



Phosphorus quantification in soil using LIBS assisted by laser-induced fluorescence

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ABSTRACT

Quantification and monitoring of phosphorus in soil plays a critical role in environmentally friendly agriculture, especially in mitigation of phosphorus leakages to water systems and subsequent risk for eutrophication. On the other hand, deficiency in phosphorus would lead to problems in development and growth of cultivated crops. Therefore, monitoring and quantification of phosphorus status in soil is essential. In this work, laser-induced breakdown spectroscopy assisted by laser-induced fluorescence (LIBS-LIF) is introduced for quantification of readily soluble phosphorus in soil and compared to the analytical performance of the conventional LIBS method. Mineral soils with variable phosphorus status were used for the analysis. The calibration curves are plotted to evaluate the detection limit of the soluble phosphorus. Compared results demonstrate improvement in detection limit from 3.74 mg/kg to 0.12 mg/kg for clay soil and from 10.94 mg/kg to 0.27 mg/kg for silt loam/loam soil in LIBS and LIBS-LIF measurements, respectively. For the LIBS-LIF measurement, detection limits are comparable with established chemical soil analyses. The proposed method would substantially reduce required sample preparation and laboratory work compared with conventional phosphorus quantification. In addition, as the calibration curves demonstrate that the calibration for soluble phosphorus holds within a soil type, LIBS-LIF has the potential to be used for high throughput soil analysis.

1. Introduction

Anthropogenic nutrient loading to water environments is a cause for eutrophication of aquatic ecosystems which may threaten drinking-water supplies, decrease recreational value of water bodies, and lead to loss of aquatic biodiversity [1]. An example of eutrophied ecosystems is the Baltic Sea that has been suffering from harmful algal blooms and “dead zones”, mainly due to the excessive loading of nutrients, i.e., nitrogen (N) and phosphorus (P) from surrounding catchments [2].

Phosphorus accumulated in agricultural land due to past excessive applications and uneven spreading of animal wastes make major contribution to nutrient loading and subsequent eutrophication of the aquatic ecosystems. This contribution can be controlled by monitoring the soil nutrient content in fields connected via drainage networks to the water bodies. Restricting the fertilizer usage when yields do not benefit from them, increasing recycling and recovery of nutrients from waste sources, timing applications according to plant development stage and critical assessment of the nutrient use in the whole food system, including animal feeds, are necessary to

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improve sustainability of the agricultural sector [3,4]. Further, monitoring of soil phosphorus is a vital step in deciding where to apply fertilizers and enable assessment of the risks for P runoff from agricultural lands [5].

There are several methodologies for quantification of soil phosphorus, including chemical extraction methods that are currently the main approaches for soil analysis [6,7]. Additionally, number of analytical methods have been utilized for soil elemental analysis, such as Inductively Coupled Plasma - Mass Spectroscopy/Atomic Emission Spectroscopy (ICP-MS/AES), X-Ray Fluorescence Spectroscopy (XRF), and Atomic Absorption Spectroscopy (AAS) [8–10]. Use of wet chemistry and the forementioned analytical techniques is time-consuming as they require pre-processing up to solubilization of the sample for the analysis.

Optical spectroscopy, that is an approach capable of handling large sample sets with no or minimal sample preparation and can offer a solution for rapid analysis of soil phosphorus, is an interesting option for high sample throughput phosphorus analysis. Near-Infrared Reflectance Spectroscopy (NIRS) has been applied for soil phosphorus detection. However, it has been noted to be too unreliable [11]. Another optical method for the phosphorus detection is Laser-Induced Breakdown Spectroscopy (LIBS) that offers a rapid micro-destructive contactless elemental analysis. LIBS method is flexible, compact, portable and requires no/minimum sample preparation, making it a good candidate also for on-site applications [12]. It is a semi-quantitative analytical technique in which a laser pulse interacts with the target sample, gas, liquid, or solid, and vaporizes a small fraction of it. The vapor is further excited and ionized leading to the formation of plasma. The cooling plasma plume emits radiation that is characteristic of the elemental content. This radiation is further transported into a spectrometer and detector via an optical fiber and are resolved into a spectrum that contains the elemental information [13]. LIBS has been applied to phosphorus detection in various environmental water [14] and soil samples [15–17]. However, due to the limitations of the technique, such as high limit of detection (LoD), sample matrix effects, self-absorption and self-reversal of spectral lines which can lead to poor accuracy [18], the method has not become common for phosphorus detection in environmental samples. On the other hand, the presence of various elements in soil, such as Si, and Cu [19], makes the choice of analytical technique very crucial as their emission lines are interfering with the phosphorus lines and, hence, with the phosphorus detection.

