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Technical procedure for using moss bags and snow as effective magnetic monitors for preliminary air quality assessment

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Abstract: Technologically advanced measuring stations are commonly used to monitor air quality, but their use is not always possible due to technical limitations. The primary aim of this study is to present a step-by-step technical research procedure as an effective method of collecting air contaminants and pollutants in locations unsuitable for standard monitoring stations. The moss bag technique was used, in which mosses were placed in a cylindrical fiberglass mesh and deployed in the field on a specially designed installation. Diamagnetic (plastic) containers were used to collect snow. This innovative approach involves both the scope of the research (natural monitors such as moss and snow, as well as seasonality) and the integration of magnetic and geochemical methods, pollution quantification parameters and meteorological data. Magnetic monitoring allows for a preliminary assessment of air quality in places that are difficult to access and/or located far from the main emission sources. A key advantage of using natural monitors (moss and snow) is the possibility of relatively long exposure times. In the case of studies focused on technogenic magnetic particles and potentially toxic elements, this approach allows for the collection of a larger amount of samples and reduces the need for frequent monitoring, which is necessary when using specialist equipment.

Introduction

Air quality, influenced by many anthropogenic and natural factors, is determined by the presence of contaminants and pollutants such as sulphur dioxide (SO_2), nitrogen oxides (NO_x), particulate matter (PM), and ozone (O_3), as well as potentially toxic elements (PTEs; Alloway 1995) and trace metals. Natural sources of air contamination and pollution include volcanic eruptions (Mazur 2022) and forest fires (Jordanova et al. 2018). In contrast, anthropogenic air pollution arises from both local and long-range sources, such as energy production, various industrial sectors, and vehicular traffic (e.g., Rachwał et al. 2024). The type and concentration of contaminants and pollutants in the air depend on the source and the distance from the emission site to the sampling location. These variations can be used to identify and classify pollution sources. Notably, air contaminants and pollutants are also associated with the presence of technogenic magnetic particles (TMPs; Magiera et al. 2011). TMPs are mainly ferromagnetic minerals *sensu lato* in the form of iron oxides, produced during high-temperature technological processes and coexist with PTEs (Hulett et al. 1980). Industrial and urban emissions are sources of fly ash and dust containing TMPs (along with PTEs) that enter the atmosphere and then accumulate in soils, sediments, and natural monitors (including moss and snow).

Thus, due to the existing relationships between specific elements and iron minerals (Petrovsky et al. 2000), magnetic susceptibility can serve as an indicator of the accumulation of various elements in the tested material (i.e., moss and snow). Previous research indicates that TPMs are potentially harmful not only due to their association with PTEs and other elements (Chaparro et al. 2020) but also because of their morphological characteristics (i.e., very small size and high surface area), which make them inhalable and harmful to humans and other living organisms (e.g., Hofman et al. 2017, Calderon-Garciduenas et al. 2019, Maher 2024).

Magnetic monitoring uses various types of monitors and magnetic measurements to analyze air contamination and pollution (Jordanova et al. 2010, Fabián et al. 2011, Winkler et al. 2019, Chaparro 2021). Examples of animal biomonitors include bees (de Oliveira et al. 2016), spiders (Rachwał et al. 2018), shrimps (Chaparro et al. 2022), and selected species of fish (Sambolino et al. 2023). On the other hand, some authors (e.g., Wawer et al. 2015, Ojha et al. 2016, Wawer et al. 2020) used special test-monitoring plots (ground-based boxes) filled with quartz sand of known chemical composition and diamagnetic properties as a neutral matrix for the accumulation of traffic pollutants.

Air quality monitoring has become increasingly widespread, reflecting growing public awareness of environmental health. In an era that emphasizes healthy lifestyle, outdoor recreation, and benefits of nature, concerns about harmful impact of air contamination and pollution on human health are more prominent than ever. Compared to costly monitoring stations that require regular maintenance, magnetic monitoring offers a much simpler and more accessible alternative. This method utilizes natural monitors, such as moss and snow to observe the negative impact of human activity on air quality.

