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To cite this version:

Roseline Bonnard, Olivier Bour. Comparison of lead concentration in surface soil by induced coupled plasma/optical emission spectrometry and X-ray fluorescence. 10. International UFZ-Deltares/TNO Conference on management of soil, groundwater & sediments (CONSOIL 2008), Jun 2008, Milan, Italy. pp.308-313. ineris-00973299

HAL Id: ineris-00973299

https://ineris.hal.science/ineris-00973299v1

Submitted on 4 Apr 2014

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COMPARISON OF LEAD CONCENTRATION IN SURFACE SOIL BY INDUCTED COUPLED PLASMA/OPTICAL EMISSION SPECTROMETRY AND X-RAY FLUORESCENCE

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Keywords : soil lead concentration, soil samples, in situ measurements, X-ray fluorescence, ICP/OES

ABSTRACT

The lead concentration in the surface soil of a French village, where a secondary lead smelter had been operating for a long time, was investigated. The objective was to define the source term of contamination for modelling the blood lead levels of the children living in that village and comparing the predicted values with the observed data.

The lead concentration was analysed by Inducted Coupled Plasma/Optical Emission Spectrometry (ICP/OES) and by X-ray fluorescence (XRF). During the first campaign, 48 composite soil samples in the first two centimetre layer were collected and prepared in lab for analysis by ICP/OES. Among these samples, 23 were also analysed by XRF. In a second campaign, field measurements by XRF were performed in 133 spots spread over the village, 24 of these spots being places sampled previously.

The analysis of these datasets showed that measurements of soil lead by XRF can provide correct estimates of the soil lead concentrations measured by the reference method.

Statistical analyses showed that ICP/OES analysis gives lower values than XRF analysis. For the samples prepared in lab, a regression coefficient equal to 0,9 was calculated between the two types of results. Regarding the common places tested by the lab method (ICP/OES) and the in-situ method (XRF), a linear regression coefficient could also be defined between the two datasets, but the regression coefficient was smaller. The larger discrepancy between the two kinds of values may be explained by the spatial variability of lead concentration at a small scale and the difference of soil volume explored by sampling and the in-situ approach.

INTRODUCTION

In a village with a long past of soil contamination by lead, the blood lead level of the children population has to be predicted and compared to the observed levels. As the ingestion of surface soil greatly contributes to the exposure of children living on a contaminated site, since a secondary lead smelter had been operating for a long time in the village and some contaminated sand was brought to the ground locally, the collection of many samples was required to have a sufficient knowledge of the source term of exposure and define a map of the lead concentrations by geostatistical methods.

Two campaigns of measurements were organized. The first one consisted of the collection of composite soil samples and analyses at laboratory by the Inducted Coupled Plasma/Optical Emission Spectrometry (ICP/OES). The second one was carried out with a X-Ray Fluorescence (XRF) portable device to perform in-situ analyses.

The present paper examines the accuracy of the concentrations measured by XRF relative to normative method.

METHODS

During the first campaign, 48 samples were taken from the first two centimetres in public areas and private gardens, spread over the village. Each sample was composed from five subsamples, four subsamples surrounding a central subsample located at a distance equal to one meter.

These samples were prepared before being analysed. They were dried, crushed and sieved to 250 µm. Then, they were mineralised according to the European standard procedure EN 13346. Lead concentration was measured by Inducted ICP/OES according to the standard ISO 11885.

Among these samples, 23 ones were selected and their lead concentration was also measured, after drying, crushing and sieving, owing a portable XRF portable device.

In a second campaign, surface soil lead concentrations were determined in 133 zones spread over the village by in situ measurement owing the same XRF portable device. Among these zones, 24 ones had been sampled previously to perform a laboratory analysis. The XRF measurement was then carried just close to the location of the central subsample. Depending on the cases, additional measurements were made next to the location of the other subsamples and/or on the bottom surface of the hollows left by the subsamples. So, according to the zones, from one to ten XRF measurements were performed on the area where surface soil had been previously sampled.

