

Laser-induced breakdown spectroscopy applied to cattle compost for phosphorus quantification

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Abstract

Purpose Agronomic and environmental reasons force farmers to know the total P concentration of composted cattle manure. Laser-Induced Breakdown Spectroscopy seems proper to obtain such information. For logistic reasons (carriage, storage, field application, etc.), a dry matter characterization is also needed.

Method Thirty samples of feedlot compost at different stages of stability and maturity were studied. Samples were dried at 50°C for dry matter characterization. As a reference method to determine total P concentration, wet digestion and colorimetry were employed. The area of the P I line emission obtained by laser-induced ablation of the samples was measured to estimate the total P concentration. Randomized calibrations through a modified version of the Kennard-Stone algorithm based on the Mahalanobis distance were performed.

Results Dry matter varied from 40% to 90%, and no pattern was found related to compost origin, maturity, or stability. The total P concentration of the studied compost ranged from 1800 ppm up to 11200 ppm. Almost 80% of the calibration fittings have an $R^2 \geq 0.895$. The mean validation error was less than 22% for about 80% of the calibrations, with a mean prediction error bound to 40%. Discarding outliers, the errors were reduced to 19% and 30%, respectively.

Conclusion Water content must be considered in addition to other characterizations due to logistic implications. Calibrations with a 30 percent of prediction error were achieved, which seems enough as a first approximation to predict the total P content in compost for utilization in farms to recycle nutrients.

Keywords Feedlot compost, Total phosphorus concentration, Laser-Induced Breakdown Spectroscopy (LIBS), Nutrient recycling

Introduction

In recent years, the number of feedlots and their cattle concentration has markedly increased in the central region of the Buenos Aires province (Argentina). Feed-

lots allow the increase in the cattle stock in the farms, shortening the time required to reach cattle fattening completion and commercialization and releasing land towards agriculture (Pordomingo 2013; Bona 2021). However, livestock confinement leads to the production of large volumes of waste in reduced areas. This fact becomes a problem for farmers, impacting on the environment and the society (Larney and Hao 2007; Hernández et al. 2016; Giroto and Cossu 2017).

On the other hand, some agricultural producers are closely related to feedlots because they act as food suppliers for these concentrated animal operations. In Argentina, regarding nutrient transfers, such agricultural producers work within a framework of a mineral-extractive production system. As a result of grain production, these agroecosystems usually present a negative soil nutrient balance because the nutrient extraction ex-

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ceeds the amounts contributed via fertilization (García 2001; Darwich 2019). One of the most extracted nutrients is phosphorus (P), which is supplied by soil minerals (native P) and, to a greater extent, by fertilizers. In the central region of Buenos Aires province, the native P has always been scarce and limited agricultural production (Pazos and Mestelan 2002; Sainz Rozas et al. 2012). However, a steady soil P build-up due to fertilizer P replenishment was observed in the last decade under agricultural soil use. On the other hand, cattle-raising agricultural systems usually have negative soil P balances (Mestelan et al. 2015).

The process of organic composting is a technique that reduces pathogens and enhances nutrient availability to plants (Almeida et al. 2019). Composting is a technique capable of generating a circular flow of nutrients, turning waste from one activity into a valuable input for others, minimizing the need to incorporate nutrients from fertilizers coming from non-renewable sources, such as phosphoric rock (Pellejero et al. 2021). As a feedlot waste treatment technology, its utilization enhances livestock production under a circular nutrient economy approach (Lett 2014; De Rosa et al. 2021). Then, composting appears as a technique that could solve the multiple problems that arise from solid waste from feedlots, such as the presence of pathogenic microorganisms, parasites, moisture excess, possible high carbon-nitrogen (C:N) ratio (associated with the manipulation of large volumes of material, N losses, and mixing of straw with soil), the concentration of some elements such as P and some micronutrients, etc. (Larney and Hao 2007). Among the properties of this type of compost, it has to be highlighted its moderate to high nutrient content in easily and moderately available forms to plants, particularly macronutrients such as N, P, and sulfur (S) (Larney and Hao 2007; Ramaglio et al. 2019). The compost can then be used as an amendment for its high organic matter levels or as manure bringing in P and N (Hernández et al. 2016; Ramaglio et al. 2019; De Rosa et al. 2021).

In Buenos Aires province, Argentina, when compost is used as manure, it is usual to adjust the amount to be applied according to the N concentration, extrapolating this information from the literature. For this reason, owing to that the general compost nutrient concentration is usually unknown, and due to that the amount of P in these materials is high, soils could quickly become saturated with P (Mazzarino et al. 2012, Hernández et al. 2016). A similar situation could occur when compost

is employed as an amendment. Then, the accumulation of material from the cleansing of the pens, which is just piled up in the feedlots occupying more and more space, could result in a source of air, water, and soil contamination without proper handling. In addition, farmers should pay attention to the quality and quantity of animal manure used as a source of nutrients to the soil. Both quality of the compost and application rate can cause an excessive input of nutrients in the soil leading to soil pollution, groundwater contamination, and soil disuse for agricultural purposes (Almeida et al. 2019). Feedlot compost can be considered somewhat concentrated in P (Ramaglio et al. 2019). The excess of P and the movement of soluble and particulate forms of P when the compost is applied in upland soils can generate undesirable effects on soils and landscapes, specifically on shallow surface water bodies (Brady and Weil 2003; Mazzarino et al. 2012; Whalen and Chang 2001; Giusti and Recuero 2018).

