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Orsay, March 16th, 2018

Report on the PhD Thesis of Monika Ciężka

The PhD Thesis of Monika Ciężka deals with a multi-parameter analysis applied on both the bioindicators (*Hypogymnia* lichens sampled on trees) and the atmospheric gases as well as metals in the Świętokrzyski National Park to assess atmospheric pollution. This is a very interesting research topic and the multi-isotope approach combined with elemental concentrations as well as Electron Paramagnetic Resonance (EPR) spectroscopy are relevant for assessing the anthropogenic pressure on the environment.

The methodologies used open new insights in environmental studies for better understanding the relative contribution of different sources (both natural and anthropogenic) on the pollution of the environment (air and bioindicators) by gases and metals. I was impressed by the scientific quality and the huge amount of theoretical and experimental work done by Monika Ciężka as well as the analysis of the literature and of her results.

This PhD Thesis document is composed of Sections and Subsections, very well structured. The general **Introduction** is short but informative, underlying clearly the context, objectives, the methods used and the relevance of the work. The Introduction is followed by a one-page section describing the **Hypotheses and Objectives** of the study. Therefore, at the very beginning of the dissertation document, the reader has a clear view of the study.

Section 3 contains **General Information** on the (i) Bioindicators and describes why the lichens are used as bioindicators of the atmospheric pollution, (ii) Elements investigated in the study (Carbon dioxide, Nitrogen dioxide, Sulfur dioxide, metals, e.g. Cu, Cd, Zn, Pb, Mg, and Mn, and free radicals), their potential sources of emission, and their impacts on the atmospheric pollution as well as on the lichens are described. This section, also contains the description of the stable isotopes and delta calculations, as well as the basics knowledge on the stable isotopes of the elements investigated in the study (their natural abundances are underlined, the graphs from literature showing the ranges of each stable isotope in different compartments of the environment as well as in the organisms are shown, and also the potential changes in their values according to the anthropogenic activities are described). All these are instructive, concise, and easy to read.

Section 4 deals with the **Study Area** description, and gives detailed information about the Geology, Vegetation, and Climate of Świętokrzyski National Park, where the study was conducted, the potential sources of pollutions in this area (e.g. traffic/transport, proximity with urban zones and with industrial activity) are precisely described and their positions well presented on the park and shown on the map, followed by the very detailed description of the sampling points (shown in a Table with details on the vegetation, elevation level, distance from pollution sources etc., of each of the 20 sampling points). This is a relevant documentation undertaken by Monika, very useful for the presented data analysis and will also be useful for any further investigation in this park.

Section 5 describes the **Protocols and Methodologies** used for both air and lichen samplings in the field, as well as the sample preparation for chemical and isotopic analyses

and laboratory measurements. Some of methodologies are detailed but some not enough. This section could thus be improved by more explanation.

Section 6 is a short section containing the **Results** presented as Tables with details of all data, but the Figures issued from those data are shown in the Discussion section only. The most important observations/findings could have been pointed out in this section to catch the attention of the reader before Discussion section.

Section 7 is the most important part of the dissertation document containing the Figures and **Discussion** of all the results. The spatial distribution of each element investigated as well as its isotopic composition both in the atmosphere and in the lichens are nicely presented. The grey nuances showing the gradient of either concentrations or isotopic compositions of the individual elements on the map of the Park together with the positions and corresponding numbers of the sampling points indicated on each map, clearly visualise the spatial variations as well as their changes between the winter and the summer sampling times. Accordingly, it is demonstrated that there is a half-a-year delay between the changes in the concentrations/isotopic compositions of the gaseous pollutants in the atmosphere and in the lichen organic matter, i.e. an increase in the pollution level during the winter (for example due to heating) can be observed on the bioindicators (lichens in the present work) only after half-a-year during summer time sampling. When the origins (sources) of pollutions are the traffic/transport (sampling points near the roads) and/or human activities (sampling points near urban zones or other anthropogenic activities near industrial zones) the results are quite clear and very well discussed and concluded.

Monika also plotted the concentration/isotopic composition of elements in lichens as a function of atmospheric data, which clearly demonstrate the half-a-year delay mentioned above between winter and summer data. However, in some cases, great variability in data between the 20 sampling points is observed. But, by looking at the individual data points, Monika visualised the groups of data (representing the sampling points) on the figures and cleverly analysed/discussed them, and suggested the possibilities of other sources of pollution (e.g. biogenic source like soil emission) or environmental factors (e.g. wind direction/velocity, precipitation rates, height) or combination of different factors, which could blur the measured values. For each element, she has also provided the literature data in a Table, indicating the ranges of values, and the sources of pollutions, and compared her data with those of literature in order to better analyse the potential causes of the observed values.