RESULTS AND DISCUSSION

Comparison of the lead concentrations measured by ICP/OES and by XRF for the samples prepared at laboratory

In figure 1, the concentrations measured by XRF (C_{XRF}) are plotted against the concentrations analysed by ICP/OES ($C_{ICP/OES}$). The horizontal bars represent the 95% uncertainty interval for the measurements carried out by ICP/OES. The correlation coefficient between the two datasets is equal to 0.99. Nevertheless, two spots have a concentration by XRF slightly higher than the upper bound of the 95% confidence interval of the corresponding concentration measured by ICP/OES.

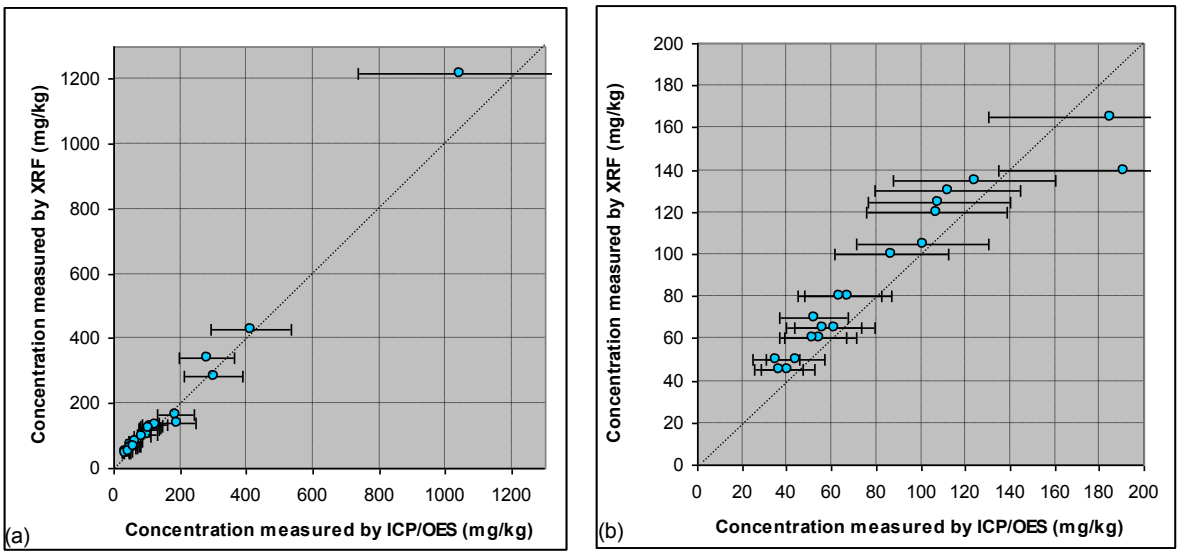

Figure 1 : Comparison of the lead concentrations measured by ICP/OES and by XRF for the samples prepared at laboratory – (a) : a view of the whole range of concentrations tested, (b) : an enlargement for concentrations inferior to 200 mg/kg

The linear regression between the two datasets were investigated.

The model obtained by the least squares method has a slope equal to 0,86 and an intercept equal to 8.32. The coefficient of determination is very high (0.99). But, the residuals do not follow a normal distribution and the property of homoscedasticity is not checked. Moreover, the residuals are slightly

negative for the soil lead concentrations ($C_{ICP/OES}$) inferior to 185 mg/kg and beyond they are much larger.

To improve the model, a least square regression weighted by C_{XRF} was tested as variability seems to improve with soil lead concentration. The relationship between the concentrations measured by XRF and those analysed by ICP/OES is the following one :

$$C_{ICP/OES} = 0.92 \times C_{XRF} - 1.12 \qquad \text{equation 1}$$

with a coefficient of determination (ρ^2) equal to 0.97.

The residuals from equation 1 have a normal and homogeneous distribution for soil concentrations inferior to 185 mg/kg. Above this value, the residuals are higher and the predicted concentrations are less accurate. Nevertheless, the low bias observed with the former model for the calculated concentrations below 185 mg/kg has disappeared and their 95% uncertainty intervals are narrower.

