

Comparison of AAS, ICP-MS, and pXRF Performance for Copper Analysis in Agricultural Soils

Usporedba AAS, ICP-MS i pXRF analitičkih tehnika za analizu bakra u poljoprivrednim tlima

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ABSTRACT

Accumulated copper (Cu) in agricultural soils is non-biodegradable and persists in the environment, which imposes the need for its regular monitoring by selective, rapid, simple, and low-cost analytical techniques. The performance of portable X-ray fluorescence spectrometers (pXRF) has significantly improved in the last ten years, and they are increasingly applied for environmental, agronomic, and soil science purposes. This study aims to compare the total Cu content determined in agricultural soil samples using three analytical methods (inductively coupled plasma mass spectrometry, (ICP-MS), atomic absorption spectrophotometry (AAS), and pXRF). The research was based on analyses of thirty-five soil samples collected from two vineyards, arable land, and a meadow located in North-West Croatia. In air-dried, milled, and homogenized soil samples, Cu content was detected using a hand-held XRF analyzer under laboratory conditions, while ICP-MS and AAS analysis were performed after open digestion by aqua-regia. Determined Cu content varied in very similar ranges from 51.2 mg/kg to 444.3 mg/kg with an average of 138.9 mg/kg for AAS; from 48.6 mg/kg to 446.4 mg/kg and an average of 139.7 mg/kg for ICP-MS and from 54.0 mg/kg to 435.3 mg/kg with an average of 141.3 mg/kg for pXRF. A high positive correlation between Cu content determined by pXRF and ICP-MS ($R^2 = 0.996$), as well as between pXRF and AAS ($R^2 = 0.997$), along with the results of Bland-Altman statistical analysis indicate that pXRF can be applied as a reliable tool for analyses of Cu-contaminated agricultural soil.

Keywords: environment, soil contamination, heavy metal, analytical chemistry, spectrometry

SAŽETAK

Akumulirani bakar (Cu) u poljoprivrednim tlima nije biorazgradiv i postojan je u okolišu, što nameće potrebu za njegovim redovitim praćenjem selektivnim, brzim, jednostavnim i jeftinim analitičkim tehnikama. Performanse prijenosnih rendgenskih fluorescentnih spektrometara (pXRF) značajno su poboljšane u posljednjih deset godina, te se sve više primjenjuju u znanstvenim istraživanjima vezanim za agronomiju, okoliš i tlo. Cilj ovog rada bio je usporediti sadržaj ukupnog Cu u uzorcima poljoprivrednih tala determiniranog s tri analitičke metode (induktivno spregnuta plazma masena spektrometrija, (ICP-MS), atomska apsorpcijska spektrofotometrija (AAS) i pXRF). Istraživanje se temeljilo na analizi trideset i pet uzoraka tla iz dva vinograda, oranice i livade koji su smješteni u sjeverozapadnom dijelu Hrvatske. U osušanim, samljevenim i homogeniziranim uzorcima tla sadržaj Cu detektiran je prijenosnim XRF analizatorom u laboratorijskim uvjetima, dok su ICP-MS i AAS analize provedene nakon otvorene digestije sa zlatotopkom. Utvrđeni sadržaj Cu varirao je u vrlo sličnim rasponima od 51,2 mg/kg do 444,3 mg/kg s prosjekom od 138,9 mg/kg za AAS; od 48,6 mg/kg do 446,4 mg/kg i prosjek od 139,7 mg/kg za ICP-MS, te od 54,0 mg/kg do 435,3 mg/kg s prosjekom od 141,3 mg/kg za pXRF. Visoka pozitivna korelacija između sadržaja Cu utvrđenog pomoću pXRF i ICP-MS ($R^2 = 0,996$), kao i između pXRF i AAS ($R^2 = 0,997$), zajedno s rezultatima Bland-Altmanove statističke analize, ukazuje da se pXRF može primijeniti kao pouzdan alat za analizu bakrom kontaminiranog poljoprivrednog tla.

Ključne riječi: okoliš, onečišćenje tla, teški metali, analitička kemija, spektrometrija

INTRODUCTION

Copper is an essential trace element for all living organisms (Fan et al., 2011; Brunetto et al., 2016), and it is naturally found in the Earth's crust in concentrations between 25-75 mg/kg (Kabata-Pendias and Mukherjee, 2007; Romić et al., 2014). Various anthropological activities such as the application of copper-based fungicides and liquid manure, discharge of analytical sludge, industrial activities, mining, released particles from car brakes, and deposition of copper from the atmosphere, lead to the accumulation of copper in the soil (Panagos et al., 2018). Copper is not biodegradable and can remain in the soil for decades and, as such, be a potential danger to the environment and human health (Apori et al., 2018; Raffa et al., 2021). Agricultural soils contaminated with copper pose an additional risk to food safety and quality (Alsafran et al., 2022). Copper concentration in agricultural soils is the highest in vineyard soils (Komárek et al., 2008; Mackie et al., 2013; Kelepertzis et al., 2016), followed by olive groves and other permanent crops (Panagos et al., 2018).

