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Spatial Distribution of Natural Enrichments of Arsenic, Selenium, and Uranium in a Minerotrophic Peatland, Gola di Lago, Canton Ticino, Switzerland

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Gola di Lago is a small (ca. 3 ha), minerotrophic peatland in Canton Ticino, southern Switzerland. Chemical analyses of peat show remarkable concentrations of As, Se, and U. Coring at regular intervals (19 sites) revealed several zones of pronounced accumulation, with As concentrations up to 350 mg kg^{-1} (2000 mg kg^{-1} on a mineral matter basis). Both Fe and S are also enriched at this depth, suggesting that redox-related transformations have affected all three elements. High concentrations of Se (up to 28 mg kg^{-1}) and U (up to 470 mg kg^{-1}) were also detected, representing on a mineral matter basis 350 and 2900 mg kg^{-1}, respectively. An intermittent stream entering the peatland contained up to 400 μg of As L^{-1}, but the permanent stream leaving the mire contains <2 μg L^{-1}. A three-dimensional map of the spatial distribution of As shows that the main source of As is the intermittent stream and not the basal, mineral sediment underlying the peatland. Arsenic is highly enriched not only in shallow peat layers at the interface between the stream and peatland today but also in deeper peat layers in the center of the mire, at what must have been the stream−peat interface in the past. By sequential extraction of fresh peat samples, 100% of the As could be extracted from a shallow sample but only 19% from a sample taken from the deeper layers. In both cases, most of the As was associated with the organic matter fraction (73% and 57% respectively). Although this peatland is an effective geochemical trap for As in the stream waters, the mechanisms of removal remain unclear.

Introduction

Arsenic (As) today is one of the trace elements of greatest environmental interest because its presence in drinking water has affected more than 400 million people worldwide (*1*). Although it is the cause of serious and well-known public health problems in developing countries such as Bangladesh, India, Mexico, and Vietnam, it also presents a number of challenges in industrialized countries such as Switzerland and the United States.

The natural abundance of As in the earth's crust is on the order of 1−2 mg kg^{-1} (*2*, *3*). Arsenic can substitute for sulfur in many sulfide minerals. It is not often found in its elemental state and is more common in sulfides and sulfosalts as arsenopyrite (FeAsS), orpiment (As_2S_3), realgar (AsS), lollingite ($FeAs_2$), and tennantite ($Cu_{12}As_4S_{13}$) (*4*, *5*). The most common arsenic-bearing mineral by far is arsenopyrite, which is often present in ore deposits; this mineral however, is much less abundant than arsenian (arsenic-rich) pyrite [$Fe(S, As)_2$], which is probably the most important source of arsenic in ore zones (*6*).

In natural waters, As is mostly found as oxyanions with oxidation states of III ($H_3AsO_3^0$ and $H_2AsO_3^-$) and V ($H_2AsO_4^-$ and $HAsO_4^{2-}$) (*7*). Transformations of As species are affected not only by chemical properties such as pH (dissociation of the protonated forms of arsenate and arsenite) and redox potential (the three possible oxidation states noted above), but biological processes may also be important, including methylation and demethylation reactions (*8*, *9*). A number of organic forms of As are also known, including arsenosugars, arsenobetaine (AsB), arsenocholine (AsC), monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), and trimethyl arsenoxide (TMAO) (*10*, *11*).

With respect to the fate of As during the weathering cycle, the migration of As from soils through aquatic systems and into sediments is also very complex. In aerobic conditions, As is removed from solution by adsorption or coprecipitation with ferric oxyhydroxides (*12*−*14*). The decomposition of organic matter and concomitant reduction in redox potential may reduce As to As(III), allowing it to become mobilized (*15*). At greater redox potentials, arsenate ($H_2AsO_4^-$) is the predominant chemical species.

Although arsenite is expected to be the dominant dissolved species in anoxic environments, under these conditions arsenate may still be present (*16*). In sulfidic sedimentary environments, the dominant sink for As is expected to be arsenian pyrite. Elevated concentrations of As are commonly found in coal, particularly in sulfur-rich varieties (*17*, *18*). Enrichments of As are also common in peat, suggesting that much of the As in coal might have become incorporated during the peat-forming stage. For example, in a study of more than 1700 Finnish peat samples, Minkkinen and Yliruokanen (*19*) found up to 4800 mg of As kg^{-1} (expressed on a mineral matter basis). Studies of complete vertical profiles of ombrotrophic (i.e., rainwater-fed) peat bogs from Canada and Switzerland have documented pronounced enrichments of As in the basal, minerotrophic (i.e., groundwater-fed) peat layers (*20*, *21*), but the enrichment process itself has yet to be studied.