Several methods are available to improve the LIBS analysis for sensitive and selective elemental detection in soil. In Double Pulse-LIBS (DP-LIBS), two laser pulses are employed for the creation and re-excitation of the plasma. DP-LIBS provides increased sensitivity compared to LIBS with a 2-fold improvement in detection limit of selected elements [20]. Similarly, LIBS assisted by spark discharge (SD-LIBS) can provide improved results to conventional LIBS [21–23]. Furthermore, light elements such as sulphur, carbon, boron, and phosphorus have stronger lines in vacuum ultraviolet (VUV) range [24]. Thus, extension of the spectral range to VUV-LIBS may improve the detection limit [25]. Phosphorus detection has been explored in several matrix such as in geological and biological samples by VUV-LIBS and a combination of VUV and classical UV-NIR LIBS [26,27]. However, VUV-LIBS setup requires a vacuum chamber, gas flow, and a pump system, which makes the setup complicated, therefore, it is not a preferable choice for applications aiming for high sample throughput.

LIBS assisted by laser-induced fluorescence (LIBS-LIF) is a relatively new approach but has shown promising results for quantification of, for example, palladium in rock ore, selenium in water samples, atomic lead and heavy metals in soils [28–32]. Fluorescence is spontaneous emission from a molecule or an atom following an excitation to a higher energy level. In LIF spectroscopy, atoms or molecules are excited by a laser light of a specific wavelength resonant to a selected transition in the target species. The excited state is relaxed typically in order of nanoseconds to a lower energy state emitting a photon characteristic to a transition that occur [33]. Fluorescence measurements provide local and selective information about an individual element or molecule, and the laser-based excitation can result a substantial improvement in signal-to-noise ratio (SNR). A combination of LIBS and LIF techniques establishes the inter-connection between the multi-elemental capability of LIBS and a sensitive selectivity for an individual element of LIF [34,35].

In this work, LIBS-LIF analysis is used for quantification of soil readily soluble phosphorus fraction. Application of LIF to the LIBS analysis has shown significant improvement in phosphorus LoD in different matrices [36,37]. Hence, LIBS-LIF is a promising approach to improve the phosphorus detection limit also in soils where a challenge has been to reach the low detection limits required by regions with low phosphorus content. A set of mineral soil samples with different phosphorus concentrations were analyzed for phosphorus quantification and to obtain calibration curve to compare the analytical performances of conventional LIBS and LIBS-LIF methods.

2. Materials and methodology

2.1. Samples

From a set of 524 soil samples collected as a part of the national soil monitoring program (Valse IV) by Natural Resource Institute Finland (LUKE) [38], 12 different mineral soil samples with variable readily soluble phosphorus content (2–50 mg/kg) were extracted. The soils were classified, based on their texture, to clay soils (>30% clay particles) and other mineral soils (<30% clay; no sandy soils were included). To obtain a relatively even distribution of samples according to P concentrations, varying from moderate to excessive agronomic P status, 6 samples from each of the two soil groups were selected to study.

After sampling, the samples were air dried and ground to pass 2 mm sieve. They were analyzed for readily soluble P using the Finnish national soil analysis [39] involving 1-h end-over-end extraction (1:10 vol/vol) of soil and 0.5 M ammonium acetate-acetic acid solution adjusted to pH 4.65. For the LIBS and LIBS-LIF analysis, the samples were after sieving pressed into pellets using a manual press to obtain a smooth measurement surface.