Accurate determination of copper in the soil is essential for minimizing the environmental and human health harm caused by pollution. Soil is a very complex matrix, so it is crucial to choose a reliable analytical method (Pan et al., 2020). There are numerous analytical methods developed that can be used to analyze copper in the soil, such as Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Atomic emission Spectroscopy (ICP-AES), Inductively Coupled Mass Spectroscopy (ICP-MS), Atomic fluorescence spectrometry (AFS), X-ray fluorescence spectrometry (XRF), Neutron Activation Analysis (NAA), D. C. Argon Plasma Multielement Atomic emission spectrometry (DCP-MAES), Scanning Electron Microscopy with Energy Dispersive X-Ray and Atomic Absorption Spectrometry (AAS) (Soodan et al., 2014, Li et al., 2021). The primary techniques for detecting heavy metals are the highly sensitive spectroscopic techniques of ICP-MS, ICP-AES, and AAS (Pan et al., 2020). According to Soodan et al. (2014), AAS has been the most widely used technique for analyzing heavy metal content in the soil matrix. This paper will focus on AAS, ICP-MS, and pXRF techniques.

AAS and ICP-MS are traditional analytical techniques for detecting heavy metals, including copper, in soil samples and require complex sample preparation by acid digestion (McComb et al., 2014). There are different methods of sample digestion, but the most often used in the spectral analysis are conventional (open) acid digestion systems and microwave-assisted acid digestion systems (Güven and Akinci, 2011; Asare, 2022). Both ICP-MS and AAS are destructive techniques (Papaefthymiou et al., 2010). AAS is an older technique developed in 1950 (Soodan et al., 2014), while the ICP-MS technique was developed about 30 years ago (Wilschefski and Baxter, 2019). The main advantage of ICP-MS compared to AAS is the multi-element capability (Wilschefski and Baxter, 2019). While AAS can measure only one element, ICP-MS can scan for several elements simultaneously in a single analysis. AAS and ICP-MS are techniques with accurate detection results and high reproducibility and, therefore, preferred over XRF (Li et al., 2021).

On the other hand, the disadvantages of the two spectroscopic techniques compared to pXRF are the device's high price, high level of staff expertise, longer sample processing time, and complex pre-treatment steps, which can affect and pollute the environment (Eser et al., 2014; Wilschefski and Baxter, 2019; Li et al., 2021). pXRF is a non-destructive technique that does not require sample digestion (McComb et al., 2014; Maeaba et al., 2020) with the possibility of determining the multi-element analysis of up to 25 elements in a sample in a short time (Maliki et al., 2017; Maeaba et al., 2020). This technique can detect elements with an atomic number greater than eight in various environmental samples (Alloway, 2013). Menšik et al. (2021) reported that spectral interferences can affect the measurement results by pXRF in the case of analyses of soils contaminated with heavy metals. The most significant advantage of the pXRF technique is the portable models used for rapid screening of contaminated sites to validate which samples and sites need further analysis in the laboratory (Radu and Diamond, 2009; Alloway, 2013). An additional advantage of pXRF instruments is easy handling, fast determination, low device costs, portability, and no negative environmental

impact (McComb et al., 2014; Maliki et al., 2017; Li et al., 2021). The sensitivity and accuracy of pXRF results are highly affected by soil properties such as soil moisture, content of organic matter and particle size (Ravansari and Lemke, 2018; Menšík et al., 2021). Samples preparation (drying and grinding to the required fineness) provides higher accuracy (Lee et al., 2016; Adler et al., 2020; Menšík et al., 2021). pXRF has a higher detection limit and poor accuracy than AAS and ICP-MS, but the pXRF technology is continuously improved (Li et al., 2021).

In this study, a comparison of two traditional analytical techniques (AAS and ICP-MS) for metal determination in soil samples was carried out to validate obtained Cu results in soil samples by the pXRF technique.