In an effort to better understand the natural accumulation of As in peat, samples were collected from Gola di Lago (GdL), a small minerotrophic (i.e., groundwater- and surface water-dominated) peatland in Canton Ticino, Switzerland. This territory is characterized by crystalline silicate rocks (gneisses, schists, amphibolites) that contain abundant As-bearing sulfide ore deposits, some of which have been mined for iron and gold in the past (*22*). Detailed studies have already been undertaken of the mobilization of As during the weathering cycle (*23*), but little work has been undertaken on the subsequent immobilization of As in organic-rich sedimentary systems such as peatlands.

At GdL, one of the intermittent streamwaters entering the mire was found to contain up to 400 μg of As L^{-1}, but the permanent waters leaving the peatland contain less than 2 μg L^{-1}. Clearly, there are natural processes operating within the peatland that are actively removing As from the inflowing waters. In a preliminary study, a single peat core collected near the centre of the peatland was found to contain up to

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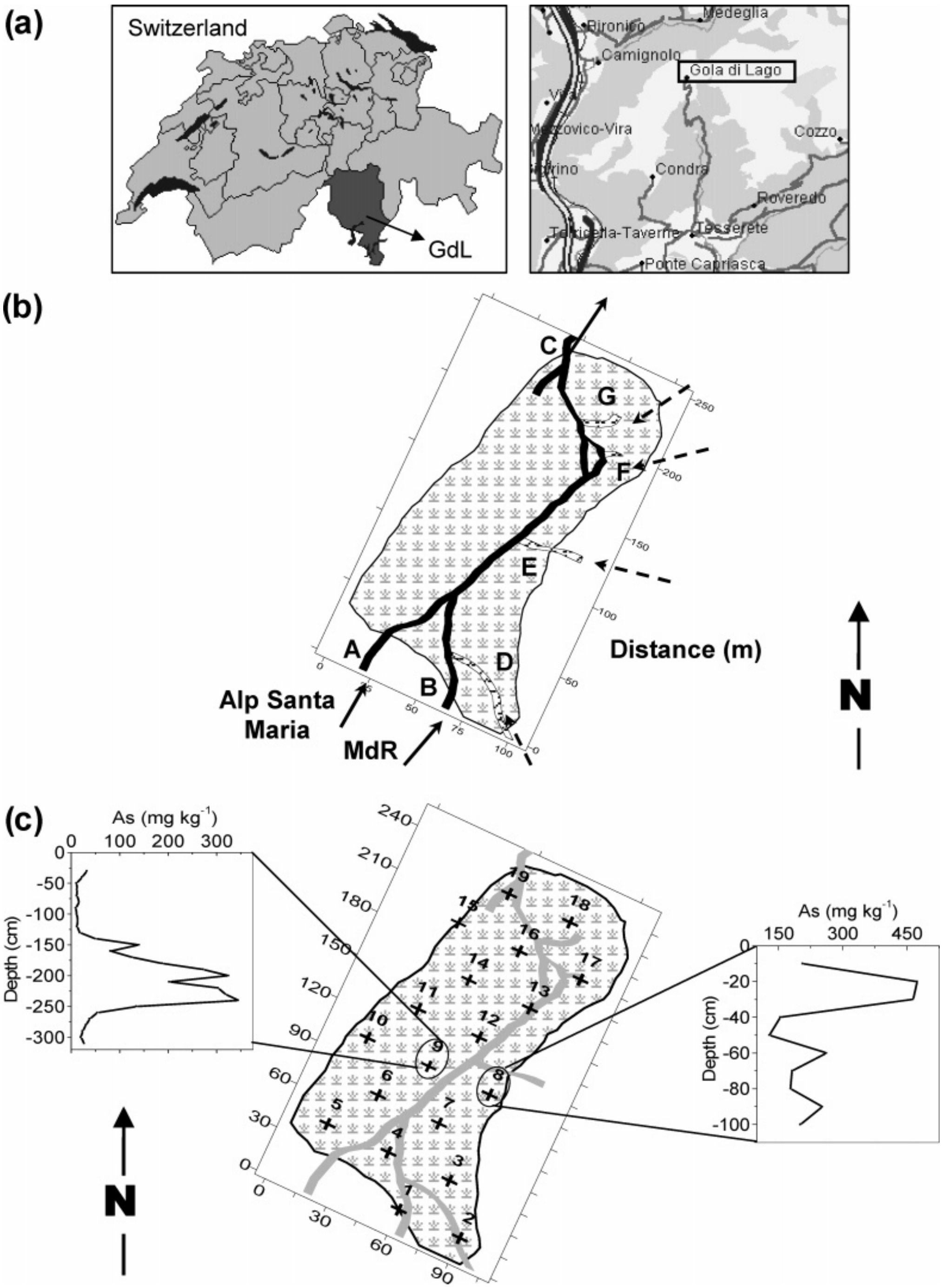

