Review of: "Probabilistic Assessment of the Heavy Metal Pollution in Debrecen's Topsoil"

Sandra Moreira[1]

1 Instituto Hidrográfico

Potential competing interests: No potential competing interests to declare.

I finished reading the manuscript entitled "Probabilistic Assessment of the Heavy Metal Pollution in Debrecen's Topsoil" by Zsolt Zoltán Fehér and Péter Tamás Nagy. Although it has good potential for publishing, I have some reservations that do not allow me to state that the current version of the manuscript is ready for publishing.

First, I recommend the authors to go over how they use the terms "contamination", "pollutant," and "trace element" throughout the manuscript. It seems that there are some misconceptions, so I suggest the reading of the study "Determining when contamination is pollution — Weight of evidence determinations for sediments and effluents," by Chapman (2017). Furthermore, I would like to point out that there is no universal standard definition for heavy metals; therefore, I avoid using this terminology and instead, I prefer to use, for example, trace elements.

One of my main concerns is regarding the analytical methodology. Handheld XRF spectrometers are frequently used as "point-and-shoot" devices, providing results with no or minimal preparation. The preparation of the sample before its analysis is a crucial step for the quality of the obtained results, and the authors had the care to remove debris that could dilute the metals' concentrations, dried the samples because moisture can decrease the fluorescence intensity of the analytes, and crushed the samples in a mortar to mitigate textural effects. Nonetheless, the samples were analyzed as loose powders in a plastic bag, which tends to provide less accurate results. Furthermore, the irradiation time of the samples was not equal, and no quality control was undertaken. Authors also need to indicate the fraction of the soil (<2 mm or <63 µm?) analyzed, the calibration method (Fundamental Parameters?), and the voltage and the current of the X-ray tube.

I have never used a Niton XL5 Plus XRF spectrometer, but based on my experience, the concentrations of Cd, Co, As, and Pb are very low, and most likely close to or below the limit of detection of the equipment, to be reliably quantified. Furthermore, it is crucial to highlight that this technique is sensitive to spectral interferences such as overlapping peaks (e.g., Fe-Co and Pb-As), which can result in poor accuracy and false positives. Although these interferences can be somewhat overcome, in this type of device, there is no control or knowledge on how the spectral processing is performed and which peaks are chosen to quantify each element. Therefore, especially for elements with very low concentrations, one must ensure that a well-defined element peak exists in the spectra before considering the result.

Despite this, I believe it is still a credible study, but it should be presented as a preliminary approach, stating that additional research is required to corroborate the main findings, and the method's limitations should be included in the

manuscript.

Given that elements like K, Ca, Ti, Fe, and even Mn are typically the primary constituents of the rocks, this study could be focused only on those that usually occur in trace concentrations.

With a dataset of 300 samples, it may be worthwhile to establish a regional baseline for the analyzed elements, which can then be used in future studies to assess the evolution of their concentrations in the topsoil. However, it is important to point out that one cannot conclude that the abundance of an element is due to anthropogenic activity (e.g., mining) without comparing it with background or baseline concentrations.

I would like to see a comparison of the concentrations of the metals in urban and non-urban areas, as well as a more in-depth discussion of the results and an attempt to link the spatial variation of the elements with the local lithologies and/or anthropogenic activities. The main findings are usually justified based on general considerations and studies from other countries without taking into account the geology of each region.

Please also see the attached document.