

This article was downloaded by: [Univ Politec Cat]

On: 31 December 2011, At: 04:45

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gche20>

Field assessment of Pb in contaminated soils and in leaf mustard (*Brassica juncea*): the LIBS technique

Meri Barbafieri ^a, Roberto Pini ^a, Alessandro Ciucci ^b & Eliana Tassi ^a

^a Institute of Ecosystem Studies, National Research Council, Pisa, Italy

^b Geostudi Astier S.r.l, Livorno, Italy

Available online: 18 Feb 2011

To cite this article: Meri Barbafieri, Roberto Pini, Alessandro Ciucci & Eliana Tassi (2011): Field assessment of Pb in contaminated soils and in leaf mustard (*Brassica juncea*): the LIBS technique, *Chemistry and Ecology*, 27:S1, 161-169

To link to this article: <http://dx.doi.org/10.1080/02757540.2010.534464>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Field assessment of Pb in contaminated soils and in leaf mustard (*Brassica juncea*): the LIBS technique

Meri Barbaferi^{a*}, Roberto Pini^a, Alessandro Ciucci^b and Eliana Tassi^a

^a*Institute of Ecosystem Studies, National Research Council, Pisa, Italy;* ^b*Geostudi Astier S.r.l, Livorno, Italy*

(Received 14 January 2010; final version received 20 October 2010)

Monitoring contaminated sites is faster and cheaper if portable analytical instruments are used rather than traditional laboratory analysis. We developed a transportable system based on the laser-induced breakdown spectroscopy (LIBS) technique for rapid on-site measurement of heavy metal concentrations. Portable instruments also offer great advantages for on-site remediation technology, where continuous monitoring is required. LIBS is especially useful when plants are used to remove or contain contaminants. Phytoremediation takes time to achieve its goals, and many analyses are required to evaluate its efficiency during the process. In this study, LIBS was used to measure Pb concentration in soils from three contaminated sites and in plant samples from phytoremediation experiments. Results obtained from LIBS show good correlation with data obtained with atomic absorption spectroscopy (AAS). In particular, in the case of contaminated site characterisation, LIBS permits delimitation of areas showing metal concentration over the legal limits, where further investigations are required. Speeding up the characterisation procedure decreases investigation costs and increases the number of analysed samples with a given economic budget, thus increasing the informational value of data. Thus reliable spatial information can be obtained, leading to lower remediation costs.

Keywords: laser-induced breakdown spectroscopy; lead; soil contamination; monitoring; plant material; phytoremediation

1. Introduction

The number of contaminated sites is increasing along with industrial development. These sites must be investigated, especially to estimate risk through better understanding of their conditions and to gather data for designing remedial or control measures [1]. Whether the goal is to contain a contaminant or to remediate an area, the site must be routinely sampled and monitored. Moreover, reliable estimation of the contaminant is critical to ensure that remediation is proceeding sufficiently to protect human health and the environment. In particular, when plants (phytoremediation) are used to remove or contain contaminants, considerable time is needed to achieve the goal and many analyses are required to choose the appropriate species and to evaluate remediation efficiency over time [2–4].

*Corresponding author. Email: meri.barbaferi@ise.cnr.it

Conventional characterisation techniques require extensive sampling and analyses, which are costly, time-consuming and can lead to high levels of personnel exposure. However, the budget often limits the number of samples used to determine the presence and degree of contamination. As stated by Crumbling [1], a much more accurate picture of the site is gained when many samples are analysed even though the analytical method is less accurate. Moreover, real-time technologies encourage the modernisation of technical practices to characterise and remediate chemically contaminated sites [5]. Thus many operators are turning to new technologies to optimise (i.e. minimise) remediation costs just starting from an effective, real-time, low-cost site characterisation.