Another factor to consider in analyzing feedlot compost as manure is the water content due to its effect on the transportation cost, which implies a considerable outlay (Ronga et al. 2020). This aspect marks the main difference with the traditionally employed fertilizers that come from chemical synthesis. These present a high nutrient concentration with low water content, allowing the use of smaller volumes of material to replenish the desired amount of nutrients.

Due to the reasons stated above, it is necessary to characterize the feedlot compost to correctly use it from an agronomic, environmental, and economic point of view.

This work focuses on the dry matter characterization of composted cattle manure samples and the measurement of its total P concentration. We aim to contribute to developing a simple methodology capable of providing information about the total P content of feedlot compost samples with different degrees of maturity and stability to adjust the application rate to the fields. In this respect, the Laser-Induced Breakdown Spectroscopy (LIBS) appears as a technique capable of producing information on the elemental composition of various matrices. This technique is widely used for the qualitative and quantitative determination of chemical elements (Hahn and Omenetto 2012; Yu et al. 2020). In particular, it has been used to detect P in diverse situations (Aras and Yalçın 2014; Li et al. 2014), including fertilizers (Marangoni et al. 2016, Nicolodelli et al. 2019). In that sense, it appears as a real possibility to quantify the total P content of compost by this method.

Materials and methods

Selection of the sampled feedlots

According to previous studies (Hernández and Rubio 2012; Hernández et al. 2016), and by request of some producers, three large-scale feedlots, located at the central region of Buenos Aires province (Argentina), were selected for sampling purposes (see locations in Fig. 1). All of them are dedicated to fattening their animals and from third parties. Still, each followed different nutritional strategies to gain animal weight, and the feeding

management was also divergent. These operations produced a large amount of residues that were piled up for composting and, in some cases, employed as manure with an uncertain degree of maturity and stability (parameters of the compost that could correlate with the total P concentration). The soils that supported these concentrated animal feeding operations, their waste management strategies and other features are briefly described in Table 1. These three well-differentiated feedlots were selected due to the provision of samples with high total P variability, which is needed to develop a methodology with a wide dynamic range.

Table 1 Description of the selected feedlots for sampling purposes in this study

Localization	Landscape - Dominant soils	Heads fed per year	Waste collection frequency	Waste treatment technology	Number of samples
Olavarria (36°37'10.15"S, 60°39'58.05"W)	A transition between <i>Sandy Pampa</i> and <i>Depressed Pampa</i> ; slopes lower than 1%; <i>Petrocalcic Natrudolls</i> and <i>Petrocalcic Argiudolls</i>	5000 to 6000	Yearly	Composting in piles with turns, with a high carbonate content from the corrals. Liners are not employed due to the reduced soil permeability: pens are underlain by <i>Petrocalcic</i> horizons.	12
Tandil (37°27'17.10"S, 59°14'33.79"W)	<i>Piedmont</i> region of the <i>Tandilia</i> sierras system, slopes greater than 3%, <i>Petrocalcic Argiudolls</i>	15000 to 20000	Yearly	Composting in windrows without turning. Liners are not employed due to the reduced soil permeability: pens are underlain by <i>Petrocalcic</i> horizons.	9
Saladillo (35°37'6.45"S, 59°53'16.87"W)	Transition to <i>Sandy Pampa</i> ; slopes between 1% and 2%, <i>Petrocalcic Hapludolls</i> and <i>Typic Hapludolls</i>	40000	Yearly or after a fattening cycle	Composting in windrows with turns, with high content of mineral material from the pen's floor, which may include materials imported from limestone quarries. Liners are not employed due to the reduced soil permeability: pens are underlain by <i>Petrocalcic</i> horizons.	9

Composite samples of about 3 kg were taken from the center of the composting piles from each establishment. These samples were adequately stored in clean bags and labeled. Additional information regarding the maturity and stability of the samples was also registered. All samples were transferred to the *Laboratorio de Análisis de Suelos*, Facultad de Agronomía, Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA) to be stored in a refrigerator for subsequent handling and processing.

Sample preparation

After each sample was homogenized, approximately 1 kg was taken and placed in a heat chamber at 50 °C. The samples were kept in the chamber until their weight variation remained below 1%. Then, the dry matter percentage was calculated from

$$DM = \frac{w_f}{w_i} \times 100, \quad (1)$$

being w_i and w_f the initial (humid) and final (dry) weight, respectively.