Moss (used as a biomonitor) is a plant with a narrow tolerance for specific external factors (e.g., contamination or pollution; Markert et al. 2003). Its surface captures PM from the air (Giordano et al. 2009). The morphological features make them highly effective bioaccumulators. Moreover, the use of biomonitors is a relatively inexpensive method for conducting preliminary research or continuous monitoring of air quality. They complement traditional physicochemical methods in assessing the impact of contamination and pollution on selected environments, including water, air, and soil. Detailed information about mosses as biomonitors can be found, among others, in studies by Kłos et al. (2018) and Varela et al. (2023). According to Harmens et al. (2010), commonly used moss species in biomonitoring include *Pleurozium schreberi* (Willd. ex Brid.) Mitt., *Hylocomium splendens* (Hedw.) Schimp., *Hypnum cupressiforme* (Hedw.), and *Pseudoscleropodium purum* (Hedw.).

In winter, under specific and favorable climatic conditions (namely frosty and snowy weather), snow can serve as an effective natural monitor of atmospheric contamination and pollution. It enables the assessment of both air quality and spatial impact of contaminant and pollutant emitters. The chemical composition of atmospheric precipitation is influenced by chemical processes occurring in one of two ways: (1) the contamination of water droplets and ice crystals within clouds, and/or (2) the removal of contaminants and pollutants from the sub-cloud layer during precipitation and subsequent sedimentation on the surface of the snow cover. While the chemical composition of cloud elements may reflect emissions from distant emitters, the amount of contaminants and pollutants removed from under the cloud and the dust deposited on the snow surface are primarily determined by local emitters. The possibility of using snow cover as a monitor depends on various factors, including the nature of the winter – it should be not only frosty but also snowy. Additionally, the concentration of individual substances in snow samples depends on factors such as duration and intensity of precipitation and the length of the preceding dry period.

To date, the use of snow as a natural monitor of magnetic enhancement has been limited to seasonal studies of traffic-related pollution (Bućko et al. 2011). The use of moss bags as a specific tool in magnetic monitoring studies of various types of pollutants was the subject of the works by Salo and Mäkinen (2014, 2019). However, the first research to use both moss and snow to monitor atmospheric pollution near a Cu-Ni smelter during the winter season was conducted by Salo et al. (2016). The research involved magnetic and chemical analyses of snow profiles and the use of moss bags to evaluate and compare the efficiency of dust pollution accumulation by both monitors. The results showed that the pollutant accumulation in snow and moss was comparable.

The aim of this work is to present, in an accessible way, a technical research procedure as an effective method of collecting air contaminants and pollutants in locations unsuitable for stations for monitoring stations. These include emissions of dust occurring in the aerosol fraction and migrating over long distances, as well as dust emissions from local sources. This approach encompasses both the scope of the research (natural monitors such as moss and snow, and seasonality) and the use of integrated magnetic and geochemical methods, pollution quantification parameters, and meteorological data.

Materials and methods

Study site

The main research site was located in the Izery Mountains (Western Sudetes), which form part of the so-called Black Triangle – a region situated at the border of Poland, the Czech Republic and Germany, and considered the most polluted areas in Europe (e.g., Błaś et al. 2008).

In addition, two other research sites were included. The first was located near Kraków (Lesser Poland Voivodeship, southern Poland), and the second in Częstochowa County (Silesian Voivodeship, in southern Poland). Research stations (bags filled with moss) were installed on private properties surrounded on all sides by low-rise buildings.

Detailed information on the characteristics of the entire research area can be found in Michczyński et al. (2022), Szuszkiewicz et al. (2023), and Szuszkiewicz et al. (in press).

Proposed technical research procedure

Due to the nature and purpose of the research, the procedure was divided into three stages.

Stage one: (1) Selection of sampling site and moss collection from reference areas. Moss samples were collected from places located far from roads and sources of industrial and urban emissions. For the purposes of the study, two moss species – *Pleurozium schreberi* (Willd. ex Brid.) Mitt. and *Pseudoscleropodium purum* (Hedw.)) were collected from coastal pine forests near the Słowiński National Park (Baltic Sea, Northern Poland). (2) Selection of research installation sites. Three field locations were selected for moss bag exposure and seasonal snow collection: the “Orle” forest glade, “Kobyła” hill, and “Granicznik” hill). (3) Preparation of moss samples and moss bags. In the laboratory, the green parts of the moss gametophyte were cleaned by placing them on a plastic sieveand washing them with distilled water (10 litres of water per 100 g of dry matter) to remove plant residues and soil residues, as well as to activate plant tissues. The cleaned moss was then placed on paper filters to remove excess moisture and dried at 50°C. The processed moss served as the baseline material for air contamination and pollution monitoring. Next, three samples were prepared for magnetic and chemical analyses (so-called reference samples). Then, 4 g of dry moss was loosely packed into cylindrical diamagnetic mesh bags (nylon, 2 mm mesh size) (Figure 1c). These bags were vacuum-sealed and stored at a temperature below 0°C until use. (4) Preparation of plastic snow collection containers. Plastic containers (45-litre diamagnetic barrels) were washed with diluted

