Hydrologic controls on DOC, As and Pb export from a polluted peatland – The importance of heavy rain events, antecedent moisture conditions and hydrological connectivity

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Abstract

Bogs can store large amounts of lead (Pb) and arsenic (As) from to atmospheric deposition of anthropogenic emissions. Pb and As are exported along with dissolved organic carbon (DOC) from these organic-rich systems, but it is not yet clear which hydrological (pre-)conditions favor their export. This study combines a one year monitoring of precipitation, bog water level and pore water concentration changes with bog discharge and DOC, iron, As and Pb stream concentrations. From this data annual DOC, As, and Pb exports were calculated. Concentrations ranged from 5 mg L^{-1} to 30 mg L^{-1} for DOC, 0.2 µg L^{-1} to 1.9 µg L^{-1} for As, and 1.3 µg L^{-1} to 12 µg L^{-1} for Pb with highest concentrations in late summer. As and Pb concentrations significantly correlated with DOC concentrations. Fluxes depended strongly on discharge, as 40% of As and 43% of Pb were exported during 10% of time with highest discharge, pointing out the over-proportional contribution of short-time high discharge events to annual As, Pb and DOC export. Exponential increase in element export from the bog is explained by connection of additional DOC, As and Pb pools in the acrotelm during water table rise, which is most pronounced after drought. Pb, As and DOC concentrations in pore water provide evidence of an increase of the soluble Pb pool as soon as the peat layer gets hydrologically connected, while DOC and As peak concentrations in runoff lag behind in comparison to Pb. Our data indicates a distinct bog-specific discharge threshold of 8 L s^{-1}, which is thought to depend mainly on the bogs size and drainage conditions. Above this threshold element concentration do not further increase and discharge gets diluted. Combining pore water and discharge data shows that As and Pb exports are not only dependent on the amount of precipitation and discharge, but on the frequency and depth of water table fluctuations. Comparing the annual bog As and Pb export with element inventories indicates that As is much more mobilized than Pb, with annual fluxes accounting for 0.85 ‰ and 0.27 ‰ of total As and Pb inventory, respectively.

1 Introduction

Peatlands provide important services in the environmental system. They play an important role in the storage of carbon and other elements such as heavy metals. On one hand the filtering function of peatlands partly prevents the input of these pollutants to streams. On the other hand, peatlands can release heavy metals as soluble DOM-metal complexes. Even though, acting as major carbon sink, peatlands are also the greatest source of dissolved organic carbon (DOC) to the aquatic system (Aitkenhead et al., 1999). Several studies demonstrated runoff, water level fluctuations and temperature to be the most important controls on terrestrial DOC production and export (Freeman et al., 2001; Hongve et al., 2004; Köhler et al., 2008; Seibert et al., 2009; Laudon et al., 2011). Recently, numerous studies describe the emerging problem of rising DOC levels in streams and lakes especially in catchment areas comprising peatlands (e.g. Worrall et al., 2004; Monteith et al., 2007), which might cause severe problems for aquatic biota and in drinking water production (Chow et al., 2003). Besides the observed general increase in concentrations, which has been attributed to the decrease in acid rain deposition or temperature rise (Freeman et al., 2001; Evans et al., 2005; Monteith et al., 2007), a flushing effect, which produces high instantaneous DOC loads during high discharge events after a summer dry period has been described (e.g. Worrall et al., 2002; Clark et al., 2007). Even though temporally limited, the high concentrations might affect the aquatic system even stronger. This effect gains more importance through the predicted climate change with enhanced dry periods and more frequent heavy rain events (IPCC, 2013). How these high DOC concentrations after re-wetting of the peatlands surface-near layer built up is not yet fully understood. Fenner and Freeman (2011) proposed that the microbial DOC production is stimulated after a drought period by reduced concentrations of phenolic compounds through an enhanced phenol oxidase activity. Moreover, release of DOC adsorbed to Fe-(oxy)hydroxides through Fe-(oxy)hydroxides dissolution after re-wetting and decreasing redox potential has shown to be an important process for DOC dynamics in peatlands (Bauer and Blodau, 2009; Knorr, 2013; Riedel et al., 2013), as well as DOC solubilization through pH rise (Grybos et al., 2009). Similarly, Clark et al. (2012) described a decrease of DOC solubility due to acidification during droughts.