MATERIAL AND METHODS

Soil samples and analytical measurements

The research was based on thirty-five archived soil samples collected in 2019 in North-West Croatia from agricultural land in Hrvatsko Zagorje (Rovno, near Krapina). Four cropland (two vineyards, arable land, and meadow) were sampled at three different slope positions (top, middle, and bottom) at three different depths (0-10, 10-20, and 20-30 cm). In our previous research, we aimed to investigate the impact of fungicide application and slope on the spatial distribution of copper in agricultural soils. Specifically, we examined how slope inclination and position on the slope, as well as soil grass coverage, influenced copper accumulation. The results revealed that slope inclination significantly contributed to the copper accumulation in vineyard soils along the entire slope gradient. Surprisingly, this effect extended beyond the vineyard area and also impacted the meadow located at the bottom of the vineyards. The results also implied that soil in vineyard with grass-covered topsoil contained significantly higher amounts of copper than freshly tilled vineyard which was partly attributed to the higher organic matter content present in the grass-covered vineyard soil. In this manuscript, we build upon our previous investigations and regardless of the organic matter content and other soil characteristics,

collected soil samples were subjected to analyses using three different analytical methods to validate the copper measurements obtained via portable X-ray fluorescence (pXRF) spectroscopy. A more detailed description of the location site and soil sample was presented in a previous study (Poljak et al., 2021). The soil samples were prepared for chemical analysis according to the ISO protocol (HRN ISO 11464:2009), which included air drying ($T < 40\text{ }^{\circ}\text{C}$), grinding, sieving through a 2 mm diameter sieve, and homogenization. pXRF measurements were conducted using a Vanta™ handheld (portable) XRF analyzer C Series (Olympus, USA, 2019) according to the loose powder method and the “point and shoot” technique (Rydberg, 2014). Specific details of analyzer specification along with steps of measurements were reported by Perčin et al. (2023). pXRF analyses were performed in dried soil samples to assure more accurate results because the presence of moisture in the sample can negatively affect the absorption of primary emitted X-rays and reduce the scattering of the secondary emitted X-rays from the analyte (López-Núñez, 2022). The soil samples for AAS and ICP-MS measurements were digested and extracted in aqua regia according to ÖNORM L1085 standard (w/V 1:12) in a digestion block (Velp Scientifica, DK 42/26, 2007), one hour at 65 °C and three hours at 150 °C. After the digestion extracts were diluted up to 50 mL with ultrapure water. Copper concentration in digested samples was determined using AAS (Solaar M5 Mk Dual, Thermo Scientific, USA, 2003) and ICP-MS (Nexion DRC-E, Perkin Elmer, USA, 2016).

Data Quality Control

Data quality control was performed by an analysis of reference soil sample ISE 989 (WEPAL, 2015) (Table 1). ISE 989 is a soil sample collected in 2015 as part of the participation of the Analytical laboratory of the Department of General Agronomy in the worldwide Wageningen Evaluating Programme for Analytical Laboratories (WEPAL) conducted by Wageningen University (Netherlands) within International Soil-analytical Exchange (ISE) program.

Table 1. The accuracy and precision of applied analytical techniques

Technique	$\bar{u}_o \pm SD$ (mg/kg)	$\bar{u}_A \pm SD$ (mg/kg)	RPD %	RSD, %
pXRF	180.7 \pm 2.49	157.0 \pm 8.3	15.3	1.38
AAS	159.4 \pm 4.60	154.9 \pm 12.5	2.9	2.88
ICP-MS	148.5 \pm 2.01	154.9 \pm 12.5	-4.1	1.35

\bar{u}_o - mean obtained value of the mass fraction of the Cu in ISE 989 soil sample; SD - standard deviation; \bar{u}_A - mean assigned value of the mass fraction of the Cu in ISE 989 soil sample (average value obtained by 35 laboratories); RSD -relative standard deviation (precision); RPD - relative percent difference (accuracy), (n = 3).

The precision of the performed measurement was calculated and presented as the relative standard deviation (RSD), while the accuracy of the measurement was estimated as the relative percent difference (RPD) between the assigned values in the reference soil sample and obtained values by each analytical technique according to the equation: $[(\bar{u}_o - \bar{u}_A) / \bar{u}_A] \times 100$. Measurements were performed in triplicate. According to the international standard, the permissible deviation in the measurements' precision and accuracy of the pXRF technique is up to $\pm 20\%$ (ISO 13196:2015). Data presented in Table 1 indicate an acceptable accuracy and precision of applied analytical techniques.

Statistical analysis

Data obtained from applying three techniques (pXRF, ICP-MS, and AAS) were subjected to descriptive statistics: minimum, maximum, mean, and standard deviation.

Linear regression was used to estimate the correlation between results obtained by using analytical techniques. Bland-Altman test was conducted to determine the 95% limits of agreement between pXRF and AAS, pXRF and ICP-MS, and AAS and ICP-MS.