Laser-induced breakdown spectroscopy (LIBS) is a powerful method for direct measurement of element concentration in nearly all materials [6–8]. The technique is based on detecting light emitted from a micro-plasma produced by a short laser pulse. The high temperature of the plasma ionises the material of the sample and after a few microseconds atomic lines are emitted. LIBS works well on heavy metals due to the strong emission of these elements in the UV and visible spectral region (200–500 nm). Little preparation of the sampled material is required. LIBS characteristics can be used to set up portable instruments as a field alternative to traditional laboratory analyses. Recently Cunat et al. [9] developed a portable LIBS and measured Pb contamination in road sediments, finding good correlations with atomic absorption spectroscopy (AAS) data. Other, still limited, studies report data on LIBS analyses of plant tissues, mostly devoted to evaluating a crop's nutritional status [10,11] or the spatial distribution of Pb within leaves [12].

Our aim was to explore the performance of LIBS technology for measuring Pb content in soil and plant samples from contaminated areas. Our data are on-site measurements of Pb from three contaminated sites carried out with a portable LIBS analyser. The ability to describe metal contamination in the sites is compared with analyses performed by a traditional technique (flame AAS), in reference to Italian legislation limits. Moreover, plant samples from Pb-phytoextraction experiments were also analysed by LIBS to verify its ability to detect and measure metals in plant materials.

2. Materials and methods

2.1. Samples

Soil samples were collected from three areas with similar soil structural characteristics, and different sources of Pb contamination. The soils were sandy loam, with a CEC ranging from 12 to 16 meq and $\sim 1\%$ org C. Site A was a former mining area, located in southern Tuscany where Pb, Cu and Ag have been extracted every now and again since the seventh century. It was characterised by heavy metal contamination due to abandoned mining waste. Site B was an industrial area in the Liguria region, characterised by Pb contamination due to the presence of a lead oxide factory. Samplings were performed at 24 points on a regular grid at both site A and site B, exploring areas of $\sim 7500\text{ m}^2$. Site C was an urban brownfield located in the Lombardy region, where for over 80 years gas-production activities (coal gasification and catalytic reforming processes of petroleum light derivatives) have contaminated the soil. Here six sampling points were fixed in a small sub-area (150 m^2) devoted to phytoremediation field trials and characterised by a low level of Pb contamination. In all three sites, at each sampling point, a composite from three samples was collected in the 0–10 cm layer using an Edelman auger. An aliquot of the composite sample was used immediately for the LIBS measurements, while the remaining material was stored in plastic bags and transported to the lab for AAS measurements.

Plant samples (*Brassica juncea*) were collected from the previous phytoremediation experiment focused on Pb uptake [13,14]. In this experiment, chelate agents were added to soil to increase

the bioavailable Pb fraction for plant uptake. Plants grew in three different conditions: (1) soil without any amendment (control plants); (2) soil amended with nitrilotriacetate sodium salt (NTA) $4.2 \text{ mM} \cdot \text{kg}^{-1}$ soil; and (3) soil amended with ethylenediaminetetraacetate sodium salt (EDTA) $2.0 \text{ mM} \cdot \text{kg}^{-1}$ soil. The different mobilising agents were distributed in soil for 4 days during irrigation in the more suitable growth period (just before the flowering stage). The aerial parts of plants (shoot/leaf) were analysed.

2.2. Conventional analyses

Soil samples were air-dried and sieved to 2 mm, while plant samples were dried for 48 h at 80°C and ground to $< 1 \text{ mm}$ size. Both soil and plant samples were digested with a nitric–perchloric acid mixture in a microwave oven (Milestone 1200) and solutions were analysed by flame AAS (Perkin–Elmer 3030) for Pb content.

2.3. LIBS analyses

The LIBS prototype used in this study can be viewed as three logical units: laser, detection apparatus and control and analysis unit (Figure 1), which can be easily transported in the rear of a van. The laser is a Nd-YAG (Quantas System) and delivers up to 300 mJ per pulse at 1064 nm with a repetition rate of 10 Hz. The beam is guided within an articulated arm into a head probe mounting the focusing lens and the collection optics. The optical signal is delivered into the entrance slit of the spectrograph via an optical fiber. The Chromex 550i spectrograph uses a holographic grating of 2400 grooves per mm that allows a 0.2 \AA sampling step. Spectra are acquired by an Andor Tech. Intensified Charge Coupled Device (ICCD). All functions of the spectrograph (slit width, grating selection, wavelength position) and ICCD detector (cooling temperature, trigger settings, etc.) are controlled by a fully integrated software package developed for the scope. The analytical software allows the acquisition and instrument control, data manipulation (smooth, peaks picking), qualitative and quantitative measurements (peak labelling, plasma temperature calculation), spectra simulation and database manager. For Pb analysis the interference free emission lines at 217 and

