Comment on "Does within-bog spatial variability of mercury and lead constrain reconstructions of absolute deposition rates from single peat records? The example of Store Mosse, Sweden," by Richard Bindler, Malin Klarqvist, Jonatan Klaminder, and Johannes Förster

William Shotyk[1]

Received 6 April 2005; revised 19 December 2005; accepted 17 January 2006; published 19 April 2006.

Citation: Shotyk, W. (2006), Comment on ''Does within-bog spatial variability of mercury and lead constrain reconstructions of absolute deposition rates from single peat records? The example of Store Mosse, Sweden,'' by Richard Bindler, Malin Klarqvist, Jonatan Klaminder, and Johannes Förster, *Global Biogeochem. Cycles*, *20*, GB2004, doi:10.1029/2005GB002528.

[1] *Bindler et al.* [2004] addressed an important question when they asked whether within-bog spatial variability of Hg and Pb constrained reconstructions of absolute deposition rates from single peat core records. In their study, they collected nine peat cores from hummocks at Store Mosse in southern Sweden and found that the Pb inventories since approximately AD 1890 varied by a factor of 2 (0.75 to 1.40 g/m2). The authors concluded that (1) ''a single peat core may not provide a record of absolute atmospheric deposition rates to the degree generally accepted''; (2) ''an individual peat core only represents a measurement of past deposition at a single point on the bog surface, and is not necessarily representative of average deposition rates for the bog area as a whole''; and (3) ''Reconstructions based on single peat records and detailed comparisons between single records should be treated more carefully.'' These statements are certainly relevant to the small but growing international community of scientists using peat bogs as archives of atmospheric deposition and climate change, and further discussion of the reported variability is warranted.

[2] At first glance, the large variation in Pb inventories within a single bog (~100%) appears to contradict findings reported earlier for Etang de la Gruère (EGR), an ombrotrophic bog in Switzerland. Peat cores collected in 1991 (2F) and in 1993 (2K) were age dated using ^{210}Pb and found to yield remarkably similar chronologies of anthropogenic Pb and its isotopic evolution [*Shotyk et al.*, 2002]. The small differences between the two cores were attributed to differential compression during core collection and to the crude method used to section the cores; these findings highlighted the need for careful site selection, peat core collection, handling, preparation, subsampling, chemical and isotopic analyses, and radiometric age dating. As a consequence of these findings, a protocol was developed which was recommended for detailed reconstructions of atmospheric deposition using peat cores from ombrotrophic bogs [*Givelet et al.*, 2004].

[3] To further explore the apparently divergent results of the studies by *Bindler et al.* [2004] and *Shotyk et al.* [2002], the inventories of atmospheric Pb since the Roman Period was calculated using five peat cores from EGR: 2F and 2G (1991), 2K (1993), 2S (2002) and 2T (2005); the collection of the 2T core this year was stimulated by the paper by *Bindler et al.* [2004] and was taken 25 m from the site where the previous samples were taken. The average Pb inventory for the five EGR cores is 1.89 ± 0.10 g/m^2 representing an RSD of 5.3%. For the calculation, the lithogenic Pb component is ignored as it represents at most 3% of the Pb deposited since the Roman Period. For comparison, the Pb inventories in peat cores from two other bogs in the Jura Mountains were also calculated: La Tourbière des Genevez (TGE) and Praz Rodet (PRD). The Pb inventories of the two cores from TGE (~4 km from EGR) are 2.14 and 2.19 g/m^2 and in the core from PRD (~100 km from EGR) 1.97 g/m^2. The Pb inventories of the eight cores from three bogs, with each core representing peat accumulation since the Roman Period, average 1.97 ± 0.14 g/m^2 with an RSD of 7.2%. The large variations within the Swedish bog (~100%) reported by *Bindler et al.* [2004], and the much smaller variations in Pb inventories within the bog at EGR and between the other Swiss bogs in the Jura Mountains described here, require us to seek possible explanations for the profound differences.

[4] *Bindler et al.* [2004] listed a number of physical and botanical reasons why Pb accumulation rates might be so variable within the surface of the bog, including e.g. differences in the structures and growth rates of plant communities which can lead to differences in interception. However, their method used to calculate the Pb inventories also deserves a second look. *Bindler et al.* [2004] reported Pb inventories since ~AD 1890. Age dating recent environmental samples such as sediments and peats is not trivial, and a more careful examination of the approach used by *Bindler et al.* [2004] to determine the depth in the peat cores corresponding to AD 1890 is warranted. One of the nine peat cores was age dated using ^{210}Pb, but the other peat cores were not. Instead, the age-depth relationship was

[1]Institute of Environmental Geochemistry, University of Heidelberg, Heidelberg, Germany.

