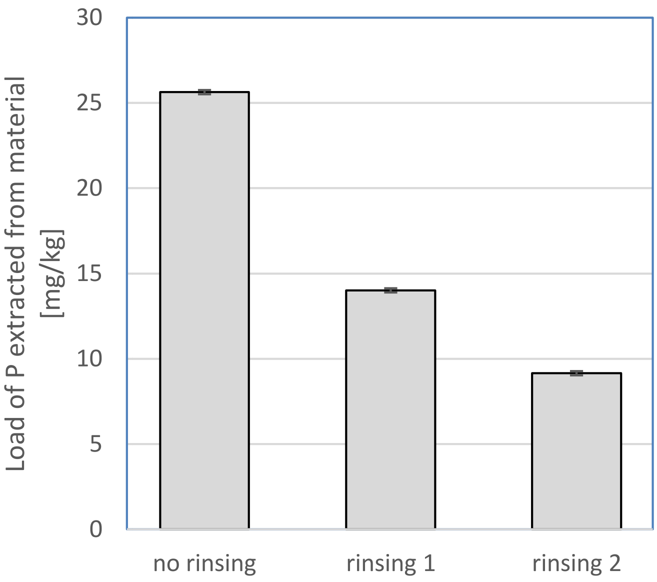

Figure 3. Effect of rinsing of on load of P extracted (gravel example). Bars show standard deviation.

Preparation of the material: fraction selection, grinding, and crushing.

In general, it is recommended to test the material fraction that will be used in practice, as grinding or crushing can affect the amount of phosphorus extracted, as shown in the case of red brick (Figure 4). The DIN standard limits the maximum particle size of tested materials to 32 mm (DIN 19529:2009-01 2009). Materials of considerable size, e.g., large stones, may pose practical challenge and should be tested in their entirety whenever technically feasible. If full-size testing is not possible, and rinsing prior to application is nor expected, it is advisable to assess PRP based on the phosphorus content in wash water obtained from these materials.

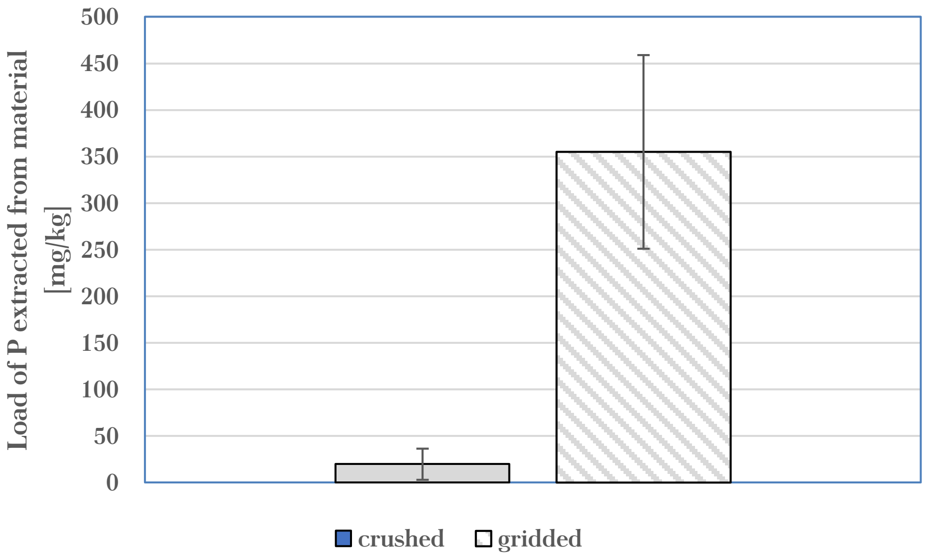

Figure 4. Effect of gridding of on load of extracted phosphorus (red brick example). Bars show standard deviation.

One-step 1n HCl extraction.

Depending on the purpose of extraction and the type of material, phosphorus (P) can be extracted using various methods (Reddy et al., 1998; Richardson and Reddy 2013; Wiegman et al. 2022) resulting in soil P enrichment and changes in vegetation communities. Sequential extraction is necessary when assessing different forms of bound phosphorus, particularly in terms of bioavailability (Wang et al. 2013). However, when the goal is to evaluate the phosphorus release potential, sequential analysis is not necessary because 1nHCl dissolves both weakly and strongly bound fractions by converting polyphosphates and some organophosphates into orthophosphates (Upmeier 2014). Omitting sequential extraction reduces the total extraction time from five to six days (Wang et al. 2013) to a single day, while also significantly decreasing chemicals consumption, waste generation, and the cost of analysis. Accordingly, the one-step extraction method, as recommended by DIN and ASC, was adopted in this study.