RESULTS AND DISCUSSION

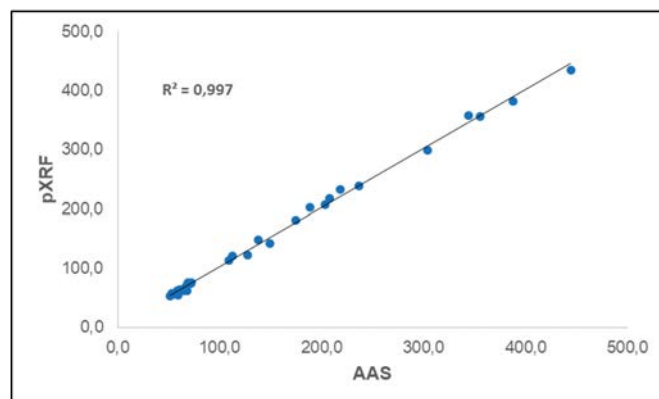
Total copper content determined by the pXRF technique in analyzed soil samples was in the range from 54.0 mg/kg to 435.3 mg/kg, by AAS technique from 51.2 mg/kg to 444.3 mg/kg, and from 48.6 mg/kg to 446.4 mg/kg by ICP-MS technique (Table 2). Due to the effects of soil depth and different land use (vineyard, arable land, and meadow) variability of detected Cu content was very high which is noticeable from similar values of mean and standard deviation, 141.3 ± 110.6 mg/kg (pXRF), 138.9 ± 110.7 mg/kg (AAS) and 139.7 ± 111.2 mg/kg (ICP-MS) (Table 2).

Table 2. Descriptive statistic for quantified total copper content in agricultural soil samples regarding the applied analytical technique (n = 35)

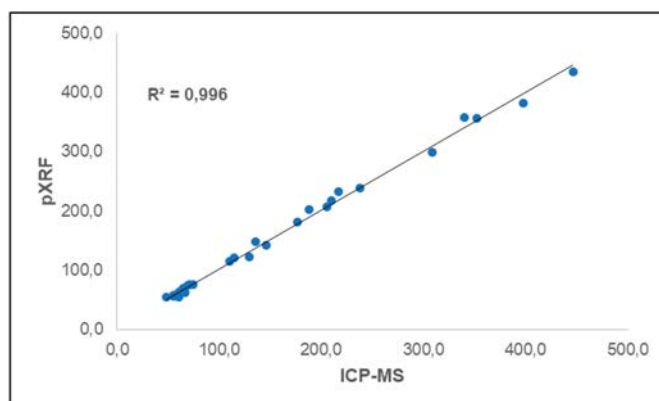
Technique	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)	SD (mg/kg)
pXRF	54.0	435.3	141.3	110.6
AAS	51.2	444.3	138.9	110.7
ICP-MS	48.6	446.4	139.7	111.2

Linear regressions were performed to establish the relationship between applied analytical techniques (Figure 1 a, b, c) especially in terms of validating results of quantified Cu content by pXRF in regards to traditional analytical techniques (AAS and ICP-MS). A high positive correlation ($r \geq 0.998$, $R^2 \geq 0.996$) was observed between the used techniques, indicating that pXRF can be applied as an appropriate tool for analyses of Cu-contaminated soil.

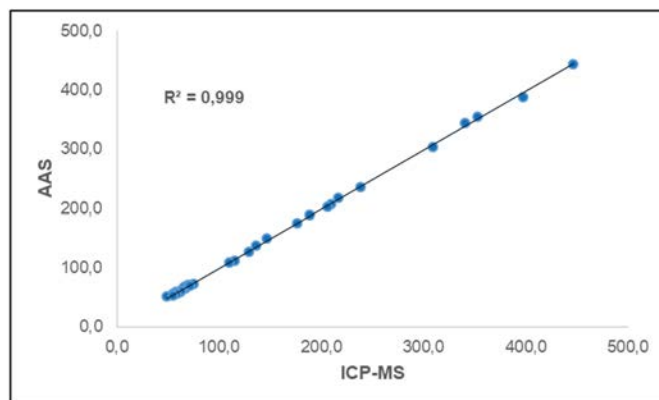
Several previous studies have found a strong correlation between Cu determined by pXRF technique with standard techniques in different soil samples. Chander et al. (2008) reported a strong correlation of Cu concentrations determined by pXRF and AAS in metal-contaminated soils near Göttingen in Germany. Radu and Diamond (2009) investigated soil samples from silver mines and abandoned mining sites in North Tipperary (Ireland) and determined a strong correlation between Cu data obtained by the mentioned techniques. Research from Italy, Campania, based on sampling and soil analysis of farmland and industrial areas, also confirms very high correlation coefficients between results of Cu obtained by pXRF and ICP-MS (Caporale et al., 2018), along with Wan et al. (2019) which investigation was performed on agricultural soil samples from Yunnan Province, southwestern China. Liu et al. (2022) analyzed industrial, residential, and agricultural soil from the western suburbs of Xi'an in the northwest of China, and observed high correlation coefficients between Cu content quantified by pXRF (in-situ) and ICP-MS. High correlation of determined Cu content by the pXRF and wet digestion techniques was also reported by other authors (McLaren et al., 2012; Rouillon and Taylor, 2016; Lee et al., 2016; Silva et al., 2019; Borges et al., 2020). Caporale et al. (2018) assert that microwave-assisted aqua regia extraction does not produce complete soil digestion because the metals that are part of mineral structures are not completely dissolved and cannot be measured. On the other side, higher Cu concentrations measured by pXRF compared to standard laboratory techniques can be the result of a lower pXRF accuracy (Menšík et al., 2021).