FIGURE 1. (a) Location of Gola di Lago. (b) Hydrographical situation of stream waters at Gola di Lago. Permanent (solid) and intermittent streams (dashed) are shown, with the arrows indicating the direction of fflow. (c) Peat core sampling locations (GdL 2004). (+)Locations of the peat cores collected (nos. 1−19). The vertical distribution of As at sites 8 and 9 is illustrated, as they yielded the greatest As concentrations. All the concentrations (milligrams per kilogram) are expressed on a dry weight basis.

ca. 50 mg of As kg^{-1} (*24*), corresponding to a concentration of 150 mg kg^{-1} on a mineral matter basis. In order to elucidate the mechanism of As enrichment, it is necessary for detailed mineralogical and chemical studies to obtain the samples containing the greatest As concentrations. Therefore the systematic collection of multiple cores at regular intervals was necessary, to identify the zone of maximum possible As enrichment. In addition, we wish to compare the spatial distribution of As within the peatland with the main source of As (an intermittent stream), to determine the vertical and horizontal extent of the enriched zone. For comparison with As, we show that other redox-sensitive elements (S, Fe, Se, and U), are similarly enriched; the accumulation of these other elements is used to help understand the geochemical controls that may be responsible for the natural enrichment of As.

Experimental Approach

Site Description. Gola di Lago (GdL) is located in Canton Ticino, Switzerland, between the Capriasca and Carcalino valleys in the territory of Camignolo, Tesserete, and Lugaggia (Figure 1a). This small peatland (29 375 m^2) was formed from a glacial lake beginning approximately 13 000 years ago (*25*).

Most of the surroundings are covered by forest of birch, beech, and chestnut, with the remainder agricultural fields, pasture, and vineyards. The bedrock is dominated by ortho-

TABLE 1. Arsenic Concentrations of Stream Water Sampled as Indicated from Gola di Lago[a]

	total As			As(III)		As(V)	
stream	June 01	June 04	April 05	June 04	April 05	June 04	April 05
A	ns[b]	0.56	0.22	0.12	0.10	0.44	0.12
B	0.5	0.34	0.21	0.10	0.07	0.24	0.14
C	1.8	1.91	0.44	0.94	0.30	0.97	0.14
D	ns	0.37	0.22	0.11	0.05	0.26	0.17
E	408	nf	36.1	nf	1.75	nf	34.4
F	ns	nf	0.15	nf	0.04	nf	0.11
G	ns	nf	0.34	nf	0.12	nf	0.22

[a] Total As was analyzed by ICP-SF-MS, As(III) was analyzed by HG-AAS, and As(V) was determined by difference. All concentrations are in micrograms per liter. The pH of these waters is 5.5−6.3. [b] ns,− not sampled; nf,− not flowing during sampling campaign.

and paragneisses of the Strona-Ceneri zone. However, at GdL there are heavily weathered amphibolites, which have been eroded by water and ice during the past 1.5 million years (*26*).

The flora within GdL is characterized by the presence of *Drosera intermedia/obovata*, *Drosera rotundifolia*, *Rhychonspora alba*, and *Trichoporum caespitosum*; *Calluna vulgaris* and *Eriphorum vaginatum* are rare. *Sphagnum compactum*, *Sphagnum nemoreum*, and *Sphagnum papillosum* are also present (*27*). The fauna consists mainly of shallow-water inhabitants, with an abundance of insects such as caddisflies, water-boatmen and beetles, grasshoppers in spring, and some dragonflies.

With respect to the peat core collected earlier (*24*), the peatland at GdL is dominated in the uppermost ca. 10 cm by *Sphagnum* (in the active zone of the peatland), along with poorly decomposed organic material (fibrous, brown). Tufted sedge (*Carex elata*), a typical fen plant, is abundant. At a depth of 15−35 cm, the peat is well decomposed (brownish-black) and intimately mixed with fine mineral material (allogenic clay and silt). A clay layer mixed with organic matter is found at a depth of 35−40 cm. At 40−60 cm the organic material is very well decomposed and mixed with very fine grained mineral material.

Two permanent streams enter GdL, one coming from the Santa Maria alp (2.95 L s^{-1}) and the other (2.24 L s^{-1}) from Motto di Ranscea (MdR), a small peatland (Figure 1b). GdL also has four intermittent streams that mainly flow between April and June but sometimes also in September and October (0.1−2.2 L s^{-1}). GdL is drained by a permanent stream leaving the peatland from south to north (*28*).