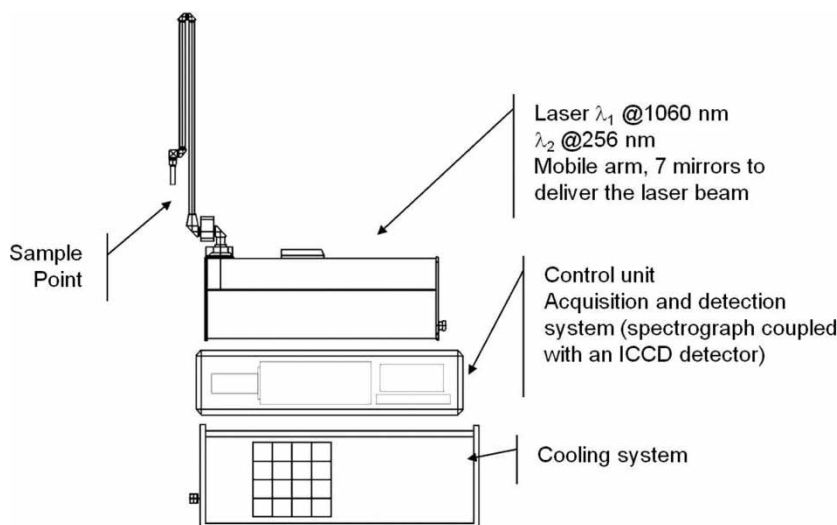


Figure 1. Schematic representation of the LIBS system used in this study.

220 nm are used. Estimation of the concentration is performed by the comparison of the intensity of resonance line of trace elements with respect to weak transition of some matrix elements [7] without the use of calibration curves. Thus, the presence of water in the samples does not affect the measurement of the metals.

LIBS works better on compacted surfaces, so soil and plant material were compacted into tablets of $\sim 1 \text{ cm}^2$. Soil moisture did not affect tablet preparation, although the water content of plant samples did not allow suitable compaction, so the plant samples were dried before tablet preparation. On each tablet, several hundreds of laser shots were performed along a 12-mm circumference. The entire procedure (tablet preparation, data acquisition, spectra analysis) lasted 10 min for each sample. Analyses were conducted on-site and results were elaborated by software developed for the purpose of producing a real time interpolated map using kriging 2D algorithm.

3. Results and discussion

3.1. Soil samples

Concentration ranges and mean values of Pb are reported in Table 1. As expected, levels of contamination in the three sites were different due to different types of exposure and activities performed in the areas. Pb concentration ranged from tens of thousands of $\text{mg}\cdot\text{kg}^{-1}$ in the mining area to thousands in the factory area to hundreds in the urban brownfield. Because of these considerable differences, LIBS performance could be appreciated in different situations and in a wide range of metal concentrations.

Differences between the mean values of AAS and LIBS were $< 10\%$ in sites A and B and $\sim 30\%$ in site C. These values are in agreement with Cunat et al. [9], where results of Pb in road sediments differed by $\sim 14\%$. The different behaviour could be ascribed to the different number of samples among the sites, and to metal content ranges. When the absolute metal content is low, as in site C, sampling errors tend to be larger and the per cent differences between analytical methods can be higher. To evaluate the accuracy of the LIBS measurements, Figure 2 shows results obtained with the portable LIBS instrument compared to those obtained with flame AAS. The square correlation coefficient (R^2) as well as the equation of the linear fit are described in the figure. All three sites reveal a reasonable correlation between the analytical methods, with R^2 always > 0.71 . Site C showed the highest R^2 , similar to that found by Cunat et al. [9], who analysed a similar number of samples to that of our sampling in site C. Again the different slopes of the three sites and their relative weights can be explained by the range of metal concentrations in which the instruments work.