(a)



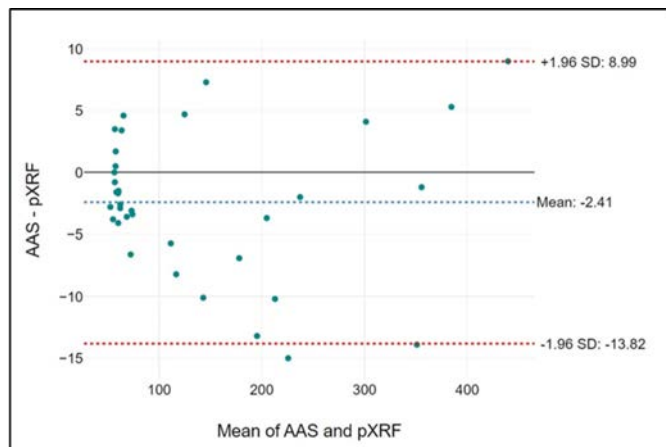
(b)



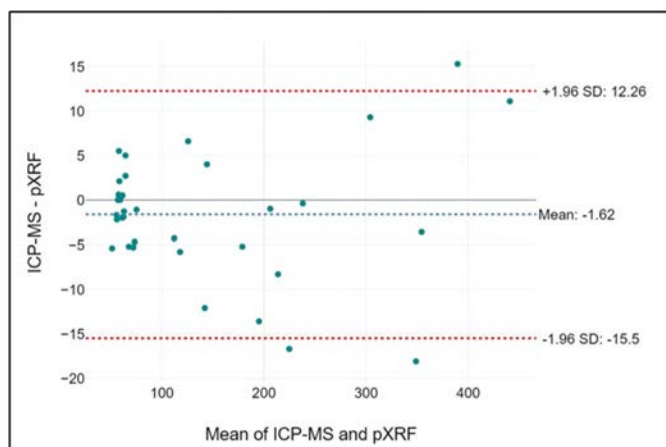
(c)

Figure 1. Linear regression analysis of total Cu content (mg/kg) determined by: (a) pXRF and AAS, (b) pXRF and ICP-MS, and (c) AAS and ICP-MS

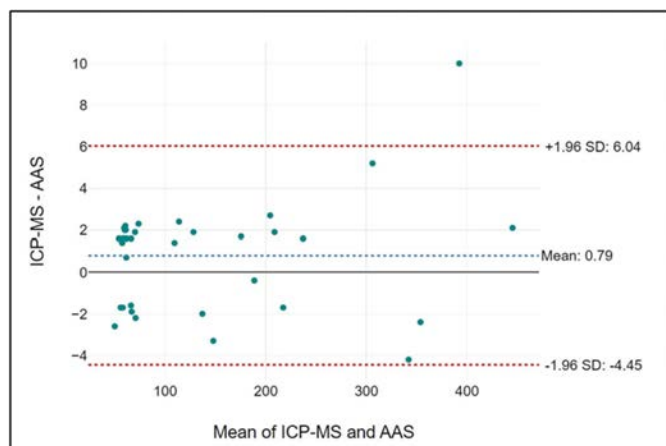
Bland-Altman analysis was used to assess the consistency of measurements (Figure 2 a, b, c). The blue dashed line indicates the mean difference, and the red dashed lines represent the lower and the upper lines of agreement.