As part of an excursion to the site in 2001, water samples were collected from two of the permanent and one of the intermittent streams and subsequently analyzed by inductively coupled plasma sector field mass spectrometry (ICP-SF-MS). The data showed that the intermittent stream had elevated As concentrations (400 μg L^{-1}) compared with the permanent streams entering and leaving the peatland, which contained less than 2 μg L^{-1} (Table 1). These findings are not discussed further here, but led to the more detailed studies that are described below.

Collection, Preparation, and Analyses of Peat Samples. In June 2004, 19 peat cores and several water samples were collected. The bottle rack grid method was used to select the peat coring sites (Figure 1c). This method consists of a rectangular fixed grid (in this case 15 m × 15 m) and equilateral triangles marked all over the grid following the peatland surface (*29*).

Complete peat profiles were cored with a stainless steel Belarus corer (5 cm $\Phi \times$ 50 cm length) at each site. Each core was sectioned in the field every 10 cm by use of a titanium spoon, resulting in a total of 293 samples. Upon returning to the laboratory, the peat samples were frozen and remained in this condition (−18 °C) until they were prepared. The peat samples were then trimmed into three subsamples. One of these subsamples was used to determine ash content, one for As and other trace elements, and the third aliquot was archived at −18 °C for future investigations.

The peat samples were weighed, dried and milled to a fine powder with an agate planetary ball mill (Pulverizette 5, Fritsch, Idar-Oberstein, Germany). Trace elements (As, Br, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Se, Sr, Th, Ti, U, Zn, and Zr) were analyzed by nondestructive X-ray fluorescence (XRF) analyses (*30*). International standard reference materials (SRM) were used to verify the measurements. For the data presented here, the error between the measured data and the certified values was between 3% and 7% for the elements of interest, in all samples. The SRMs used to evaluate accuracy were NIST 1515 (apple leaves), GBW 07604 (poplar leaves), CTA-VTL2 (Virginia tobacco leaves), NIST 1573a (tomato leaves), NIST 1547 (peach leaves), GBW07602 (bush leaves), BCR60 (olive leaves), and NIST1632b (coal bituminous). In the case of As, the maximum concentration in plant SRM is 8 ppm (BCR60), so the instrument was also calibrated with AAS (atomic absorption spectrometry) standards, employing As standard solutions with concentrations of 50, 100, 150, 200, 300, 500, and 1000 mg kg^{-1}.

The ash content was determined by use of a high-temperature muffle oven (MLS 1200 pyro, Microwave Laboratory Systems, Leutkirch, Germany) at 550 °C.

After the samples containing the greatest As enrichments were determined, powdered samples were directly analyzed with X-ray diffractometry (XRD) to detect any crystalline phases present. These samples were also analyzed with a scanning electron microscope (SEM; type 440, Leo) plus an energy-dispersive X-ray (EDX) system (Oxford Instruments, Wiesbaden, Germany) to identify any As-containing particles. For the SEM analyses, a fraction of the powdered sample was taken and deposited on the SEM sample holder and then covered with a carbon film under vacuum. The microphotographs were taken by use of the SE1 detector to prevent interference from secondary electrons.

Sequential Extraction of As. A sequential extraction method was employed to evaluate samples GdL 8 (20−30 cm) and GdL 9 (230−240 cm). The method (Table S1, Supporting Information) was a modification of those proposed by Keon et al. (*31*) and Tessier et al. (*32*). The samples evaluated were (a) fresh (60% water content), (b) milled and dried (105 °C), and (c) freeze-dried. Three aliquots of each sample and two blanks at each step were evaluated.

An inductively coupled plasma optical emission spectrometer (ICP-OES) (Vista MPX, Varian) was used for As analyses [limit of detection (LOD) 1 μg L^{-1}]. Samples containing concentrations below this LOD were measured with a hydride generation atomic fluorescence spectrometer (HG-AFS) (Millennium Excalibur, PS Analytical Ltd., Orpington, Kent, England) coupled with an As boosted-discharge hollow cathode lamp (BDHCL); the LOD for As with this method was 30 ng L^{-1}. The As in the sample was first reduced to As(III) according to the method described elsewhere (*33*). For quality control, NIST 1573a (pine needles) was used as SRM: the concentration measured by this method was 0.23 ± 0.04 μg g^{-1} compared to the certified value of 0.21 ± 0.04 μg g^{-1}.