HNO_3 and distilled water, dried, and stored in plastic bags until deployment. (5) Construction of research installations. At each selected site, research installation approximately 3 m high were constructed using PVC pipes and other diamagnetic elements such as rings, lines, and tapes. (Figures 1 and 2). (6) Exposition of moss bags and plastic snow containers (45-litre barrels). Moss bags (Figures 1, and 2a-b) were suspended approximately 3 m above ground surface at each research plot, with 3 bags per research installation. Snow collection barrels were placed approximately 1 m above ground level (Figure 2a), with 1 barrel per plot. The moss bags were exposed in 8-week cycles during both spring–summer and autumn–winter seasons (Figure 1). Seasonal snow collection (Figures 2a-c) was conducted over a 6 month-month period (autumn–winter season), in 4-week intervals. After each exposure cycle, the moss bags and snow containers were collected, replaced with new ones, secured and transported (Figure 2d) to the laboratory at the Institute of Environmental Engineering, Polish Academy of Sciences in Zabrze.

Stage two: (1) Preparation of moss bags for laboratory measurements and analyses. In the laboratory, moss samples from the collected bags (after the exposition cycle) were dried at 50°C and then ground in an agate mortar. Melted snow samples were filtered using a Sartorius vacuum pump (Sartorius AG, Göttingen, Germany) and cellulose filters with a 0.2 μm pore size to isolate dust contaminants. (2) Magnetic measurements (in moss samples and dust isolated from snow). Prepared samples were placed in 10 ml diamagnetic plastic containers for magnetic susceptibility measurements using a Kappabridge MFK1-FA (AGICO, Brno, Czech Republic). Next, tested material was used for further analyses, which included hysteresis loop measurements, acquisition of remanent magnetization, back-field remagnetization measurements using the EV9 VSM with the maximum applied field of 2 T (Vibrating Sample Magnetometer; DSM Magnetics, ADE Corporation, Lowell, MA, USA), and thermomagnetic measurements using MFK1-FA Kappabridge with a CS-L cryostat (AGICO, Brno, Czech Republic). (3) Determination of the content of selected elements (in moss samples and dust isolated from snow). After magnetic measurements, the same samples (from the 10 ml containers) were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). The samples were mineralized using microwaves in concentrated nitric acid (V) HNO_3 and hydrogen peroxide H_2O_2. Moreover, the melted snow was analyzed for pH and conductivity.

Stage three: (1) Magnetic data analysis. (2) Geochemical data analysis (obtained content of tested elements). (3) Analysis and comparison of the obtained data with meteorological data from the meteorological station operated by the Institute of Meteorology and Water Management – National Research Institute (IMWM – NRI). (4) Statistical interpretation. The analysis was conducted using Statistica 13.3 (TIBCO Software Inc.) incorporating the obtained magnetic, geochemical and meteorological data. (5) Application of parameters and geostatistical methods (e.g., Łyszczarz et al., 2020). To quantify contamination and pollution levels the following parameters were calculated: enrichment factor (EF) (Chester and Stoner, 1973), geoaccumulation index (I_{geo}) (Müller, 1969), contamination factor (CF) (Cesa et al., 2009), and pollution load index (PLI) (Tomlinson et al., 1980). (6) Inter- and multidisciplinary interpretation of the obtained results.

Results and discussion

The research results, supported by data from earlier studies (Michczyński et al. 2022), Szuszkiewicz et al. 2023), and Szuszkiewicz et al., in press), are based on a relatively large amount of data collected in research plots. A total of 153 samples were collected from the applied contamination monitors), yielded more than 3,300 instances of magnetic data and over 2,100 instances of geochemical data.

The parameters used for the quantitative determination of environmental pollution were compared with the results of measurements and magnetic and geochemical analyses. This approach enabled the demonstration of how different research methods can contribute to the accurate interpretation of magnetic and geochemical signals in monitors used (snow and moss) from areas affected by long-range and local contamination and pollution. Determining the chemical composition of contaminants and pollutants present in regularly collected snow samples made it possible to indicate the role of the most important factors influencing the chemical profile of a given area. Thus, in turn, enabled an estimation of the total load of contaminants and pollutants present in the snow cover and subsequently introduced into the environment. In addition, snow cover analysis proved valuable for monitoring local climate changes. Furthermore, comparing the obtained results from the spring–summer period (non-heating season) and autumn–winter (heating season) revealed seasonal differences in magnetic and geochemical properties in the analyzed samples.