2.2. Experimental setup

A detailed schematic diagram of experimental setup is illustrated in Fig. 1. The soil samples are ablated by a standard Q-switched Nd:YAG laser (Ultra 100, Quantel), operating at third harmonic wavelength, 355 nm with repetition rate of 10 Hz and pulse duration of 8 ns in atmospheric conditions. The laser output energy is software controlled and is set to 30 mJ per pulse. The laser pulse was guided by a pair of mirrors and focused on the sample surface by a fused silica plano-convex lens with a focal length of 50 mm. LIBS measurements were carried out by analyzing the plasma formed by the Nd:YAG laser. The plasma emission is transmitted via an optical fiber to a Czerny-Turner spectrometer (Kymera 328i, Andor) for analysis. The spectrometer is equipped with an iCCD camera (istar, Andor) for signal detection. For LIBS analysis, the observation window was optimized at gate delay of 300 ns and gate width 2 μ s. For LIBS-LIF analysis, the formation of the laser-induced plasma is spatially and temporally synchronized with another laser pulse produced by another laser equipped with an optical parametric oscillator (OPO) (NT340 Ekspla, 210–2200 nm). A plano-convex lens was used to focus the fluorescence-inducing laser beam 1 cm behind to the plasma formation spot parallel to the sample surface, thus, covering the plasma plume with the exciting laser beam. A sample was placed on a motorized stage to avoid over ablation of the target surface resulting fresh sample surface after every five laser pulses. To minimise the random and systematic errors due to the matrix effect of the sample and variance in shot-to-shot spectra, spectral averaging over 500 shots is performed to improve the precision of the results. The fluorescence emission of phosphorus neutral line at 213.62 nm is used for the phosphorus quantification and it is excited with wavelength of 253.6 nm. There are two phosphorus lines listed in NIST database in the proximity of the 213.6 nm; 213.5465 nm and 213.6182 nm [40]. These are degenerate energy levels and correspond to the same upper energy state. The lines are overlapped and are not resolved with the current LIBS instrument. The LIBS-LIF spectrum is acquired at 57 ns of gate delay, including the trigger propagation and internal device delays, from the fluorescence inducing pulse and with 200 ns of gate width. The optimal inter-pulse delay for phosphorus quantification between the ablating and fluorescence inducing laser pulses was found to be 2 μ s. The fluorescence behavior is further discussed in Section 3.2.

3. Results

3.1. Comparison of LIBS and LIBS-LIF phosphorus spectra

A spectral region without emission features was used to determine the background level and it was subtracted from the obtained spectrum [41]. Background subtracted plasma emission from LIBS and LIBS-LIF measurements on soil collected in the wavelength range 210–225 nm are shown in Fig. 2. The spectra have an accumulation of 500 shots and the measurement parameters for both techniques are independently optimized. It is observed that, in the LIBS signal, Phosphorus line P I (213.6 nm), that is used for the quantification, suffers spectral interference from the iron emission line Fe I (213.85 nm). Finnish soil contains high amounts of iron and, hence, the iron interference is a typical problem in soil LIBS experiments. Additionally, lines P I (213.55 nm), W I (213.56 nm), Cu II (213.6 nm), and Si II (213.64 nm) are in the proximity of the desired phosphorus emission line and may interfere in LIBS experiments [36]. In the LIBS-LIF spectrum, a significant relative enhancement in phosphorus line to other elements can be observed with negligible spectral interference. Similar observation of reduced interference was reported by Yi et al. [35] in the case of lead detection.

For further analysis and method comparison, the phosphorus signals were acquired with the same signal acquisition parameters. The obtained spectra are shown in Fig. 3. The inter-pulse delay between the ablation and the exciting LIF pulse was 2 μ s, gate delay from the LIF laser pulse was 57 ns, and gate width was 200 ns in both cases. To obtain LIBS spectrum, the fluorescence-inducing laser was blocked. The phosphorus signal enhancement of LIBS-LIF is substantial in comparison to the conventional LIBS laser pulse. From these spectra, it can be noted that the used excitation wavelength of 253.6 nm is also resonant to Fe I that leads to enhanced Fe I emission at 216.7 nm. This resonance was reported also by Shen et al. [36]. In addition, increased emission intensity after the LIF