Although the general focus in most studies is set on changing DOC dynamics, it is also known that some elements are mainly exported by transport with DOC to the discharging stream. Lead (Pb) strongly binds to organic matter (Tipping, 1998; Rothwell et al., 2007) and high DOC concentrations increase Pb mobility (Jordan et al., 1997). In spite of the high affinity of arsenic (As) to iron(oxy)hydroxides, recent mechanistic studies revealed a strong binding of As to sulfhydryl groups of organic matter in the anaerobic peat layer (Langner et al., 2011, 2014). Due to the low pH (<4.5 pH) and the low amount of mineral phases in peat, a correlation of DOC and As concentrations in bog draining streams has been observed (Rothwell et al., 2009; Neubauer et al., 2013). Moreover, As is known to be subjected to post-depositional mobilization due to water level fluctuations and resulting redox changes (Blodau et al., 2008; Rothwell et al., 2009; Langner et al., 2014).

Bogs, which receive element inputs exclusively by atmospheric deposition, and also other peatland types have the potential of accumulating As and Pb in the peat. The anthropogenic deposition rate of those two elements largely exceeds pre-industrial background fluxes (Shotyk, 1998; Bindler, 2006). Mining activity, fossil fuel combustion, especially emissions from burning of leaded gasoline, often resulted in high As and Pb concentrations in peat layers, which developed over the past centuries. Based on observed metal concentrations some peatlands especially those influenced by mining areas would even have to be classified as highly contaminated soils.

The near surface layer of a bog, the acrotelm, is the most active part, and conducts most of the bogs discharge (Evans et al., 1999; Holden and Burt, 2003) and DOC production (Clark et al., 2008). Due to high porosity, the acrotelm has a high hydraulic conductivity and is characterized by recurrent water table drawdowns and aeration resulting in higher biological activity. Moreover, this surface-near peat layer, which often hosts large amounts of atmospheric derived metals, is the main source of metal release from ombrotrophic peatlands.

Up to now, most studies on heavy metal release from contaminated peatlands have focused on discharge, only. Studies connecting DOC export with *in-situ* pore water chemistry measurements are rare or lacking in regard of Pb and As. Clark et al. (2005) found a strong correlation between peat soil solution DOC and stream water DOC concentrations over a ten-year record. Many field or laboratory studies focused on DOC production in view of water level, redox-state, acidification, temperature or microbial conditions (e.g. Grybos et al., 2009; Clark et al., 2012; Evans et al., 2012) without a connection to discharge measurements or they were conducted in mineral soil environments (e.g. Kokfelt et al., 2009; Singh et al., 2014, for Pb see Vinogradoff et al., 2005). In regard of As, Blodau et al. (2008) found a higher release of As in minerogenic peat mesocosms after a drought period, which is in line with leaching experiments described by Tipping et al. (2003). Rothwell et al. (2009) observed higher As concentrations during late summer storm flow after the summer dry period in a bog catchment.

The aim of this study is to gain further understanding in the generation and controls of Pb and As export from ombrotrophic peatlands. If the export of Pb and As is mainly controlled by DOC production and transport, higher metal concentrations and fluxes are expected during periods of elevated DOC concentrations. Moreover, export dynamics should strongly depend on peatland hydrology. This study tries to unravel the importance of hydrologic conditions like antecedent bog water levels, as well as precipitation, temperature and pH for the export of

As and Pb. We expect that these factors mainly control hydrologic pathways, DOC production and the hydraulic connection of different As and Pb pools. We thus aim to investigate to which extent As and Pb export is constrained by supply of DOC and related soluble metal organic complexes or discharge quantities.

To tackle these questions we chose a bog, which is heavily contaminated by As and Pb through historic mining activities and is known to exhibit high As and Pb concentrations in the acrotelm. We continuously monitored direct bog discharge at a first order stream to gain information of the DOC, Pb and As export dynamics dependent on precipitation. To combine discharge generation and element concentrations with (pre-)conditions within the peat catchment, we sampled pore water to investigate time- and depth resolved DOC and metal release patterns and monitored temperature, precipitation and water level at the bog. For an estimation of the overall export and mobilization potential from the bog we calculated fluxes and peat As and Pb inventories. To examine the importance of storm flow events we conducted high resolution measurements occasionally during snowmelt and rain events in spring and fall.