Sample mass to eluent volume ratio.

The DIN standard recommends a 1:2 weight-to-volume ratio of the material to 1nHCl solution, noting that this ratio minimizes the risk of dilution effects. Furthermore, these guidelines specify a minimum dry weight of 100 g for analysis (DIN 19529:2009-01 2009). Extracting samples of this size requires large vessels (up to 10 L) and appropriate shakers - rotary for vessels up to 2 L or horizontal for 5 and 10 L containers (FLL 2013; Upmeier 2014) (Table 2). Such equipment is not commonly available in standard environmental laboratories, thereby limiting the number of samples that can be processed simultaneously. The use of large sample masses, and consequently large volumes of acid, substantially increases the environmental impact of the analysis due to high consumption of resources (chemicals, water, and tested material) and the generation of waste (residual material and extract, both analyzed and discarded). An attempt to simplify the DIN method was made by Sýkora (2015), who proposed reducing the sample weight to 15 g (with a material fraction of 11-22 mm) while maintaining the weight-to-volume ratio of 1:2. This adjustment significantly decreased reagent use and was justified based on the extract volume required for analytical procedures (Sýkora 2015). A review of existing and draft standards for determining soluble phosphorus in soil, sludge, and wastes indicates the use of higher weight-to-volume ratios such as 1:5, 1:10, and 1:20 (Janßen 2004).

In this study, for environmental and technical reasons, material samples weighing 1, 2, 5, 10 20, 30, 50, and 100 g were used in batch tests. The results indicated that the 1:2 weight-to-volume ratio recommended by the DIN standard is not always sufficient to provide an adequate extract volume for analysis when using small samples (a few grams). In the case of materials with high water absorption, it was sometimes impossible to obtain a sufficient extract for analysis after the prescribed extraction period. This limitation is also related to the dilution issue discussed later in the paper. Specifically, insufficient extract volume was observed when applying the DIN-recommended 1:40 dilution for a 1g sample at a 1:2 mass-to-volume ratio. In the absence of pre-analysis dilution, insufficient extract volume was also noted for a 1g sample, at a 1:5 ratio, and 2g sample at 1:2 ratio (Table 3).

When determining the appropriate mass-to-volume ratio, it is important to consider how this ratio affects the

Table 2. Recommended weights of tested samples and volume of test vessels depending on aggregate fraction (FLL 2013)

Aggregate fraction [mm]	Weight of the sample [g]	Volume of the test vessel [L]
≤ 2.0	100 ±5.0	0.5
> 2.0÷10.0	250 ±12.5	1.0
>10.0÷16.0	500 ±25.0	2.5
>16.0÷22.4	1000 ±50.0	5.0
>22.4÷32.0	2500 ±125.0	10.0

Table 3. Availability of extract for analysis in case of different mass to volume ratios

	mass of sample [g]								
mass to volume ratio m:V [g:mL]		1	2	5	10	20	30	50	100
	01:02	x	xx	o	o	o	o	o	o
	01:05	xx	o	o	o	o	o	o	
	01:10	o	o	o	o	o			
	01:20	o	o	o	o				
	01:30	o	o	o					
	01:50	o	o	o					

x – insufficient sample volume for analysis using DIN recommended dilution (1:40)
xx – insufficient sample volume for analysis without dilution
o – sufficient amount of sample for analysis by the method used in the work

detectability of phosphorus in the extract. The risk of non-detection is discussed further in the "Extraction Time" section (Table 5). The choice of mas-to-volume ratio may also depend on the particle size of the tested material, particularly in the case of large fractions, where complete immersion in the extractant must be ensured. The use of large-mass samples, as recommended by DIN, is justified by the heterogeneity of materials, as largeer samples provide more averaged results. However, larger samples require greater volumes of acid, which has both economic and environmental implications due to increased consumption and waste generation. In this context, it may be more practical to avoid heterogeneity-related errors by increasing the number of repetitions rather than increasing sample size. Further discussion on the optimal mass-to-volume ratio requires a qualitative comparison with the results obtained for the same material using Uppmeier's method (see: "*Comparison of extraction results using DIN and the modified method*" section).

Repetitions.