The concentrations of all the gaseous pollutants (CO_2, NO_2 and SO_2) analysed were higher during the winter time (heating season, with fossil fuel combustion) compared to the summer time (vegetation season). According to the information about the different sampling points in the Park, Monica concluded that the highest CO_2 concentration was observed at the highest elevations, the highest NO_2 concentrations were along the roads thus due to the pollution by traffic/transport, and the highest SO_2 concentrations were rather observed along roads and vicinity of houses. According to the isotopic composition analyses of ^{15}N and ^{34}S in the lichen organic matter, she concluded that the lichens collected along roads are influenced by transport/traffic pollutants, while those sampled on the peaks reflect the long-range transport of pollutants, respectively. The analysis of ^{13}C in lichen organic matter suggested a link with natural factors like the elevation due probably to higher O_3 concentration, precipitation amount and light level, masking the impact of anthropogenic pollutants.

Concerning the metals investigated in this work (Pb, Cd, Mn, Fe, Mg, Zn, and Cu), their measured concentrations in the lichens are in the range of the geochemical background values reported in the literature, suggesting that the lichens sampled in this park may not have reflected the human activities concerning the metals. However, using the isotopic composition analyses and mass balance calculations, Monika showed that the investigated area was affected by the industrial sediment source of pollution like the smelters (long-range

transported by wind). In addition, Pb concentration in lichens increased with elevation in both seasons. This was linked to the higher precipitation levels at elevated zones because the uptake of heavy metals by lichens is greater under moisture. Therefore, for metals both natural and anthropogenic activities are the pollution sources. For metals, more than one year investigations are needed to better understand the impact of anthropogenic pollution on lichens.

The Electron Paramagnetic Resonance (EPR) spectroscopy analysis showed that the concentrations of the radicals were low in the lichens sampled in the investigated area. A previous work in 1999 had shown concentrations 10 times higher than the present ones, and it had also shown good relationship between radicals and the pollutant gases (mainly SO_2), suggesting that an increase in SO_2 concentration in the atmosphere could increase free radicals in lichens. In the present work the concentrations of free radicals were lower but correlated with SO_2 concentration in the atmosphere only during heating season and not during the summer. In vegetation season, the variability in free radicals was much higher while the SO_2 concentration was very low and not really changing between different sampling points. She suggested that the oxides like SO_2 may lead to the formation of reactive oxygen species (ROS) which could alter the SO_2 concentration in the atmosphere while increasing radicals in the lichens.

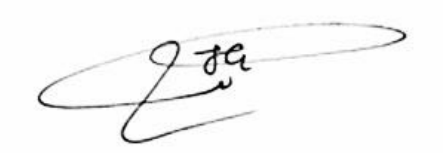
The statistical analyses (PCA) confirmed the half-a-year shift between the element concentrations in the atmosphere and in the lichens for N and for S. But for carbon, it was controlled rather by natural than anthropogenic sources.

The final section synthesises the main findings and conclusions mentioned above. It is also concluded that although the investigated area is localised in a National Park, where the human activity should be low, the anthropogenic pressure is measured (mainly local fossil fuel combustion by traffic and houses, and the long-distance transport of pollutants from industrial zones). A short criticism and a few perspective/insight for future investigations would have been useful. This could be recovered during oral presentation.

Although Monika has already published two papers on her PhD results in *Journal of atmospheric Chemistry*, and in *Geoscience Records* (both as first author), her Thesis has a great merit to be a complete PhD document rather than a compilation of papers. She has another paper (first author too) under review. The Thesis is well documented and will be very useful for students and researchers who will continue the work. This is a beautiful contribution to both scientific and technical progress in this domain. I suggest to add the papers as annexes to this document.

Therefore I conclude, that the presented dissertation meets the usual and formal requirements made to the PhD theses (Act of 14 March 2003 on academic degrees and academic title, and degrees and title in the field of art.). Hence, I request the admission of Ms Monika Ciężka to the subsequent stages of the procedure, including the public defense.

Sincerely,
Jaleh Ghashghaie (Professor)



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