2 Materials and Methods

2.1 Study Area

The Odersprung bog (OS, 52°46.383’N, 10°33.816’E; 800 m asl, 1500 mm mean annual precipitation and 5°C mean annual temperature) is an ombrotrophic peatland located within the nature protection area in the Harz Mountains in Northwestern Germany. The treeless part of the bog covers an area of about 17 ha and has a mean peat depth of 3 m (Beug et al., 1999). Vegetation is dominated by *Sphagnum magellanicum* and *Sphagnum rubellum*. *Eriophorum angustifolium* and *Molina caerulea* occur less frequently (Baumann, 2009). The bog is drained by a small erosion rill, which originates within the bog. Discharge sampling was conducted at the rill outflow of the bog where all water is exclusively received from the bog. Former studies on the effect of past local mining activities in the Harz Mountains reported Pb and As peat concentrations of up 2300 mg kg^{-1} and 100 mg kg^{-1}, respectively, which is by a factor of 10,000 (Pb) higher than background values (Biester et al., 2012).

2.2 Sampling and Field Measurements

Seasonal discharge sampling was conducted from April 2013 to November 2013 covering the time from snowmelt to begin of snowfall. Water samples were taken in a six day interval by an automated water sampler (ISCO autosampler 3700), equipped with 0.5 L PE bottles and a Teflon hose, which was automatically rinsed with sample water prior to each sampling. Further grab samples as well as pH and electric conductivity measurements were conducted every two to three weeks. For grab samples new 50 mL PE tubes were used and previously rinsed with sample twice before sampling. For all sampling techniques blank controls were run. Several storm flow events were sampled at high frequency (every 3 hours) over a period of three days, respectively. At all sampled events the catchment was free of ice and snow.

Pore water samples at the Odersprung bog were taken using a suction sampler described in Broder et al. (2012). In short, the sampler consisted of PE-sinter slides (5x0.5x1 cm) inserted in a 3.5 m long rod. Slides were connected by tubing to a stop-cock above the peatland surface. Samples were taken by means of PE syringes and transferred to new PE tubes, which were rinsed with sample before. Sampling resolution was 20 cm until 60 cm depth and 30 cm until 210 cm depth. The suction sampler was installed within the catchment area of the erosion rill (Fig. 1). Close to the pore water sampler a peat core was extracted using a Russian peat corer (Eijkelkamp Agrisearch Equipment). Cores were collected down to 300 cm depth, sliced in 2.5 cm sections, frozen and freeze dried. For the calculation of As and Pb inventories in the acrotelm 15 short cores (30 cm depth) were sampled by means of a Wardenaar peat profile sampler (Eijkelkamp Agrisearch Equipment).

Discharge at the bog outlet was quantified using a V-notch weir. Stage was recorded every 15 min by a water level logger (Odyssey dataflow systems) for the recalculation to the actual discharge. Water level at the bog site was monitored in close proximity to the pore water sampler using PVC piezometer tubes of 4 cm diameter, fully slotted until 120 cm depth and a water level logger (Odyssey dataflow systems). Temperature, relative humidity and precipitation (using a tipping-bucket rain gauge) were monitored (tinytag tgp 4500 and 4810, Gemini) at the site.

2.3 Laboratory Analyses

Water samples were filtered with 0.45 µm nylon filters (Merck, Millipore) within the laboratory and stored at 4°C. All water samples were analyzed for total dissolved organic carbon by a thermo-catalytic total carbon analyzer (Analytik Jena multi N/C 2100S) using the NPOC method. As, Fe and Pb concentrations were determined by an ICP-MS (Agilent 7700). Instrumental drift and quality was checked by certified reference materials (SPS-SW 1 and SLRS-4, riverine water, National Research Council, Canada). Detection limits for Fe, As and Pb were 0.01 µg/L, 0.001 µg/L and 0.001 µg/L, respectively.

All peat samples were freeze dried, milled and further analyzed with a resolution of 2.5 cm until 50 cm depth and 10 cm resolution below. Peat As and Pb concentrations were determined by an energy-dispersive miniprobe multielement analyzer (EMMA-XRF, see Cheburkin and Shotyk, (1996)). Carbon and nitrogen concentrations in peat were measured using an elemental analyzer (Euro EA 3000, HEKAtech).

