

If microcracks indeed catalyze the reaction, then lasers, among other techniques, could be used to scribe fine patterns and microcircuits on the surface that would be preferentially filled with the B-group element. If scratched above the melting point of Ga, scratches immediately fill up with molten Ga. Once patterned, the B-group elements could then be doped to form semiconductor-based devices. For example, Ga could be nitrided to form GaN and hence GaN-based devices. Finally, the results of this work further reinforce the notion that the B-group element is relatively weakly bound in the structure (3–5) and hence easily chemically

displaceable. Consequently, it is not unreasonable to assume that this replacement-displacement reaction could also be carried out electrochemically. It is thus anticipated that a majority, if not all, of the 312's and 211's could potentially be useful intercalation compounds.

References and Notes

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9. We thank T. Twardowski and A. Zavaliangos for stimulating discussions and T. El-Raghy for carrying out some experiments and for many very fruitful discussions. The help of M. Gamarnik in carrying out the Laue experiments is appreciated.

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Mercury in a Spanish Peat Bog: Archive of Climate Change and Atmospheric Metal Deposition

A. Martínez-Cortizas,^{1*} X. Pontevedra-Pombal,¹
E. García-Rodeja,¹ J. C. Nóvoa-Muñoz,¹ W. Shotyk²

A peat core from a bog in northwest Spain provides a record of the net accumulation of atmospheric mercury since 4000 radiocarbon years before the present. It was found that cold climates promoted an enhanced accumulation and the preservation of mercury with low thermal stability, and warm climates were characterized by a lower accumulation and the predominance of mercury with moderate to high thermal stability. This record can be separated into natural and anthropogenic components. The substantial anthropogenic mercury component began ~2500 radiocarbon years before the present, which is near the time of the onset of mercury mining in Spain. Anthropogenic mercury has dominated the deposition record since the Islamic period (8th to 11th centuries A.D.). The results shown here have implications for the global mercury cycle and also imply that the thermal lability of the accumulated mercury can be used not only to quantify the effects of human activity, but also as a new tool for quantitative paleotemperature reconstruction.

Mercury is an important trace metal in the environment because of its complex behavior and the high potential toxicity of its methylated species. Gaseous elemental Hg has a long atmospheric residence time (1 year), which favors long-range transport and homogenization on a hemispherical scale. Global mercury emissions have increased substantially at least during the past 100 to 150 years, and they have accumulated in various ecosystems (1). Although local decreases have been seen in some locations (mainly because of the reduction of emissions of regional sources), in general, Hg burdens have not declined. These observations suggest that atmospheric

Hg emissions are complicated and that it can be difficult to separate natural and anthropogenic Hg emissions (1, 2). Evaluating the impact of anthropogenic emissions requires a knowledge of the natural background values and cycling processes (2). As a liquid at room temperature (melting point, 234.28 K) with a low enthalpy of vaporization ($\Delta H_{\text{vap}} = 59.15$ kJ/mol), physical transformations of Hg (such as volatilization, condensation, and so forth) may have been important in pre-anthropogenic times because of the dramatic climate (especially temperature) changes that characterize the Holocene (3).

Here, we present a record of Hg deposition in the peat bog of Penido Vello (PVO), which extends to 4000 radiocarbon years before the present (^{14}C yr B.P.). Cadmium, Zn, and Pb were previously analyzed (4) in a core from this bog, which is situated in Galicia, northwest Spain ($43^{\circ}32'\text{N}$, $7^{\circ}34'\text{W}$). This site is 600 km northwest of Almadén, the site of the largest Hg mine in the world. Mining activity here extends

to Roman times and perhaps even earlier. In addition, the bog is ombrotrophic (4), meaning that elements such as Hg were supplied to the peat exclusively by atmospheric deposition.

A core of 2.5 m was sampled at intervals of 2 cm in the upper 1 m and at intervals of 5 cm below that depth. Total Hg concentrations were measured in wet samples (Hg_T) and in samples that were dried for 2 weeks at 30°C ($\text{Hg}_{30^{\circ}}$) and 105°C ($\text{Hg}_{105^{\circ}}$) (5).