(a)



(b)



(c)

Figure 2. The Bland-Altman analysis of the difference (mg/kg) between: (a) AAS/pXRF, (b) ICP MS/pXRF, and (c) ICP MS/AAS for Cu quantification

The 95% limits of agreement between pXRF and AAS are determined from -13.82 to 8.99, which includes more than 95% (34/35) of all data. The differences between results were within acceptable limits, and those two applied techniques were in good agreement. The 95% limits of agreement between pXRF and ICP-MS are determined from -15.5 to 12.26. Most sample points are within the limits of agreement, but three results were outside the boundary. In this case, 91% (32/35) of all data are within the limits. However, Bland and Altman (1986) recommended that 95% of the data points should lie between $\bar{d} + 1.96sd$ and $\bar{d} - 1.96sd$ (\bar{d} = mean difference, (sd) = standard deviation) to establish an acceptable agreement between the two methods. In terms of two traditional analytical techniques (AAS and ICP-MS) 34/35 of all data were within acceptable limits, which imposes the conclusion that results obtained by those two techniques were also in good agreement.

CONCLUSION

Results indicate that portable X-ray fluorescence (pXRF) revealed great potential for the determination of total copper content in agricultural soil samples, especially in the range from 51.3 mg/kg to 442.0 mg/kg. Copper content quantified by ICP-MS and AAS indicates that those two methods corroborated the pXRF technique for Cu measurements in agricultural soil samples. All impose the conclusion that the pXRF technique could be imposed as a suitable technology for rapid detection and quantification of Cu in contaminated soils. Compared to ICP-MS and AAS techniques, the pXRF technique is more cost-effective, less labor-intensive, and more eco-friendly while giving an accurate quantification of copper content promptly.

REFERENCES

- Adler, K., Piikki, K., Söderström, M., Eriksson, J., Alshihabi, O. (2020) Predictions of Cu, Zn, and Cd concentrations in soil using portable X-ray fluorescence measurements. *Sensors*, 20 (2), 474. DOI: <https://doi.org/10.3390/s20020474>
- Alloway, B. J. (2013) Methods for Determining Heavy Metals and Metalloids in Soils. In: Alloway, B., ed. *Heavy Metals in Soils*. Dordrecht: Springer, pp. 97-140. DOI: https://doi.org/10.1007/978-94-007-4470-7_21