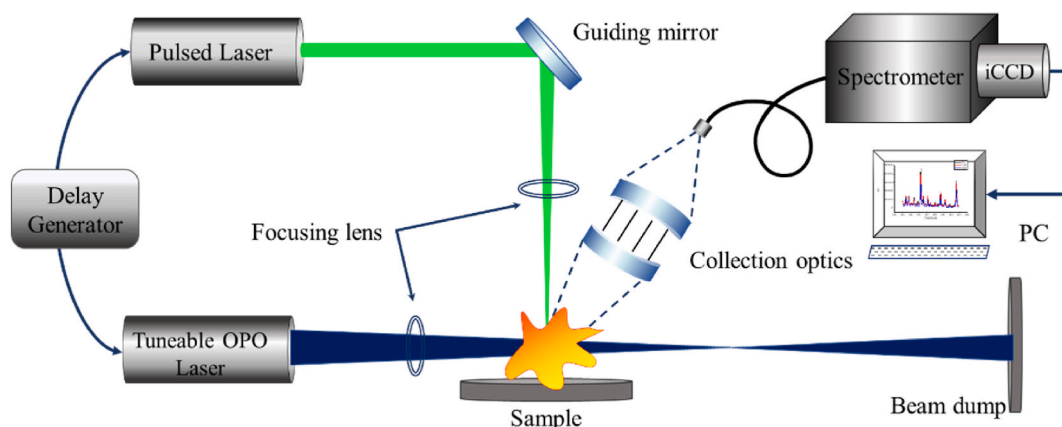


Fig. 1. Schematic diagram of laser-induced fluorescence assisted LIBS.

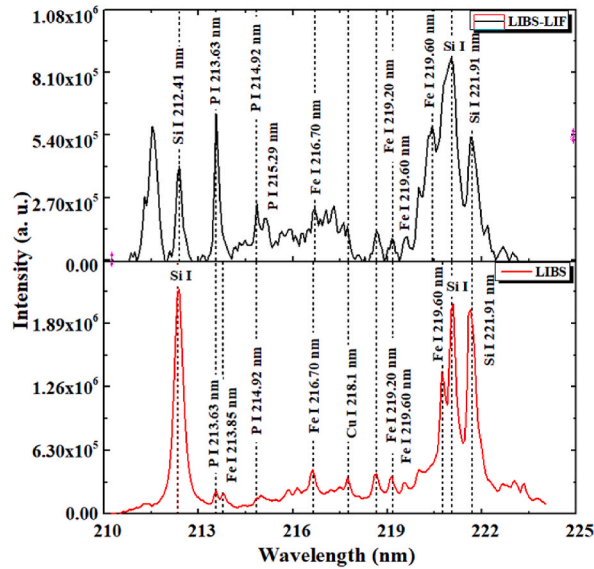


Fig. 2. Comparison of parameter optimized LIBS and LIBS-LIF spectra. Spectra is obtained from clay soil with soluble phosphorus quantity of 7.7 mg/kg. LIBS measurements were performed at a gate delay of 300 ns and gate width of 2 μs while LIBS-LIF were measured at an inter-pulse delay of 2 μs, gate delay of 57 ns relative to the LIF pulse and gate width of 200 ns.

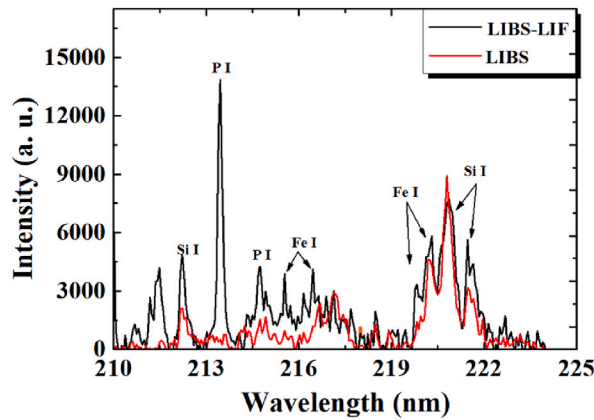


Fig. 3. Comparison of LIBS and LIF-LIBS spectrum at same parameters; gate delay = 2 μs, gate width = 200 ns. Spectra is obtained from silt loam/loam sample of phosphorus quantity of 2.3 mg/kg.

excitation is observed at wavelengths around 211.8 nm. This spectral feature is a result of multiple overlapping emission lines that may be attributed to, e.g., Fe I-II, Co II, and Mn II that all have resonant lines at the proximity of the used excitation wavelength and are present in the soil matrix. The enhancement in the other lines does not cause issues for phosphorus detection and quantification due to the clear separation between the emission lines.

