Comment on: “A novel approach to peatlands as archives of total cumulative spatial pollution loads from atmospheric deposition of airborne elements complementary to EMEP data: priority pollutants (Pb, Cd, Hg)”

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Abstract

A recent paper by Miszczak et al. (2020) examines metal contamination in mires in Poland and Norway. The authors conclude that lead (Pb) records in ombrotrophic peatlands cannot be used to reconstruct the chronological history of anthropogenic activities due to post-depositional mobility of the metal. We contest this general conclusion which stands in contrast with a significant body of literature demonstrating that Pb is largely immobile in the vast majority of ombrotrophic peatlands. Our aim is to reaffirm the crucial contribution that peat records have made to our knowledge of atmospheric Pb contamination. In addition, we re-iterate the necessity of following accepted protocols to produce reliable records of anthropogenic Pb contamination in environmental archives.

Keywords

Lead, immobility, ombrotrophic peatland, bog, geochemistry, enrichment factor, metal accumulation rate

1. INTRODUCTION

Ombrotrophic peatlands are well-established archives of past atmospheric deposition of trace elements. After more than 40 years of investigation (see Table SI1), there is a consensus that Pb is largely immobile in ombrotrophic peatlands. We contend that some of the conclusions reached by Miszczak et al (2020) are based on misinterpretation or incorrect sampling and data analysis approaches. To avoid such confusion, we seek to clarify here how ombrotrophic peatlands have allowed the reconstruction of past patterns of atmospheric metal contamination in the environment. We however do not aim to provide a complete review of Pb in mires, because the trophic status of a peatland is crucial to studies of past atmospheric metal deposition (see Supplementary Material for further details), we refer to a selection of studies relevant to ombrotrophic peatlands, also known as bogs. Due to their high atmospheric fidelity, ombrotrophic peatlands have special utility for reconstructing metal contamination records. This was also the type of peatland investigated by Miszczak et al. (2020).

2. THE BEHAVIOUR OF LEAD IN OMBROTROPHIC PEATLANDS

While some studies have suggested that Pb can be mobilized in minerotrophic, riparian, drained or degraded peatlands (e.g. Syrovetnik et al., 2007; Smieja-Król et al., 2010, 2019; Rothwell, 2011; Broder and Biester, 2017) the majority of more than 40 years of literature suggests that Pb is largely immobile in pristine ombrotrophic peat profiles (e.g. De Vleeschouwer et al., 2010a; Marx et al., 2010, Shotyk et al., 2016a,b; Longman et al. 2018; Fiałkiewicz-Kozieł et al., 2020 and references therein). Although Miszczak et al. (2020) cite literature to support their conclusion of Pb mobility in the bogs they examine, that literature pertains to minerotrophic or disturbed peatlands (e.g. Syrovetnik et al., 2007; Smieja-Król et al., 2010, 2019) and the processes that can promote Pb mobility in those systems are not applicable to ombrotrophic peatlands.

The similar elemental and isotopic trends encountered in ombrotrophic peat, lake sediment, ice and herbaria samples (e.g. Rosman et al., 1997; Weiss et al., 1999; Renberg et al., 2001;