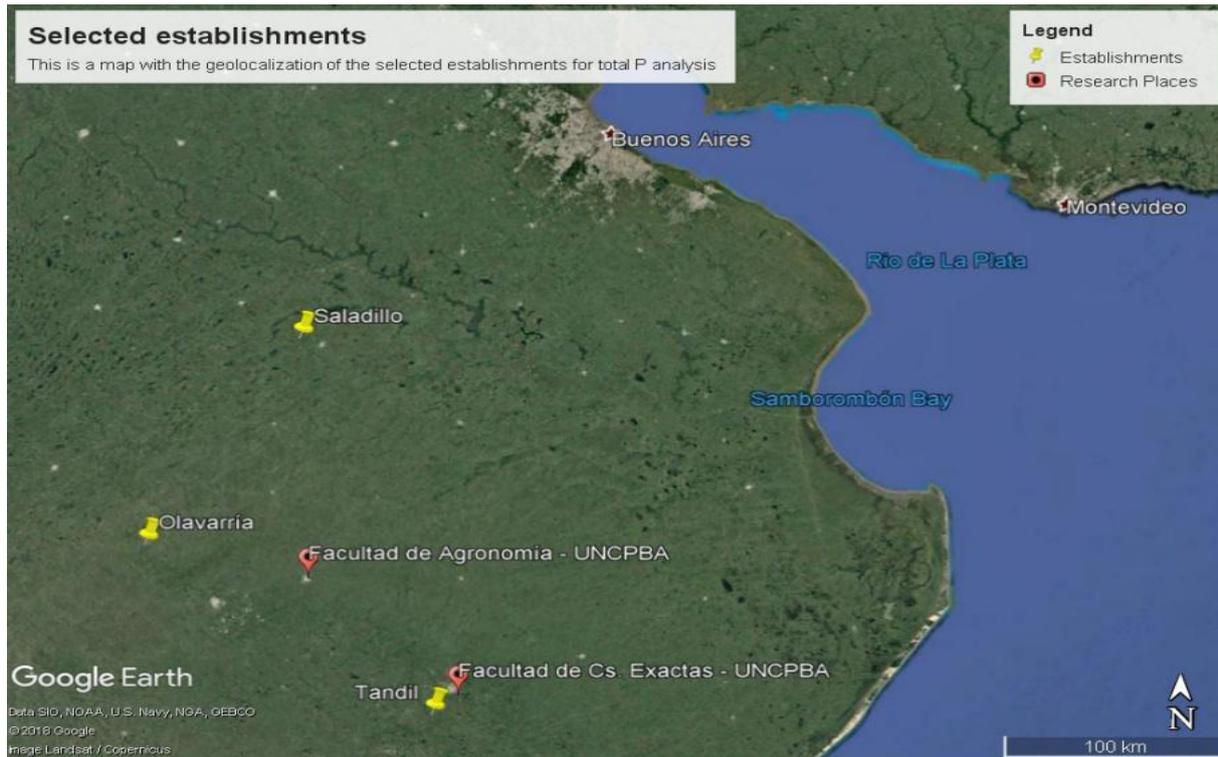


Fig. 1 A map with the georeferenced concentrated animal feeding operations (Google, n.d. 2021)

Once all the samples were dried, they were milled and sieved to pass a 2 mm sieve.

Total P sample determination - Standard method

The total P determination was carried out by the *Laboratorio de Análisis Bioquímicos y de Minerales*, Facultad de Ciencias Veterinarias, UNCPBA. The modified Braselton et al. (1997) and Henry et al. (1974) procedures, involving wet digestion and colorimetry, were used.

Three subsamples were wet digested in a mixture of acids (HNO_3 and HClO_4 , in a 3:1 relationship), first at room temperature for six hours and then at 95°C for at least eight hours, according to an adaptation of the method of Braselton et al. (1997). Once the digestion process ends, each subsample was diluted down to a concentration of around $50 \mu\text{g}\cdot\text{mL}^{-1}$ of P. Then, the P concentration was determined according to a modification of the Henry et al. (1974) method. The P reacts in an acid medium with molybdate to generate a phosphomolybdic complex measured by spectrophotometry at 340 nm. The results were expressed as *ppm* of P in a dry compost basis.

Sample preparation (pelletization) for LIBS

LIBS technique has some requirements regarding the samples: they must have a plane, smooth and compact surface that does not disperse dust when the laser hits them and must be stable over time. For these reasons, it was decided to prepare pellets. Thirteen grams of each dried and sieved sample were taken and placed in a cylindrical metal tin of 3 cm diameter and 5 cm height and then pressed with a piston to approximately 140 MPa. In some cases, mainly in samples with high sand content (Saladillo samples), the pressure was not enough to obtain the pellets. In these situations, a small quantity of polyvinyl alcohol was added as a binder (it is known that this compound does not affect LIBS records for measurement purposes; Sabara et al. 2011).

LIBS technique

Fundamentals

Assuming that the total P was detected in the samples through chemical analysis, it is hypothesized that the LIBS technique would detect and measure the atomic

emission of P present in the samples, and the values obtained with both procedures could be comparable.

LIBS is mainly an atomic emission spectroscopic technique. A laser pulse is directed and focused on a sample (as seen in Fig. 2). When the laser pulse hits the sample surface, it heats up, and some material is ablated. There, the generation of a shock wave (acoustic) and the appearance of a spark occurs. The shock wave results from the ablated material. The spark is a consequence of the high temperature achieved in that region, which excites the atoms. When they return to their background state, light emission with wavelengths precisely defined for each element appears. This light is collected by a spectrophotometer and measured for different wavelengths according to the device resolution and detector configuration. The measured light intensity and wavelength data are sent to a PC, and a spectrum is built.

It is recognized that there is a high-intensity emission line for P I at 253.56 nm (I denote neutral atoms) (Aras and Yalçın 2014; Kramida et al. 2020; Li et al. 2014). Then, by measuring around this wavelength, it should be possible to detect the amount of P present in the sample.