3.2. Influence of measurement parameters to phosphorus fluorescence intensity

The phosphorus emission intensity I_N was evaluated by Trapezoidal method and normalized according to Equation (1) [17];

$$I_N = \frac{I_p}{I_B} * \frac{x}{y} \tag{1}$$

where I_N is the normalized intensity, I_p and I_B are the intensity of emission line and the background, respectively, x and y are the widths of the background and emission-line base respectively. The effect of excitation wavelength to the phosphorus LIF signal intensity is studied by tuning the OPO laser’s emission wavelength across the phosphorus line at 253.6 nm. The phosphorus atoms in the plasma plume are illuminated by the OPO laser operating at 253.6 nm and further the atoms are excited to the upper energy state following a spontaneous emission resulting in fluorescence emission signal at 213.6 nm [36,37]. The fluorescence emission intensity is sensitive to

the wavelength and energy of the fluorescence-inducing laser pulse. The wavelength dependency is shown in Fig. 4, where it is shown that the strong fluorescence emission signal is observed only when the wavelength of OPO laser is tuned to the 253.6 nm that is the resonant wavelength for phosphorus excitation. Some LIF effect was observed in the wavelength range 253.4–253.7 nm where the bandwidth of OPO emission partially overlapped with the phosphorus lines at 253.39 nm and at 253.56 nm.

Acquisition parameters highly affect the LIBS-LIF signal as can be seen in Fig. 5 showing the influence of the gate delay of the iCCD camera with respect to the fluorescence-inducing laser pulse. The optimal gate delay was 57 ns that included the trigger propagation delays in the cables and in the hardware. The gate width was kept at 200 ns. The effect of inter-pulse delay between the ablating and fluorescence-inducing pulses on SNR is illustrated in Fig. 6. The noise level for LIBS-LIF phosphorus line is defined as the standard deviation in 213.6 nm P I line region in the spectrum recorded with 2 μ s gate delay but with LIF inducing laser pulse blocked, i.e. from the LIBS spectrum in Fig. 3. It can be considered as a blank measurement as no phosphorus peak is visible providing the noise level at the P I emission peak for the SNR determination. In LIBS spectrum, the phosphorus emission at 213.6 nm day rapidly and is indistinguishable after 2 μ s as could be seen in Fig. 3. However, the phosphorus atoms remain in the plasma much longer and can be observed utilizing the LIF. Fig. 6 demonstrates that in the early dense plasma plume the SNR is relatively low, due to the high background radiation, and, thus, the maximum SNR is obtained at 2 μ s of inter-pulse delay. The LIF intensity shows exponential decay thereafter but can be observed with up to 40 μ s of inter-pulse delay.

