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Comment

## Comment on “The biosphere: A homogeniser of Pb-isotope signals” by C. Reimann, B. Flem, A. Arnoldussen, P. Englmaier, T.E. Finne, F. Koller and Ø. Nordgulen

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Reimann et al. (2008) recently published a study on Pb-isotope signature along a 120 km long transect cutting the city of Oslo. Based on concentration but also isotope data, they misinterpret Pb concentration of the biosphere in rural places and explain these large enrichments of Pb as being due to natural processes. The study ignores numerous previous studies either on local, regional or global scales (see reviews by Shotyk and Le Roux, 2005; Callender, 2003, and references therein), which clearly demonstrate that anthropogenic Pb emitted in the atmosphere from different sources (leaded gasoline, coal burning, metallurgy, etc.) was and is dispersed worldwide. The study also ignores work on Norway by the Steinnes and colleagues group (Harmens et al., 2008; Steinnes et al., 2005a, b; Åberg et al., 2004), and measurements and modelling by the EMEP network ([www.emep.int/](http://www.emep.int/), EMEP, 2005). The study also neglects numerous works on preanthropogenic Pb deposition rate and isotopic signature using continental archives of atmospheric deposition like peat bogs (Shotyk et al., 1998; Klaminder et al., 2003; Kylander et al., 2005; Le Roux et al., 2005). These studies have shown that preanthropogenic Pb atmospheric deposition rate and its Pb isotopic signature is regionally defined, but also that those signals are negligible compared to past 2 ka and recent Pb atmospheric fluxes (Table 1).

Reimann et al. (2008) argue that the Pb isotopic signatures of their biogenic samples ( $^{206}\text{Pb}/^{207}\text{Pb}$  of 1.14–1.17) are possibly explained by mass-dependent and mass-independent stable isotope fractionation processes during biogeochemical cycling, rather than by source mixing of 20th

century anthropogenic Pb and local geogenic background Pb. In doing so, they ignore basic knowledge on Pb-isotope geochemistry. In contrast to Zn, Fe or Hg isotopes, 3 Pb-isotopes ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ) are radiogenic and are end-members of U–Th decay chains. Therefore the variability of Pb isotopic compositions due to combined U–Th radioactivity and U–Th/Pb elemental fractionation is up to 200 times larger than the variability due to mass-dependent equilibrium and kinetic isotope fractionation (Faure, 1986). In addition, Reimann et al.’s argument that the recently proposed mass-independent nuclear field shift mechanism (Schauble, 2007) could induce large natural variations in the very heavy stable isotopes, such as those of Hg and Pb, is similarly flawed. The nuclear field shift effect (also known as nuclear volume effect) is a theoretical concept invoked to explain experimental U isotope fractionation (Biegeleisen, 1996). Schauble (2007) theoretical predictions of nuclear field shift fractionation factors for Hg and Tl are <1‰ per atomic mass unit. Although nuclear field shift fractionation has potentially been observed at a very limited level (<1‰) in experimental liquid Hg evaporation (Estrade et al., 2007), it remains to be detected in natural samples. Rather, recent work on Hg isotopes notes the notorious absence of the nuclear field shift effect in mass-independent Hg isotope fractionation in biological samples (Bergquist and Blum, 2007; Laffont et al., 2007; Epov et al., 2008). Finally, the predicted mass dependent and mass-independent isotope fractionation of Pb and neighbouring heavy elements of <1‰ per amu, is smaller than the long-term analytical reproducibility of Reimann et al.’s sector field ICP-MS Pb-isotope analyses (2‰, 2SD), and therefore undetectable. Moreover, Reimann et al. (2008) point out that Fe and Zn isotopes are fractionated

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**Table 1**

Pb atmospheric accumulation rate (AR) estimated using peat bogs in Europe for “preanthropogenic” periods (adapted from Kylander et al., 2005 and Le Roux et al., 2005) and recent measured wet deposition

Study	Country	Pre-anthropogenic AR $\mu\text{g m}^{-2} \text{a}^{-1}$	$^{206}\text{Pb}/^{207}\text{Pb}$ signature	Period
Le Roux et al. (2005)	Southern Germany	$30 \pm 14$ (1–90, $n = 51$ )	1.18–1.19 ( $n = 10$ )	5800–1300 cal. BC
Shotyk et al. (1998)	Northern Switzerland	$10 \pm 2$ (5–14, $n = 18$ )	1.199–1.21	7000–4100 cal. BC
Klaminder et al.(2003)	Southern Sweden	1–10	1197–1212	4000–1500 cal. BC
Kylander et al. (2005)	Galicia, Spain	$32 \pm 30$ ( $n = 11$ )	$1.25470 \pm 0.02575$	6100–3200 cal. BC
Shotyk et al. (2005) and unpublished data	Faroe Islands	$0.2\text{--}10$ ( $n = 12$ )		8000–3500 cal. BC
Study	Country	AR $\mu\text{g m}^{-2} \text{a}^{-1}$	$^{206}\text{Pb}/^{207}\text{Pb}$ signature	Period
Le Roux et al. (2005)	Southern Germany	$2500 \pm 1500$	1.14–1.16	2003
EMEP (2005)	Southern Germany	1500		2003
EMEP (2005)	Southern Norway	800–2300		2003
EMEP (2005)	Southern Sweden	700–1100		2003