The lowest Hg_T concentrations of the PVO core is 22 ng g^{-1} at 170 to 175 cm, and the maximum is 436 ng g^{-1} in the uppermost peat sample. These values exceed the concentration in bedrock (1.52 ng g^{-1}) by 14 to 290 times and imply that the rock was not an important source of Hg to the overlying layers. High Hg concentrations are found at the surface and at depths of 17 cm (191 ng g^{-1}), 41 cm (65 ng g^{-1}), and 97 cm (45 ng g^{-1}) (Fig. 1, A and B). The concentrations in the deeper layers are far from constant (Fig. 1B). In general, there is an increase in Hg_T from 70 cm to the top of the core, but there are also higher values between 195 and 250 cm, followed by other local maxima (of ~40 to 45 ng g^{-1}). These deeper Hg_T peaks are not related to the ash content or bulk density of the peat, these properties being almost constant throughout the profile. They can only be partially explained by the history of mining and metallurgy in Almadén (6). The peak at 17 cm, dated between 600 and 200 years ago, cannot be fully explained by mining or metallurgy activities as there is no agreement between Hg production and the higher concentrations for those times and because the relatively higher values below 190 cm, in samples older than 2800 ^{14}C yr B.P., predate by centuries any known mining activities in Spain.

A comparison of the Hg_T profile with those of dried samples shows that some Hg was lost during heating. For example, the peak at 17 cm and the higher values of the deeper section of the core are represented entirely by Hg that volatilizes at the lowest temperature (30°C). Between 15 to 25 and 190 to 250 cm, peat layers contain Hg that has low thermal stability;

¹Departamento de Edafología y Química Agrícola, Facultad de Biología, Campus Sur s/n, E-15706 Santiago de Compostela, Spain. ²Geological Institute, University of Bern, Baltzerstrasse 1, CH-3012 Berne, Switzerland.

*To whom correspondence should be addressed. E-mail: edantxon@usc.es

these layers lost large proportions of Hg, and almost all Hg was lost at 30°C. In contrast, the central section of the core (50 to 180 cm) is mainly represented by layers with moderate to high thermal stability; these layers lost relatively small proportions of Hg (some less than 20%), and most of the Hg was lost at temperatures greater than 30°C. This thermal behavior is not related to any of the investigated morphological or physicochemical properties of the peat and is also independent of the Hg concentration of the samples.

To quantify these losses, we define the proportion of Hg lost/retained at various temperatures as the following stability classes:

$$L_{\text{Hg}} = [(H_{\text{gT}} - H_{\text{g30}})/H_{\text{gT}}] \times 100 \quad (1)$$

$$M_{\text{Hg}} = [(H_{\text{g30}} - H_{\text{g105}})/H_{\text{gT}}] \times 100 \quad (2)$$

$$H_{\text{Hg}} = [H_{\text{g105}}/H_{\text{gT}}] \times 100 \quad (3)$$

L_{Hg} , M_{Hg} , and H_{Hg} represent the proportions of low, moderate, and high thermal stability Hg, respectively. On the basis of the results of pyrolysis studies on Hg desorption (7), L_{Hg} is likely to be represented exclusively by elemental Hg (Hg^0), whereas M_{Hg} is represented mainly by Hg^0 and small proportions of Hg chlorides, and H_{Hg} is represented by Hg chlorides and Hg bound to organic compounds.