Furthermore, for all the samples, the 95% uncertainty intervals calculated owing to this linear model based on the XRF measurements overlap with the 95 % confidence intervals of the soil lead concentrations determined by the ICP/OES method (see figure 2).

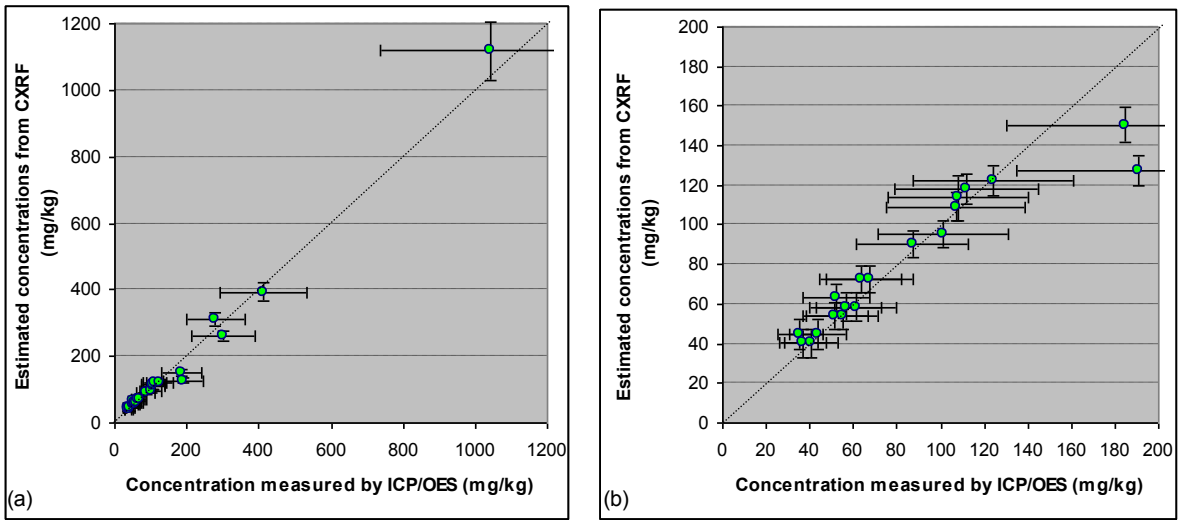

Figure 2 : Comparison of the lead concentration measured by ICP/OES with the predicted concentrations based on equation 1 - (a) : a view of the whole range of concentrations tested, (b) : an enlargement for concentrations inferior to 200 mg/kg

Comparison of the lead concentrations measured in situ by XRF with the lead concentrations measured at laboratory by ICP/OES in the samples taken at the corresponding locations

The lead concentration measured in situ by XRF in an area was estimated as the mean of the different (from one to ten) measurements carried out in this area. The coefficient of determination between this dataset and the lead concentrations measured at the laboratory ICP/OES in the corresponding samples is equal to 0.97. But in a quarter of the cases, the mean of the concentrations measured by XRF is not included in the 95% confidence interval of the measurement determined by ICP/OES at laboratory (figure 3).