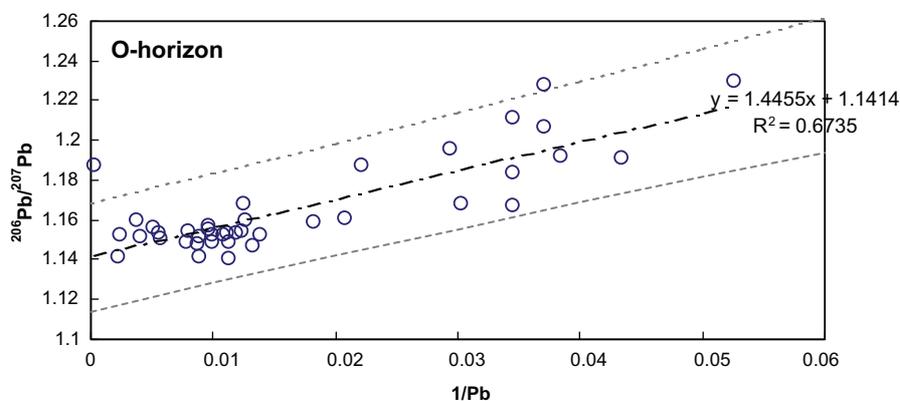
in biological systems but the variation is again within a few ‰ per amu (e.g: Cloquet et al., 2008; Guelke and Von Blanckenburg, 2007; Weiss et al., 2005; Viers et al., 2007). A lower or in the best case a similar variation would be expected for Pb which will change the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in the third decimal. These observations lead to the same conclusion that such variations could not be detected and are in any case a possible explanation for Pb “homogenisation”.

In summary, stable isotope fractionation cannot, by any physico-chemical means, be responsible for the terrestrial variation in stable Pb-isotope ratios, nor in the variation in Reimann et al.’s samples. Reimann et al.’s conclusion that biological activity fractionates and homogenizes stable Pb-isotope signatures, and that therefore the “20th century airborne pollution signal as defined by Bindler et al. (1999) ( $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of c.a 1.15) ... is not related to anthropogenic sources.” is therefore entirely based on a misconception.

Another hypothesis by Reimann et al. is a preferential leaching of some minerals, which will have another isotope composition than the bulk soil. Lead will be taken up by plants from this soil solution and therefore have a different isotope composition than bulk soil. That is right and this was verified for other isotopic systems (i.e.  $^{86}\text{Sr}/^{87}\text{Sr}$ ), however this is negligible in comparison with atmospheric deposition of anthropogenic Pb (Klaminder et al., 2003).

This was also clearly shown by Bacon et al. (2005), when they investigated the isotopic composition of grass in a field enriched in  $^{207}\text{Pb}$ . They showed that in rural places in Scotland, >80% of Pb in grass was derived from atmospheric deposition. In soils, Pb, even in rural places, mainly comes from atmospheric deposition of anthropogenic Pb apart from specific geological settings. Lead soil inventories, which are closely related to atmospheric precipitation, are even used in forested and mountainous areas as indicator of total atmospheric deposition (Weathers et al., 2000, 2006).

Once it is concluded that plants do not “homogenise” the Pb-isotope signal, the data from Reimann et al. (2008) can be looked at differently and indeed using the same results, inverse conclusions supported by numerous recent studies (i.e. Lahd Geagea et al., 2008; Cloquet et al., 2006) can be adopted. In fact, Reimann et al. (2008) ignore their own data. The discussion about Fig. 5 in Reimann et al. (2008) is especially short and only points out that “completely different processes determine Pb concentrations and isotope ratios in the geosphere and in the biosphere”: for sure, because the biosphere and the surface soil layers are influenced by atmospheric deposition of anthropogenic Pb. If only the O-Horizon samples are considered, it appears clearly that there is a relationship between Pb concentration and Pb-isotope composition (Fig. 1). This allows definition of the the isotope composition



**Fig. 1.** Pb isotope composition vs. Pb concentration<sup>-1</sup> in O-horizons.

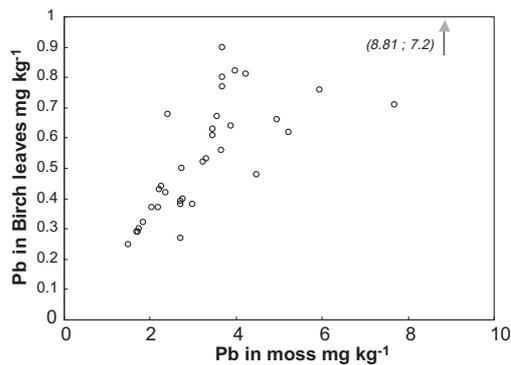


Fig. 2. Pb concentrations in birch leaves vs. Pb concentrations in mosses.

tion of an end-member enriched in Pb between 1.14 and 1.16 for  $^{206}\text{Pb}/^{207}\text{Pb}$ .