0886-6236/06/2005GB002528

inferred using the ratio of $^{206}Pb/^{207}Pb$ in the peat, obtained using Q-ICP-MS following acid digestion, and comparing this to published values for the temporal evolution of $^{206}Pb/^{207}Pb$ in England and Scotland. Specifically, *Bindler et al.* [2004] used the variation in $^{206}Pb/^{207}Pb$ published for archived grass samples from Rothamsted Experimental Station [*Bacon et al.*, 1996] determined using TIMS, and from herbarium specimens of *Sphagnum* moss from the Edinburgh Botanical Garden [*Farmer et al.*, 2002] using Q-ICP-MS. On the basis of these studies, *Bindler et al.* [2004] assumed that the first sample in the Swedish peat cores with $^{206}Pb/^{207}Pb$ below 1.17 corresponds to the year 1890.

[5] The isotopic composition of Pb in acid digests of peat using Q-ICP-MS is notoriously imprecise, with RSDs typically on the order of 0.3 to 0.7% [*Shotyk and LeRoux*, 2005]. Assuming that the precision of the measurements is 0.5%, an average Q-ICP-MS measurement of 1.17 has an uncertainty associated with it in the range 1.164 to 1.176. If the range of the errors in $^{206}Pb/^{207}Pb$ are plotted in Figure 3 of *Bindler et al.* [2004], it becomes clear that the depth at which samples contain $^{206}Pb/^{207}Pb$ in the range 1.164 to 1.176 are variable not only between individual peat cores, but also within a single peat core. While a number of consecutive samples could conceivably have the same isotopic composition, they cannot have the same age. These variable depths represent a wide range in Pb concentrations (because of the rate of change of atmospheric Pb deposition during the 19th and 20th centuries), and therefore also variable Pb inventories. Although it is possible that the Pb inventories within Store Mose since 1890 vary by a factor of 2 (0.75 to 1.40 g/m^2) for some or all of the reasons given by *Bindler et al.* [2004], it is not clear how much of the variation in the Pb inventories is simply because the age-depth relationship was poorly constrained in eight of the nine cores.

[6] The fundamental problem in the approach used by *Bindler et al.* [2004] to infer age dates using the $^{206}Pb/^{207}Pb$ ratio can be illustrated by considering the isotopic composition of Pb in four Swiss peat bog profiles which were dated using ^{210}Pb [*Weiss et al.*, 1999a]. The isotopic composition of Pb in these peat cores was measured using TIMS which provides an accuracy and precision of measurements of $^{206}Pb/^{207}Pb$ of ~0.1 and 0.01%, respectively. Taking the value of $^{206}Pb/^{207}Pb = 1.170$ as a point of reference, it is clear that the corresponding ^{210}Pb ages of the peat cores range from the early 1880s until 1930 (dotted vertical arrows in Figure 1). In these cores, however, the cumulative Pb inventories since 1930 are up to 50% greater than those since 1880. Assuming that the measurements of Pb concentrations and peat bulk density are done properly, the accuracy of the calculated Pb inventory in any given time increment of a peat core will depend in a sensitive way on the accuracy of the age-depth relationship.

[7] Taking into account the precision of the TIMS data shown in Figure 1, the ^{210}Pb age dates of the first samples with $^{206}Pb/^{207}Pb < 1.17$ are 1905 ± 6 at EGR, 1923 ± 6 at TGE, and 1921 ± 5 at PRD. Had these samples been measured using Q-ICP-MS, and even assuming that precision of the Q-ICP-MS measurements was 0.3%, the first samples corresponding to $^{206}Pb/^{207}Pb < 1.17$ would have

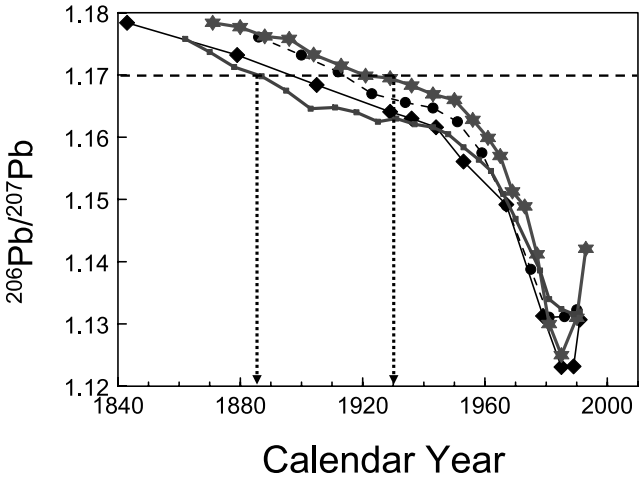

Figure 1. Plot of $^{206}Pb/^{207}Pb$ (obtained using TIMS) for four peat cores from Switzerland versus the age dates obtained using ^{210}Pb [*Weiss et al.*, 1999a]. The horizontal line at $^{206}Pb/^{207}Pb = 1.170$ intersects peat samples ranging in age from the early 1880s to ~1930 (dashed vertical arrows).