A comparison of H_{gT} concentrations and the relative abundance of the thermal stability classes with paleoclimatic evolution for this part of Europe generally indicates that Hg accumulation was promoted during cold climate phases and hindered during warm periods and that the nature of Hg deposited also varied. The

basal section of the core corresponds to the Neoglacial Period (NP), a time of globally cool climate (8); here, L_{Hg} (the fraction of Hg lost at 30°C) represents a large proportion of H_{gT} (up to 50%) (Fig. 1C). After this phase, temperatures increased, culminating in the Roman Warm Period (RWP) (2100 to 1500 ^{14}C yr B.P.) (9); in this section of the core, H_{Hg} (proportion of Hg retained by the peat after heating at 105°C) dominates, but M_{Hg} (fraction of Hg lost between 30° and 105°C) also attains substantial proportions. Similarly, Hg amounts of high and moderate stability are the dominant fractions in peats corresponding to the Medieval Warm Period (MWP). In peats corresponding to the Little Ice Age (LIA) (the coldest period of the late Holocene), which started at ~1400 A.D. (9, 10), L_{Hg} is dominant (up to 60%) (Fig. 1C). In summary, during cold to very cold climatic periods, a large proportion of the accumulated Hg is in the form of thermally unstable Hg, and vice versa (11). During warm and wet climates, both H_{Hg} and M_{Hg} are abundant (12). This variation, if it holds regionally, may thus provide a proxy of environmental conditions at the time of atmospheric deposition. However, a full demonstration that these indicators are a robust proxy will require comparable analyses at several sites. This notion is consistent with data on modern Hg accumulation patterns in remote northern areas (13) and with predictive models of the fate of atmospheric Hg in response to temperature (14). It is also consistent with data on Hg accumulation in Antarctica over the past 34,000 years (15). In Dome C (Antarctica), Hg concentrations are high during the Last Glacial Maximum (LGM) (18,000 years ago), between 5 and 12 times those of the Holocene (up to 2.2 pg g^{-1} during the LGM, compared with ~0.4 pg g^{-1} during the Holocene). Although this finding was suggested to be related to increased Hg emissions due to enhanced oceanic productivity (15) in cold periods, a simple temperature control is also worth considering.

For peat samples older than 2200 ^{14}C yr B.P., a multiple regression function that includes the climatic signal contained in the Hg lability classes explains 95% of the variation of H_{gT} (16)

$$H_{\text{gNAT}} = 4.0M_{\text{Hg}} + 38.2(L_{\text{Hg}}/H_{\text{Hg}})$$

$$- 1.5(M_{\text{Hg}}/L_{\text{Hg}})$$

$$- 198.6(M_{\text{Hg}}/H_{\text{Hg}}) + 11.5 \quad (4)$$

Here, $L_{\text{Hg}}/H_{\text{Hg}}$, $M_{\text{Hg}}/L_{\text{Hg}}$, and $M_{\text{Hg}}/H_{\text{Hg}}$ are the ratios L_{Hg} to H_{Hg} , M_{Hg} to L_{Hg} , and M_{Hg} to H_{Hg} , respectively. Because these are pre-anthropogenic concentrations of H_{gT} , the function predicts the natural component of the accumulated Hg (H_{gNAT}), and it can be used as a model to reconstruct the concentration of Hg of natural origin for the whole PVO core (Fig. 2). The data (Fig. 2) show that until ~2500 ^{14}C yr B.P., the Hg concentrations can be considered to be

