Review Report on the PhD Thesis submitted to Charles University in Prague

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Title: Wildfires in Polluted Areas: Mineralogical Transformations and Remobilization of Metal(loid)s

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The present review report is organized in the following sections: Introduction, Originality of the research, Brief description of the thesis, Scientific quality of the research chapters and overall assessment.

Introduction

Wildfires have been an important natural process affecting the Earth's system for over 350 million years. However, nowadays the present regimes are not driven by natural or controlled process and as so, they are consider an accelerating problem causing serious environmental and economical impacts. Another important issue is the problematic associated to soil contaminated places, mainly surroundings of mines and smellers, which may be exposed to wildfires and having the possibility to contribute to the remobilization of metal(loid)s. Both issues are of huge relevance, and should be investigated. Understanding the dynamic of metal(loid)s remobilization on anthropogenic contaminated places is essential for ecosystems management and risk assessment and sustainability.

The PhD thesis of Marek Tuhý explore one of the possible negative side effects of wildfire, namely the problem related to their impacts on contaminants in highly polluted places in semi-arid areas, which may cause remobilization of metal(loid)s. Several important issues affecting remobilization of these inorganic elements are addressed with the focus on experimental wildfires simulation to obtain information's regarding this possible remobilization. Thus, this thesis addresses highly relevant and vital areas of wildfire research.

Originality of the research

The thesis present original research results in the area of the impacts of wildfires on contaminated biomass-rich soils systems, a phenomenon that has vaguely been studied so far. It makes a substantial contribution by addressing and solving relevant questions that are interesting for others within the field.

Brief description of the thesis structure

The thesis is well written, clear and concise, but balance with sufficient detail, with very attractive, functional figures and layout. A very interesting and positive feature of this thesis is the "boxes" that allow the readers to have general and specific complementary information that are fundamental for a comprehensive understanding of the topic. The structure of the dissertation is correct and chapters are well structure and presented in logical order.

The thesis comprises the abstract (in English and Czech), 57 pages of text, including figures and tables, structured in seven chapters, one chapter of References and five annexes (with the scientific outcome of the Author: three published papers in IF journals, one unpublished data set and one published news in the magazine Geochemie, in Czech).

Scientific quality of the research chapters

Taking the thesis as a whole, Mr. Marek Tuhý demonstrated the ability to choose justified methods for reaching the research goals, to apply them and to produce reliable results. The thesis begins with the abstract and the introduction (chapter 1) to the subject and well as the motivation for the study of the topic. Chapter 2 consists of a literature review of the wildfires in the environmental systems that is short and to point. Although this chapter covers sufficiently the research area and some of the most relevant references of the topic, I miss reading in more detail the effects of the remobilization of metal(loid)s on soil functioning and the possible off-site effects on the aquatic systems (even if it was beyond the scope of this thesis). Furthermore, this chapter clearly identified the topic, the hypothesis and the research questions, which directly leads to a list of several main aims of the thesis. In my opinion, the aims are carefully presented, convincing and of scientific relevance.

The research methodology is credible and includes a very good description of the research work that was developed as describe in chapter 3. The methods and techniques applied in the execution of the work are appropriated, effective and properly applied. A combination of different techniques, from bulk chemistry (e.g. spectroscopic techniques: CV-AAS, ICP-OES, ICP-MS) to mineralogical analysis (X-ray diffraction, scanning electron microscopy and electron microprobe and automated mineralogy- autoSEM) were used to obtain detailed information about samples structure, composition and metal(loid) speciation. A particularly interesting and important feature of this thesis is the application of the thermodesorption technique with novel experimental setups to better simulate the potential metal (loid) remobilization from the topsoil during wildfires under laboratory conditions. Furthermore, he optimize and validate the automated SEM (autoSEM) technique for obtaining quantitative data on the partitioning of metal(loid)s.