Despite the fact that the installed research plots were characterized by similar locations and topographic conditions (for more information, see Szuszkiewicz et al. in press), the amount of TMPs accumulating in natural air contamination and pollution monitors varied depending on the research plot (i.e., the contaminant and pollutant absorption installation). However, this accumulation remained consistent in terms of seasonality (determined based on the climatic conditions of the studied area and the specificity of the local environment), specifically the heating season (autumn–winter, from October to April) and the non-heating season (spring–summer, from May to September). A comparison of the research results from the three research plots (installations) and datas from the meteorological station (IMWM – NRI) located in Lower Silesia (southwestern Poland), in the Izery Mountains (western Sudetes), revealed the following key findings: (1) The natural atmospheric contamination and pollution monitors used (snow and mosses) proved to be effective. (2) The results obtained were comparable for both dust isolated from snow and for moss samples. (3) the mass of particulate matter in the snow samples ranged from 0.00004 g to 0.06 g per barrel of snow (13–22 L of meltwater); (4) the total concentration of the analysed elements in the samples ranged from 2 μg/L to 17.5 μg/L; (5) the lowest concentration was observed for cadmium (Cd), which reached values around 0.0004 μg/L, while the highest concentrations were observed for iron (Fe), with values of approximately 14 μg/L; (6) the concentration of individual elements depended, among other factors, on the month in which the samples were collected. (7) There were no significant differences in the capture of atmospheric contaminants and pollutants between the two moss species used – *Pseudoscleropodium purum* (Hedw.) and *Pleurozium schreberi* (Wild. ex Brid.) Mitt. (8) The highest concentrations of TMPs (as expressed by magnetic susceptibility values) and the highest contents of iron and selected PTEs – As, Cd, Cu, Mo, Ni, Pb, Se and Zn, were observed during the heating season. (9) The highest contents of Ti and V, observed in the spring–summer (non-heating) period, were most likely the effect of local geological conditions (the presence of the Karkonosze–Izera granitoid, which forms the geological background and includes numerous exposures and outcrops). (10) The decreasing order of iron and PTE contents in the tested samples was as follows: Fe > Zn > Pb > Cu > As > Ti > Ni > V > Zr > Cd > Mo > Se. (11) The decreasing order of wind frequency from directions associated with potential long-range air contamination and pollution sources (mainly coal-fired power plants from Germany, the Czech Republic and Poland), based on meteorological data from Jakuszyce (IMWM – NRI) during the monitoring period (21/09/2018 to 19/11/2021), was as follows: S (29.3%) > SW (25.3%) > NW (10.8%) > W (8.6%).

The implementation of an efficient filtration system and the transition to higher-quality resources have contributed to a significant reduction in industrial emissions over recent decades. This trend was demonstrated in the study by Szuszkiewicz et al. (in press), which employed active biomonitoring using the moss bag technique as an effective preliminary research method for monitoring selected air contaminants and pollutants, and identifying trends. Previous magnetic studies of the Black Triangle region were based on historical records contained in soil or anthropogenic layers (e.g., Zawadzki et al. 2016, Magiera et al. 2019, 2020), not in natural monitors.

However, the accumulation of TMPs and PTEs remains evident in the form of historical magnetic and geochemical records in the " Torfowiska Doliny Izery" (Michczyński et al.

Figure 1. Photographs: (a) research installation on research plot in the spring–summer season (near the "Kobyła" hill, Izery Mountains), (b) fragment of the installation with moss bags (during the exposition cycle) in the spring–summer season (near the "Kobyła" hill, Izery Mountains), (c) moss bag (during the exposition cycle) in the spring–summer season (in the "Orle" forest glade, Izery Mountains), and (d) research installation on research plot in the spring–summer season (near the "Granicznik" hill, Izery Mountains)

2022). This is further supported by pollutant quantification parameters such as the EF and Igeo. The main aim of the work was to characterize TMPs and PTEs originating from both historical long-range emissions and local sources, based on peat archives located at the edge of the Black Triangle region in the Izery Mountains. As such, research conducted in this historically industrialized area provides an excellent reference material for research on the use of natural contamination and pollution monitors (e.g., snow and moss) as recorders of magnetic (TMPs) and geochemical (PTEs) signals related to industrial activities in the study area. In the analyzed samples, enrichment in TMPs and PTEs was observed (Michczyński et al. 2022), which corresponds to historically documented anthropogenic activity (long-range atmospheric transport in the Black Triangle area throughout the 20th century and local transport dating back to the 18th century).