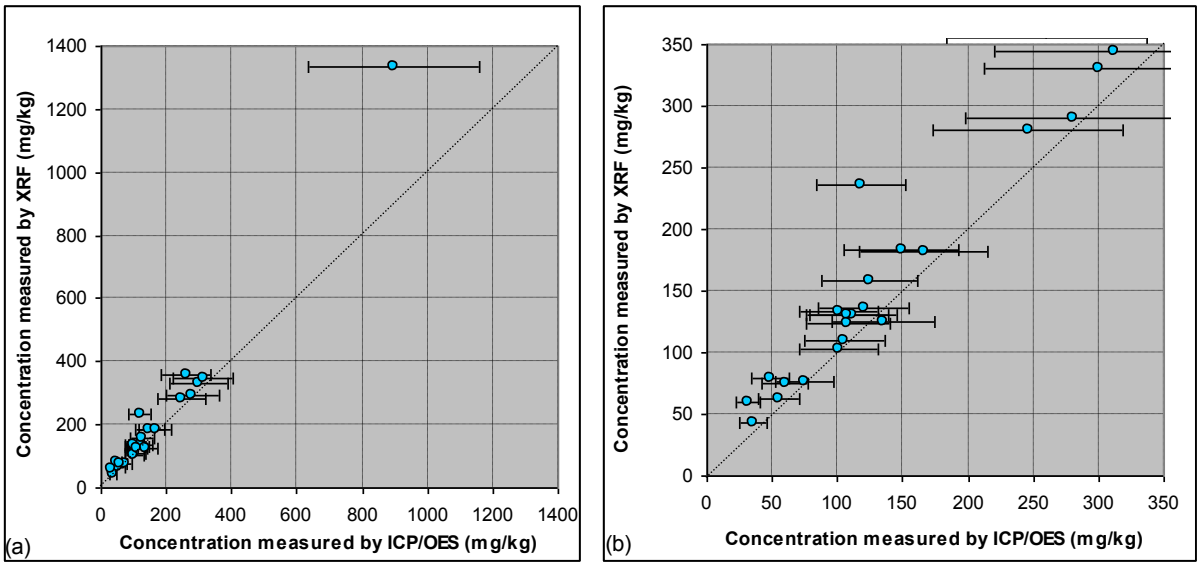

Figure 3 : Comparison of the lead concentrations measured by XRF with the concentrations measured in the corresponding samples prepared at laboratory – (a) : a view of the whole range of concentrations tested, (b) : an enlargement for concentrations inferior to 350 mg/kg

The equation of the linear regression between the two datasets can be written as follows :

$$C_{ICP/OES} = 0.67 \times C_{XRF} - 25.6 \qquad \text{equation 2}$$

The coefficient of determination (ρ^2) is equal to 0.97 and the residual standard deviation has a value of 29.7.

In spite of the high coefficient of determination, this model is not good because there is a clear linearity of the residuals versus the XRF concentrations. The least-squares regression weighted by C_{XRF} slightly reduces the relative errors attached to the predicted concentrations, but the linearity of the residuals, even for low concentrations, can still be observed.

In fact, the different measurements made by XRF in the area of a composite sample reveal a local variability of the soil lead concentration, the discrepancy between the different measurements being able to go up above 100%.

Besides, in the ten sampling areas where measurements by XRF were performed in the hollows left by the composite samples, the mean concentrations measured in these hollows differ from the mean concentrations determined next to their locations from 2% to 70%.

When the gap between these two means was superior to 40%, the lower of them was used to replace the mean calculated from all the XRF measurements performed in a sampling area. Thereby, four values were removed, three being replaced by the mean concentration in the hollows. The relationship between the concentrations measured in-situ by the XRF method and the concentrations measured by ICP/OES in the samples brought to laboratory was then reinvestigated.

In these conditions, the new regression model obtained by least -squares analysis is the following one :

$$C_{ICP/OES} = 1.0 \times C_{XRF} - 22.0 \qquad \text{equation 3}$$

The coefficient of determination (ρ^2) is equal to 0.99 and the residual standard deviation has a value of 16.3.

Owing to these changes, the residual standard deviation has decreased with respect to equation 2. The residuals calculated from this relationship are normal and do not reveal linearity. Notwithstanding, a group of a few negative residuals can be observed for concentrations superior to 200 mg/kg. These findings can be explained by the absence of measurement performed in the sampling hollows of the corresponding areas. If some ones had been carried out, lower mean concentrations may have been found, yielding higher residuals, since contamination by atmospheric fallouts tend to induce higher concentrations at the surface of soil.

Unlike the results obtained with equation 2, the 95% uncertainty intervals of the predicted concentrations calculated owing to this model overlap the 95 % confidence intervals of the soil lead concentrations determined by the ICP/OES method for the all 24 spots tested (figure 4).