2.4 Flux calculations and As and Pb inventory estimates

DOC, As and Pb annual fluxes were estimated by calculating the total annual load from analyzed water samples and the continuous discharge record using method 5 according to Walling and Webb (1985) and Littlewood (1992):

$$Load = K \times Q_r \left(\frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \right) \quad (1)$$

Where K is a conversion factor (here number of seconds per year), Q_r here the annual mean discharge from the continuous record, C_i the instantaneous concentration, Q_i the instantaneous discharge and n the number of samples ($n = 112$). Load estimates were divided by catchment size to gain fluxes in g ha^{-1}a^{-1}.

The rill catchment area is mainly covered by an open and treeless part of the bog (8 ha, see Fig. 1). Catchment boundaries were determined by topographic conditions and the occurrence of perennial streams, which required including a part of a hillslope with shallow podsolic forest soils. However, it was perceived that small pools build up between the domed bog and forested areas, which drain downslope during rain events, and do not discharge into the bog (see also Fig. 1). Therefore, the chemical characteristic from the bog stream should not be biased by forest soil draining water. Flux calculations from high-frequency concentration measurements during snowmelt and discharge events were calculated according to method 3 (Walling and Webb, 1985), where instantaneous loads were calculated by the measured concentration and the integrated discharge data of the preceding sampling interval (3h) to obtain a robust discharge estimate. To further improve flux estimates the annual record was separated either by season or by hydrograph and was additionally calculated by method 2 (after Walling and Webb, 1985). Standard error and 95% confidence limits of flux calculations were conducted after Hope et al. (1997). As and Pb inventories for the peatland catchment were calculated from the median value of the upper 30 cm As and Pb inventories of all 16 peat cores to estimate an inventory per unit area of the bog surface. Uncertainties of the inventory calculations were estimated by the standard deviation from the mean of all As and Pb inventories of the 16 peat cores.

3 Results and Discussion

3.1 Hydrologic conditions

The year 2013 was characterized by strong snow melt and several intense rain events (Fig. 2). The precipitation record before day of the year (doy) 100 (mid of April) and after doy 289 (end of October) was affected by snowfall, which produces exceptionally high precipitation values that distorts quantification as we used a tipping-bucket. At two other occasions the rain gauge got clogged, thus for a few high flow discharges and water level rises no rainfall was recorded (doy 150-162 and doy 256-270). During the snow-free record from mid-April to mid-October the catchment received 537 mm rain. Monthly precipitation totals recorded highest rainfall in fall,, while a longer dry period prevailed in summer.

In total, 36 discharge events with high flow could be distinguished after the end of snowmelt. High flow events partly followed shortly after a preceding event, especially in fall where rain was frequent. The two main discharge events of the 2013 record triggered by a longer rain fall period, occurred in spring and peaking at a discharge of 44 L s^{-1} and 55 L s^{-1}. The three largest events in fall peaked at 23-24.5 L s^{-1}. High discharge values at the beginning of the record indicate that snowmelt contributed an important portion to the annual discharge (Fig. 2). As a quantification of the complete snowmelt discharge was impossible, calculated annual element fluxes might be underestimated (Dyson et al., 2011). A typical event hydrograph exhibits a steep rising and falling limb with a slow decline as the event subsides. Setting a low flow limit at 0.3 L s^{-1} by thorough visual hydrograph separation, low flow occurred during more than 28% of the time record but contributed only 2.5% of total discharge. This is indicative of an event runoff regime with negligible groundwater contribution. In fact, constant base flow over longer periods could never be observed, as flow steadily declined without rain fall until it almost ceased when the accessible water pool in the acrotelm was depleted. Therefore, we do not refer to base flow conditions, but rather use the term low flow as no steady groundwater component seem to contribute to the bog's discharge. The flashy hydrograph response fits to a rapid runoff generation by surface-near and surface flow. The dominance of this kind of runoff generation is similar to previously reported flashy regimes at blanket bogs (Evans et al., 1999; Holden and Burt, 2003).

Lag times from the beginning of rainfall to discharge were short with a mean response time of 1.3 h ±0.5 h. Shortest lag times occurred when discharge was still high at the beginning of a new high flow event similar as has been observed for a blanket bog (Daniels et al., 2008). This instantaneous response indicates that at wet preconditions surface runoff prevails as this is the most rapid runoff component.