Moreover, another study (Szuszkiewicz et al. 2023) showed that an innovative approach, both in research design and methodology, enabled the collection of unique research material related to the long-range transport of Saharan dust in atmospheric aerosols. This phenomenon was observed across southern and central Europe from 5 to 7 February 2021. As a result, a magnetic and geochemical record of the Saharan dust episode was captured in the snow cover at one of the seasonal snow accumulation sites (Szuszkiewicz et al. 2023).

Conclusions

This study presents a step-by-step, technical research procedure as an effective approach for collecting air contaminants and pollutants in areas unsuitable for conventional monitoring stations.

The magnetic monitoring method used in the research allows for the assessment of the size and type of contaminants and pollutants released into the environment, particularly in locations that are difficult to access and/or situated far from

Figure 2. Photographs: (a) research installation on research plot in the autumn–winter season (near the "Kobyła" hill, Izery Mountains), (b) fragment of the installation with moss bags (during the exposition cycle) in the autumn–winter season (near the "Kobyła" hill, Izery Mountains), (c) container (barrel) for snow collection (after the exposition cycle) in the autumn–winter season, and (d) transport of moss bags and filled snow container from the research plot (after the exposition cycle) in the autumn–winter season

the main emission sources. As such, it offers a promising complement to traditional measurement (monitoring) stations.

An important advantage of using natural contamination and pollution monitors (moss and snow) is the potential for relatively long exposure times. In studies focusing on TMPs and PTEs, this approach allows for the collection of a larger sample volumes and reduces the need for frequent monitoring, which is necessary in the case of using specialist equipment.

Moreover, an important element of the conducted research is the analysis of the differentiation of the magnetic signal due to its origin (source) and the implications related to the interdisciplinary and multidisciplinary interpretation of the obtained results. This highlights the potential of environmental magnetism as a valuable tool in environmental research.

The characteristic features of TMPs and the occurrence of specific elements, including PTEs, transported by TMPs allow for the extraction of individual magnetic and geochemical signals associated with long-range transport versus local emissions, while taking into account seasonal variations.

To sum up, due to the use of natural contamination and pollution monitors, the obtained results are of great importance not only for atmospheric science and geophysics, but also for soil science, geology and climatology. In particular, the results contribute to the understanding of local climate changes – an area where magnetic methods have, until now, seen limited application.

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Techniczna procedura wykorzystania woreczków z mchem i śniegu jako efektywnych monitorów magnetycznych do wstępnej oceny jakości powietrza

Streszczenie. Do monitorowania jakości powietrza powszechnie stosuje się zaawansowane technologicznie stacje pomiarowe, jednak ich wykorzystanie nie zawsze jest możliwe ze względu na ograniczenia techniczne. Głównym celem niniejszego opracowania jest przedstawienie, krok po kroku, technicznej procedury badawczej jako skutecznej metody zbierania zanieczyszczeń powietrza w miejscach nieodpowiednich dla standardowych stacji monitorujących. Zastosowano technikę woreczków z mchem, w której mchy umieszczono w cylindrycznej siatce z włókna szklanego i rozmieszczono w terenie na specjalnie zaprojektowanej instalacji. Do zbierania śniegu wykorzystano diamagnetyczne (plastikowe) pojemniki. Innowacyjne podejście obejmuje, zarówno zakres badań (naturalne monitory, takie jak mech i śnieg; sezonowość), jak i integrację metod magnetycznych i geochemicznych, parametrów kwantyfikacji zanieczyszczeń oraz danych meteorologicznych. Monitoring magnetyczny pozwala na wstępną ocenę jakości powietrza w miejscach trudno dostępnych i/lub oddalonych od głównych źródeł emisji. Kluczową zaletą stosowania naturalnych monitorów (mchu i śniegu) jest możliwość stosunkowo długiego czasu ekspozycji. W przypadku badań skoncentrowanych na technogenicznych cząstkach magnetycznych i pierwiastkach potencjalnie toksycznych, takie podejście pozwala na pobranie większej liczby próbek i zmniejsza potrzebę częstego monitoringu, który jest konieczny przy użyciu specjalistycznego sprzętu.