



Isotopic signature of atmospheric phosphate emitted from coal combustion



Roi Weinberger, Tal Weiner, Alon Angert*

The Institute of Earth Sciences, The Hebrew University of Jerusalem, Jerusalem, 91904, Israel

HIGHLIGHTS

- Fly coal ash phosphate oxygen isotopes ($\delta^{18}\text{O}_\text{P}$) is within a narrow range.
- Ash $\delta^{18}\text{O}_\text{P}$ values are higher than source coal, due to exchange with atmospheric O_2 .
- The coal source country strongly controls the $\delta^{18}\text{O}_\text{P}$ of the ash and the coal.
- Small ash particles, which dominates the emission, are significantly P-richer.

ARTICLE INFO

Article history:

Received 4 February 2016

Received in revised form

3 April 2016

Accepted 6 April 2016

Available online 10 April 2016

Keywords:

Coal
Fly ash
Phosphorus
Phosphate
Isotopic signature

ABSTRACT

Atmospheric deposition of phosphorus (P) serves as an important nutrient input for many terrestrial, marine and freshwater ecosystems, influencing their biogeochemistry and primary production. Fossil fuel combustion, principally coal, is estimated to be a major source of atmospheric-P in industrialized regions. In this research, we aim to find a distinct isotopic signature for fly coal ash, the by-product of coal combustion that is emitted to the atmosphere. This signature could be used to identify coal's contribution to atmospheric-P. For this aim, ten fly coal ash samples from different coal sources, collected by power station filters, were analyzed for P concentrations and stable oxygen isotopic composition ($\delta^{18}\text{O}_\text{P}$). Two inorganic phosphate fractions were analyzed: HCl-extractable and resin-extractable (bioavailable P). High HCl-P concentrations of up to 3500 $\mu\text{g P/g}$ ash were found with a distinct $\delta^{18}\text{O}_\text{P}$ range of 17.1–20.5‰. The resin-P concentrations were substantially lower (<8 $\mu\text{g/g}$) with a wider and significantly lower $\delta^{18}\text{O}_\text{P}$ range of 10.6–16.5‰. The ash samples were found to have HCl-P $\delta^{18}\text{O}_\text{P}$ higher in ~ 0 – ~ 9 ‰ relative to the source coal. Similar isotopic values were found for ash with the same coal source country, regardless of the power station. Despite the low bioavailable P concentrations, fly ash could still be an important atmospheric P source to the biosphere since these combustion products likely acidify in the atmosphere to become bioavailable. This is also supported by our finding that smaller particles, which are more indicative of the particles actually emitted to the atmosphere, are significantly P-richer. Natural dust sources' $\delta^{18}\text{O}_\text{P}$ overlap fly ash's range, complicating the assessment of coal's contribution. Nonetheless, our results provide a new tool for identification of fossil fuel combustion sources in local and global atmospheric P deposition.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Phosphorus (P) functions frequently as a main limiting or co-limiting factor for photosynthetic organisms in terrestrial, marine and freshwater ecosystems. Thus, its fluxes have strong influence

on the biogeochemistry of soils and water bodies and the ecosystem primary production (Elser et al., 2007; Peñuelas et al., 2013). Therefore, understanding and managing the P inputs is critical for maintaining healthy ecosystems. While riverine nutrient inputs affect many ecosystems, such as lakes and coastal environments, atmospheric deposition (dust) serves as a major input for oligotrophic ecosystems such as the Saharan dust for the Atlantic Ocean (Okin et al., 2011) and the Amazon rainforest (Swap et al., 1992). Also, dust serves as an important secondary input to freshwater lakes (Gross et al., 2013; Camarero and Catalan, 2012).

* Corresponding author. The Institute of Earth Sciences, The Hebrew University, Edmond J. Safra Campus, Givat Ram, Jerusalem, 91904, Israel.

E-mail address: angert@gmail.com (A. Angert).

While most of the atmospheric-P are mineral aerosols that originated in soils, recent estimations of global P budget have shown that combustion of biomass, biofuels and fossil fuels has a significant role as well. Mahowald et al. (2008) estimated by modeling that $0.06 \text{ Tg P yr}^{-1}$, less than 5% of global Total Phosphorus (TP) depositions, are from anthropogenic combustion (fossil fuels, biofuels and biomass) (Table 1). On the other hand, Wang et al. (2015) estimated that 1.1 Tg P yr^{-1} originate for anthropogenic combustion, from which $\sim 0.5 \text{ Tg P yr}^{-1}$ originate from fossil fuels, making it a significant contributor ($\sim 15\%$) to global TP deposition (Table 1). Despite the large difference between the studies, both show that in industrialized regions, fossil fuel combustion is the main atmospheric-P source. Based on the P content of emissions of different fossil fuels and fuel consumption data, coal burning supplies most of the P in fossil fuels (Wang et al., 2015).

In order to validate these estimates and to fully assess the contribution of coal combustion to P deposition, it is necessary to be able to differentiate between the atmospheric-P sources in atmospheric samples. Our group has developed a method based on stable oxygen isotopes in inorganic phosphate ($\delta^{18}\text{O}_\text{P}$), to identify different atmospheric-P sources. This is possible since the P-O bonds in phosphate (PO_4^{3-}) are not dissociated under normal environmental conditions ($T < 80^\circ\text{C}$) except by biological processes (Tudge, 1960). This method, which is an extension of methods used for soil $\delta^{18}\text{O}_\text{P}$ determination (see Jaisi and Blake (2014) and references within) was tested successfully to identify sources of natural and agricultural soils (Gross et al., 2013) and to identify distinct Saharan dust sources (Gross et al., 2015). In this research, we aim to find a distinct isotopic signature for fly coal ash, the by-product of coal combustion that is emitted to the atmosphere, which could be used to identify coal's contribution to atmospheric-P.