Despite high rainfall events in summer, only small corresponding discharge events were recorded. Here, the water pool of the bog's surface-near layer is recharged before discharge takes place. The process is clearly depicted in Fig. 2 where the water level rose almost immediately after beginning of rainfall at doy 205. Over the entire record the water table ranged between 3.5 cm above and 36 cm below the peat surface with a median depth of 10.5 cm. The lowest water level occurred during the summer drought (36 cm depth) after 20 days without precipitation.. From the 36 discharge events 22 could be classified as following wet and 13 as following dry preconditions based on the median water level of 10.5 cm as threshold value. Estimated runoff to precipitation ratios for discharge events were lowest for those events with exceptionally dry preconditions following the summer drought. In general, dry precondition events exhibited lower runoff to precipitation ratios than wet precondition events.

3.2 DOC, As and Pb stream concentrations

DOC release patterns from the Odersprung bog were similar than those reported from other peatlands (e.g. Worrall et al., 2002; Laudon et al., 2004; Clark et al., 2008). Lowest DOC concentrations (5 mg L^{-1}) were observed in the middle of April during snowmelt when dilution was highest, whereas highest DOC concentrations (~30 mg L^{-1}) occurred in late summer to fall when DOC production was highest and mostly low flow conditions occur (Fig. 2). DOC concentration decreased thereafter until begin of winter and the end of the annual record. This general seasonal trend with lower concentrations in winter and spring and increasing concentrations during summer can be attributed to reasons unrelated to discharge, but to the seasonal temperature dynamics and therefore, enhanced biological activity, organic matter decomposition and solubility. The low DOC concentrations during snowmelt can be attributed to a dilution effect, but also to a smaller extent to the low DOC production and storage during winter (Dyson et al., 2011).

Concentrations of As ranged from 0.2 µg L^{-1} to 1.9 µg L^{-1}, whereas Pb concentrations were significantly higher (1.3 µg L^{-1} to 12 µg L^{-1}) and in some cases even exceeded the WHO threshold value for drinking water (10 µg L^{-1}; WHO, 2011). Highest Pb concentrations occurred during a rain event in fall, which is discussed further below. Concentrations of As showed the same seasonal trend as observed for DOC with highest concentrations in summer (Fig. 2). This trend was recognizable for Pb as well, but less pronounced (Fig. 2). Both, As and Pb concentrations significantly correlated with DOC (r^2: 0.96 and 0.87, respectively), which supports the assumption that both elements are mainly transported along with DOC within and out of this organic-rich system. Pb is known to strongly bind to organic matter (Tipping, 1998). As forms soluble DOM-complexes (Buschmann et al., 2006), but also shows sorption to iron(hydr)oxides or formation of As-Fe-NOM colloids or complexes (Ritter et al., 2006; ThomasArrigo et al., 2014). Accordingly, Fe concentrations significantly correlate with

DOC and As (Fig. 1; r² Fe/DOC: 0.86; r² Fe/As: 0.80). At the bog's outflow, acidic conditions (< pH 4.5) prevail over the whole sampling period. Under these conditions iron-DOM complexes such as a ternary complex of As-Fe-DOM, dominate the soluble fraction (Tipping et al., 2002; Lofts et al., 2008; Neubauer et al., 2013). Exports of As, Fe, and DOC thus seem to be strongly linked and it is likely that both elements are mobilized by the same processes and originate from the same source area within the bog.

3.3 DOC, As and Pb concentrations during storm flows

Three high frequency samplings of storm flows were conducted at the bog outlet in 2013. The first spring event started after a longer low flow period and a low water level within the bog of around 13 cm below surface, indicating dry preconditions (doy 137; 18/5/13; Fig. 3). The second event followed shortly after the first, but with wet preconditions (doy 150; 31/5/13). The third sampled storm flow event occurred in fall with again dry preconditions and a water level of around 12 cm below surface (doy 251; 9/9/13; Fig. 3). In general, concentration changes of all elements during high discharge events were rather small compared to the annual variations indicating that high precipitation and increased runoff do not necessarily cause dilution, but seem to mobilize or connect additional pools of DOC, As and Pb.