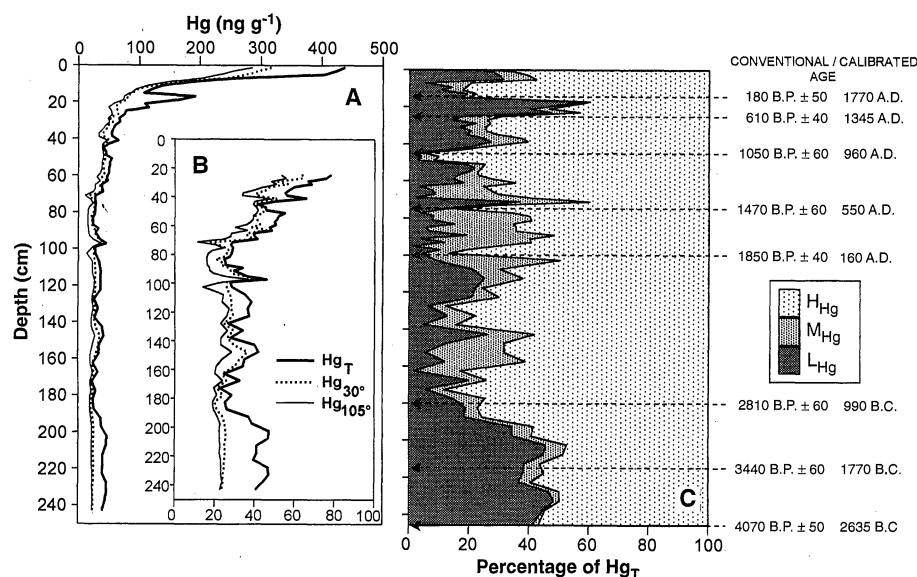
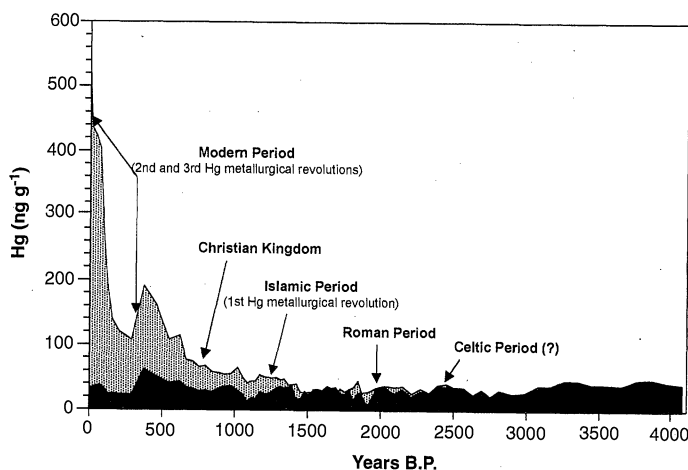


Fig. 1. (A) Mercury concentrations in the peat bog of PVO in wet (H_{gT}) and dried samples (H_{g30} and H_{g105}). (B) Magnified section of the core with Hg concentrations for peat samples below 25 cm. (C) Thermal lability of Hg: L_{Hg} , percentage of Hg lost at 30°C; M_{Hg} , percentage of Hg lost between 30° and 105°C; H_{Hg} , percentage of Hg retained by the peat after drying at 105°C. Radiocarbon and calibrated ages are also shown. Calibrated ages were calculated using CALIB REV, version 3.03 (29), and are reported here as intercepts (without standard deviations).

Fig. 2. Total Hg (H_{gT}) and the natural component of Hg accumulation (H_{gNAT} , black area) in PVO. The anthropogenic component of accumulation (H_{gANT} , shaded area) is estimated as the difference between total Hg and the natural component ($H_{\text{gANT}} = H_{\text{gT}} - H_{\text{gNAT}}$). The main prehistoric and historic phases of the Hg exploitation in Spain are indicated.



the result of natural emissions. For these pre-anthropogenic times, net Hg flux varied between 1.5 and 8.0 $\mu\text{g m}^{-2} \text{ year}^{-1}$, with an average of $3.3 \pm 1.1 \mu\text{g m}^{-2} \text{ year}^{-1}$ (17).

Samples of cold to very cold climate phases have Hg_{NAT} concentrations of 37 to 50 ng g^{-1} , except for the coldest episode of the LIA, which has a concentration of 65 ng g^{-1} . Samples of warm and wet climate phases have Hg_{NAT} concentrations between 15 and 37 ng g^{-1} , and samples of warm and dry phases have concentrations of 13 to 33 ng g^{-1} . Very warm periods are those with the lowest concentrations of Hg_{NAT} , and very cold periods are those with higher Hg_{NAT} concentrations. Thus, the natural variation between cold and very warm periods is as great as 50 ng g^{-1} , and accumulation during the coldest episode was five times that of the warmest episode. These results indicate that, at least at our site, Hg accumulation is mainly controlled by temperature variations, and humidity (that is, net surface moisture) is a secondary factor. It also has to be considered that climatic effects might influence Hg accumulation in an indirect way by affecting peat growth and decomposition rates, suggesting a certain degree of site dependency on the Hg record and the need for further extensive work to establish the limits of this methodology. Nevertheless, ratios between Hg species, as we used them here, are not likely to be affected by changes in peat growth, decomposition, or degradation.