Measurements

Pellets were placed on a rotary stage to ensure that laser hits do not ablate the same place of the sample. The laser employed was an Nd: YAG Q-switched (Continuum Surelite II) operating at the fundamental wavelength, 1064 nm. The pulse had, on average, a width of 7 ns and an energy of 100 mJ. In the experimental setup, a delay of 10 μ s and an integration time of 15 μ s were employed for the acquisition. The light coming from the spark was collected by a quartz lens and focused onto a JobinYvon THR 1500 (Czerny - Turner configuration, focal length 1.5 m) monochromator (Fig. 2). Three spectra were acquired for each sample (Fig. 3). The spectra are made up of one hundred points with steps of 0.00132 nm around the 253.56 nm P I line. For each wavelength measured (because the monochromator has only one photodetector and to avoid heterogeneity noise from the sample), three laser hits were averaged on an A/D converter and sent to a PC where the line spectra were recorded.

Line analysis

Considering the collision process is the major contributor to the broadening and shape of spectral lines (Corney

1977), the high resolution of the monochromator, and the characteristics of the plasma generated, the spectra can be described by a Lorentz function. Then the Origin® software was employed to fit the Lorentz function

$$I = I_0 + \frac{2A}{\pi} \frac{\omega}{4(\lambda - \lambda_c)^2 + \omega^2}, \quad (2)$$

to the intensity data (Fig. 3), being I_0 the offset, λ_c the peak center, ω the half-width, and A the area. The last parameter contains relevant information related to the P content of the sample. The three fitted areas for each sample were averaged, and this value was compared to that obtained by the standard or reference chemical method.

Area error

The error assigned to the averaged areas was calculated according to the following expression

$$\Delta A_a = \text{Max} \left\{ \sqrt{\text{Mean}[\Delta A_j^2]}, \text{Abs}[A_j - A_a] \right\} \quad (3)$$

having, $\text{Max}\{\dots\}$, $\text{Mean}[\dots]$ and $\text{Abs}[\dots]$ their usual meaning, being ΔA_j the area error resulting from the areas A_j obtained in the fitting procedure and A_a the area average.

Calibration procedure

Once the LIBS averaged areas (with the associated error) resulting from the fitting procedure were obtained, calibrations with the chemically determined total P were performed (taking these later values as standards). Then, the samples were separated into three groups: calibration, validation, and prediction. This separation uses the calibration data to fit a linear relationship between the LIBS averaged areas and the chemically determined total P values. Then, the second group is employed to validate the calibration with the obtained slope, and a *validation error* is calculated. Finally, the last group is used to predict the values given by the calibration, and a *prediction error* is also determined.

The choice of the data for the three groups is not a trivial task because it cannot be made arbitrarily, and the bias must be minimized. Then, the following procedure was carried out:

1) From the ensemble of samples, it was determined that the group size would be: for calibration 70% of the samples, for validation 20%, and for prediction 10%.

2) The samples for prediction were randomly selected.

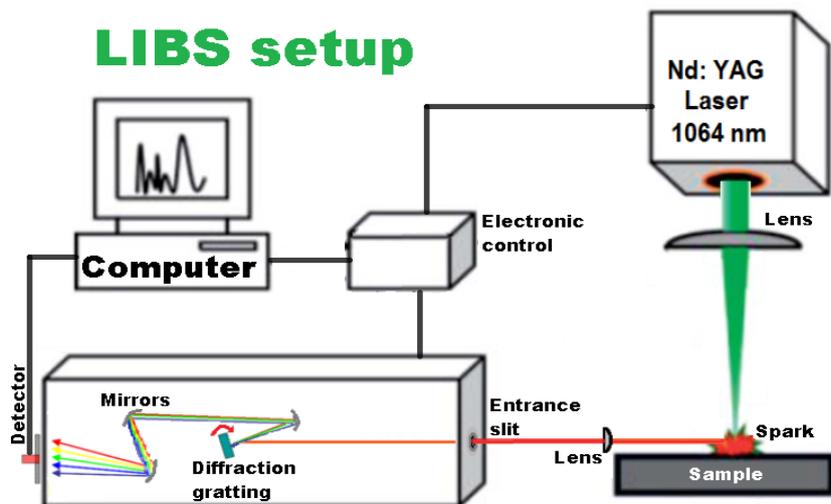


Fig. 2 LIBS setup for emission spectra acquisition

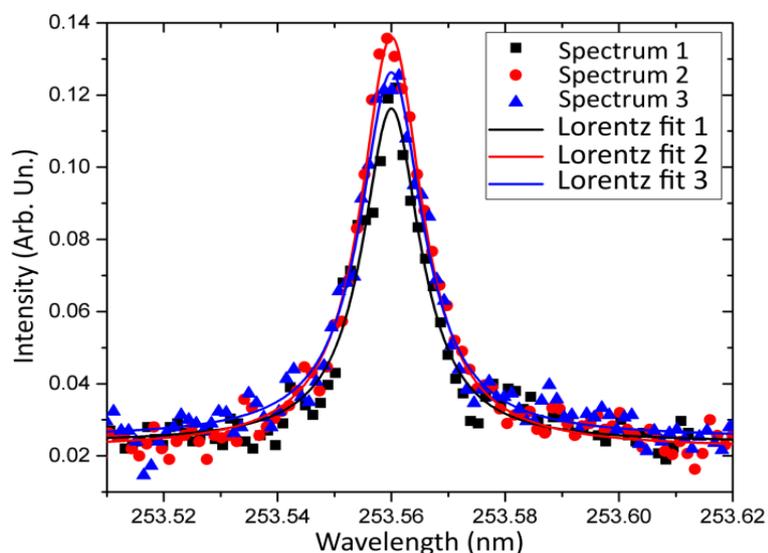


Fig. 3 Example of three spectra acquired for a sample with their corresponding Lorentz fit

3) The samples for calibration and validation were chosen by employing a modified version of the Kennard-Stone algorithm based on the Mahalanobis distance (Saporo et al. 2012).