At the first event, DOC and As concentration started to decrease immediately after the onset of high flow from 26.8 mg L^{-1} and 1.5 µg L^{-1} to 21.8 mg L^{-1} and 1.0 µg L^{-1}, respectively at the end of the event. No flushing effect with increasing stream water concentrations was visible (Fig. 3). Pb concentrations however, immediately increased with rising water level and discharge. Water levels rose from 13 to 6 cm depth, while Pb concentrations increased from 5 µg L^{-1} to 7 µg L^{-1}. With the falling limb of the hydrograph Pb concentrations also decreased to concentrations of about 4 µg L^{-1}. The reason for the different behavior of Pb compared to As and DOC is unknown. The increase in Pb concentrations with increasing water level indicates that there is no dilution but that additional Pb pools are mobilized as surface-near peat layers get hydrologically connected to discharge. It is still unknown how the Pb pool evolves during the winter months, probably by mineralization of organic matter in the acrotelm. In case of DOC concentrations, which did not increase with increasing water level, we assume that a potentially mobile DOC pool had not yet been built up in spring when temperature and thus biological productivity were still low. The role of redox induced formation or dissolution of mineral Fe-phases for As mobilization during water level changes is not yet understood. One explanation could be that As and DOC, as well as As-organic complexes are adsorbed to precipitated Fe-oxides when water levels are low. The re-establishment of anoxic conditions after water level rise causes a reductive dissolution of Fe-oxide and a release of DOC and As. However, these processes are assumingly too slow to be effective within a storm flow event (Grybos et al., 2007). This hypothesis will be further discussed in the pore water section further below.

The second storm flow event exhibited low concentrations compared to the annual concentration record at this site, starting with concentrations of 13 mg L^{-1} DOC, 2 µg L^{-1} Pb and 0.7 µg L^{-1} As, when low flow conditions had just re-established after a greater rain event. During the low flow regime, concentrations slightly increased until the onset of the high discharge event. DOC and As concentrations peaked at 18 mg L^{-1} and 1 µg L^{-1}, respectively at the onset of the event, while Pb concentrations only peaked 3 hours later coinciding with maximum flow and a water level rise from 9.5 cm to 5.6 cm depth. Regardless of further smaller discharge peaks, DOC, As and Pb stream concentrations decreased to former low flow concentration levels until the end of the discharge event. Even though a distinct rise in concentrations of DOC, As and Pb caused by this rain event was evident, concentration ranges for all three elements were low and of the same magnitude as lower concentrations before the first event in May. This indicates a strong depletion of all three elements through the directly preceding event, which exhibited the highest recorded discharge of the whole record. The obvious exhaustion of potentially mobile DOC, As and Pb here, induces an element export constrained by production rates. As low flow established again after this rain event, concentrations started to slowly rise again as it has been observed under low flow just before the rain event.

At the fall event concentrations before the event were higher than in spring with 33.5 mg L^{-1} DOC, 8 µg L^{-1} Pb and 1.5 µg L^{-1} As. During this event, DOC, Pb and As behave differently (Fig. 3). DOC concentrations first decreased at the onset of the rising limb of the hydrograph and rising water level within the bog, but thereafter DOC concentrations started to rise until discharge peaked (Fig. 3) and remained high at 35 mg L^{-1} to 37 mg L^{-1} until discharge increased even further. Unfortunately, the automated sampler failed to sample a part of the following main event, but DOC concentrations after the event were again much lower (27 mg L^{-1}, doy 255) than concentrations before the whole event. The As concentration dynamics during this fall event followed that of DOC with a peak concentration of 1.9 µg L^{-1}. For Pb, the first decrease in concentration was not apparent, but an immediate rise to higher concentrations and a second discharge peak resulted also in distinctly higher Pb concentrations of up to 11.9 µg L^{-1}. After the event As and Pb concentrations were slightly lower than before the event (6 µg L^{-1} Pb and 1.2 µg L^{-1} As). In line with the different discharge peaks, the water level responded immediately to rain fall with a stepwise rise up to a level of 1 cm above the peat surface. DOC and As concentrations evidently peaked shortly after the discharge peak and even decreased with increasing discharge, which can be indicative of a fast runoff component with less intense DOC and As mobilization or dilution. However, Pb concentrations were not diluted, but increased with first discharge peak, which is contradicting the pattern observed for DOC and As. Similarly, Rothwell et al. (2007) also observed variable peak dynamics for Pb amongst other metals over several fall discharge events. Summarizing the response of Pb stream water concentrations for all three rain events, Pb concentrations seem to respond immediately to water level rise within the bog with an increasing in concentrations. As fast surface runoff at the beginning of the event can be ruled out as a reason for the initial decrease in As and DOC stream concentrations, the different behavior of the three elements indicates that DOC and As seemed to be controlled by different mobilization processes than Pb. Concentrations of DOC, As and Pb thus do not respond entirely similar to rain events. This difference in the dynamics cannot be explained based on our data set and prompts the question why the strong correlation of DOC with As and Pb concentrations observed for the annual low resolution record is not valid for the rain events.