In samples that are more recent than ~ 2500 ^{14}C yr B.P., total Hg concentrations in the peats (Hg_T) exceed the value for Hg_{NAT} as determined with Eq. 4. There are no obvious additional natural sources of Hg at this time, and the coincidence of this time with the start of Celtic mining in Spain at ~ 2400 to 2500 ^{14}C yr B.P. (18) suggests that the difference between Hg_{NAT} and Hg_T values represents anthropogen-

ic Hg (Hg_{ANT}). Since 1500 ^{14}C yr B.P., the Hg_{ANT} concentrations rose steadily to reach a maximum between 300 and 400 ^{14}C yr B.P.; this was followed by a small decrease, but since ~ 200 ^{14}C yr B.P., there has been a further pronounced increase. The average net Hg flux for the industrial period is $56.0 \pm 25.7 \mu\text{g m}^{-2} \text{ year}^{-1}$, with a maximum of $87 \mu\text{g m}^{-2} \text{ year}^{-1}$ in the uppermost samples of the peat (17).

This evolution is consistent with the history of Hg mining and metallurgy in Spain. Mining in the Almadén region is thought to have begun at 430 B.C. in the Celtic period (18). This is when Hg_{ANT} first became significant, representing 10 to 15% of Hg_T . A sharp increase to 30% of Hg_T occurred during the first phase of the Roman exploitation (the Republican period, in which there was no ore refinement); in samples that correspond to the Roman Empire, when cinnabar refining was introduced (19), values of Hg_{ANT} are up to 80% of Hg_T . Hg_{ANT} decreased with the fall of the Roman Empire in the fourth century A.D., increased during the Germanic period, decreased during the Islamic conquest of Spain, and increased again after the establishment of the Islamic kingdom, when metallurgy was first introduced. Since the final reconquest of Almadén by the Christian kingdom, Hg_{ANT} has dominated Hg_T and has steadily increased (18–20). Some of these features are shared by the Pb accumulation pattern in PVO (4).

The data above imply that the thermal lability of Hg is a good indicator of paleoclimate evolution. To establish a relation, we grouped samples in the following classes of climates in Spain (9, 21, 22): very cold to cold, cold to mild (described in the literature as irregular climatic conditions, transitions from warm to cold periods, or transitions from cold to warm periods), mild to warm and dry, warm and dry, and warm and humid.

We performed a discriminant analysis using

the climate classes as the grouping variable and the Hg stability classes as well as the ratios between them as predicting variables (23). Three canonical functions were needed to explain all the variance represented by the climate evolution of the past 4000 years, but the first two accounted for 96.5% of the total variance

$$F1 = 6.07(L_{\text{Hg}}/H_{\text{Hg}}) + 10.69(M_{\text{Hg}}/H_{\text{Hg}})$$

$$+ 0.22H_{\text{Hg}} - 0.17L_{\text{Hg}} - 15.93 \quad (5)$$

$$F2 = -2.74(L_{\text{Hg}}/H_{\text{Hg}}) - 22.81(M_{\text{Hg}}/H_{\text{Hg}})$$

$$- 0.67H_{\text{Hg}} + 0.48L_{\text{Hg}} + 60.53 \quad (6)$$

L_{Hg} and the $L_{\text{Hg}}/H_{\text{Hg}}$ ratio showed significant correlations to $F1$, whereas $M_{\text{Hg}}/H_{\text{Hg}}$ and H_{Hg} are correlated with $F2$ (23). Considering the relations between the Hg thermal stability classes and climate, $F1$ primarily represents temperature variations, and $F2$ mainly represents humidity variations (Fig. 3). The humidity function was not well defined for cold or for mild to cold periods, as the dispersion in $F2$ appears only for climates classified as mild or warm (24).