Collection, Preparation, and Analyses of Water Samples. The stream waters were sampled in June 2004 and in April 2005. They were filtered in the field with plastic syringes (10 mL) and syringe filters (0.45 μm) and acidified with 6 drops of 65% concentrated HNO_3 (analytical reagent-grade, Merck, Darmstadt, Germany). All samples were stored in the dark and kept cold (4 °C) until analysis. In these samples total arsenic concentrations were obtained by ICP-SF-MS (Element2, Thermo Electron, Bremen, Germany). For quality

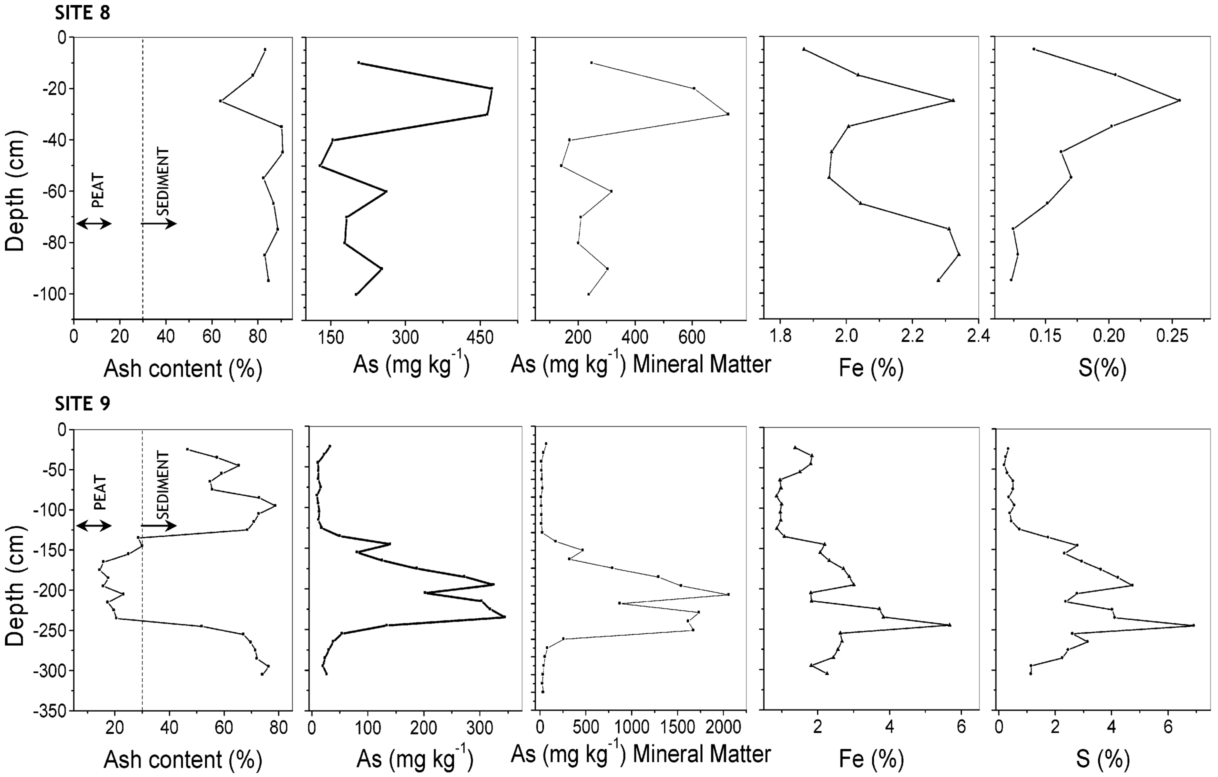

FIGURE 2. Vertical distribution of ash (%), As (milligrams per kilogram), Fe (%), and S (%) at sites 8 and 9. Calculated As abundance in mineral matter is simply the arsenic concentration in the sample, normalized to 100% ash. All of the concentrations are expressed on a dry weight basis.

control, a riverine water reference material (SLRS-4, National Research Council Canada, Ottawa, Canada) was analyzed, yielding a mean concentration of 0.66 ± 0.03 μg L^{-1} ($N = 4$) compared with the certified value of 0.68 ± 0.06 μg L^{-1}. In addition, As(III) was determined with hydride generation atomic absorption spectrometry (HG-AAS) (FIAS 200, AAS 4100, Perkin-Elmer) by the method of Ruede (*34*). For quality control, a prepared standard of As(III) (5 μg L^{-1}) was measured after every 10th sample, yielding a concentration of 5.00 ± 0.25 μg L^{-1} ($N = 4$). As(V) was calculated as the difference between total arsenic (ICP-SF-MS) and As(III) concentrations (HG-AAS).

Results and Discussion

Spatial Distribution of Arsenic. The complete peat profiles yielded enough information to generate a three-dimensional map of peat depth at GdL (Figure S1, Supporting Information). This map revealed that the geomorphology is very irregular, ranging from a site with 15 cm of peat to the deepest zone in the middle of the peatland with a depth of 310 cm.