As mentioned above, fly coal ash which is composed of the fine particles that are carried with the flue gas, has relatively high P concentrations with reported values of 0.22–1.31% (Mahowald et al., 2008). But, the majority of ash particles are filtered by electrostatic precipitators (ESP) or other types of filters before they reach the chimneys and released to the atmosphere. Wang et al. (2015) used a value of 59% removal of fly ash for their calculations for the years 1960–2007, but mentions that ESPs remove 83–97%. Furthermore, in the Israeli coal power stations ESPs are claimed to remove 99.75% of the fly ash (NCAB, 2015). Since the amount of ash filtered has a major influence on the budget calculation, different removal efficiencies should be accounted for. Due to the complexity of emission sampling from power stations, the fly coal ash collected by the ESPs provides a good available indicator of the actual particles emitted, and thus, it was used in this study.

P is a minor constituent of coal ranging 0.001–0.229% for most coals (based on US coals, Rao and Walsh, 1997). In coal, phosphorus is usually inorganic, constituting minerals such as apatite (Ca-P) or crandallite group minerals (Ca and/or Al bound phosphate along with Sr and Ba). Also, rare-earth phosphate minerals such as monazites were reported (Rao and Walsh, 1997). The efficient combustion in power stations and industrial boilers burns most of

the coal, leaving behind ash with high P content (Beck and Unterberger, 2006).

During combustion, the P-bearing compounds liberate, vaporize or melt depending on the compound, its initial particle size and the combustion temperature. In the $<1 \mu\text{m}$ (PM_{10}) fraction of fly ash, high P concentrations were found in which P appears as Ca-P or as an aggregate of P-oxide, alkali elements- P and P/Al-silicates. These probably form by vaporization followed by possible oxidation and other chemical reactions and finally condense to PM_{10} (Zhang and Ninomiya, 2007). Ca-P in this range might form by the condensation of phosphates on Ca particles or by another physical or chemical process. Experimental work confirmed that the majority of the gaseous P is the soluble orthophosphate (H_3PO_4) (Beck and Unterberger, 2006). In larger particles of ash, 1–10 μm , P constitutes mostly apatites and complex compounds of Si, Al, Ca, Fe and P. The apatites are formed by direct liberation of the apatites in the coal. However, the complex species are probably the product of melting and solidification (Zhang and Ninomiya, 2007).

Not all the P in the aerosols is available for biological uptake. The common preferred state for biological processes is inorganic phosphate (PO_4^{3-}). But since it is primarily bound to Ca in apatite and other minerals and somewhat to Fe and Al oxides, most of it is not labile (Hinsinger, 2001). The different P fractions can be defined by the chemical extraction. In this study we focused on the HCl-extractable (HCl-P) and the anion-exchange-resin-extractable (resin-P). The latter fraction is considered to be readily bioavailable and represents the labile inorganic P, which is lightly adsorbed to outer surfaces of particles (Cooperband et al., 1999). HCl-P contains this fraction as well as inorganic P that is Ca-bound and some Fe-bound P (Gross et al., 2015). Nenes et al. (2011) suggest that the bioavailable fraction of dust increases during atmospheric transport as a result of acidification by HNO_3 and H_2SO_4 . This effect is expected to be stronger for ash particles, which are emitted together with nitrogen and sulfur oxides. Such abiotic solubilization causes only negligible isotopic fractionations (Kolodny et al., 1983), so the isotopic signature of the inorganic fraction should remain unchanged.

In this study, we analyzed ten different fly coal ash samples produced at Israeli power stations during 2014 for P concentrations and $\delta^{18}\text{O}_\text{P}$ in the HCl-P and resin-P fractions. The source coal of the ash was also analyzed in order to understand what governs the isotopic composition. Further, we separated the ash to different particle size bins and measured their P concentrations in order to estimate the P concentration of the actual PM emitted. Finally, we compared the results with other dust-P sources and tried to evaluate them in the context of global and local atmospheric-P deposition.

2. Materials and methods

2.1. Coal and fly coal ash

We used 10 different fly ash samples that cover the different types of coal burned in Hadera and Ashqelon power stations in 2014 (see Table S1 in Supplementary Material), and 9 samples of coal that was the source of this ash. The coal burned in Israel is mostly bituminous coal with carbon content of 60–80% (NCAB, 2015). The ash was sampled two days after that coal was burned. Chemical composition (including Total P) of the fly ash and its source coal was carried by the Geological Survey of Israel for the Israeli National Coal Ash Board (NCAB) using Lithium Metaborate Fusion, HNO_3 and ICP-OES. Coal samples were burned in 900°C prior to the Lithium Metaborate Fusion in order to remove organic material, thus the element concentrations in coal refer to the inorganic fraction but the elements constituted both organic and

Table 1
Estimations of global Total Phosphorus atmospheric deposition by combustion sources. Anthropogenic combustion excludes natural fires (part of biomass).

TP Tg P yr ⁻¹	Mahowald et al., 2008	Wang et al., 2015
Global Total	2.7	3.5
Combustion	0.07	1.8
Biomass	0.025	0.87
Biofuels	0.021	0.46
Fossil fuels	0.024	0.45–0.62
Anthropogenic Combustion	0.06	1.1

Download English Version:

<https://daneshyari.com/en/article/6336649>

Download Persian Version:

<https://daneshyari.com/article/6336649>

[Daneshyari.com](https://daneshyari.com)