Intrinsic matrix composition, humidity or grain size could carry differences in both analytical techniques. Moreover, the acidic digestion involved in AAS analyses measures the pseudo-total concentration against the total obtained with analyses such as LIBS. These features can induce positive or negative bias when comparing both techniques, as reported in Figure 2. Each national legislation gives different limit values that define soil contamination, so it is important to compare

Table 1. Pb concentration ranges and mean values in sites A, B and C ($\text{mg}\cdot\text{kg}^{-1}$).

		Site A		Site B		Site C	
		AAS	LIBS	AAS	LIBS	AAS	LIBS
Pb	Range	450–23,500	190–18,576	0–2175	0–3048	147–821	65–1170
	Mean	6488	6326	521	565	430	564

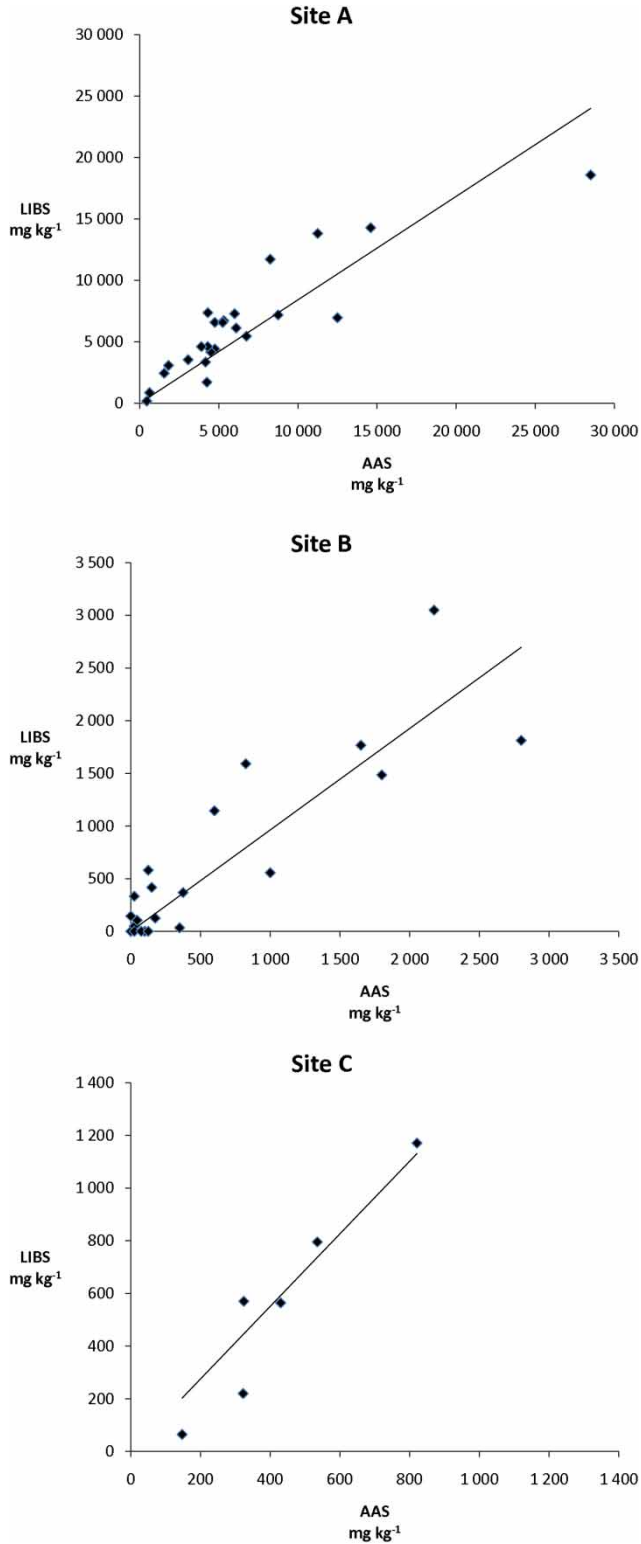


Figure 2. Correlations of results obtained with the field LIBS instrument vs. those obtained by flame-AAS for sites A ($y = 0.8516x$, $R^2 = 0.7067$), B ($y = 0.9628x$, $R^2 = 0.7739$) and C ($y = 1.3767$, $R^2 = 0.8860$).