We built a relative scale [temperature index (TI)] (Fig. 4) by correcting the scores of the $F1$ function to that of the uppermost sample of the peat, making it the reference zero value (25). Positive values may represent periods of higher temperature, and negative values may represent periods of temperature lower than the average experienced during the past 30 years (25). Previous studies have estimated that temperature relative to the present was as follows: between 1° and 2°C lower during the LIA, 1.5°C higher during the MWP, 2°C higher during the RWP, and between 1° and 2°C lower during the NP (9, 21, 22). For comparison, the average TI values for these same periods are -1.7 for the LIA, +1.9 for the MWP, +2.2 for the RWP, and -1.3 for the NP. Long records at Spanish

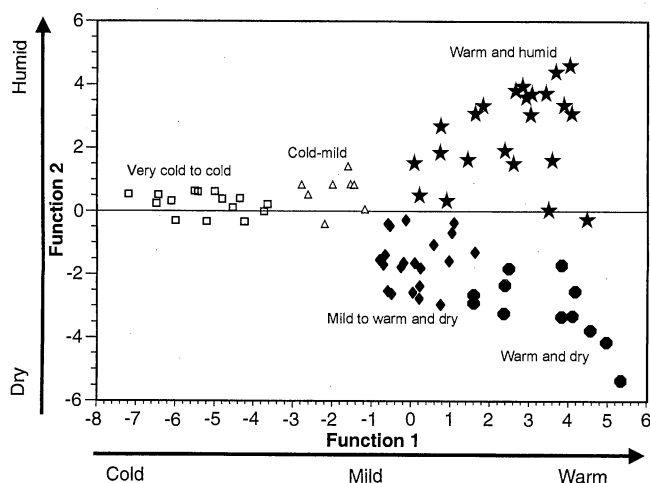


Fig. 3 (left). Bidimensional projection of the discriminant analysis using functions 1 and 2 ($F1$ of Eq. 5 and $F2$ of Eq. 6, respectively). Function 1 shows a variation from negative to positive values associated with temperature, and function 2 shows a variation associated with humidity.

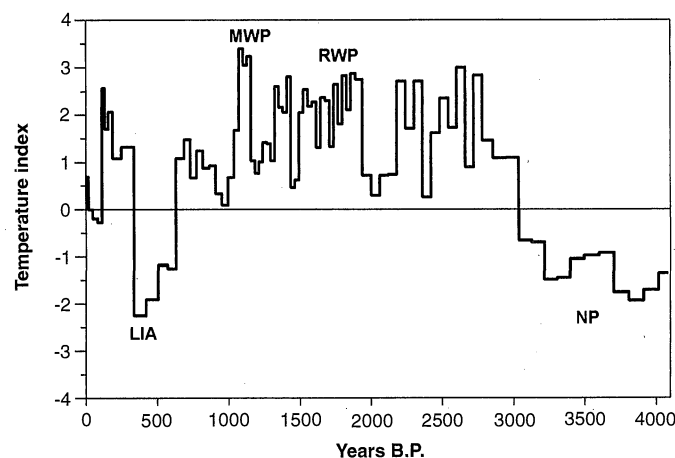


Fig. 4 (right). Evolution of the TI values for the late Holocene in northwestern Spain. Because of its good agreement with published data, it can be considered as a record of relative temperature variations for the past 4000 years in Spain.

meteorological stations show a temperature decrease of 2° to 3°C from the end of the 19th to the beginning of the 20th century (26). During the same period, the TI drops 2.7 units, from 2.5 in the 19th century to -0.2 at the beginning of the 20th century, and increases ~1.0 unit from the beginning of the 20th century (27). This result is consistent with the climate warming observed at a global scale and in Spain (28).

The record implies that, for the past 4000 years (Fig. 4), the NP and the LIA were the most prominent cooling periods and the RWP and the MWP were the most important warming periods. The reconstruction also shows some regional climatic peculiarities, such as that from 1500 to 1200 ^{14}C yr B.P., when it was generally cool in Spain except for north-western areas, where temperatures recovered after an initial cooling (9). In addition, the record shows high variability, with intense changes occurring at different time scales (3).

