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Review of PhD thesis by MSc. Christopher Ash

Title: The behaviour and fate of potentially toxic elements of anthropogenic origin in the environment, as influenced by soil properties and various leaching solvents

The thesis by Christopher Ash is focused on a scientifically sound topic, but the title is too general. The author says in the Preface that the central theme of the thesis is the application of low-molecular-mass organic acids (LMMOA) in experimental research, but three of the the attached papers, dealing with Cu in vineyard soils (paper #1), soils from shooting ranges (paper #2) and forest soils of the Jizera Mountains (paper #5) are out of the this topic. It would be more consistent and easier to read, if the manuscript would contain only papers dealing with LMMOAs and the title of the thesis would be more focused.

The first part of the manuscripts corresponds to the extended “thesis methodology”, which I have already reviewed 1 year ago. I only repeat that this literature review is well written, namely the chapter devoted the role of humic substances and simple organic acids in the environmental systems. Here, I have only few comments: (i) chapter 1.1.2 on the mining and smelting in Kutná Hora does not logically fit into the very introductory parts of the text; it should be either moved to chapter entitled “Areas of study” (which is in my opinion too short with only few lines describing each locality) or supplemented with similar text devoted to other study areas (e.g., mining and smelting in the Příbram area); (ii) page 6, second para: redox states should not be given in Arabic numbers (thus As^{III} or As(III) should be used instead of As³⁺); (iii) there is a couple of “et al.” missing in the text (e.g., Table 3).

Hypotheses and aims are well structured and the summary describing major findings from the published papers is very clear. Despite the fact that all the papers have already been reviewed by external reviewers, I have several comments and questions, which could be helpful for clarifying some of the points during the defence of the thesis:

- (i) It is a pity that the slag material was not better characterized (bulk chemistry, bulk mineralogy) and numerous papers from the literature, which have previously described these slags from the chemical and mineralogical point of views have even not been cited (e.g., Manasse and Mellini, 2002, N. Jb. Miner. Mh. 2002(8), 369-384). In my opinion, the use of 2 M HNO₃ extraction used in papers #3 and #4 is not convenient for studying metal(loid)s of anthropogenic origin in soils and is totally unsuitable for slags. It would be much better to have total concentrations for all these materials.
- (ii) Paper #7 is a technical study, but rationale for real-life application is missing. It seems to me that soil washing as a remediation option has been abandoned and chemical stabilization with amendments is currently more and more used for polluted soils. The

understanding of processes and mechanisms of retention of contaminant-organic complexes could be greatly enhanced by thermodynamic modelling, which unfortunately has not been done (there can also be extensive competition for organic ligands in the solutions).

- (iii) It seems to me that it would be better to see all the sequential extraction data expressed as absolute concentration in mg/kg rather than % of the total (papers #6 and #8). The description of differences in Pb and As release from soils by LMMOA is the major finding. However, the relationship of As leaching and ligand-promoted dissolution of Fe-oxides could also be supplemented with presentation of Fe leaching curves (given for instance in the Supplementary Material of the paper) and not only as correlation coefficient in the table. Is there any other approach besides BCR sequential extraction, which could potentially be used to verify the hypothesis of Fe-oxides dissolution?

Overall, based on the above consideration and despite several critical comments, I am convinced that Christopher Ash demonstrated the ability to design and perform the laboratory experiments, to use a variety of analytical techniques, to assess and discuss the obtained data and to write scientific papers. Number of papers and quality of the journals, where the results have been published is far exceeding criteria for a PhD thesis. I highly recommend this thesis for the defence by the candidate.

In Lučkovice, September 20, 2016



Vojtěch Ettler