The arsenic concentrations obtained from the XRF analyses were plotted in contour maps at depth increments of 10 cm by use of Surfer for Windows (v. 7). These maps illustrate the spatial variation in As concentrations (Figure S2, Supporting Information). Two of these maps showed the greatest As concentrations at site 8, at a depth of 10−20 cm (300 mg kg^{-1}), and at site 9, revealing the maximum concentrations of As (450 mg kg^{-1}) at 230−240 cm. In both cases the zones of maximum arsenic concentration are found in close proximity to the intermittent stream, which contained up to 400 μg of As L^{-1} (Figure 1c). This finding is important, as it shows that the basal mineral sediment underlying the peatland is not the predominant source of As to the peat.

Horizontal Variations in Depth and Arsenic Concentrations. Sites 8 and 9 contain the greatest As concentrations (Figure 1c). The variation in As concentrations as a function of depth at these two sites along with the ash contents and concentrations of Fe and S are shown in Figure 2. There are profound variations in the abundance of mineral matter within a given profile and between profiles. Because of the possible influence of this parameter on the variation in As concentrations, the As concentrations are also expressed on a mineral matter basis (MMB) (milligrams per kilogram), which is calculated simply as

$$\text{As (MMB)} = [(100[\text{As}])\ ([\text{ash}]^{-1})] \qquad (1)$$

where As concentrations are given in milligrams per kilogram and ash content is given in percent by weight.

While these two sites have several features in common (elevated concentrations of As, Fe, and S), there are also some pronounced differences. First, at site 8, all of the samples contain very high ash contents (64−90% by weight). According to the American Society of Testing and Materials (ASTM) definitions, “peat” is a substance containing less than 25% by weight mineral matter, organic-rich sediments contain between 25% and 75% mineral matter, and sediments contain more than 75% mineral matter (*35*). While it is true that site 9 has much lower ash content than site 8, at both sites the highest As concentration is found in the layer containing the least ash (Figure 2). The significance of these differences between the two sites for the mechanism of As accumulation is not yet clear.

A second difference between the two sites is that the greatest As concentrations at site 8 are in the subsurface of the core (ca. 20 cm), whereas the maximum As concentration at site 9 is much deeper (ca. 200 cm) in the peat column. Both (site 8 and site 9) are relatively close to the intermittent stream, which was found to be rich in As (Figure 1c). Given that sediments and peat have been accumulating here for ca. 13 000 years, and that sedimentation rarely proceeds uniformly, we assume that thousands of years ago, site 9 was closer to the stream than it is today, and the present-day zone of As enrichment was closer to the surface of the

TABLE 2. Sequential Extraction Results for As[a]

	sample GdL 8 (20–30 cm)			sample GdL 9 (230-240 cm)		
fraction	dry	fresh	freeze-dried	dry	fresh	freeze-dried
anion exchange	75 ± 2	20 ± 1	19 ± 2	15 ± 1	7 ± 0.2	9 ± 0.5
water wash	3 ± 0.2	<0.01	2 ± 0.6	13 ± 0.3	<0.01	<0.01
associated with Fe hydroxides, Mn oxides, etc.	5 ± 0.3	<0.01	3 ± 0.5	5 ± 0.4	<0.01	<0.01
water wash	<0.01	<0.01	0.5 ± 0.2	<0.01	<0.01	<0.01
bound to organic matter	5 ± 1	73 ± 6	10 ± 4	48 ± 4	12 ± 1	86 ± 7
residual	<0.01	7 ± 2	<0.01	3 ± 0.3	<0.01	5 ± 1
total, %	**88**	**100**	**35**	**84**	**19**	**100**

[a] All data are expressed as percent of total arsenic extracted in the indicated fraction. Values shown in underlined and boldface type indicate the highest As concentration extracted in the specified fraction. For a description of the experimental procedure, see Table S1 in Supporting Information.

peatland at that time. In other words, thousands of years ago, site 9 might represent the interface between the stream and the peatland. Since then, the peatland has been expanding both in depth and in width, with the zone of greatest As concentration always at the interface between the intermittent stream, which supplies most of the As, and the edge of the peatland. Although there are differences in the distribution of As between site 8 and site 9 today, we assume that the biogeochemical process responsible for the removal of As is common to both sites.

Comparison of As, Fe, and S. The distribution of As at both sites 8 and 9 resembles the distribution of Fe and S (Figure 2), suggesting a possible connection between all three elements. Not only are the As concentrations strongly elevated, but the abundances of Fe and S are also very high, relative to the values commonly reported for freshwater peats. For example, Casagrande et al. (*36*) reported S concentrations no greater than 1.1 wt %, and Naucke (*37*) indicated that peat typically contains no more than 2.3% Fe. At Gola di Lago, therefore, the peat has become profoundly enriched not only in As but also in Fe and S. In fact, the maximum concentrations of Fe (5.5%) and S (7%) are so great as to imply the in situ formation of pyrite.