The presentation and analysis of the work performed by Mr. Marek Tuhý is described in chapter 4-6 (and corresponding annexes I-IV), each addressing a specific scientific problem. It should be emphasize that most of the chapters of this thesis are published in international scientific journals in the field: *Environmental Pollution* (chapter 4), *Chemosphere* (chapter 5) and *Journal of Environmental Management* (chapter 6) and the part of the results of chapter 6 that are not still published (annex IV) are for sure, likely to be, since they cover an important research gap and representing cutting edge research in the study field.

The outcome of chapter 4 and annex I is of major importance as it provides a new generating tool (novel "dot" mapping approach): automated mineralogy (autoSEM), that, despite the limitations, proved to be a convenient tool for obtaining data on the partitioning of metal(loid)s in the heavy mineral fraction of a mineralogical complex soil systems. This information is not only fundamental to understand the fate of metal(loid)s during wildfires, but also in other fields of soil science.

Chapter 5 and annex II brings us a subject of major concern that is the mercury emissions into the atmosphere. Once emitted or released, mercury persist in the environment where it circulates between air, water, sediments, soils and living creatures. It can travel long distances to areas far from any production or use, like the Artic or Antarctic regions. Although, wildfires has already been identified a diffuse source of mercury to the environment, their remobilization (due to the

occurrence of wildfires) from soils and biomass in higher polluted areas near smelting/mining sites has been poorly study. The results obtained in this thesis, although obtained in wildfire simulations, provide valuable information to understand and predict the risks of wildfires on this kind of polluted areas. I would like to congratulate the candidate for bearing in mind that the main value of studies conducted in control a controlled environment (in this case, laboratory simulation of mercury remobilization during wildfires), consists in the detailed description of the obtained results. And thus, further work, as field measurements of Hg fluxes should also be applied for better understand the role of wildfires in Hg cycling near the active smelters in semi-arid regions.

The work developed in chapter 6 and annex III provide important knowledge, relating the release of metal(loid)s (Cu, Zn, Cd and Pb) from burnt soil and biomass in smelter-polluted semi-arid areas. Furthermore, it appoints this areas as significant sources of metal(loid)s remobilization. This study has an excellent design with two novel experimental setups of laboratory burning experiments (a single-step combustion set-up and a set-up with continuous temperature increase and on-line ICP-OES detection) combined with chemical and multi-methods mineralogical investigations of the initial materials (soil and biomass), ashes and aerosols. Once again, the candidate demonstrates knowledge about the limitation of the results obtained in laboratory wildfire simulations. Some reservations and criticism should, however, be applied for the extrapolation of this results to real-scale condition. The candidate suggest ideas for further experimental work to try (for example, an integrative approach using laboratory-based large scale wildfires experiments and/or in-situ experiments (prescribe fires)could be applied) to overcame some of the limitations and to better understand the mechanisms and processes controlling the remobilization of metal(loid) from burnt soils and biomass on type of areas.

As demonstrated in chapter 7, the main goals and aims of this thesis have been achieved. Here, the candidate integrates and consolidate the issues investigated in all the chapters and annexes of the thesis, including also some questions raised by his study. Furthermore, he highlights the contribution of the thesis and also indicates its limitations, showing clearly that he has a comprehensive understanding of the context of his work. Mr. Marek Tuhý identifies several futures research suggestion that emanate from her research can contribute to fill some knowledge gap. I agree that Mr. Marek Tuhý thesis provide useful additional and valuable information's to

the body of research concerning the impacts of wildfires on contaminated anthropogenic areas and their environmental implications, namely understanding the individual processes driving the wildfire-induced remobilization of metal(loid)s.

Overall assessment

The work of this thesis demonstrates originality of conception and execution and represents a great deal of results, which are very well presented, and their interpretation is at a high scientific level. Based on the above considerations the overall quality of the thesis is very good and fulfills the requirements for obtaining the PhD degree. In my opinion, Mr. Marek Tuhý should be allowed to defend his thesis.

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