Since the initial selection of calibration, validation, and prediction samples could be fortuitously favorable (or unfavorable, regarding validation and/or prediction errors), steps 2) and 3) were repeated. Due to the 4060 chances to choose three samples from an ensemble of thirty elements, steps 2) and 3) were repeated 3000 times to ensure evaluating 70% of the possible calibrations. All calculi were implemented in Python.

Fitting procedure

The samples in the calibration group were fitted to a linear regression through the origin, i.e., $A_a = bP$, where

P represents the total phosphorus concentration chemically determined, A_a the averaged LIBS areas, and b was the fitted slope calculated according to Press *et al.* (1992) (setting the intercept at zero) which is given by $b = \frac{S_{PA}}{S_{PP}}$ where

$$S_{PA} = \sum_i P_i A_{ai} \Delta A_{ai}^2, \tag{4}$$

and

$$S_{PP} = \sum_i P_i^2 \Delta A_{ai}^2, \tag{5}$$

being A_{ai} the averaged fitted LIBS areas for each sample (see Sub. Sec. *Line Analysis*), ΔA_{ai} stands for its corresponding error given by Eq. (3), and P_i refers to the chemically determined total phosphorus concentration of such a sample (see Sec. Total P sample deter-

mination - Standard method), with i spanning all the calibration samples. Errors were considered as *direct weighting*, which resulted in the best fitting situation.

The goodness of fit index (also called the coefficient of determination) was estimated from (Eisenhauer 2003; Chatterjee and Hadi 2012):

$$R^2 = \frac{\sum_i A_{pi}^2 \Delta A_{ai}^2}{\sum_i A_{ai}^2 \Delta A_{ai}^2}, \quad (6)$$

where A_{pi} is the area predicted by using the fitted slope b . Errors were included by following the Origin® guidelines (Origin n. d 2021).

Errors estimation

As stated above, once the slope was estimated, the Mean percentage absolute errors (de Myttenaere et al. 2016) of the validation and prediction were evaluated. In both cases, the evaluations were performed through the same expression

$$Err = \frac{100}{h} \sum_{j=1}^h \frac{|(A_{aj} - A_{pj})|}{A_{aj}}, \quad (7)$$

being $h = v, p$ the number of validation or prediction samples, according to the case.

Results and discussion

Table 2 summarizes the main determinations and results of this work. Samples are labeled according to the establishment which belongs: "O" for Olavarría, "T" for Tandil, and "S" for Saladillo. The number only identifies the sequence in which they were collected. Dry matter is represented in percentage, Total P in ppm, and LIBS values in Arbitrary Units proportional to the Lorentz function area. The third row displays the variable names according to the previous section.

Fig. 4 presents the chemically determined total P concentrations (left axis) and the dry matter content (right axis) for all the collected samples. The samples were ordered according to their P content in an increasing pattern. Each establishment is differentiated by a color: Olavarría (blue), Tandil (green), and Saladillo (red). As expected, the different weight gain strategies, the associated nutritional management, and the composting procedures created a wide range of total P values, starting around 1800 ppm up to 11200 ppm. There is also a significant variation even for the samples within a feedlot.

From Fig. 4, it is apparent the difference of about 10000 ppm of P between the minimum and maximum value. This fact highlights the need for a proper characterization of the cattle compost before using it. If a value obtained in one establishment is assumed for the application of the compost in another one, a significant error could be made. Note that the total P content of 1 ton of sample S-7 is around six times of 1 ton of sample O-10. This extreme example shows that if the nutritional carrying capacity of a compost is unknown, it is almost impossible to design a sound administration of manure to the fields. Due to possible imbalances, this situation can result in nutrient underestimation or, on the contrary, in nutrient overdoses leading to environmental and then social risk situations, as discussed at the beginning of this work.

Fig. 4 also depicts the dry matter content, which noticeably varies among the different samples, even those corresponding to the same establishment. Among the factors that can explain this situation, the technique used for composting (windrows in Tandil and Saladillo and piles in Olavarría), which generates differences in the exposure of the surface of the composting structure to rain, sun, or wind, can be mentioned. Moreover, the location of the samples taken from the piles or windrows according to the landscape also matters: it is not the same if they are located in a runoff area or in a flat or concave ground. For example, in the feedlot located in Tandil, some samples (T1 to T5) were taken from a windrow situated perpendicular to the land slope. In particular, samples T3 to T5 were extracted from the windrow's center, resulting in the lowest dry matter content.

The dry matter differences could increase the total P variability if this is not considered or the compost is assumed dry. The water dilutes the nutrients, which are usually expressed on a dry matter basis. There lies the importance of measuring the dry matter of these materials.