The weak flushing effect during the spring events indicates a lack of supply of DOC and As caused by a low biological productivity early in the year. The stronger flushing effect of Pb will be discussed further below in relation to the results of pore water analysis. The fall event followed after the summer dry period and the time of highest productivity. When bog water level rises to the surface, the entire previously aerated peat layer gets hydrologically connected and contributes to near-surface flow. Therefore, a much greater amount of DOC, As and Pb can be mobilized and exported by such discharge events resulting in the highest discharge concentrations of all three elements of that year. High frequency sampling revealed a great dependency of DOC, As and Pb discharge concentrations on pool exhaustion within the bog. This is evident by decreasing concentrations during an event, but also a decline in DOC, As and Pb concentrations, when rain events follow up over a short time interval. This exhaustion effect can be explained by a lack of supply of readily mobile element pools, when peat layers are hydrologically connected over a longer time period and constant bog water levels. These results are congruent with Rothwell et al. (2007), who sampled subsequent discharge events at a bog draining stream in fall. In addition, the observed high concentration levels of DOC, As, and Pb highlight the role of seasonal dynamics of productivity.

Figure 4 displays an element concentration to discharge (c/Q) plot for DOC, As and Pb. Here, it is apparent that above a threshold of discharge of about 8 L s^{-1} concentrations of DOC, As and Pb decrease or remain at constant. This indicates that at a discharge above 8 L s^{-1} element concentrations get diluted, most likely because all available pools have been connected. As this threshold is distinct and uniform for all three elements, pool exhaustion might be less likely, as the pool size is expected to differ over the vegetation period with a longer supply in summer and fall. Also, mobilization processes are probably different for DOC, Pb and As depending on binding types, which result in different responses depending on moisture and temperature preconditions of discharge events. However, rain water concentrations of DOC, As and Pb are much lower than pore water concentrations and hence dilution by precipitation should affect those elements all in the same way, as was observed here. Assuming that surface runoff takes place after saturation of the entire peat layer, the particular discharge at which surface runoff commences and dilution takes place should be similar over the whole year. This conclusion also implies that at this bog, surface runoff is generated after peat saturation and not through infiltration excess.

3.4 Peat decomposition and solid phase As, Pb and Fe concentrations

Solid phase Pb and As concentration exhibited a similar general trend with depth with higher contents in the uppermost meter (Fig. 5 A). Pb concentrations peaked in 40 and 72.5 cm depth with 1,200 mg kg^{-1} and 706 mg kg^{-1}, respectively. These two peaks has been reported before for other bogs in the Harz Mountains (Biester et al., 2012) and can be clearly related to mining activities in the past. Kemptner and Frenzel (2000) related those peaks to regional mining activities in the 12th/13th century and 17th century by ^{14}C dating in a bog within 5 km distance from our sampling site. Due to the strong historic mining influence the recent decrease in Pb concentrations in the uppermost cm was very pronounced. Also below 75 cm Pb concentrations sharply decreased to non-anthropogenic background levels and < 20 mg kg^{-1} below 100 cm depth. Concentrations of As were also highest in the uppermost 75 cm and show peaks at similar depths as Pb with maximum concentrations of 65 mg kg^{-1} and 38 mg kg^{-1} at 30 cm and 72.5 cm depth. Peak concentration of Pb and As were high, even compared to other contaminated sites (e.g. Rothwell et al., 2009). While Pb is no redox-sensitive element, As might be mobilized after deposition and gets enriched in the surface-near layer due to redox changes, especially, when strong water level fluctuations prevail (Rothwell et al., 2010). As As(V) associates with Fe-(hydr)oxides, As mobility is known to be controlled by the reductive dissolution of Fe-(hydr)oxides, which causes the release of As into pore waters and would lead to an enrichment in the surface-near layer along with precipitated Fe-(hydroxides). Fe enrichment at the redox boundary occurs through the upward diffusion of dissolved Fe(II) and precipitation where oxic conditions prevail. The Fe depth profile here showed enrichment in the uppermost peat layer with a peak concentration of 5.5 g kg^{-1} at 5 cm depth and decreasing concentrations down to 1.3 g kg^{-1} at 32.5 cm depth. Lowest Fe concentrations were found below 100 cm depth with concentrations less than 1.3 g kg^{-1}. In general Fe concentrations were low compared to other peatlands (Riedel et al., 2013) and much lower than in studies describing Fe as an important factor for DOC and As retention. Concentrations of As showed no enrichment in the upper peat layer as did Fe, indicating that As is not coupled to redox induced changes of Fe phases here. We assume that As in our bog is predominately bound to organic matter similar as observed in other peatlands, where As is mainly bound to organic matter by reduced organic sulphur groups under reducing conditions (Langner et al., 2011).