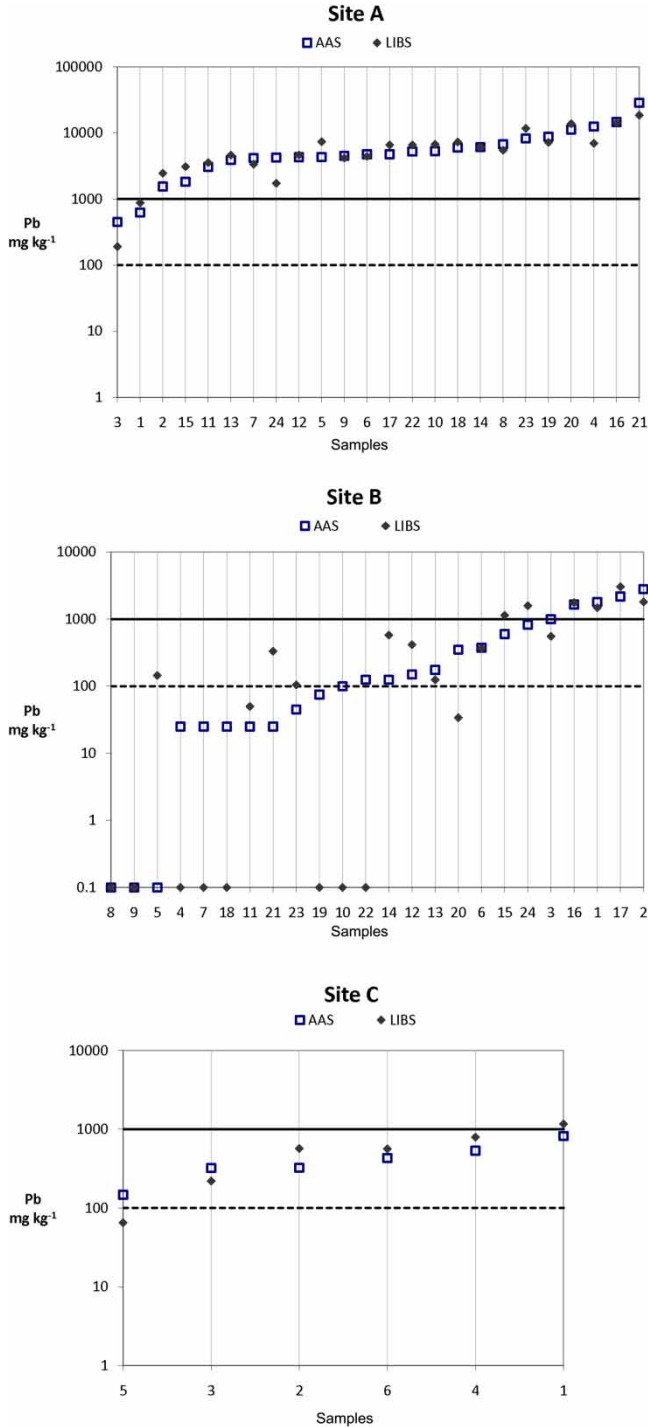


Figure 3. Pb concentrations (mg·kg⁻¹) at each sampling point of site A, B and C. Lines at 100 mg·kg⁻¹ and at 1000 mg·kg⁻¹ represent the Italian legal limits in public parks and gardens, and industrial areas, respectively.