Fig. 4 also depicts some distinctive features of each establishment. It is observed that Olavarría and Tandil feedlots (blue and green dots) presented lower to medium values of total P. In contrast, Saladillo has the samples with the highest concentration of total P, being these differences observed since the beginning of the composting. For example, from fresh piles waiting to be transported to their final composting destination, two samples taken from inside the pen could be

Table 2 Details of the main determinations and results obtained in this study

Sample	Dry matter (%)	Total P (ppm)	Average LIBS area (-Arb. Un)	Error Av. LIBS area (-Arb. Un)	Sample	Dry matter (%)	Total P (ppm)	Average LIBS area (Arb. Un.)	Error Av. LIBS area (Arb. Un.)
		P_i	A_i	ΔA_i			P_i	A_i	ΔA_i
O-10	82.7	1794	1.10	0.27	T-7	66.5	4745	0.90	0.27
O-8	78.5	2089	1.19	0.05	T-1	61.8	4764	0.68	0.01
O-12	90.6	2993	1.11	0.22	T-2	56.0	4922	1.80	0.16
O-1	84.3	3192	1.39	0.17	S-5	68.3	5053	1.53	0.08
T-5	41.7	3542	1.15	0.08	O-6	65.8	5053	1.52	0.07
T-8	75.5	3585	1.32	0.11	O-5	64.4	5188	1.61	0.22
O-2	69.9	3754	1.04	0.05	S-3	78.2	5283	2.32	0.15
S-1	85.2	3769	1.38	0.03	O-4	63.4	5448	1.59	0.22
S-9	79.3	4236	2.23	0.07	S-4	69.9	5483	1.85	0.04
O-11	70.5	4236	1.17	0.11	S-2	64.1	6424	2.17	0.07
T-4	43.1	4340	1.85	0.04	T-9	71.6	6529	0.98	0.04
O-3	72.7	4390	1.24	0.09	T-6	60.0	7806	1.44	0.05
O-7	68.9	4689	1.26	0.11	S-8	70.1	8678	1.73	0.11
O-9	62.4	4691	1.37	0.22	S-6	54.4	9958	1.69	0.06
T-3	39.1	4702	1.09	0.04	S-7	72.9	11180	2.42	0.20

compared: sample O-8 presented a 25% of total P than sample S-8. This difference could be ascertained by the diet and nutrient balance established in each feedlot. Another reason could be that different amounts of the pen floor were pulled and mixed with the waste in the cleansing maneuvers. More samples of fresh compost should be collected and analyzed to enlighten the ques-

tion if the total P differences in mature compost were correlated to differences in their P content at the initial stages. However, these subjects are out of the scope of the present work. Information about the P supplied in the diet could also be interesting to understand the differences in nutrient efficiency use among feedlots and fattening bovines.

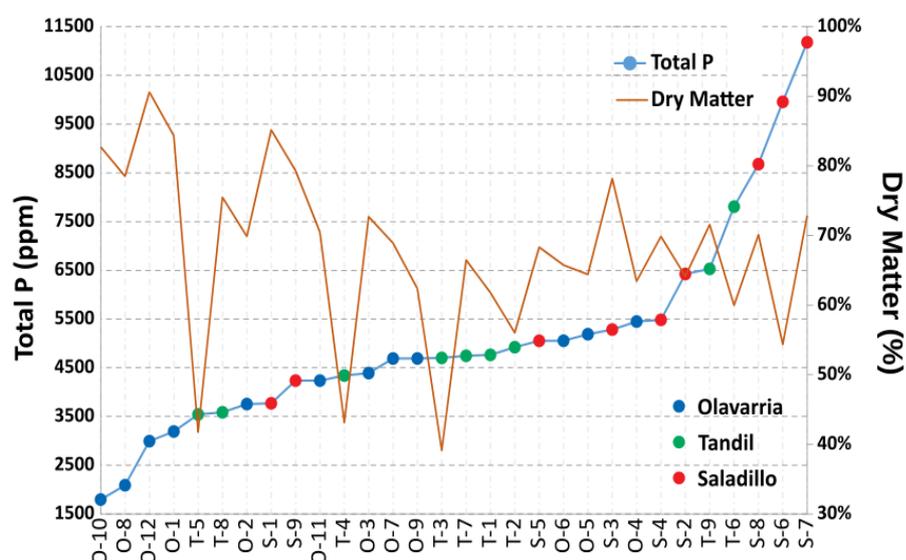


Fig. 4 Chemically determined total P (left axis) and dry matter content (right) for all samples

Besides the total P variations among establishments, differences within a feedlot can be observed. Such differences could arise from the compost volume reduction of piles or windrows as long as time elapses. This reduction is due to the active emission of gases (due to microbial decomposition of the organic matter) and leaching (leachates from compost piles are common under humid climates, and soluble P can be lost with them). However, these ideas should be supported with specific research, which is out of the objectives of this work.

The previous paragraphs presented a characterization of the samples on which the LIBS calibration was performed. In the following, the focus is placed on the relationship between LIBS areas to the chemically determined total P. The analysis is stated in terms of four main features: the slope of the calibration, the goodness of fit, and the mean percentage absolute errors for validation and prediction. Fig. 5 shows the results obtained by running 3000 times the calibration process.