The ASC guidelines recommend performing extractions on a minimum of 3 parallel samples. If three results are of the same order of magnitude, or if two are similar and one is lower, the result is considered acceptable. In other cases, the test should be repeated (ASC-A-0003 2012). For naturally occurring materials, which are often high heterogeneous, a larger number

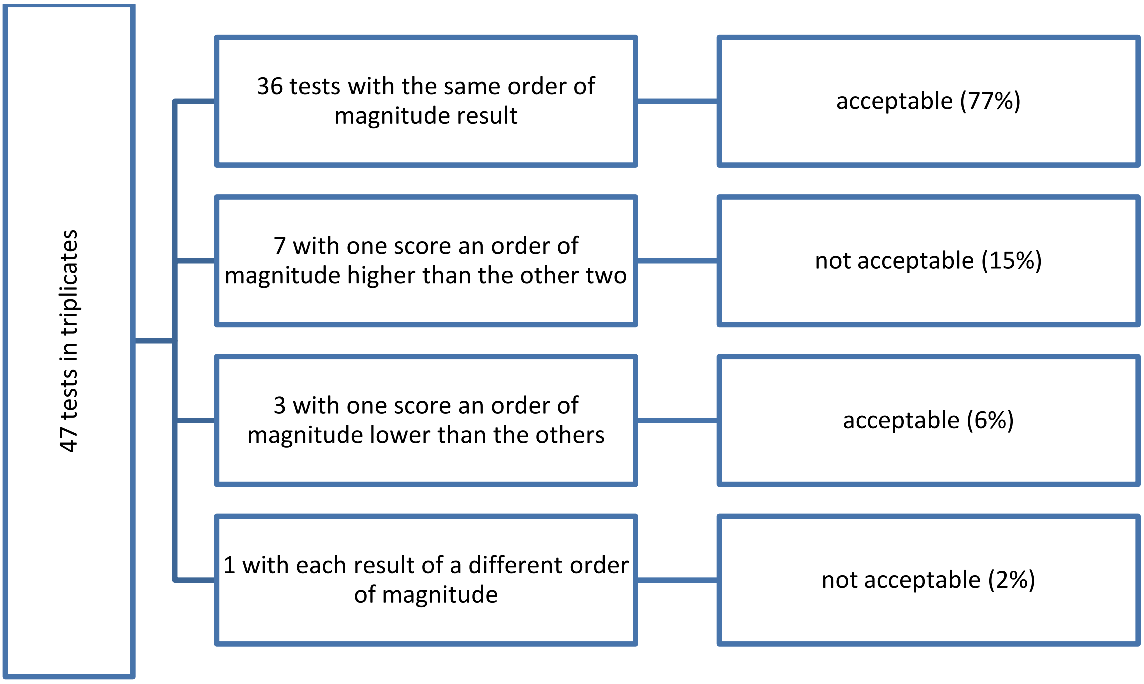

Figure 5. Frequency of achieving an acceptable test result using three replicates

Table 4. Correlation between values of P release potential obtained in different extraction times

Contact time [h]	**1**	**16**	**24**
1	1	0.68	0.69
16		1	0.86
24			1

of replicates may be necessary. Of the 47 tests performed in triplicate on different materials, 36 yielded results of the same order of magnitude; 7 had one result an order of magnitude higher than the other two; 3 had one result an order of magnitude lower than the others; and one test had each result of a different order of magnitude (Figure 5). Consequently, 17% of these tests had to be repeated. For the 14 tests performed in four or more replicates, 50% of the results could be accepted without further verification, while 100% could be accepted after excluding outliers and retaining a minimum of 3 results of the same order of magnitude. For tests involving small sample weights, it may be advisable to perform four replicates. However, adherence to the ASC-A-0003 guidelines with three replicates is also acceptable, albeit with a higher risk of requiring retesting.

Extraction time.

The recommended extraction time is 16 h (ASC-A-0003 2012) or 24 h (DIN 19529:2009-01 2009). Sýkora (2015) made an attempt to shorten the material evaluation process by using a one-hour extraction, obtaining approximately 50% of the phosphorus released after eight hours of extraction. However, this study did not include 16- or 24-hour contact times, making direct comparisons to DIN or ASC-recommended protocols impossible. In the present study, the impact of contact time on the phosphorus release was assessed by taking samples after 1, 16 and 24 h. A strong correlation (r=0.86) was observed between the phosphorus release potential measured at 16 and 24 h. Moderate correlations (r=0.68 and 0.69) were found between the one-hour measurements and those at 16 and 24 hours, respectively (Table 4). Despite these significant statistical correlations, the number of samples in which phosphorus was detected increased with longer extraction times, highlighting the advantage of a 24-hour contact period. Specifically, phosphorus

