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Review of the PhD Thesis
of Dr. Juliana Souza-Kasprzyk,
entitled:

"Biogeochemistry of chemical elements in Arctic soils: multi-factor effects on element concentrations from different locations in Billefjord, Svalbard"

The basis for issuing the opinion is the letter of Dean of the Faculty of Chemistry of Adam Mickiewicz University in Poznań, Prof. dr. hab. Maciej Kubicki (L. dz. WCH/25/KZ/2023).

The mentioned above doctoral dissertation was conducted under the supervision of Prof. Przemysław Niedzielski at the Faculty of Chemistry of Adam Mickiewicz University in Poznań.

The researchers conducted by Dr. Juliana Souza-Kasprzyk are related to current and relevant topic, which is the assessment of the impact of human activities on the state of the environment, and the extremely dynamic development of modern technologies.

The Author focused her considerations on the area of the Arctic (Svalbard), perceived as free from pollution.

The manuscript was properly organized and written in good scientific English. The whole dissertation has been written on 180 pages and enriched with 49 figures, which show the sampling sites, the apparatus used and the detailed results obtained. In addition, 24 tables were included that present the classification of the analytes determined, procedures for sample leaching/decomposition, analytical parameters of the instrumentation used, detection limits

obtained and analyte content in soils samples with comparison of the results with other studies. The bibliography section shows more than 170 pertinent references.

The whole dissertation begins with an abstract (written in English and Polish) and in subsequent chapters the Arctic environment was characterized: geographical location, atmospheric conditions as well as the impact of climate change and other factors (ozone depletion, habitat fragmentation, overexploitation, biological invasion and chemical disturbance).

The Author then characterized the Svalbard Archipelago geographically, geologically, historically and politically, considering the role of this area as a source of mineral and hydrocarbon exploration.

In the second chapter Dr. Juliana Souza-Kasprzyk clearly defined the purpose of the work, which was to identify and investigate factors that may affect the accumulation of essential elements (EEs, i.e.: calcium, copper phosphorus, iron magnesium, potassium, sodium and zinc), potentially toxic elements (PTEs, i.e.: aluminum, antimony, arsenic, cadmium, cobalt, chromium, lead and manganese), rare earth elements (REEs, i.e.: cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum and lutetium) and other elements (OTs, not classified in the previous groups, i.e.: boron, barium, beryllium, caesium, gallium, lithium, strontium and titanium) in soils from Billefjord (central Spitsbergen, Svalbard, Arctic).

The main objective has been detailed in the following points:

- To carry out a spatial investigation of the levels of EEs, PTEs and OEs from topsoils collected in eight locations in northern Billefjord during 6 boreal summers (2014-2019);
- To verify the accumulation profile of elements among different geographic locations;
- To investigate concentrations of the EEs, PTEs and OEs in addition to the REEs from soils with animal influence obtained from the western (Elsa Valley) and eastern (Ebba Valley) coasts of Petunia Bay, Spitsbergen;
- To evaluate the contribution of vertebrate animals to the flux of chemical elements in different soil profiles;
- To assess the organic matter content of the soil of both valleys to correlate with the influence of vertebrate animals;
- Generate insights into the possible accumulation trend associated with the multiple factors that can affect the elemental concentration of the studied region such as anthropogenic pressure , animal influence and glacial meltwater;

- Results comparison with available data from other polar and Svalbard soils.

The experimental part, described in chapter called *Experimental Methods*, covers wide range of researches, from the stage of sampling, through leaching/decomposition procedures, to the final stage, which was the determination of selected elements using both Inductively Coupled Plasma Optical Emission and Mass Spectrometry techniques (ICP OES and ICP-MS). The analytical techniques used were described in details, with all the components, the principles of obtaining an analytical signal and the range of applications. The Author took into account a number of parameters (variables, such as: different sample preparation/decomposition procedures and reagent mixtures, interferences, calibration method) affecting the individual stages of the entire analytical procedure.

Soil samples were chosen as an indicator of the level of contamination in this region. Since it is in the soil toxic components can accumulate, affecting its functions in the ecosystem. In addition, soil samples can also be easily collected, transported, stored and then prepared for analysis using developed procedures.

Dr. Juliana Souza-Kasprzyk undertook a difficult task, requiring not only the proper selection of sampling sites, selection of the appropriate research material, sample preparation methods and procedures, but also the use of appropriate analytical instrumentation.

The selection of material for the studies conducted involved obtaining representative analytical samples from the locations precisely defined.

Topsoil samples were collected (at depths of 0-10 cm) during six fieldworks in the northern part of Billefiord, Spitsbergen (Svalbard). In total almost 600 samples were collected over the period 2014-2019 in areas with different levels of antropopressure, from the northwest coast, in Mimer Bay, where the abandoned Russian coal mining town of Pyramiden is located, entering Petunia Bay and heading to the northeast, to Adolf Bay where the Nordeskiöld is located. Samples from Elsa and Elba valleys were collected (two depth layers: 0-5 cm (upper layer) and 6-10 cm (deeper layer) from areas under the clear animal influence (e.g. visible faeces of mammals).