Fig. 5a) shows the histogram and cumulative functions (direct and reverse) obtained from the calibration process. As can be seen, the histogram is slightly asymmetric with a median value of 2.64×10^{-4} LIBS

Arb. Un. / (mg/kg). The Fig shows that around 80% of the slopes are within the interval $2.56 - 2.76 \times 10^{-4}$ LIBS Arb. Un. / (mg/kg). The histogram of the R^2 of the fittings is displayed in Fig. 5b). The Fig also presents the cumulative function. From the Fig, it is apparent that almost 80% of the fittings have a value higher than 0.895. This result suggests a high correlation between the LIBS areas and the chemical determinations of P, which is well described by a linear model. Fig. 5c) depicts the histogram and cumulative function of the mean percentage absolute validation error. As can be seen, 80% of the calibrations have a mean percentage absolute validation error of less than 22%. Finally, Fig. 5d) shows the histogram of the mean percentage absolute prediction error accompanied by its cumulative function. The Fig reveals that almost 80% of the calibrations have a mean percentage absolute prediction error bound to 40%. This last result seems, at first glance, discouraging. However, it should not be forgotten that this is the first approach to a complex problem due to the nature of the samples, concerning their different origins, the techniques used to deal with solid pen residues, and the variability of the matrix where P is found.

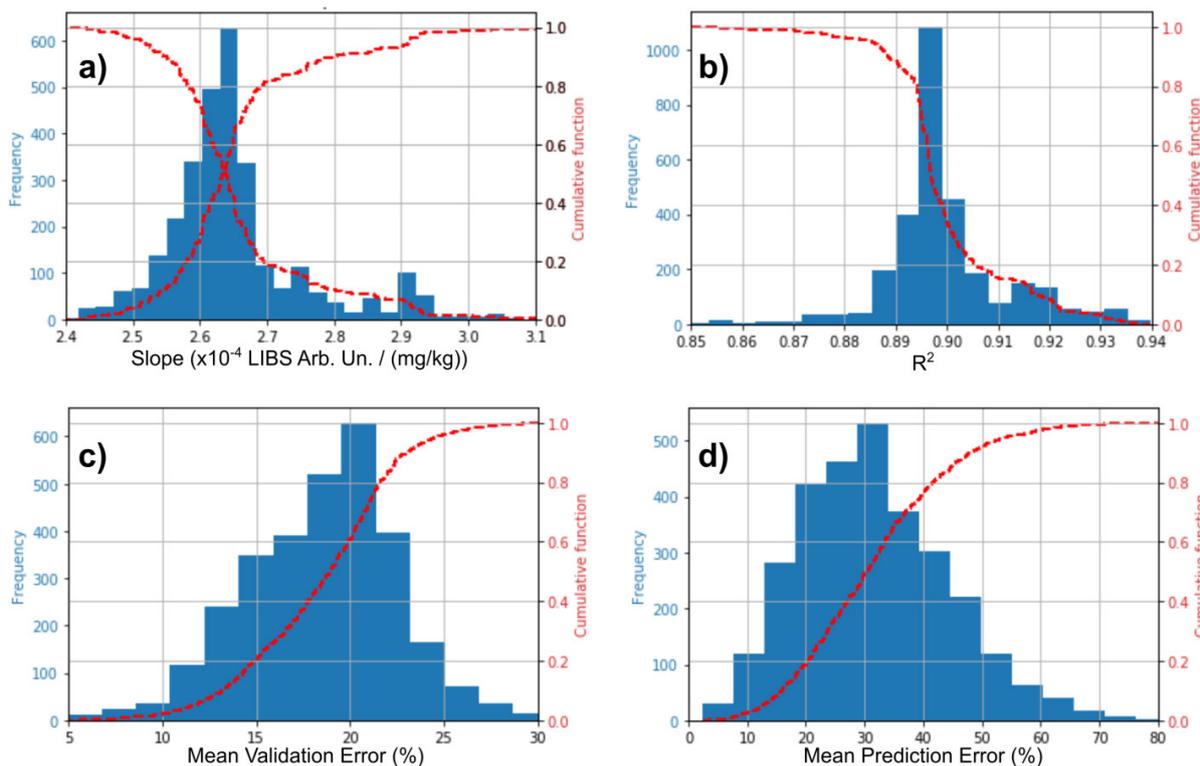


Fig. 5 Histograms and cumulative functions obtained from the calibration, validation, and prediction performed after 3000 repetitions over the samples ensemble
a: Fitted slopes, b: R^2 of the fittings, c: Mean percentage absolute validation errors, d: Mean percentage absolute prediction errors