Table 5. The efficiency of detecting phosphorus in the extract vs. extraction time and mass to volume ratio

	mass of sample [g]								
mass to volume ratio m:V [g: mL]		1	2	5	10	20	30	50	100
	extraction time 1h								
	01:02	x	ND	D	D	ND	ND	ND	ND
	01:05	D	ND	D	ND	ND	ND	ND	
	01:10	D	D	ND	ND	ND			
	01:20	D	D	ND	ND				
	01:30	D	ND	ND					
	01:50	ND	ND	ND					
	extraction time 16h								
mass to volume ratio m:V [g:mL	**01:02**	x	ND	D	D	D	ND	ND	ND
	01:05	D	D	ND	ND	ND	ND	ND	
	01:10	D	D	ND	ND	ND			
	01:20	D	ND	ND	ND				
	01:30	D	ND	ND					
	01:50	ND	ND	ND					
	extraction time 24h								
mass to volume ratio m:V [g:mL	**01:02**	x	ND	D	D	D	D	D	D
	01:05	D	D	D	ND	D	D	D	
	01:10	D	D	D	D	D			
	01:20	D	D	D	D				
	01:30	D	D	D					
	01:50	D	D	D					

x – insufficient sample volume for analysis

D – phosphorus determined in the extract (in min 2 on 3 samples)

ND – phosphorus not determined in the extract

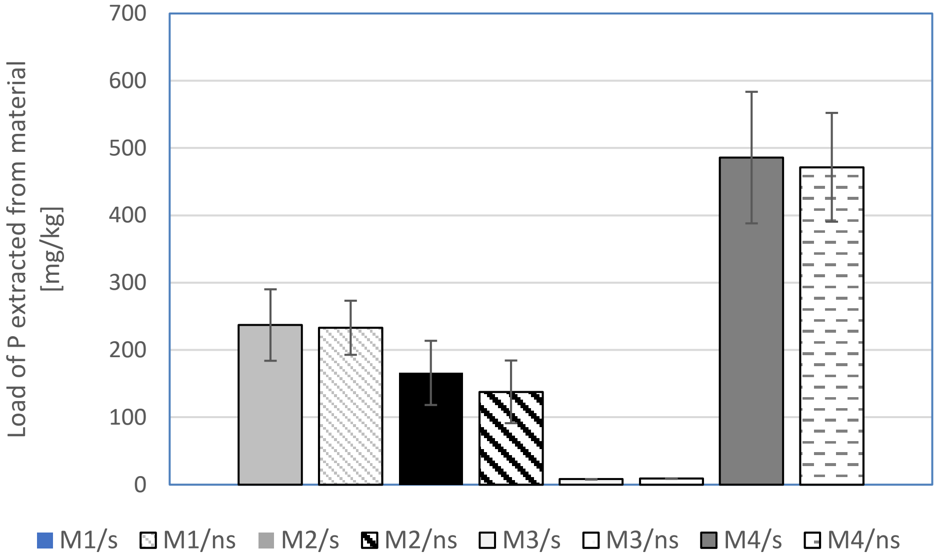

Figure 6. Results of obtained phosphorus release potential from four different materials (M1-4) with (s) and without (ns) shaking. Bars show standard deviation.

was detected in 27 out of 29 samples fter 24 hour, compared to ony 9 samples after 1 hour (Table 5). Using contact times shorter than 24 hours carries the risk of failing to detect phosphorus leaching, even in materials with significant release potential. Furthermore, a 24-hour extraction period is practical, as it aligns well with the daily work schedule of most laboratories.

Shaking/Agitation.

Upmeier recommends using a rotary shaker at 5-10 rpm or a horizontal shaker at 60-70 rpm (Upmeier 2014). In this study, tests were performed using an orbital shaker (PSU-20i) at 70 rpm and under static conditions (without shaking). The results for four different materials, each extracted in parallel under both shaken and static conditions, showed no statistically significant differences in phosphorus extraction (Figure 6). As the results were comparable, it can be concluded that shaking is not necessary for the tested sample masses and mass-to-volume ratios. Omitting shaking represents a significant simplification of the procedure and reduces the time required for testing a large number of materials simultaneously. It should also be noted that magnetic stirrers or similar devices, which could cause mechanical crushing of the sample during mixing, should be avoided.

Analysis of P in the extract.