Farmer et al., 2002; Cloy et al. 2009; Bindler, 2011) and their agreement with anthropogenic emission patterns (e.g. Shotyk et al., 1998; Mighall et al., 2002; Kylander et al., 2006; De Vleeschouwer et al., 2009a; Marx et al., 2010; Bindler 2011; Cloy et al., 2008, 2009; Allan et al., 2013; Martínez-Cortizas et al., 2016) provide a body of evidence supporting the view that Pb is largely immobile in bogs. Significantly, stable Pb isotopes records from bogs have consistently been found to accurately reflect temporal variability in source signatures in numerous studies (e.g. in reference *op. cit.*). This would not be the case if post-depositional mobility/isotope mixing were taking place. Furthermore, in most ombrotrophic peat cores ^{210}Pb ages, as determined from the constant rate of supply (CRS) age-depth models (Appleby and Oldfield, 1978; Appleby, 2001), are in very good agreement with pollen chronological markers (Appleby et al., 1997), fallout radionuclide chronostratigraphic makers (e.g. from ^{14}C Bomb Pulse Curve, ^{137}Cs and ^{241}Am), and tephrochronology (e.g. Goodsite et al., 2001; Piotrowska et al. 2009; Li et al., 2017; Davies et al., 2018), providing *prima facie* evidence that Pb and its isotopes are largely immobile in bogs. Experimental studies lend further support to this (e.g. Vile et al., 1999; Novak et al., 2001). For example, Pb concentrations in the aqueous phase of ombrotrophic peatlands are low (<0.01% of total Pb), while the limited vertical water movement in bogs together with the size of the metal-containing particles in solution limits Pb redistribution (e.g. Shotyk et al., 2016b). Down-washing experiments have also demonstrated that Pb has limited mobility (Hansson et al. 2014, 2015). The limited mobility that may occur is not sufficient to compromise the use of Pb to reconstruct pollution histories over millennia. We note, however, the spatial distribution of Pb must be carefully addressed in cases where decomposition and compression integrate signals over longer (decadal and more) timespans (Bindler et al, 2004; Martinez Cortizas et al., 2012). Additionally, Pb behaviour in ombrotrophic peats has been demonstrated to differ from that of mobile elements such as Zn which, in contrast to Pb, displays evidence of vertical diffusion/advection as well as upward plant uptake (e.g. Shotyk 1988; Twardowska et al., 1999; Nieminen et al., 2002; Weiss et al., 2007).

In summary, there is a significant body of evidence demonstrating that Pb is largely immobile in bog profiles (see Table S1 and Supplementary Material) that stands in contrast to the conclusions of Miszczak et al. (2020).

3. HOW TO USE LEAD DATA TO ACCURATELY RECONSTRUCT HISTORICAL CONTAMINATION

In the following sections we outline what we consider to be the best practices to ensure accurate reconstruction of atmospheric Pb deposition. We also discuss appropriate approaches to use Pb pollution records constructed from peatlands to examine contaminant sources and to compare with emissions data. The approaches we outline are well established and have been described before (e.g. Givelet et al., 2004; De Vleeschouwer et al., 2010b). We hope that this overview corrects any misapprehensions arising from the approaches used by Miszczak et al. (2020).

3.1. Sampling and sub-sampling – Data resolution and geochronology

Correct coring and sub-sampling protocols are important for accurately reconstructing metal contamination records from mires. The slow accumulation rate of ombrotrophic peatlands means that peat sections on the order of one vertical centimeter can represent decades of metal accumulation. For example, in European ombrotrophic peatlands, long-term mean peat accumulation rates (i.e. excluding surface vegetation growth) have been estimated to range from c. 0.18 to 1 mm yr^{-1} (e.g. Gorham, 1991; Mäkilä, 1997; Malmer and Wallén, 2004; Pontevedra-Pombal, et al., 2017) depending on the vegetation and climate (e.g. Charman et al., 2013; Pontevedra-Pombal et al., 2019). Because of this, it is commonplace for studies to both sample and date the living vegetation at the bog surface (e.g. Farmer et al., 2006; Kempter et al. 2007; Olid et al., 2008). This point was illustrated by Givelet et al. (2004) who stated: "*the historical record of atmospheric Pb … can depend to a large extent on the methods used to collect, handle, and prepare the samples for analysis*". As a result, high-resolution sub-sampling and dating are required to reconstruct decadal-scale atmospheric pollution records.

Here Miszczak et al. (2020) compare metal contaminants in their peat records to European Monitoring and Evaluation Program (EMEP) data (annual trace metal emissions, https://www.emep.int). Although potentially a very useful undertaking, their sampling approach unfortunately greatly reduces the utility of their comparison. This is because Miszczak et al. (2020) followed the coring protocol of Steinnes and Sjøbakk (2005) where "*Sphagnum moss … and other plant material growing on the surface were removed…before the coring, and the reference surface level is thus the interface moss/peat. The thickness of the Sphagnum layer, if present, was always less than 10 cm".* In other words, the authors removed the living/surface vegetation which is an integral part of the ombrotrophic peat deposit, potentially accumulating decades of information.