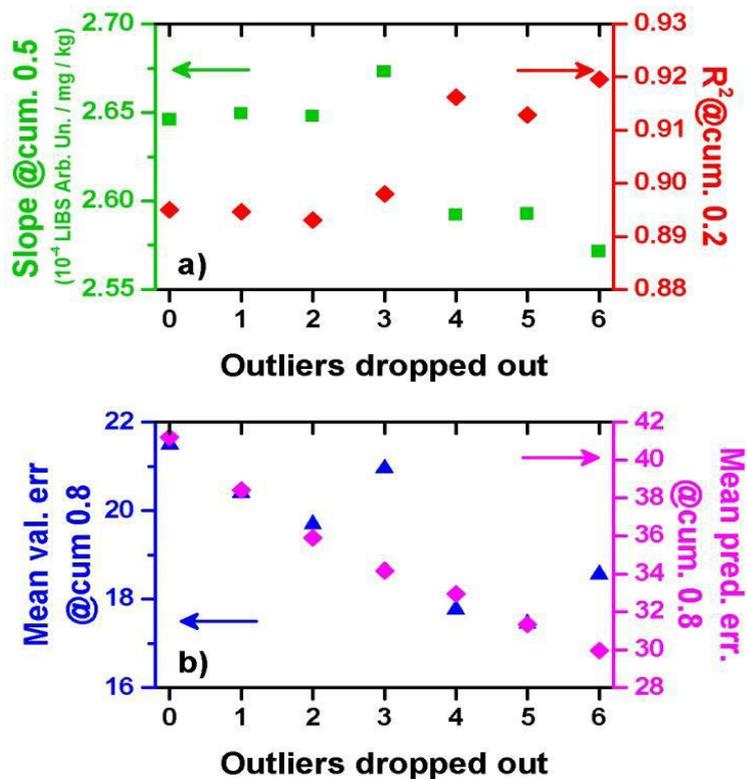


Fig. 6 Analysis of the outlier's effect on the four main statistical indicators. a) Left (right) axis: values of the slope (R^2) for which the cumulative function is 0.5 (0.2). b) Left (right) axis: mean validation (prediction) error for which the cumulative function is 0.8

To further understand this calibration process, as a next step, it was necessary to study the effect of the outliers, focusing on the possibility of lessening the mean validation error. The procedure to reach this goal was the following: a linear fit was applied all over the samples, looking for the sample of maximum percentage absolute error $\left| \frac{(A_{oi} - bP_i)}{A_{oi}} \right|$. Once the sample was identified, such a point was dropped out. Then, the calibration process described earlier was again performed. Four statistical indicators were evaluated to describe the calibration process results: the median of the slopes; the value of the R^2 at which its cumulative function is 0.2; and the values of the mean validation error and the mean prediction error at which their cumulative functions are 0.8. The role of the outliers was explored by dropping out up to 20% of the total samples. Fig. 6a depicts the median of the slopes and the R^2 value for which the cumulative function is 0.2. From the Fig, it is apparent that no appreciable changes are observed by dropping out up to two outliers. However, from the third point onwards, slope and R^2 changes are ob-

served. In particular, a noticeable fit improvement is observed when three to four outliers were dropped out. Fig. 6b) shows the mean validation and prediction errors at which the cumulative function reaches 0.8. Note that whereas the mean validation error had a behavior that resembled those observed in the slopes and R^2 , the mean prediction error monotonously decreased from ~40% to ~30%. This result shows the importance of dealing with outliers.

Table 3 summarizes the main features of the outliers. From the table, it can be seen that there is not a clear pattern that allows us to understand why these points behave as such. These points belong to deep or surface samples, mature or fresh compost, with high amounts of soil or calcium carbonates from the floor of the pens or with evidence of vermicomposting made by different provenance. This diversity in the samples suggests that more research must be performed to fully comprehend these kinds of samples, and more has to be understood about P dynamics during the composting process.

Table 3 Description of the outlier samples

Sample	Dry matter (%)	Chem. total P (mg/kg)	LIBS Area (Arb. Un.)	Maturity (months)	Description
T-1	62	4764	0.677	12	Surficial sample from the top of a windrow perpendicular to the land slope.
T-9	72	6529	0.982	36	Deep sample from a shallow windrow covered with dry grasses. Several earthworms were observed. Coprogenic P concentration inferred.
S-6	54	9957	1.692	6	.Deep sample from a tall windrow
O-10	83	1794	1.096	1	A surficial sample of a pile of materials recently scraped from the pen, with high soil content, including calcium carbonate from quarries nearby (added to seal the floor of the pen).
O-8	79	2088	1.194	1	Surficial sample of a pile recently scraped from the pen and ready to be moved. Presents high content of pieces of calcium carbonate from <i>Petrocalcic</i> horizons quarries nearby or excavated "tosca" used to seal the pen's floor.
O-11	70	4235	2.228	6	Surficial pile sample.

Conclusion

In this work, the LIBS technique was applied to quantify the total P concentration of cattle compost. As a reference standard, chemically determined total P was considered. A significant difference (10.000 ppm) between the minimum and maximum values was observed; Olavarría and Tandil establishments had lower to medium P values, whereas Saladillo showed the highest concentrations. The differences could result from the nutrient balance and/or the pen cleansing management, and further research should be focused on these topics. On the other hand, owing to the diversity in the water content of the samples, a dry matter characterization was previously performed. It was found that dry matter varies from 40% up to 90%. This fact evidences the necessity of considering water content in compost samples in addition to other characterizations to employ it properly. Water content matters not only to avoid nutrient dilution effects but also for carriage costs. Regarding the total P quantification by LIBS technique, a modified version of the Kennard-Stone algorithm based on the Mahalanobis distance was employed to split samples ensemble into calibration and validation groups. Prediction samples were previously taken at random. This procedure achieved a 30% mean percentage absolute validation error calibration after dropping out six outlier samples. This result is considered a first approximation to delineate an expeditious method to measure total P content in compost valuable for farmers. Although this result is not proper of an analytical approach, it paves the way to further research to develop a portable device to perform this technique for total P characterization on farms.

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Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study.

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