DIN-based guidelines (Figure 1) recommend determining released phosphorus as either inorganic or organic (Upmeier 2014). Inorganic phosphorus is measured in an extract from a sample dried at 105°C to constant weight, whereas organic phosphorus is calculated as the difference between total phosphorus determined in an extract from a sample calcined at 550°C for 24 h and the inorganic fraction. The preferred analytical method for phosphorus determination is ICP-MS (Upmeier 2014). This approach is particularly suitable for hydrochloric acid extractions of limestone materials, where the reaction produces calcium chloride and carbon dioxide, resulting in high extract salinity. A slightly different and more elaborate procedure is presented in the ASC-based guidelines (Figure 1). This method involves softening the extract by shaking it for 1 min with an ion exchange resin (≥1 eq/kg) in a volume equal to that of the sample, to remove high calcium content that may interfere with the analysis. The softened solution is then diluted in the proportion of 1:40, treated with 5% potassium persulfate solution, and incubated at 130°C for 30 minutes in an autoclave. After cooling, phosphorus is determined using the Murphy and Riley method (ASC-A-0003

Table 6. Highest dilution at which phosphorus was determined in a sample

m:V [g:mL	1	2	5	10	20	30	50	100
01:02	1:40	1:40	1:40	1:5	1:40	1:5	1:5	1:40
01:05	1:40	1:40	1:5	1:5	1:5	1:5	1:5	
01:10	1:40	1:40	1:5	1:5	1:5			
01:20	1:40	1:5	1:5	1:5				
01:30	1:40	1:5	1:3					
01:50	1:5	1:5	1:3					

2012). When using this procedure, it should be noted that a portion of the extract is irretrievably absorbed by the resin. Some samples may also require degassing, e.g., using an ultrasonic cleaner. Direct analysis of the extract without additional treatment provides orthophosphate concentrations, which, in the case of mineral materials, can be compared to established phosphorus limits. The choice of analytical method depends largely on the laboratory's capabilities but should be adapted to the specific material, particularly considering other potential impurities that could interfere with the measurement.

Justification of dilution of samples in a ratio of 1:40.

The results of this research show that the 1:40 extract dilution recommended in the ASC procedure can cause situations where phosphorus concentrations fall below the detection level, even though phosphorus has been released from the material and is physically present in the extract. The highest dilution at which phosphorus was still detected is presented in Table 6. For quartzite, using high dilutions of 1:40 and 1:20 resulted in phosphorus concentrations below detection limit for 18 of the 30 mass-to-volume ratios tested. Dilution may be appropriate when the analytical method requires neutralization of the sample pH or when the phosphorus concentration exceeds the method's measurement range. In other cases, indiscriminate dilution should be avoided. It should also be noted that dilution increases the volume of liquid waste needed for disposal. Conversely, when using ICP-based methods, the low pH of the sample is not only non-interfering but often necessary for accurate analysis, making dilution potentially undesirable. Therefore, any dilution used should be determined based on the analytical method, its range, and laboratory's capabilities.

Interpretation of results / permissible amount of leached phosphorus.

Although the main goal of this study is to develop a method for selecting materials for GI facilities, interpretation of the results required reference to recommendations for swimming ponds, due to the absence of specific guidelines. According to the ASC guidelines, a "worst case scenario" approach is used, assuming that all phosphorus measured by this method during a single season is dissolved and converted into biomass. The guideline assumes that the phosphorus content in biomass is approximately one-thousandth of its mass, for example, 10 g of phosphorus would correspond to an expected biomass of 10 kg (ASC-A-0003 2012). To assess the total phosphorus contribution to the system, the amount of phosphorus extracted from each material [mg/kg] is multiplied by its weight [kg] used in construction. This calculation also accounts for the phosphorus load introduced with the water used to fill the system. For swimming ponds of type I-III (FLL 2013), the recommended phosphorus input should not exceed 0.5 g per cubic meter of water (Table 7).

Czech standards for swimming ponds recommend that the phosphorus introduced with construction materials should not exceed 200 g per 100 m^2 of pond surface or 50 g per 1 m^3 of water. Individual materials with a phosphorus release potential greater than 6 mg/kg are not permitted (Standardy 2014). The FLL guidelines set a stricter limit of 5 mg/kg for bulk materials (> 4 mm) used at the edge and bottom of the pond, as well as decorative materials and filter substrates (FLL 2013). Upmeier provides threshold values for materials based on the release potential of inorganic and organic phosphorus, as summarized in Table 8 (Upmeier 2014). Sýkora (2015) proposes an alternative classification, defining three quality classes for building materials used in backyard ponds, according to the amount of phosphorus released from apatite (Table 9).