Given the slow accumulation rates of bogs, the 40 years of EMEP data are likely, at best, to represent approximately 4 cm of peat accumulation (if surface vegetation is excluded and assuming a 1mm yr^{-1} peat accumulation rate). Therefore, the sampling resolution of Miszczak et al. (2020), where peats were subsampled in multi-centimeter increments, combined with their limited use of radionuclide dating, preclude any assessment of recent Pb deposition or comparison with EMEP data from their study. This is especially the case if surface vegetation were removed. Slow growth rates, combined with the demonstrated importance of surface vegetation in accumulating metal contaminants means that Miszczak et al. (2020) assumption that the peat/vegetation interface represents the year of coring (in that case 1999) is incorrect. Their approach therefore leads to large uncertainties in chronology and any inventory calculations performed thereafter. As previously stated, we consider comparing EMEP data with data from ombrotrophic peatlands to be a very worthwhile undertaking, but it requires high-resolution sub-sampling and dating, which is unfortunately not achieved by Miszczak et al. (2020).

3.2. Interpreting data in elemental ratios, enrichment factors (EFs) and metal accumulation rates,

Reconstructing Pb contamination in ombrotrophic peatlands requires an understanding of how they respond to environmental change. This is because changes in Pb concentrations may result from changes in the peat bog density/accumulation rate rather than changes in the extent of contamination. In the following section we outline the importance of understanding density changes in peat records and the need to consider the variability in natural Pb from aeolian mineral dust deposition. We provide a brief overview of techniques to account for such changes, allowing Pb to be reliably used as a tracer of past anthropogenic activity.

3.2.1. Density, accumulation rate and Pb concentration

The importance of understanding and accounting for changes in peat density and dust input are illustrated by De Vleeschouwer et al. (2009a,b) in their study of the Slowinskie Blota ombrotrophic peatland (Poland). In this peatland, a section of higher than average bulk density was present between 50 and 35 cm depth (De Vleeschouwer et al., 2009a,b). It corresponds to the timing of the Little Ice Age, when colder temperatures promoted a decrease in peat accumulation rates coeval with increased windiness and dune activity (i.e. increased aeolian lithogenic inputs). This combination of reduced organic accumulation rates and increased dust input resulted in an increase in bulk density. The effect of these changes was an increase in Pb concentration within the peat profile. Although part of this Pb increase is attributable to increased pollution in the Industrial Revolution, the majority of the Pb increase results from the decrease in peat accumulation causing an apparent increase in pollution Pb accumulation. This occurs because that section of the peat profile represents a greater period of time than sections below 50 cm depth or above 35 cm depth. In addition, increased dust inputs during the drier conditions of the Little Ice Age mean there was an increase in natural Pb input during that period. Miszczak et al. (2020) incorrectly assumed the increase in Pb in the Slowinskie Blota peatland at that time resulted from the movement of Pb from higher in the peat profile (i.e., Pb mobility in the bog). But, by appropriately accounting for the change in density and increased dust input during the Little Ice Age (i.e. using EFs accumulation rates and isotopic ratios, which are discussed in the next section), De Vleeschouwer et al. (2009a) demonstrated the maximum Pb concentration in the Slowinskie Blota record occurred at AD 1960-70s, and not between 50 and 35 cm depth as the raw Pb concentration data would suggest. The maximum Pb contamination therefore coincided precisely with maximum Pb emissions from leaded gasoline, just prior to Pb being banned and phased out beginning in the 1980s (e.g. Pacyna and Pacyna, 2000). De Vleeschouwer et al. (2009a,b), match the known history of anthropogenic Pb emissions in Europe clearly demonstrating that it is not related to any post-depositional mobility. The approach to accurately reconstruct Pb contamination (as separate from total Pb concentrations) is outlined in the following section.