Mineral Occurrences. Samples from site 8 (10–20 cm) and site 9 (220–230 cm) were analyzed by XRD. The spectra obtained for GdL 8 showed the presence of quartz (SiO_2), chlorite [$(Mg, Fe)_5(Al, Si)$], muscovite [$KAl_2(Si_3Al)O_{10}(OH, F)_2$], and albite ($NaAlSi_3O_8$). In addition, pyrite ($FeS_2$) was also found in GdL 9 (Figure S3, Supporting Information). There was no arsenopyrite found in the XRD spectra, which suggests that if indeed this mineral is present, its abundance is below the limit of detection, which is ca. 1% by weight.

Samples (GdL 8 and GdL 9) were also analyzed by use of the SEM which confirmed the presence of pyrite framboids in GdL 9, with diameters typically on the order of ~20 μm (Figure S4, Supporting Information). Energy-dispersive X-ray analyses confirmed the abundance of Fe and S in the framboids, but no As was found. The lower limit of detection for trace elements determined by use of the XRF spectrometer of the SEM is approximately 1000 mg kg^{-1}. Although As might be present in the pyrite framboids, the concentrations must be below this limit of detection.

Arsenic and Organic Matter. The results of the sequential extractions (Table 2) show some remarkable differences between GdL 8 and GdL 9. In fresh samples from GdL 8, where the enrichment of As is near the surface of the peatland (20–30 cm), 100% of the As could be extracted, with 73% of total As found in the organic matter fraction and 20% exchangeable. When this sample was dried, however, 75% was exchangeable, which suggests that the majority of the As at this site is comparatively labile and vulnerable to transformations. In contrast, in fresh samples from GdL 9 where the As concentrations are deep in the profile (230–240 cm), only 19% of the As could be extracted, with most (12/19 = 63%) of this being organically bound. When this sample was dried, 84% could be extracted, but most of this (48/84 = 57%) was still in the organic matter fraction. In summary, although both sites contain anomalous enrichments of As, the mechanisms by which the As has become entrapped and retained appear to be fundamentally different, with much more stable binding forms of As found in the deeper peat layers. Despite the profound differences, organically bound forms of As predominate at both sites.

To further contribute to a better understanding of the behavior and fate of As in the peat, in a separate but relevant study, As was extracted from selected peat samples of three Finnish cores by use of high-purity water (*38*). The strategy behind this approach was to mimic the leaching ability of the natural pore fluids of the peat to provide insight into the binding mechanism and fate of As in peat. For fresh peat samples containing approximately 90% water, between 1% and 12% of the total As could be extracted. The extraction yield increased up to 23% for peat dried at 105 °C. The generally low extraction yield of As from fresh peat samples supports the finding of strong retention of the element in the peat column and favors stable bindings of As to the organic matrix.

Stream Waters. Both permanent (A–C) and intermittent (D–G) streams are found at GdL (Figure 1b). During the June 2004 sampling campaign, there was no flow at stream E. However, the permanent streams and one of the intermittent stream (D) were sampled, revealing concentrations of arsenic less than 2 μg L^{-1}, with the majority in the form of As(V) (Table 1).

In April 2005, all the streams were flowing, so they were sampled and analyzed. The results show that the concentrations of arsenic are below 1 μg L^{-1} except for stream E, which contained 36 μg L^{-1}. Although this concentration is a factor of 10 lower than the concentration detected in 2001, it is far greater than the other streams and indicates that this is the single most important source of As to the peatland. Moreover, it demonstrates the great variability in the rate of As supply to the peatland. In this water sample (E, 2004), 95% of the total dissolved As was in the form of As(V).

The As concentrations of the permanent stream waters are less than 2 μg L^{-1}, and one of the intermittent streams delivers As to the peatland in unpredictable concentrations. When this stream (E) does flow, however, it is dominated by As(V). At stream C, however, leaving the peatland, As(III) is the dominant redox state. This demonstrates that the arsenic is entering the peatland as As(V) and in the peatland is being reduced to As(III).

Selenium and Uranium. The peat cores collected at sites 7 and 10 revealed up to nearly 20 and 30 mg of Se kg^{-1}, respectively (Figure 3). Expressed on a mineral matter basis, the samples from site 10 contain up to ca. 350 mg of Se kg^{-1}.