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5. Mercury concentrations were measured in wet and dried samples with a LECO-ALTEC AMA-254 Hg analyzer (Altec, Praha, Czech Republic) connected to an automatic sampler. This equipment is a single-purpose atomic absorption spectrophotometer for Hg determination in solid and liquid samples without sample chemical pretreatment. It uses a Hg vapor generation technique and attains exceptionally high sensitivity. The detection limit is 0.01 ng of Hg, and the working range is 0.05 to 600 ng. Each sample was measured in triplicate. Differences between replicates never exceeded 0.5 ng g⁻¹, being always less than 1% of the mean value of the sample. Standard reference materials (SRMs) were run within each set of analysis. All the determined values were in the precision range for each SRM, and mean reproducibility for triplicates was 5.2%. Radiocarbon age dating was previously described (4). All radiocarbon age dates presented here are given as conventional radiocarbon years before present (¹⁴C yr B.P.).
6. Mercury and Hg minerals have been exploited for centuries in Spain, with the first reference dating to 430 B.C. in the region of Sisapo (a Celtic word that means "the mine"), later identified as the Almadén area, where vermilion (HgS) of first quality was extracted; mining began to be intensive during the Roman times (first century B.C. to fourth century A.D.), and metallurgy was introduced during the Islamic period (eighth and ninth centuries A.D.) (78). Available data on Hg production extend to 500 years ago.
7. Mercury pyrolysis studies of contaminated soils and synthetic standards [H. Biester and C. Scholz, *Environ. increasing humidity (net surface moisture) can be the result of an increase in the input of Hg chlorides. The bog is located only 20 km south of the coast, and more precipitation would correspond with an enhanced marine influence (especially the ionic strength of wet deposition).*
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16. To obtain this function, we performed a regression analysis (SPSS version 6.1, SPSS, Chicago, IL) on 24 samples with ages older than 2200 years, which is before the beginning of the Roman exploitation of Almadén. A stepwise regression method was used, with *F* probabilities of 0.05 and 0.10 (in and out, respectively). Analysis of variance and Student *t* analyses indicated that the regression function and the regression coefficients of independent variables are significant (*P* < 0.01). The correlation coefficient is 0.97, and the standard error of the estimate is 2.2 ng g⁻¹.
17. The Hg flux calculation is based on accumulation and has to be considered as a crude estimation of the actual Hg flux, because accumulation is not exclusively the result of deposition processes but is the result of a balance between inputs to and outputs from the bog. Our data suggest that part of the deposited Hg is reemitted to the atmosphere, with the proportion increasing with increasing temperature.
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- The water content of the atmosphere as temperature drops; therefore, the colder the climate, the drier it tends to be. But this cannot be fully assessed because PVO is located in an oceanic region only ~20 km from the sea, and there is no clear evidence of an intense humidity decrease in northwestern Spain during the cold spells of the late Holocene. For example, during the LIA (the most recent cold period), extreme humid and dry conditions seem to have been of common occurrence (21), and on the basis of the results shown in Fig. 3, the average trend reflected by the *F2* scores is one of humidity that is similar to or only slightly higher than that at the present.
25. The TI values were calculated as $(F_1/F_1)_{-1}$, in which *F*₁ is the score of *F*₁ for each individual peat sample and *F*₁ is the score of the uppermost sample of the peat. The latter is a sample with a thickness of 2 cm, which represents the past 25 to 30 years of peat accumulation, based on the growth rate. At the place where PVO is located, the mean annual temperature for this period is 10.3°C (5.4°C in winter and 16.5°C in summer), and annual precipitation is 1600 mm (575 mm in winter and 170 mm in summer) [A. Martínez-Cortizas and F. Castillo, *Geographica* **33**, 127 (1996)].
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27. It is not certain whether the TI of the peat-vegetation interface sample is a correct value because it may be not in equilibrium with present conditions and it is still subjected to Hg volatilization. In this case, the TI would be lower, and a more reasonable estimate for the change during the present century would be an increase in TI on the order of 0.5 to 1.0 units.
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