The calculated concentrations are obtained with a relative error (for a 95% confidence level) comprised between +/- 3 and 44%, the larger relative error being found for the lower soil concentration of the dataset. Regarding the uncertainty linked to the reference method (29.4% at the 95% confidence level), this error seems to be acceptable. Yet, if the lead concentration of a new spot needs to be predicted from this model, the equation's error has to be added, which increases the width of the uncertainty on the predicted value. According to the parameters of the model, it appears that the soil lead concentrations measured by XRF should be superior or equal to about 150 mg/kg to get uncertainties on the predicted values inferior or equal to those attached to the values obtained by the reference method.

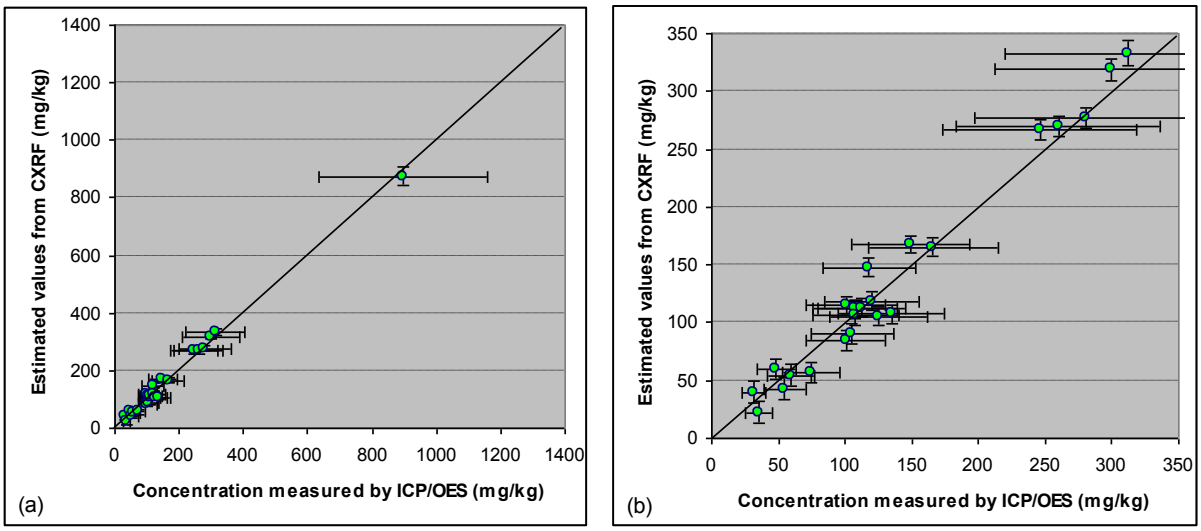

Figure 4 : Comparison of the lead concentration measured by ICP/OES with the predicted concentrations based on equation 3 - (a) : a view of the whole range of concentrations tested, (b) : an enlargement for concentrations inferior to 350 mg/kg

Finally, the increase of the regression coefficient from equation 2 to equation 3 (higher closeness) between the concentrations of the two datasets may be explained, on one hand by the difference of soil volume explored by sampling and the in-situ approach, and on the other hand by the low mobility of lead in soil, since lead contamination can be diluted in the samples with respect to the volume analysed by the XRF portable device.

CONCLUSION

The analysis of these datasets showed that measurements of soil lead by XRF can provide correct estimates of the soil lead concentrations measured by the reference method.

Nevertheless, the in-situ measurements can give deviating results because of the small surface investigated by the XRF device during each measurement compared to the area covered by soil sampling. Because of the variability of the soil concentrations at small scale, several points of measurements should be examined in a same area to get a composite result, following the example of what is made for sampling.

On the other hand, the small quantity of soil explored by the XRF technique may provide a more representative estimate of the children's exposure by direct ingestion of soil than an approach by sampling, in which the depth of soil removed is most of the time superior to the one in real contact with children.

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