- Alsafran, M., Saleem, M.H., AL Jabri, H., Rizwan, M., Usman, K. (2022) Principles and Applicability of Integrated Remediation Strategies for Heavy Metal Removal/Recovery from Contaminated Environments. *Journal of Plant Growth Regulation*, 42, 3419–3440. DOI: <https://doi.org/10.1007/s00344-022-10803-1>
- Apori, O. S., Hanyabui, E., Asiamah, Y. J. (2018) Remediation Technology for Copper Contaminated Soil: A Review. *Asian Soil Research Journal*, 1 (3), 1-7.
- Asare, E. A. (2022) Comparative Study of Two Acid Digestion Protocols for Evaluating Potentially Toxic Elements in Surface Sediments Influenced by Sewage Discharge and Sand Mining Activity. *Chemistry Africa*, 5 (3), 731-744.
- Bland, M. J., Altman, D. G. (1986) Statistical Methods for Assessing Agreement Between Two Methods of Clinical Measurement. *The Lancet*, 327 (8476), 307-310. DOI: [https://doi.org/10.1016/S0140-6736\(86\)90837-8](https://doi.org/10.1016/S0140-6736(86)90837-8)
- Borges, C. S., Weindorf, D. C., Nascimento, D. C., Curi, C., Guimarães Guilherme L.R., Carvalho, G. S., Ribeiro, B. T. (2020) Comparison of portable X-ray fluorescence spectrometry and laboratory-based methods to assess the soil elemental composition: Applications for wetland soils. *Environmental Technology & Innovation*, 19, 100826. DOI: <https://doi.org/10.1016/j.eti.2020.100826>
- Brunetto, G., Bastos de Melo, G.W., Terzano, R., Del Buono, D., Astolfi, S., Tomasi, N., Pii, Y., Mimmo, T., Cesco, S. (2016) Copper accumulation in vineyard soils: Rhizosphere processes and agronomic practices to limit its toxicity. *Chemosphere*, 162, 293-307. DOI: <https://doi.org/10.1016/j.chemosphere.2016.07.104>
- Caporale, A. G., Adamo, P., Capozzi, F., Langella, G., Terribile, F., Vingiani, S. (2018) Monitoring metal pollution in soils using portable-XRF and conventional laboratory-based techniques: Evaluation of the performance and limitations according to metal properties and sources. *Science of The Total Environment*, 643, 516-526. DOI: <https://doi.org/10.1016/j.chemosphere.2016.07.104>
- Chander, K., Hartmann, G., Joergensen, R. G., Khan, K. S., Lamersdorf, N. (2008) Comparison of methods for measuring heavy metals and total phosphorus in soils contaminated by different sources. *Archives of Agronomy and Soil Science*, 54 (4), 413-422.
- Eser, A., Kahraman, E., Demiray, M. (2014) Comparison of Atomic Absorption Spectroscopy and Energy Dispersive X-Ray Fluorescence Spectrometer Methods for Chemical Analysis. *Asian Journal of Chemistry*, 26 (20), 6982-6988.
- Fan, J., He, Z., Ma, L. Q., Stoffella, P. J. (2011) Accumulation and availability of copper in citrus grove soils as affected by fungicide application. *Journal of Soils and Sediments*, 11, 639–648.
- Güven, D. E., Akinci, G. (2011) Comparison of Acid Digestion Techniques To Determine Heavy Metals In Sediment And Soil Samples. *Gazi University Journal of Science*, 24, 29-34.
- ISO 13196 (2015) Soil Quality - Screening Soils for Selected Elements by Energy-Dispersive X-ray Fluorescence Spectrometry Using a Handheld or Portable Instrument. Technical Committee ISO/TC 190. International Organization for Standardization: Geneva, Switzerland, 1–12.
- Kabata-Pendias, A., Mukherjee, A. B. (2007) Trace Elements from Soil to Human. Berlin: Springer-Verlag, pp. 257-268
- Kelepertzis, E., Hashimoto, Y., Wang, S-L., Ban, T. (2016) Copper Accumulation in Vineyard Soils. *Bulletin of the Geological Society of Greece*, Volume 50 (4), 2192–2199.
- Komárek, M., Száková, J., Rohošková, M., Javorská, H., Chrástný, V., Balík J. (2008) Copper contamination of vineyard soils from small wine producers: A case study from the Czech Republic. *Geoderma*, 147 (1-2), 16-22.
- Lee, H., Choi, Y., Suh, J., Lee, S. H. (2016) Mapping copper and lead concentrations at abandoned mine areas using element analysis data from ICP-AES and portable XRF instruments: A comparative study. *International Journal of Environmental Research and Public Health*, 13(4). DOI: <https://doi.org/10.3390/ijerph13040384>
- Liu, S., Peng, B., Li, J. (2022) Ecological Risk Evaluation and Source Identification of Heavy Metal Pollution in Urban Village Soil Based on XRF Technique. *Sustainability*, 14 (9), 5030. DOI: <https://doi.org/10.3390/su14095030>
- Li, W., Niu, N., Guo, N., Zhou, H., Bu, J., Ding, A. (2021) Comparative Study on the Determination of Heavy Metals in Soil by XRF and ICP-MS. *Journal of Physics: Conference Series*, 2009 (1), 012075. DOI: <https://doi.org/10.1088/1742-6596/2009/1/012075>
- López-Núñez, R. (2022) Portable X-ray Fluorescence Analysis of Organic Amendments: A Review. *Applied Sciences*, 12 (14), 6944. DOI: <https://doi.org/10.3390/app12146944>
- Mackie, K. A., Muller, T., Zikeli, S., Kandeler, E. (2013) Long-term copper application in an organic vineyard modifies spatial distribution of soil micro-organisms. *Soil Biology and Biochemistry*, 65, 245-253.
- Maeaba, W., Kumari, R., Prasad, S. (2020) Spectroscopic assessment of heavy metals pollution in roadside soil and road dust: a review. *Applied Spectroscopy Reviews*, 56 (7), 588-611.
- Maliki, A. A., Al-lam, A. K., Hussain, H. M., Al-Ansari, N. (2017) Comparison between inductively coupled plasma and X-ray fluorescence performance for Pb analysis in environmental soil sample. *Environmental Earth Sciences*, 76, 433. DOI: <https://doi.org/10.1007/s12665-017-6753-z>
- McComb, J. Q., Rogers, C., Han, F. X., Tchounwou, P. B. (2014) Rapid screening of heavy metals and trace elements in environmental samples using portable X-ray fluorescence spectrometer, A comparative study. *Water, air, and soil pollution*, 225 (12), 2169. DOI: <https://doi.org/10.1007/s11270-014-2169-5>
- McLaren, T. I., Guppy, C. N., Tighe, M. K., Forster, N., Grave, P., Lisle, L. M., Bennett, J. W. (2012) Rapid, Nondestructive Total Elemental Analysis of Vertisol Soils using Portable X-ray Fluorescence. *Soil Science Society of America Journal*, 76 (4), 1436-1445.
- Menšík, L., Hlisenikovsky, L., Nerušil, P., Kunzová, E. (2021) Comparison of the Concentration of Risk Elements in Alluvial Soils Determined by pXRF In Situ, in the Laboratory, and by ICP-OES. *Agronomy*, 11 (5), 938.
- Panagos, P., Ballabio, C., Lugato, E., Jones, A., Borrelli, P., Scarpa, S., Orgiazzi, A., Montanarella, L. (2018) Potential Sources of Anthropogenic Copper Inputs to European Agricultural Soils. *Sustainability*, 10, 2380.
- Pan, F., Yu, Y., Yu, L., Lin, H., Wang, Y., Zhang, L., Pan, D., Zh, R. (2020) Quantitative assessment on soil concentration of heavy metal-contaminated soil with various sample pretreatment techniques and detection methods. *Environmental Monitoring and Assessment*, 192 (12), 800. DOI: <https://doi.org/10.1007/s10661-020-08775-4>
- Papaefthymiou, H., Papatheodorou, G., Christodoulou, D., Geraga, M., Moustakli, A., Kapolos, J. (2010) Elemental concentrations in sediments of the Patras Harbour, Greece, using INAA, ICP-MS and AAS. *Microchemical Journal*, 96, 269–276.
- Perčín, A., Zgorelec, Ž., Karažija, T., Kisić, I., Župan, N., Šestak, I. (2023) Metals Contained in Various Formulations of Mineral Nitrogen Fertilizers Determined Using Portable X-ray Fluorescence. *Agronomy*, 13 (9), 2282. DOI: <https://doi.org/10.3390/agronomy13092282>