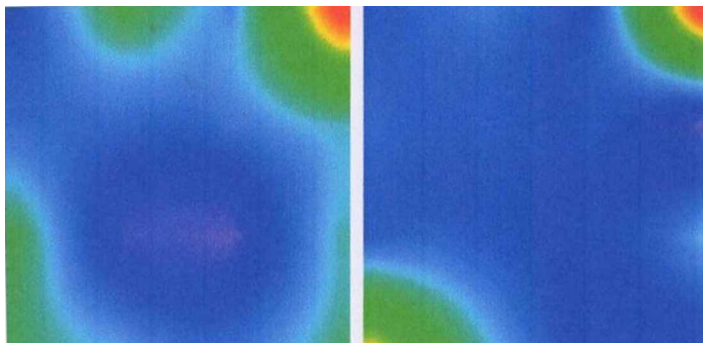


Figure 4. Isoconcentration maps of Pb in site B obtained with data from LIBS (left) and AAS (right). Scale blue–red, 0–5000 mg·kg⁻¹ (colour online).

analytical data with the legal limits. The Italian limits for soils in public parks and gardens and for soils in industrial areas are reported in Figure 3, as dotted and continuous lines, respectively. The data show that LIBS was just as efficient as AAS in classifying each sampling point with respect to both limits.

Results obtained using both techniques were also software processed, and interpolated maps could be made of the on-site localisation. Figure 4 shows the Pb isoconcentration map of site B obtained with data from AAS and LIBS. The maps revealed very similar positions for a hot spot in the right upper corner of the pictures and a zone of low Pb concentration in the central sampled area.

3.2. Plant samples

Phytoextraction is a mild, long-lasting procedure for removing heavy metals from a contaminated site. This process requires plants that accumulate high quantities of metals in their tissues. Several vegetative cycles are required to give measurable differences in total metal concentrations in soils before and after plant growth. However, at the end of a vegetative cycle, the plant's efficiency in accumulating metals can be evaluated. Our test compared measurements with AAS and LIBS of Pb accumulation in plants of *Brassica juncea* grown on contaminated soil with different mobilising agents. Pb concentrations in plant samples measured by AAS and LIBS are reported in Figure 5(a). Plant samples with low Pb concentrations (samples 1–3) refer to plants grown in unamended soil. Higher Pb concentrations were found in shoots of plants grown in soil amended with NTA (samples 4–7) and EDTA (samples 8, 9). Sample 10 refers to analysis of leaves alone, after EDTA treatment. Pb concentration increased in the following sequence: control (shoots) < NTA (shoots) < EDTA (shoots) < EDTA (leaves), as reported previously [13,14]. LIBS was able to measure these increasing concentrations the same way as AAS. Our results are in good agreement with data obtained by *Galiova et al.* [12] where the overall Pb concentration in leaves measured using LIBS increases by the increased Pb availability. The correlation between AAS and LIBS was very high ($R^2 = 0.97$, slope = 1.0045), as shown in Figure 5(b), although this information must be considered with caution, because of the low number of samples.

4. Conclusions

LIBS is still an experimental technique, but it appears promising for environmental science. Our approach to quantitative analysis of metals involves comparison with respect to an internal