3.3. Quantitative analysis of phosphorus in soil

Soils from two textural classes are used to demonstrate the phosphorus detection with LIBS-LIF in soils. The soil samples are classified as clay soils and silt loam/loam soils. The calibration curves are plotted for both types using the observed intensities at 213.6 nm and are shown in Figs. 7 and 8. The red curve represents the calibration curve for LIBS and black curve represents the calibration for LIBS-LIF measurements. The experiments are repeated four times and the error bars indicate the variations in the intensity with different measurements. A clear improvement in the fitted slope can be seen in LIBS-LIF measurements compared to the conventional LIBS for both types of soil. LIBS-LIF shows also slightly improved linearity with the R2 value of 0.9686 compared to the conventional LIBS case of R2 = 0.8737 for silt loam/loam soil. The LoD was evaluated using $3\sigma/S$ requirement where σ is the standard deviation in the background signal and S is the slope of the calibration curve [12]. The LoD's of soluble phosphorus for clay soil are evaluated as 3.74 mg/kg and 0.12 mg/kg for LIBS and LIBS-LIF, respectively. For silt loam/loam soils, the LoD's are 8.87 mg/kg and 0.27 mg/kg for LIBS and LIBS-LIF, respectively. The obtained improvement in LoD is typical for phosphorus LIBS-LIF applications [36,37]. The obtained results are compared in Table 1 to the previously reported phosphorus LoD's in soil and fertilizers with different variations of LIBS. The LoD for the readily soluble phosphorus achieved with LIBS-LIF is in the same range as the established chemical methods and potentially lower than in previously demonstrated method combining LIBS and Vis-NIRS method [43] enabling rapid optical phosphorus analysis also in low phosphorus containing samples. Many of the previous approaches have concentrated on total soil phosphorus estimation. However, the readily soluble phosphorus fraction is the most crucial when considering nutrient availability to crops and plants and, on the other hand, when assessing the risk of nutrient runoff to surrounding environment. The soluble phosphorus fraction determined in this work corresponds typically 3–5% of the total phosphorus mass. As the obtained calibration results show, the soluble phosphorus fraction compared to total phosphorus is constant within the clay and silt loam/loam soil types.

LIBS-LIF arrangement used in this study provided up to 40-fold improvement in the soluble phosphorus LoD compared to conventional LIBS arrangement. In addition, it improved the selectivity of the measurement as the spectral overlap with the iron emission is mitigated. Detection limits less than 1 mg/kg for readily soluble phosphorus fraction in soil are sufficiently low for soil phosphorus testing purposes. The use of two different soil types in the current study demonstrates that separate calibration is required for the different soil types. It is likely that including coarser sandy soils and organic soils would also require separate calibration and, therefore, requires further investigation. However, as all the individual soil samples were collected from geographically different

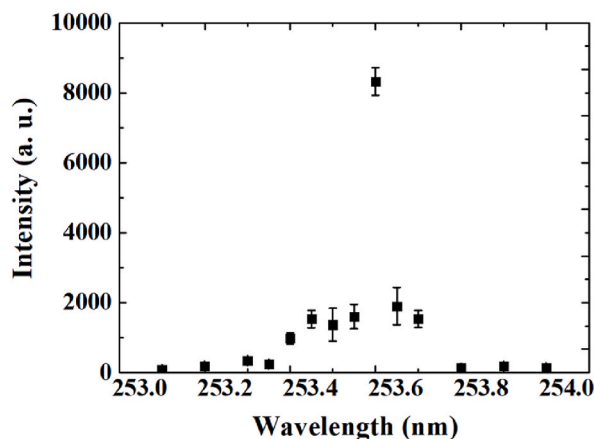


Fig. 4. Variation in phosphorus line intensity (213.6 nm) on different OPO wavelengths.

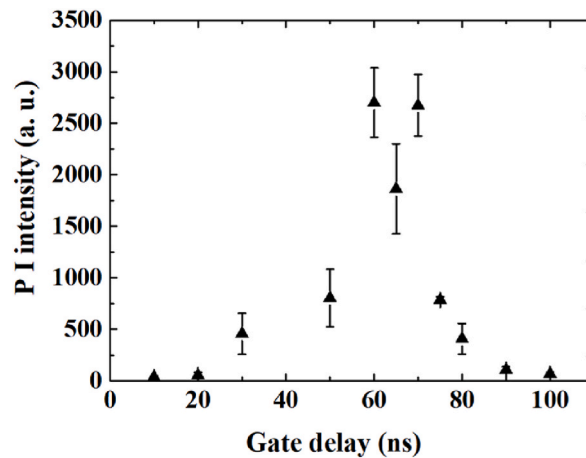


Fig. 5. Influence of Gate delay on P-I (213.6 nm) intensity in LIBS-LIF signal.