- Poljak, M., Kisić, I., Zgorelec, Ž., Šestak, I., Galić, M., Kuharić, Ž., Jukić, M., Galić, A., Šikić, S., Perčin, A. (2021) Utjecaj fungicida i nagiba padine na prostornu akumulaciju bakra u poljoprivrednim tlima. Proceedings of 56th Croatian and 16th international Symposium on agriculture. Rozman, V., Antunović, Z. (ed.). Vodice: Faculty of Agrobiotechnical Sciences of Josip Juraj Strossmayer University in Osijek, pp. 128-133.
- Radu, T., Diamond, D. (2009) Comparison of soil pollution concentrations determined using AAS and portable XRF techniques. *Journal of Hazardous Materials*, 171 (1-3), 1168–1171.
- Raffa, C. M., Chiampo, F., Shanthakumar, S. (2021) Remediation of Metal/Metalloid-Polluted Soils: A Short Review. *Applied Sciences*, 11 (9), 4134. DOI: <https://doi.org/10.3390/app11094134>
- Ravansari, R., Lemke, L.D. (2018) Portable X-ray fluorescence trace metal measurement in organic rich soils: pXRF response as a function of organic matter fraction. *Geoderma*, 319, 175-184.
- Romić, M., Matijević, L., Bakić, H., Romić, D. (2014) Copper Accumulation in Vineyard Soils: Distribution, Fractionation and Bioavailability Assessment. U. In: M. C. Hernandez Soriano, ed. *Environmental Risk Assessment of Soil Contamination*. London: Intech publication, pp. 800–825.
- Rouillon, M., Taylor, M. P. (2016) Can field portable X-ray fluorescence (pXRF) produce high quality data for application in environmental contamination research?. *Environmental Pollution*, 214, 255-264.
- Rydberg, J. (2014) Wavelength dispersive X-ray fluorescence spectroscopy as a fast, non-destructive and cost-effective analytical method for determining the geochemical composition of small loose-powder sediment samples. *Journal of Paleolimnology*, 52, 265–276.
- Silva, E. A., Weindorf, D.C., Silva, S.H.G., Ribeiro, B.T., Poggere, G.C., Carvalho, T.S., Gonçalves, M.G.M., Guilherme, L.R.G., Curi, N. (2019) Advances in Tropical Soil Characterization via Portable X-Ray Fluorescence Spectrometry. *Pedosphere*, 29 (4), 468-482.
- Soodan, R.K., Pakade, Y. B., Nagpal, A., Katnoria, J. K. (2014) Analytical techniques for estimation of heavy metals in soil ecosystem: A tabulated review. *Talanta*, 125, 405-410.
- Wan, M., Hu, W., Qu, M., Tian, K., Zhang, H., Wang, Y., Huang, B. (2019) Application of arc emission spectrometry and portable X-ray fluorescence spectrometry to rapid risk assessment of heavy metals in agricultural soils. *Ecological Indicators*, 101, 583-594.
- WEPAL (2015) Evaluating Programme for Analytical Laboratories International Soil-Analytical Exchange (ISE) Program; Annual Report for 2015; Wageningen University Environmental Sciences: Wageningen, The Netherlands, pp. 24 and 66.
- Wilschefski, S. C., Baxter, M. R. (2019) Inductively Coupled Plasma Mass Spectrometry: Introduction to Analytical Aspects. *The Clinical Biochemist Reviews*, 40 (3), 115-133. DOI: <https://doi.org/10.33176%2FAACB-19-00024>