3.2.2. Pb as a tracer of past anthropogenic activity

Since the pioneering paper of Lee and Tallis (1973), practices have developed to ensure the accurate use of trace metal data to reconstruct past environmental pollution. It has been demonstrated that using concentration data to reconstruct past anthropogenic activity is problematic because, as shown above, peat accumulation rates alter total Pb concentrations. Additionally, because the rate of dust deposition in bogs (from wind erosion of soils) varies, it is necessary to separate natural Pb in dust from anthropogenic Pb. Therefore, it is common practice to use metal to lithogenic element ratios, enrichment factors (EFs), or elemental mass accumulation rates (e.g. Shotyk et al., 1998; Le Roux et al., 2010; Allan et al., 2013) to reconstruct contamination histories. These approaches are important to avoid misinterpretations based on examining concentration data alone. Miszczak et al. (2020) did not apply these standard approaches. By comparison De Vleeschouwer et al. (2009a) use EFs and Pb accumulation rates (combined to Pb isotopes and high-resolution sampling and dating including the surface vegetation) to come to a different set of conclusions regarding the utility of Polish ombrotrophic peatlands for reconstructing Pb contamination histories. Consequently the latter represents a more accurate picture of the extent of Pb contamination in Poland over the past 1400 years, demonstrating *i)* the Pb accumulation rate in the topmost centimeter of the peat is of the same order of magnitude as 2009 European Pb deposition (www.msceast.org, www.emep.int), *ii)* the main sources of anthropogenic Pb are from metallurgy, coal and gasoline and, *iii)* the peak in Pb contamination matches the history of European Pb emissions. That work therefore provides another example amongst many others, (Table SI1) of Pb being largely immobile in ombrotrophic peatlands and shows peatlands to be excellent recorders of anthropogenic activities.

4. CONCLUSIONS

Due to their fidelity ombrotrophic peatlands have been extensively used to study current and past patterns of atmospheric metal contamination and metal use, in particular for Pb. Despite their utility there are some key considerations required when constructing contamination histories from bogs. The aim of this comment was to highlight some these considerations. The impetus for this arose from the recent paper by Miszczak et al (2020) who used nonstandard sampling and analysis techniques and, as a result, came to what we consider to be erroneous conclusions. Additional discussion on the effect of pH on Pb mobility and the relationship between peat age and the history of Pb contamination is provided in the supplementary material. Over the past 40 years many investigators have developed or applied a range of analysis and sampling techniques necessary to construct metal contamination records in ombrotrophic peatlands. These approaches include undertaking high resolution sampling and dating, including sampling the living vegetation of the surface of bogs and the use of short-lived radionuclides (such as ^{210}Pb) to accurately reconstruct metal contamination over the past ~100 years or less. They also include calculating enrichment factors (EFs), elemental ratios, or using accumulations rates (as opposed to raw metal concentration data) to take account of changes in peat density/growth rates and changes in natural metal input. Studies of Pb contamination have also benefitted from the use of Pb isotopes to decipher emission sources at a regional to continental scale. Many of these steps are also necessary when accurately determining contaminate loads and patterns in other environments including in ice, lakes and soils and within direct atmospheric samples. We therefore wish to reiterate the particular value of ombrotrophic peats for reconstructing atmospheric metal contaminant chronologies due to their wide distribution and high fidelity. We maintain that 40 years of literature demonstrate that

Pb is largely immobile in ombrotrophic peatlands (i.e. bogs) and that peat cores extracted from this type of mire represent reliable archives for reconstructing past natural changes in Pb deposition from natural processes and anthropogenic activity. The approach is supported by experimental work and similar reconstructions of metal contamination in other environmental archives (herbarium samples, lake sediments, ice cores). We conclude by noting that reconstructions of Pb contamination from bogs provide unequivocal evidence of the global scale of atmospheric Pb contamination and a reliable record of the timing of changes in atmospheric deposition extending from pre-history until the present day.

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