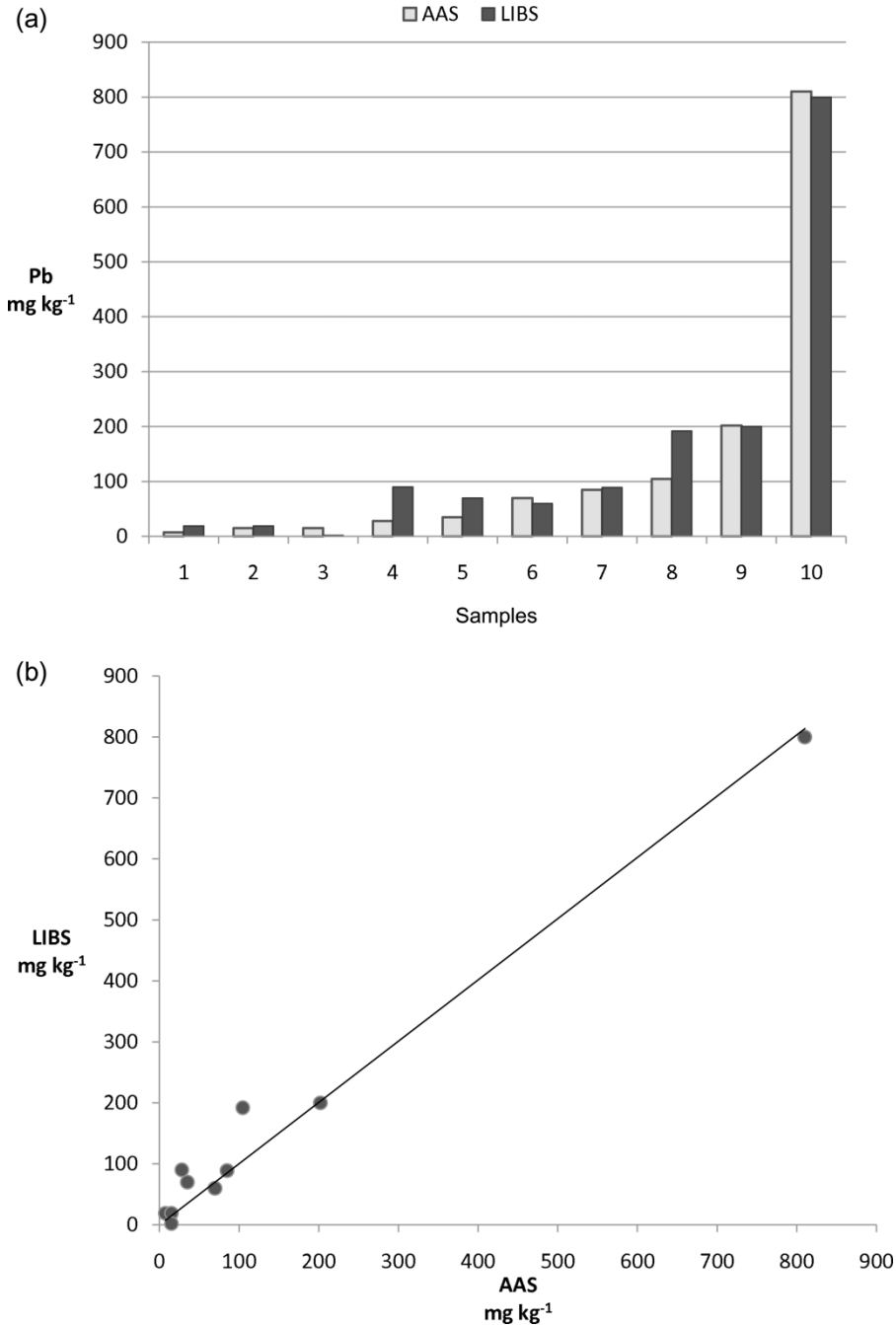


Figure 5. Results obtained with LIBS and AAS for the plant samples: (a) Pb concentrations (mg kg⁻¹); (b) correlation between LIBS and AAS ($y = 1.0045x$, $R^2 = 0.9738$).

reference, producing results that are less accurate, but are suitable for field application. The system is easily transported by car. Results obtained with LIBS showed acceptable correlation with data obtained using AAS. In particular, in the characterisation of contaminated sites, LIBS permitted easy delimitation of areas showing metal concentrations above the legal limits, where

further investigations are required. The major advantages of using LIBS as a semi-analytical tool are rapid analysis, a low-cost approach to site characterisation because the system needs no gas or replacement parts, and the possibility of obtaining an optical signal from any solid matrix (rocks, soils, plants) without laborious and time-consuming pre-treatments. Speeding up the characterisation procedure decreases cost and increases the number of samples analysed within a given budget, increasing the informational value of data. Thus, a more reliable spatial information can be obtained, leading to lower remediation costs.

Our results analysing plant materials with LIBS are encouraging. When confirmed, LIBS will be useful for the rapid screening of heavy metal accumulating plants and for monitoring phytoremediation activities.

Acknowledgements

Research funded by CNR-RSTL project "SPIN - SPetroscopia IN situ: un metodo per la misura speditiva in campo dell'inquinamento da metalli pesanti nei suoli".