Table 7. Sum of extracted P possible to be introduced into a pond with a volume of 100 m^3 depending on the type of pond (ASC-A-0003 2012)

Pond type	For a volume of 100 m³	Unit P
I-III	< 50 g	0.5 g/m³
IV-V	< 10 g	0.1 g/m³
V+	< 1 g	0.01 g/m³

Table 8. Limit values for materials used in swimming ponds construction (Upmeier 2014)

Tested material	inorganic P [mg/kg]	organic P [mg/kg]
suitable	< 2.5	< 0.5
conditionally suitable	< 20	< 5.0
unsuitable	> 20	> 5.0

Table 9. Limit values for materials used in backyard ponds (Sýkora 2015)

Tested material	P [mg/kg]
appropriate	< 15
less suitable	< 30
unsuitable	> 50

The above recommendations were developed for systems with closed water circulation, which are very sensitive to elevated phosphorus concentrations. Consequently, they cannot be directly applied as limits for materials used in flow-through systems, such as green roofs. Nevertheless, to protect receiving water bodies, particularly those located in urban areas, where altered hydrology limits natural self-cleaning capacity, the use of materials with low phosphorus release potential is extremely important.

Previous studies examining the usefulness of determining phosphorus leaching potential using the discussed method for assessing the eutrophication potential of green roof substrates have shown that it can be a useful and recommended test for selecting substrates based on potential phosphorus leaching. Although phosphorus leaching observed in column experiments simulating the first vegetation period of green roof use accounted for only 1.74–2.41% of the total phosphorus content in the substrate estimated by HCl extraction, a good correlation (r = 0.993, p = 0.002) was observed between these values for all five tested fresh substrates (Karczmarczyk et al. 2018). These findings indicate that the method presented here should be considered indicative; the obtained values are suitable for comparing different materials but should not be used to estimate the total phosphorus outflow into water from various structures.

Comparison of extraction results using the DIN and the modified method.

A positive correlation was observed between results obtained according to the DIN guidelines (sample weight of 250 g, mass-to-volume ratio 1:2) and those obtained using a modified method for samples weighing 2 g (r=0.795), 10 g (r=0.822), and 30 g (r=0.979). Correlations were statistically insignificant ($p < 0.05$) for other sample weights. Quantitative comparison of the results showed that samples weighing less than 10 g yielded higher phosphorus leaching values, 20 g samples produced results of the same order of magnitude, and 30 g samples provided quantitatively comparable results to the DIN method (Figure 7). A 30 g sample ensured sufficient extract volume for analysis at a 1:2 mass-to-volume ratio (Table 3), allows detection of leached phosphorus at a 24-hour contact time (Table 5), and is compatible with a 1:5 dilution (Table 6). Based on these findings, a 30 g sample is considered optimal in terms of both analytical reliability and comparability with the method recommended for swimming pond materials.

Sustainability of the estimation of phosphorus release potential.

In the procedure, phosphorus is extracted using hydrochloric acid, a chemical with significant environmental impacts. The production of hydrochloric acid generates substantial emissions due to the large material and energy inputs required (Vahidi and Zhao 2017). Laboratory use of hydrochloric acid can contribute to acidification, chemical waste generation, resource depletion, energy consumption, and air emissions. Although these impacts are typically localized, minimizing them is important for sustainable development. This consideration is particularly relevant in university laboratories, where sustainability is increasingly integrated into research and education. Consequently, in the development of a simplified procedure for determining PRP, special attention was given to reducing the environmental footprint of the tests. A primary objective was to minimize resource consumption and waste generation, achieved by reducing both the sample mass and the volume of solutions used in the tests.

Quartzite in the 2-8 mm fraction, used in most experiments in this study, would require testing according to the DIN procedure on 250 g samples with 500 mL of 1N HCl solution (Table 2). When run in triplicate, this corresponds to a resource input of 750 g of aggregate and 1500 mL of 1n HCl solution (comprising 123 mL of 37% (w/w) hydrochloric acid stock solution and 1377 mL of deionized water), producing an equivalent volume of waste and wastewater for utilization. By contrast, using the mass-to-solution ratio of 1:2 and a sample mass of 30 g recommended in this study, the total solution required to test one sample in triplicate is 180 mL. This represents an 88% reduction in both 1nHCl consumption and material mass requiring disposal after analysis, yielding a positive environmental impact.

