



Dissertation review

A study of the behavior of selected metals in affected environments using an isotopic approach

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Doctoral student Rafael Santos Baieta dealt with the biogeochemical fate of selected metals in the environment including isotopic tracing. The dissertation thesis constitutes of 72 pages of summarizing text with references, amended with 3 published papers included as annexes. Two of the annexes were first authored by Rafael Santos Baieta in respected scientific journals with impact factors from 2.47 to 7.42.

After reading the summarizing text, I can conclude that it has a logical structure reflecting the diversity of the published papers. The introduction described the general topics connected with pollution of environment by metals, storage of metals in soil, wildfires, tree rings and metal isotopes. I read with interest but several times I was attracted by statements with obsolete reference(s). Was there a particular reason? For example, on page 3 sentence “Today this development is recorded in polar ice cores, which we can study (Dickson et al., 1972).” It says today but the reference used to support this is 50 years old. I believe there are dozens of much recent papers on metals in ice cores. Another example, page 4 again “Soil Pb concentrations are now decreasing concentrations worldwide are now decreasing, a first in recorded history (Friedland et al., 1992; Trefry et al., 1985). The text says “now” but the references supporting this statement are 30 and 37 years old, respectively. Please comment.

Furthermore, there were some inconsistent statements for example: On page 6, it says “Metal-bearing particles may be wind-blown and transport contaminants far away from the source (Csavina et al., 2014, 2011), or they can be pulverized.” I do not understand this. Please explain. Finally, on page 11 “This single article (Lepp 1975) gave rise to the field of dendrochronology, which today helps researchers composite a more accurate picture of past events.” My textbook of dendrochronology says that this field of research (i.e. dendrochronology) was started by Andrew. E. Douglass in late 1800s or early 1900s. Please comment.

The thesis continues with Methodology section including sampling procedures, treatment and analytical part. I have two questions in terms of soil analysis methods. Milled soil samples were then dissolved using 0.5 ml of HClO₄ (70–72 %) and 10 ml of HF (50 %) and evaporated to dryness at 170 °C for two hours. It seems to me there could be missing something here, what was the concentration of organic material in the soils samples?

The first paper in Annex II describes migration of Pb and Cu in semi-arid soils together with the differences in behavior of these metals based on isotopic analysis. The next study first authored by applicant connects the soil survey and tree ring assessment near the smelter and mining waste dumps. For the tree ring study presented in annex III I have several critical comments and question for discussion. First of all, concerning relatively extensive discussion I am concerned about the number of trees (only two). There are several recent papers indicating that you need at least 3 different trees from a site to draw some meaningful conclusions. This is of course frequent critical comment by many reviewers but of course I understand that there could be only single tree at each site. Is that so? Please comment. Second of all, each tree was cored three times but I could not find an information on the usage of individual tree cores (i.e. were they pooled or was each used for another analysis?) Please explain, I am interested how much material is needed for $\delta^{13}\text{C}$. Third of all, several recent papers dealing with metals in tree rings indicate importance of the heartwood-sapwood boundary (not “hardwood” as stated on page 10). Thick heartwood trees were not recommended for dendrochemical studies. Does *Pinus Montezuma* belong to the trees with thin or thick sapwood? Some works indicated abrupt increase of analytes on the heartwood-sapwood boundary (e.g. Pearson et al. 2006, Applied Geochemistry), could this explain high concentrations in your most recent tree rings? And for the last, I understood that the younger tree had elevated concentrations of contaminants in tree rings and greater $\delta^{13}\text{C}$, could the delta be used as a proxy for normalization? For general discussion, what is the concept for Pb atmospheric uptake by assimilatory organs and how it is transported to the tree rings.

The third paper in annex IV described the effect of burning temperature onto the Pb isotopic composition of the topsoil. From the conclusions in this valuable paper it seems that the fire severity or burning temperature plays an important role in the fractionation process. For the discussion, I understood that the soil burn severity value is based on visual assessment. Could you think or propose an analytical method that could be used for assessment of the fire severity?

With respect to the extensive forest fire this year in the Czech Republic will the results (isotopic changes) of presented study be applicable to local soils?

Despite the critical comments above, the presented thesis as a whole together with the published scientific papers demonstrated the abilities of applicant to conceptualize research questions, evaluate and present scientific data. The submitted papers by applicant Mgr. Rafael Santos Baieta are his original contributions and extended the general knowledge on behavior of environmental contaminants and isotopic tracing of pollution. Thus it is my pleasure to recommend this Ph.D. thesis as a base for graduation in a doctoral study program and after a successful defense award the doctoral degree.

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Tomáš Navrátil