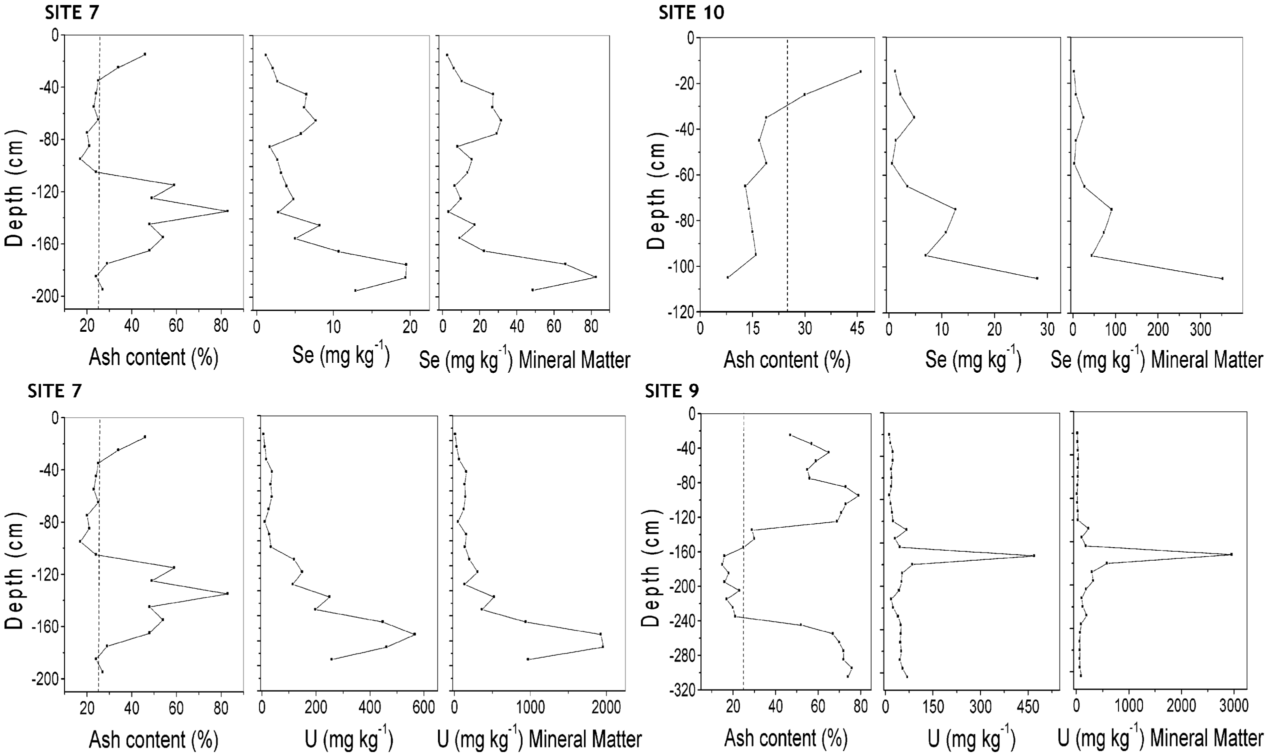

FIGURE 3. Vertical distribution profiles of Se (milligrams per kilogram) at sites 7 and 10 and U (milligrams per kilogram) at site 7 and 9. All of the concentrations are expressed on a dry weight basis.

It is difficult to put these values into perspective when there have been so few measurements of this element in peat samples from continental mires. However, using the EMMA XRF spectrometer with a limit of detection of 0.5 mg kg^{-1} for Se (*30*), we have measured trace elements in peat cores from eight Swiss peatlands (*39*), but we have never before encountered such high Se concentrations. In fact, all of the Se concentrations, except for the samples from GdL, have been below 1 mg kg^{-1} (unpublished data). Even in a peat core from a maritime blanket bog, which is strongly influenced from marine aerosols, Se concentrations are in the range of 5−15 mg kg^{-1} (*40*). In the peats from GdL, therefore, there is a truly remarkable Se enrichment that warrants further study.

The peat samples from GdL are also frequently enriched in uranium. At site 7, for example, U in the deeper layers exceeds 500 mg kg^{-1} (Figure 3), which corresponds to 0.2% on a mineral matter basis. In contrast to Se, which suffers from a lack of quantitative studies, there have been many published studies of the natural enrichment of U in peat (*41*). The reduction of aqueous U species from U(VI) to U(IV) and the precipitation of this element as UO_2 (uraninite) is a possible mechanism of enrichment, but complexation by organic matter also may be involved.

Gola di Lago is an effective geochemical trap for As, Fe, S, Se, and U. Arsenic is of special interest because the waters entering the peatland can contain up to 400 μg of As L^{-1}, but the waters leaving the mire contain less than 2 μg L^{-1}. This phenomenon suggests that peatlands might have the potential for remediating As-bearing waters, regardless of whether the As is derived from natural or anthropogenic sources. To take advantage of the phenomenon, however, the mechanism of the process needs to be understood.

Acknowledgments

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Supporting Information Available

Complementary figures and tables as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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