Summary of the simplified method for assessment of phosphorus release potential.

In summary, this study demonstrates that the phosphorus release potential (PRP) of mineral aggregates can be determined using small samples of 30 g. Tests should be run in triplicate, which can guarantee acceptable results in over 80% of cases. This efficiency may increase due to the staff experience, knowledge of the aggregate's behavior, and origin. When determining the volume of extractant, both the technical capacity of the laboratory and the weight and particle size of the

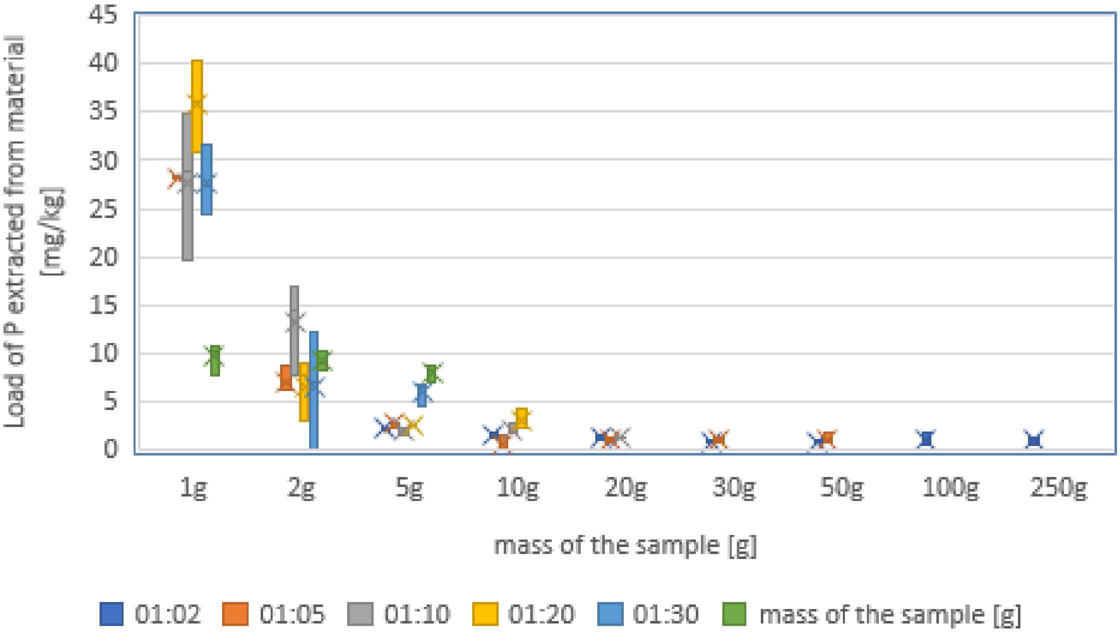

Figure 7. Comparison of test results conducted at different m:V ratios (see legend) and different sample masses.

