

Review report of the dissertation theses entitled
„Effects of phosphate on the mobility of arsenic
in contaminated areas“
submitted by the PhD student
MSc. Petra Stubbe (by birth Venhauerova)

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Introduction

The role of phosphorus (P), especially in the form of phosphate (PO_4^{3-}) in the retention of inorganic forms of arsenic (As), and thus, also in their mobility in soils and sediments is generally known and has been studied for a long time by many authors all over the world; however, its role is less recognised regarding to the inorganic forms of antimony (Sb). The present dissertation theses build on this issue and based on a series of laboratory and field observations coupled with really deep mineralogical characterisation of the studied soils/sediments, investigate the effect of phosphates on the retention of As, but also Sb in soils and sediments. To understand the effect of P on the mobility of these two metalloids, the author used various standard methodologies, selective chemical extractions, mineralogical methods, especially microprobe (EMP) analysis and Raman spectroscopy, as well as thermodynamic modelling with PHREEQC software. Moreover, the last work is world-unique contribution to the knowledge of geochemical stability of two arsenates: yukonite and amorphous ferric arsenate under the presence of high-concentration PO_4^{3-} solutions.

Evaluation of originality and comments/questions on the dissertation theses

The work is based on the results of three published articles in scientific journals with a high rating and a rigorous review process, which itself guarantee high originality, innovative aspect and international acceptance of the science presented in these dissertation theses. As a reviewer, I consider it very beneficial to compare the mobility of As with Sb in soils with increasing concentration of phosphates where the author offers an alternative explanation why Sb behaves differently than As. It is explained by the preferential sorption of Sb by Fe-rich clay minerals under the high As concentrations.

Another interesting result comes from a field study published in Environmental Pollution (2022), pointing to the competitive behaviour of As and PO_4^{3-} in the approximately 70 m long stream (Viničný potok), into which waste water from the WWTP flows. Here, **I would be interested in whether these findings are stable over time as the research was**

conducted in a limited time period. I missed at least a brief mention of how this interaction develops further beyond the mouth of the stream into the next stream as illustrated in Fig. 2.1. *Can we expect a similar situation or will this competitive behaviour between As and phosphates “break down” due to dilution by stream waters and sediments? What are the concentrations of As and P in the water and sediment after the confluence of the streams?*

Please, present in detail how “theoretical As concentrations in water (C_F) after mixing were obtained. This is shown neither in the article nor in accompanying text in the dissertation theses.

In addition to the above-mentioned comments on the dissertation work, I would like to add some other observations or questions that the doctoral student could kindly clarify during the defence.

When studying the mobilisation effect of increasing PO_4^{3-} concentration on As (or Sb) in soils and sediments, one could probably consider the own adsorption of externally added P in these solid phases because the adsorption of phosphates itself has an effect on the competitive behaviour against the adsorption of As and could clarify also differences in its extracted fractions between soils and sediments. I think that when the adsorption of externally added PO_4^{3-} in a given soil or sediment is higher than in another soil or sediment, the extracted proportion of As would be higher due to competition for adsorption sites on solid phases and vice versa. Did not you plan to consider this option or at least read about it? I would be also interested in this for the following reason: **“When I compared the 24-h extraction data with a PO_4^{3-} solution of sediments from the Viničný potok with soils from the Příklad and Krásna Hora, it is obvious that in percentage terms, more As is released from the sediments than from the soils at approximately the same concentration of PO_4^{3-} (please, compare Fig. 2.4 with Fig. 3.6).”** *Or these differences can be explained “only” in terms of different mineralogy?*

Although you did single-step, even selective extractions, sequential extractions could also be considered in the future, which, in connection with a very detailed mineralogical characterisation of the studied materials, could bring a deeper clarification of the function of P in the retention and mobility of As and Sb. Here, it would be nice to consider the possibility of studying sequential extractions of As or Sb before extraction and after extraction with PO_4^{3-} solutions, at least at their concentrations when higher mobilisation of As and Sb occurs compared to the control, i.e., at zero concentration of PO_4^{3-} . This could clarify from which reservoirs As is released by the action of phosphates.

My another comment and question is: *Why did you use different reagents (oxalate solution versus 1 M HCl) to determine the content of reactive Fe oxides and the proportion of As, Sb and P in different studies?* In the study in Environmental Pollution from the year 2022, it is an oxalate solution and in the study in Applied Geochemistry (2023) it is 1 M HCl. *Are these two reagents for determining the content of reactive forms of Fe oxides comparable?*

Finally, I found that the concentration evolution of As and P with time shown in Figs. 4.2 and 4.3 was fitted to some kind of chemical kinetics equation, here so called “two pool

first-order model". It would be useful to discuss this "model" in detail during your defence, particularly, to show the parameters describing the rate of change. It seems from Fig. 4.2 and 4.3 that for example, the rate of As release is the highest at the highest PO_4^{3-} concentration used because the slope of the curves seems to be steeper than at lower PO_4^{3-} concentration or at zero concentration. *What mechanisms of As release from the studied solids lie behind this equation?*

Final remark

The dissertation theses as a whole seem to me to be a high-quality and balanced contribution to world science for understanding the interaction of phosphates with ions of toxic metalloids, As and Sb. The candidate MSc. Petra Stubbe for the doctoral degree has demonstrated the ability to work independently and in a team. I recommend her dissertation theses for defence and after their successful defence, **I propose to reward her with the doctoral degree PhD. in study programme Applied Geology.**

In Bratislava, 23rd of May 2024


prof. Edgar Hiller