It should be emphasized that the methodologies used have been thoroughly validated using many materials of the highest metrological value - the certified reference materials (CRMs): NIST-2709-San Joaquin Soil, NIST-1515-apple leaves, NIST-2790-inorganic constituents in hardwood biomass material supplied by US National Institute of Science and Technology; IAEA-405 - estuarine sediments from the International Atomic Energy Agency; BCR-667 - estuarine sediments from Community Bureau of Reference; LGC-6187 – river

sediment (extractable metals) from LGC; CNS392 – trace elements on fresh water sediment from Supelco; INCT-TL-1 – tea leaves from Institute of Nuclear Chemistry and Technology (Poland).

The CRMs have been properly chosen to represent liquid and solid sample matrices and selected because they were closest in nature to real samples analyzed.

Dr. Juliana Souza-Kasprzyk presented a rigorous manner a large number of results (figures and tables) and succeeded in organizing the discussion in a clear way. The major point of this discussion was that the interactions between the localities of sampling and the determined concentrations of elements seem to be more complex and interconnected with each other than previously expected. For example, the expected effect of increased concentrations of elements determined in soils collected in Pyramiden was not observed. Although this area, according to available data, was subjected to anthropogenic exploration. The effect of the release of elements (including toxic ones, e.g. As, B, Cd, Cr, Li, Sb, Se, Sn, Sr, Ti, Tl, U, V and Zr) in the process of glaciers melting and transfer to soils with the flow of meltwater was observed. This trend was present in the vicinity of the Nordenskiöld glacier, which, due to its retreat, left new areas of exposed sediment.

The influence of vertebrate animals (e.g. Arctic fox, reindeer and polar bears), based on studies of samples from Elsa and Ebba Valleys, on the transport of the elements has not been confirmed. However, a positive correlation was found between soil organic matter (SOM) content and the content of the analytes determined, indicating that this factor should be considered important in assessing the availability and mobility of these elements in soils.

Additionally, some perspectives for further monitoring of this Arctic area were given at the end of the summary based on new samples collected in 2022.

The reviewer's duties also include finding inaccuracies, incorrect wording or typographical errors in the work. The work was edited very carefully and, apart from a few minor errors, I did not notice any major shortcomings. Below is a list of question that can be addressed during the public defense of the PhD thesis:

- p.p. 55. Certified reference materials were properly selected and used to validate the methodologies applied. These materials have a defined grain size. Was this parameter taken into account when determining elements in real samples?
- p.p. 56. "*Among the sample extraction techniques, acid leaching methods are widely used to extract elements from variety of matrices*" - Analytes might be leached from samples not from matrices.

- -p.p. 56...*they do not extract the total elemental concentration from the samples...*" – should be:... *the total content.*
- p.p. 57., Table 3 and Table 4. What is the difference between microwave-assisted acid nitric leaching and sample digestion procedures indicated? Do both terms refer to processes conducted in a closed-vessel system?
- p.p. 64. How was the internal standard introduced during determinations? Was a multi-channel nebulizer used? This is not shown in Figure 9.
- p.p. 63-69. The basic principles of analytical techniques used could be omitted. On the other hand, the method of internal standard solution introduction (ICP OES, Figure 9), collision/reaction cell and vacuum pump (ICP-MS, Figure10) were not indicated.
- ICP OES is not a coupled technique, so the abbreviation should not be written with a hyphen

The above comments do not detract from the high scientific level of the dissertation, but are only meant to contribute to the discussion.

The publication output Dr. Juliana Souza-Kasprzyk is significant: the co-authorship of seven publications in journals listed in the *Journal Citation Reports* (JCR) database with high values of Impact Factor (IF): *Science of the Total Environment, Environmental Pollution, Chemosphere, Polar Biology and Polish Polar Research.*

In addition, She was honored with awards (pro-quality scholarship from Adam Mickiewicz University, selected to the "*100 Women in Polar Science*" project), held internships (Gdansk University of Technology (1 week), Federal University of Rio de Janeiro (6 months) and Porto University (3 months)) and presented the results of her research in the form of numerous presentations (including conference presentations) and also participated in fieldwork expeditions (Adam Mickiewicz Polar Station "Petuniabukta" on Spitsbergen, Svabald, Arctic in 2019 and 2022; Antarctic Base Camp in Hennequin Point in 2013 and 2014; Brazilian Antarctic Station Comandante Ferraz, Keller peninsula in 2012).

All the reasons detailed above lead me to express a positive opinion about the PhD work of Dr. Juliana Souza-Kasprzyk and I strongly support the oral defense of this work by the Candidate for the attribution of the title of Doctor of Philosophy in Chemical Sciences discipline.

Considering the valuable results obtained by Dr. Juliana Souza-Kasprzyk, good mastery of the research technique and correct interpretation of the research results, herein it

can be concluded that her doctoral dissertation meets all conditions specified in Article 187 of Act of July 20, 2019 Law on Higher Education and Science (Journal of Law of 2018, item 1668, as amended), and thus I conclude that fully deserves to be admitted to the further stages of the doctoral process.

At the same time, due to the wide range of studies, high quality and importance of the results of the dissertation and high level of scientific achievements the reviewed work deserves a distinction.

Poznań, March 10, 2023