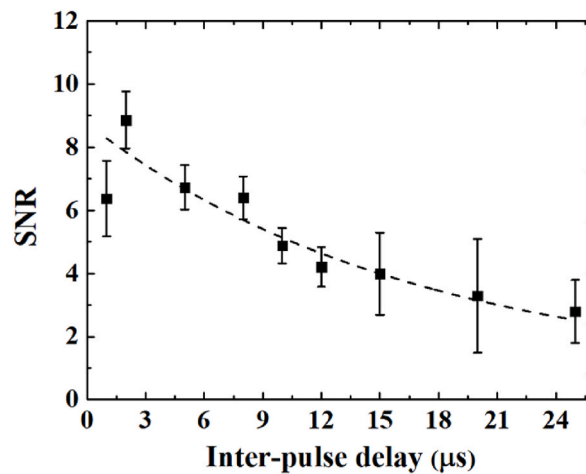


Fig. 6. Effect of inter-pulse delay between Nd:YAG laser pulse and OPO laser pulse on signal to noise ratio (SNR).

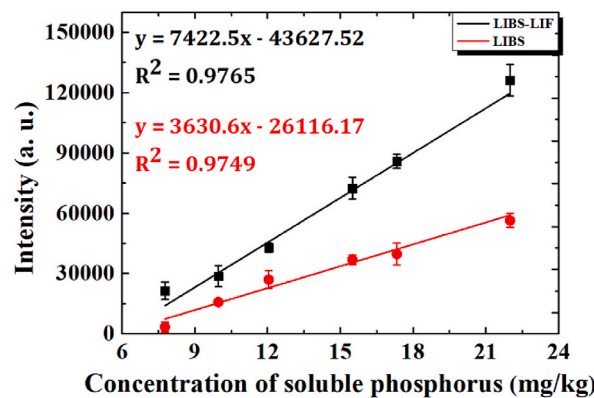


Fig. 7. Calibration curve for phosphorus line at 213.6 nm in clay soils. X-axis concentrations refer to readily soluble phosphorus determined in agronomic soil testing.

locations and, thus, include variation in their geological properties (parent materials), the good linearity in the calibration curve shows that the same calibration line can be utilized to soil samples of the same type. The observation on the generalizability of the calibration over similar soil types including samples that are not milled or sieved was recently presented also in the case of carbon detection in soil

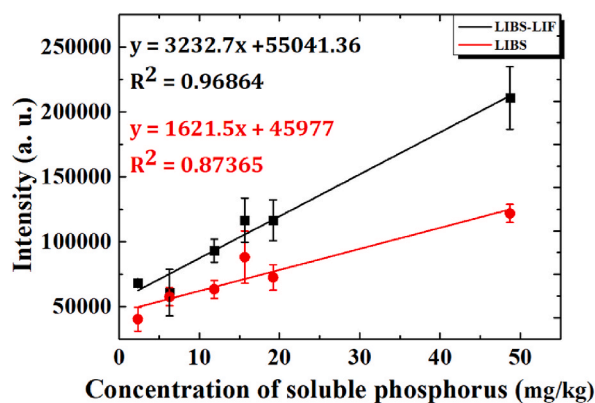


Fig. 8. Calibration curve for phosphorus line at 213.6 nm in silt loam/loam soils. X-axis concentrations refer to readily soluble phosphorus determined in agronomic soil testing.

Table 1

Phosphorus quantification in different soil and fertilizer matrices with different LIBS-based methodologies. Units are changed to mg/kg where applicable.

Sample	Methodology	P fraction	LoD	Lowest P concentration	Reference	
Soil	Sandy	LIBS	Total	10 mg/kg	100 mg/kg	[16]
	Clay	LIBS	Total	122 mg/kg	100 mg/kg	
Soil	LIBS	Total	46 ppm	4300 ppm	[17]	
Biochar-Fertilizers	SD-LIBS	Total	2100 mg/kg	0 mg/kg	[22]	
River Sediments	SP LIBS	Total	709 mg/kg	802 mg/kg	[23]	
	DP LIBS	Total	349 mg/kg			
Fertilizers	SP LIBS	Total	5000 mg/kg	0 mg/kg	[42]	
Soil	LIBS + Vis-NIRS	Soluble	NA	1.5 mg/kg	[43]	
Soil	Silt loam/loam	LIBS	Soluble	10.94 mg/kg	2.32 mg/kg	This work
		LIBS-LIF	Soluble	0.27 mg/kg		
	Clay	LIBS	Soluble	3.74 mg/kg	7.7 mg/kg	
		LIBS-LIF	Soluble	0.12 mg/kg		