The raw results by Reimann et al. (2008) are also interesting in order to validate or develop bioindicators of atmospheric deposition. Mosses are often used as bioindicators of atmospheric deposition, however in some areas, they can be rarely found. A comparison between the concentrations in mosses and birch leaves (Fig. 2) from the data of Reimann et al. (2008) show that birch leaves would possibly be good alternatives, even if they represent a shorter time of aerosol interception. The isotopic shift (Fig. 3) of leaves leads to a more radiogenic component compared to mosses. This can be perhaps explained by an additional uptake of Pb from the soil via the tree roots to the leaves (Fig. 4) if it is considered that mosses represent the atmospheric Pb isotopic signature. Further investigations with more precise Pb-isotope measurements and adapted protocol are needed to explain this shift. Other bioindicators such as wood or bark (Fig. 5) may be interesting, especially in order to understand the Pb biogeochemical cycle on a longer time-scale, but then it can be expected that the Pb contamination in the wood is dependent on the history of the tree and its environment. Recently analyses of tree bark using a dedicated sampler and protocol have shown, however, that they can be used to monitor atmospheric pollution and corresponds to 2–8 a of accumulation (Lahd Geagea et al., 2008). Here

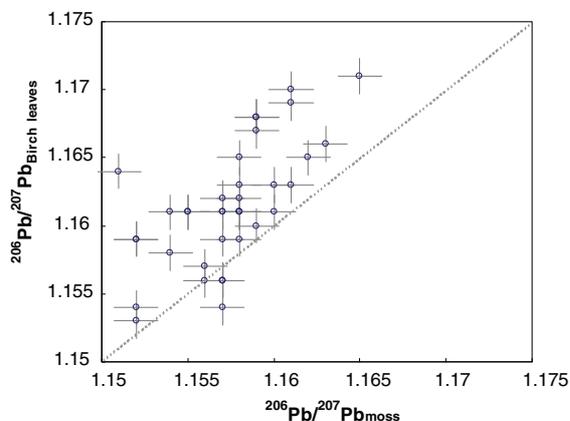


Fig. 3.  $^{206}\text{Pb}/^{207}\text{Pb}$  in birch leaves vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  in mosses.

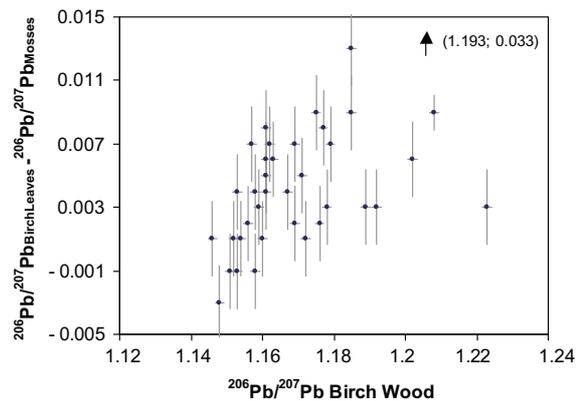


Fig. 4. “Isotopic shift” of birch leaves compared to the atmospheric signal (mosses) vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  in birch wood.

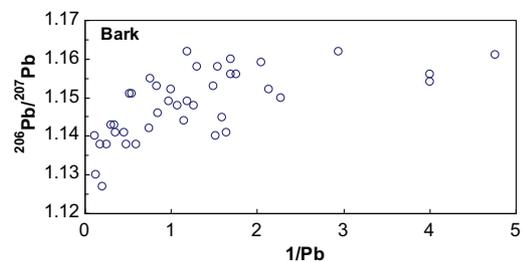


Fig. 5. Pb isotope composition vs. Pb concentration in birch bark.

(Fig. 5), the data of Reimann et al. (2008) again show a relationship between concentration and isotopic composition.

To conclude, the set of data from Reimann et al. (2008) is inappropriately interpreted and should be revised in order to integrate results and conclusions from previous studies on environmental archives. In rural and remote places from western Europe far from any point source, the isotopic chronology of atmospheric Pb deposition and consequently ecosystem contamination displays a similar history mainly dominated by the dispersion of submicron aerosols carrying Pb from leaded gasoline before its recent banishment.

Consequently to that and to other environmental improvements, Pb emissions in the atmosphere have decreased over 10 a in western Europe along with Pb deposition in rural places. This is causing other previous “minor” sources of Pb to influence the isotopic composition of Pb in the environment. Will it spatially differentiate this isotopic composition of Pb? This should be verified in the near future using a similar approach to Reimann et al. (2008), combining isotopic measurement and GIS but without ignoring previous studies specifically on environmental archives.

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