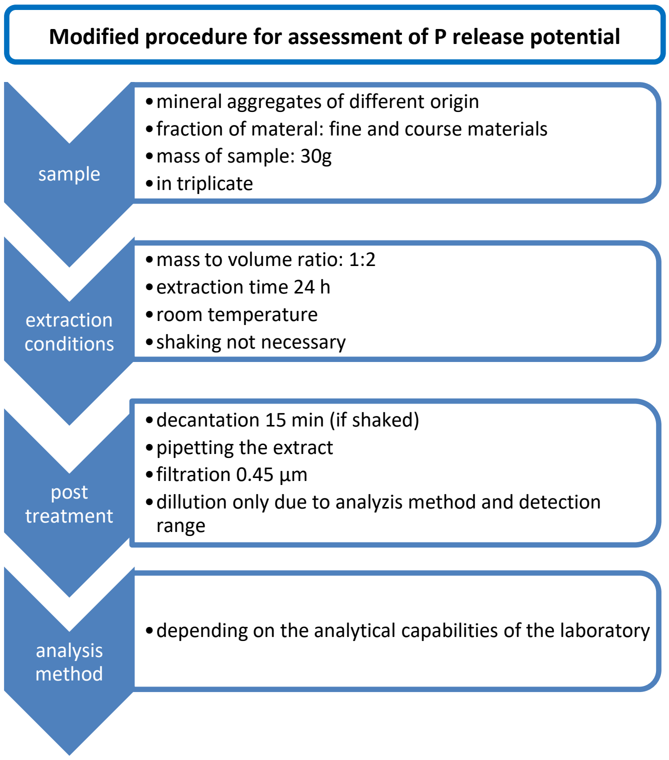

Figure 8. Modified procedure for assessment of P release potential

tested aggregate should be considered. Laboratory capabilities, including available equipment, dictate the extract volume required to measure phosphorus concentration, accounting for repetitions and potential losses due to water absorption, filtration, and other factors. FIA or ICP methods typically require several milliliters of sample per analysis, while older analytical tools may need 5-20 mL. Based on this study, the recommended extract volume for a 1:2 mass-to-volume ratio of is 60 mL, providing a generous safety margin. Using a 30 g sample eliminates problems encountered with smaller samples (1-2 g) in obtaining sufficient extract for analysis. The particle size of the tested aggregate is also important, particularly to ensure complete immersion in the extract, which can be challenging for coarse-grained materials. In specific cases, higher mass-to-volume ratios than 1:2 may be appropriate. The extraction should be carried out for 24 hours, as this duration provides the highest efficiency for phosphorus detection. Shaking of samples is unnecessary, and dilution should be avoided unless dictated by the analytical method, measurement range, or sample pH. It is not recommended to dilute samples unless the method and range of analysis or pH determine it. A graphical overview of the modified method is shown in Figure 8, and the procedure for recording and calculating the results is summarized in Table 10.

Conclusions

The simplified procedure developed in this study can be widely used as a support tool for selecting mineral materials for various applications, including GI. Its major advantage is its feasibility in a standard environmental laboratory, combined with significantly reduced test costs and environmental impact due to the lower sample mass. Reduced material and chemical usage, along with minimized wastewater and solid waste generation, make this method more sustainable.

At the preliminary material preparation stage (rinsing, fraction selection, crushing, or grinding), it is recommended to test the materials in the form in which they will be used in the structure. Providing strict guidelines at this stage is unjustified, as it may substantially influence the impact of the material on the quality of the water it contacts.

Several factors were considered in determining the extraction parameters, including sample mass, mass-to-volume ratio of acid, contact time, the required extract volume for analysis (accounting for water absorption), the need for shaking, the number of repetitions, and the appropriateness of dilution. The aim was to reduce the sample mass while producing results comparable to previously used methods and minimizing the environmental impact. A 30 g sample was identified as optimal, as it can be obtained for most mineral materials (fine and coarse grains) while maintaining a 1:2 mass-to-volume ratio. This ensures sufficient extract for most laboratory phosphorus analysis methods and allows for reduced (previously used 1:40) or no dilution, minimizing dilution errors and increasing the likelihood of phosphorus detection. Dilution may still be appropriate in some cases to address interfering substances or pH constraints. A 24-hour contact time was found to be optimal for phosphorus detection in extracts and is comparable with laboratory workflow logistics. Test should be performed in at least three replicates, applying the ASC acceptance criteria. For highly heterogenous materials, increasing the number of replicates may be justified based on laboratory staff experience. The study also showed that shaking is unnecessary, as differences between shaken and static samples were statistically insignificant, facilitating simultaneous testing of multiple samples without equipment limitations.

Phosphorus values obtained via 1nHCl extraction should be treated as indicative and can be used as a basis for material selection according to FLL limits. The method is also useful for comparing different materials should not be used to

Table 10. Calculation formulae

Name or Number of sample	Mass of sample; m [g]	Volume of 1nHCl; V[L]	Concentration of P; C [mg/L]*	Load of P in extract; L [mg]	P release potential; PRP [mg/kg]
Sample 1	m	V	C	$L = V * C$ (eq. 2)	$PRP = \frac{L}{m} * 1000$ (eq. 3)

*including recalculation due to dilution calculate phosphorus loads in water systems. Previous study (Karczmarczyk et al. 2018) have shown that the values of P loads from extraction tests exceed actual leaching under water-rinsing conditions.

It should be noted that the scope of this work is limited to the laboratory testing phase and does not include the sampling stage. Sampling procedures should be appropriate for the type and origin of material, particularly for natural heterogeneous materials or solid waste used in GI facilities.

Overall, it is crucial to increase the prevalence of testing of mineral materials used in structures and installations in contact with water, in particular those discharging into sensitive receivers. This is particularly important for GI facilities such as green roofs, rain gardens, and constructed wetlands. Uncritical selection of materials for the construction of such systems significantly limits their positive environmental effect, and their holistic assessment should demonstrate the sustainability of such installations. This issue is especially significant when excess rainwater is discharged into sensitive urban water bodies, such as housing estate ponds or watercourses.

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