the following ^{210}Pb age dates: EGR, 1929 ± 3; TGE, 1934 ± 4; PRD, 1950 ± 2 [*Weiss et al.*, 1999a]. In other words, on the basis of the ratio $^{206}Pb/^{207}Pb$, peat from EGR dating from 1905 could not be distinguished from that of peat from PRD dating from 1950, and yet the cumulative Pb inventory of the latter is more than 50% greater than that of the former. Given the range in ^{210}Pb ages for samples which are not significantly different with respect to their measured $^{206}Pb/^{207}Pb$ ratios, it is fair to ask to what extent the $^{206}Pb/^{207}Pb$ ratio can be used to reliably quantify variations in cumulative atmospheric Pb deposition.

[8] In addition to Swiss peat cores, herbarium specimens of *Sphagnum* moss from the University of Geneva were also analyzed using TIMS [*Weiss et al.*, 1999b]. A sample dating from 1895 had a $^{206}Pb/^{207}Pb$ of 1.1742 ± 0.0002 and a sample from 1951 a ratio of $^{206}Pb/^{207}Pb$ of 1.1620 ± 0.0002. Even though these two moss specimens differ with respect to age by more than 50 years, it would be difficult to distinguish one from the other using Q-ICP-MS.

[9] The data and arguments presented here suggest that the "within-bog spatial variability" reported by *Bindler et al.* [2004] for Pb inventories since AD 1890 at Store Mose may have been overestimated because of the inaccuracy of the approach used to determine the depth corresponding to AD 1890. The question of variation in atmospheric Pb inventories within a given bog warrants further study, but the accuracy of the method employed to date the cores should be duly considered.

References

Bacon, J. R., K. C. Jones, S. P. McGrath, and A. E. Johnston (1996), Isotopic character of lead deposited from the atmosphere at a grassland site in the United Kingdom since 1860, *Environ. Sci. Technol.*, *30*, 2511–2518.

Bindler, R., M. Klarqvist, J. Klaminder, and J. Förster (2004), Does within-bog spatial variability of mercury and lead constrain reconstructions of absolute deposition rates from single peat records? The example of Store

Mosse, Sweden, *Global Biogeochem. Cycles*, *18*, GB3020, doi:10.1029/2004GB002270.

Farmer, J. G., L. J. Eades, H. Atkins, and D. F. Chamberlin (2002), Historical trends in the lead isotopic composition of archival Sphagnum mosses from Scotland (1838–2000), *Environ. Sci. Technol.*, *36*, 152–157.

Givelet, N., et al. (2004), Protocol for collecting, handling, and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses, *J. Environ. Monit.*, *6*, 481–492.

Shotyk, W., and G. LeRoux (2005), Biogeochemistry and cycling of lead, in *Biogeochemical Cycles of the Elements, Metal Ions Biol. Syst.*, vol. 43, edited by A. Sigel, H. Sigel, and R.K.O. Sigel, pp. 240–275, CRC Press, Boca Raton, Fl.

Shotyk, W., D. Weiss, M. Heisterkamp, A. K. Cheburkin, and F. C. Adams (2002), A new peat bog record of atmospheric lead pollution in Switzerland: Pb concentrations, enrichment factors, isotopic composition, and organolead species, *Environ. Sci. Technol.*, *36*, 3893–3900.

Weiss, D., W. Shotyk, P. G. Appleby, A. K. Cheburkin, and J. D. Kramers (1999a), Atmospheric Pb deposition since the Industrial Revolution recorded by five Swiss peat profiles: Enrichment factors, fluxes, isotopic composition, and sources, *Environ. Sci. Technol.*, *33*, 1340–1352.

Weiss, D., W. Shotyk, M. Gloor, and J. D. Kramers (1999b), Herbarium specimens of *Sphagnum* moss as archives of recent and past atmospheric Pb deposition in Switzerland: Isotopic composition and source assessment, *Atmos. Environ.*, *33*, 3751–3763.

W. Shotyk, Institute of Environmental Geochemistry, University of Heidelberg, INF 236, D-69120 Heidelberg, Germany. (shotyk@ugc.uni-heidelberg.de)