References

- [1] D.M. Crumbling, *Applying the concept of effective data to environmental contaminated sites, USA EPA 542-R-01-013 Current Perspectives in Site Remediation and Monitoring*, Office of Solid Waste and Emergency Response, Washington, DC, 2001. Available at http://www.clu-in.org/download/char/effective_data.pdf.
- [2] M. Barbaferi, *Phytoremediation*, in *Bonifica di siti contaminati – Caratterizzazione e tecnologie di risanamento*, L. Bonomo, ed., McGraw Hill, New York, 2005, pp. 409–424.
- [3] F. Pedron, G. Petruzzelli, M. Barbaferi, and E. Tassi, *Strategies to use phytoextraction in very acidic soil*, *Chemosphere* 75 (2009), pp. 808–814.
- [4] E. Tassi, J. Pouget, G. Petruzzelli, and M. Barbaferi, *The effects of exogenous plant growth regulators in the phytoextraction of heavy metals*, *Chemosphere* 71 (2008), pp. 66–73.
- [5] D.M. Crumbling, *Summary of triad approach*, White Paper, Office of Superfund Remediation and Technology Innovation, U.S. Environmental Protection Agency, Washington, DC, 2004. Available at <http://triadcentral.org/ref/doc/triadsummary.pdf>.
- [6] A. Ciucci, V. Palleschi, S. Rastella, R. Barbini, F. Colao, R. Fantoni, A. Palucci, S. Ribrezzo, and S. Van der Steen, *Trace pollutants in soil by a time resolved laser induced break down spectroscopy*, *Appl. Phys. B* 63 (1996), pp. 85–190.
- [7] A. Ciucci, M. Corsi, V. Palleschi, S. Rastella, A. Salvetti, and E. Rognoni, *New procedure for quantitative elemental analysis by laser-induced plasma spectroscopy*, *Appl. Spectrosc.* 53(8) (1999), pp. 960–964.
- [8] C. Haish and U. Panne, *Laser-induced plasma spectroscopy (LIBS) in action*, *Atom. Spectrosc.* 9(3) (1997), pp. 8–14.
- [9] J. Cunat, F.J. Fortes, and J.J. Laserna, *Real time and in situ determination of lead in road sediments using a man-portable laser-induced breakdown spectroscopy analyzer*, *Anal. Chim. Acta* 633 (2009), pp. 38–42.
- [10] L.C. Trevizan, D. Santos Jr, R.E. Samad, N. Dias Vieira Jr, C.S. Nomura, L.C. Nunes, I.A. Rufini, and F.J. Krug, *Evaluation of laser induced breakdown spectroscopy for the determination of macronutrients in plant materials*, *Spectrochim. Acta B* 63 (2008), pp. 1151–1158.
- [11] L.C. Trevizan, D. Santos Jr, R.E. Samad, N. Dias Vieira Jr, L.C. Nunes, I.A. Rufini, and F.J. Krug, *Evaluation of laser induced breakdown spectroscopy for the determination of micronutrients in plant materials*, *Spectrochim. Acta B* 64 (2009), pp. 369–377.
- [12] M. Galiova, J. Kaiser, K. Novotny, O. Samek, L. Reale, R. Malin, K. Palenikova, M. Liska, V. Cudek, V. Kanicky, V. Otruba, A. Poma, and A. Trucci, *Utilization of laser induced breakdown spectroscopy for investigation of the metal accumulation in vegetal tissues*, *Spectrochim. Acta B* 62 (2007), pp. 1597–1605.
- [13] E. Tassi, C. Mastretta, L. Rizzi, and M. Barbaferi, *PHYTODEC: European project for the use of vegetation in the management of heavy metal polluted sites. Enhancing metal bioavailability for phytoremediation strategy*, CONSOIL – 8th International Conference on Contaminated Soil, Gent, Belgium, 2003.
- [14] E. Tassi and M. Barbaferi, *Testes de fitoextração em campo em um contexto do projeto europeu PHYTODEC, in Revitalização de áreas contaminadas, tecnologias de Remediação e gerenciamento tecnico, legal e gurdico de passivos ambientais*, E. Moeri and D. Rodrigues, eds., Sigmus Editora, Sao Paulo, 2005, pp. 93–104.