[44]. Due to the low number of samples used in this study, it cannot be assessed how soil matrix effects will affect the reliability of the phosphorus quantification using LIBS-LIF. The improved R^2 value from LIBS calibration curve to LIBS-LIF however suggests that it could be more resilient to changes in the sample matrix within the same soil type when compared to conventional LIBS analysis of phosphorus.

Addition of LIF assistance to any LIBS configuration is possible when suitable light source is available. Therefore, LIF is an interesting option to improve phosphorus detection limits also in other environmental samples, such as water streams that require sensitive phosphorus detection [14]. However, when compared to conventional LIBS arrangement, addition of the wavelength tuneable light source will increase the physical size of the arrangement substantially. Thus, LIBS-LIF will inherently be laboratory-based technique requiring sampling and the sample transportation to the laboratory. LIBS-LIF is also expensive as one-time investment, but the light sources have lifespan of >10 years. On the other hand, the time required for the LIBS-LIF measurement is ~ 1 min including the laser operation and signal analysis. Use of LIBS-LIF would reduce the need of wet chemistry substantially and, consequently, need of labour reducing the price of the phosphorus analysis. Thus, the most importantly, LIBS-LIF would enable sensitive high throughput analysis of soil and other environmental samples enabling frequent and spatially vast monitoring of phosphorus. The next steps in the pursuit of extensive soil nutrient and quality monitoring will be combining the sensitivity of LIBS-LIF phosphorus analysis with the LIBS method's ability to detect multiple elements simultaneously. This combination has the potential to provide information rapidly on, for example, soil P, K, Ca, N, C, and Mg content. Furthermore, LIBS-LIF will be demonstrated for phosphorus monitoring in water samples where knowledge of the phosphorus load plays crucial role in mitigation of eutrophication of water systems.

4. Conclusion

Soluble fraction of soil phosphorus is analyzed using two different laser-based approaches: LIBS and LIBS-LIF. Three phosphorus lines were successfully detected with both methodologies: 213.6 nm, 214.91 nm and 215.29 nm. However, P I emission line at 213.6 nm was used for further analytical assessment in this work. For LIBS-LIF analysis, a tunable nanosecond OPO laser is tuned at 253.6 nm to induce fluorescence emission from the phosphorus atoms available in the laser-induced plasma plume. A substantial improvement in the SNR was observed with insignificant elemental interference in the LIBS-LIF spectrum in comparison to conventional LIBS.

Quantification of readily soluble phosphorus was performed with both methods for two soil types. The LoDs were found to be 3.74 mg/kg and 0.12 mg/kg in clay and 10.94 mg/kg and 0.27 mg/kg in silt loam/loam soil for LIBS and LIBS-LIF, respectively. Thus, the addition of LIF excitation improved the LoD of readily soluble phosphorus fraction up to 40-fold. Due to low number of samples, the reliability of the calibration for determination of readily phosphorus content in unknown soil samples was not assessed. Soil samples with low concentration of phosphorus were used in this study to demonstrate the abilities of the LIBS-LIF method. The results shows that the LIBS-LIF method has better selectivity and sensitivity over conventional LIBS. This study is the first step towards selective and sensitive laser-based readily soluble soil phosphorus analysis. The method has the potential to be further utilized as a high throughput optical detection method of soluble phosphorus in environmental samples.

Author contribution statement

Shweta Soni: Conceived and designed the experiments, Performed the experiments, Analyzed and interpreted the data, Wrote the paper, Jan Viljanen: Conceived and designed the experiments, Analyzed and interpreted the data, Wrote the paper Risto Uusitalo: Contributed reagents, materials, analysis tools or data, Wrote the paper Pavel Veis: Analyzed and interpreted the data, Wrote the paper.

Data availability statement

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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