In previous studies peat decomposition has been found to enrich particular element concentrations through mass loss (Biester et al., 2003; Biester et al., 2004; Biester et al., 2014). Figure 5 A displays C/N ratios of the organic matter as proxy for peat decomposition (Kuhry and Vitt, 1996; Broder et al., 2012; Biester et al., 2014). In the upper 12.5 cm C/N ratios were high (88-128) with a distinct decrease to a value of 54 in 15 cm depth (Fig. 5 A). Further below, C/N ratios remained low between 23 - 50 with higher values between 70 cm and 150 cm (50-100). This indicates that the upper 15 cm are less decomposed, while with decreasing C/N with depth the degree of decomposition increases with again a lower degree of decomposition between 70 - 150 cm depth. A straight influence of decomposition on As and Pb distribution was not found here and concentrations were rather determined by enhanced deposition rates or in case of Fe by redox processes than by peat decomposition.

3.5 Pore water DOC, As and Pb concentrations

DOC concentrations in the pore water profile ranged from 20 mg L^{-1} to 250 mg L^{-1} (Fig. 5). Highest concentrations were found at the down most sample in 225 cm depth. DOC concentrations in the upper 50 cm, where most discharge is generated, were low in spring under wet conditions (doy 147: 34-41 mg L^{-1}; Fig. 6) and much higher in fall after rewetting following the dry summer period with concentrations of 119 mg L^{-1} in 20 cm depth and 100 mg L^{-1} in 40 cm depth (Fig. 6, doy 254). In late fall concentrations decreased again, but were still much higher than in spring. This is in line with the recorded seasonal trend of DOC concentrations at the discharging stream and the fact that DOC stream concentrations are dependent on temperature and microbial activity to built up potentially mobile pools (Clark et al., 2005), but also to the hydraulic connectivity of the surface-near peat layers. Normally, within a couple of weeks after rewetting acidity is consumed in pore waters through anaerobic respiration processes, like sulfate- or iron reduction (Fenner and Freeman, 2011). This should favor DOC solubility through higher pH, but also by release of formerly Fe-(hydr)oxid-bound

DOM (Grybos et al., 2009). Moreover, anaerobic conditions suppress peat mineralization and the described enzymatic latch of phenol oxidase activity favors DOC production after rewetting (Fenner and Freeman, 2011). In line with these assumptions, DOC concentrations were highest several weeks after the summer drought in fall, when the water level had fully recovered again (doy 254, Fig. 6). However, the lower DOC concentrations measured during this rewetting, at an intermediate water level depth of 14 cm, probably reflect a limitation in DOC supply and an exhaustion of the DOC pool through export, as the sampling just followed two rain events, which already had triggered high DOC stream concentrations.

During the summer drought, the amount of pore water was too low to obtain sufficient sample volume for DOC measurements at 20 cm depth. At 40 cm depth DOC concentrations during drought and following rewetting (doy 254) were higher than in spring and during rewetting (doy 236). On the one hand, this might contradict the concept of Fenner and Freeman (2011) or Clark et al. (2012) who stated low DOC concentrations during drought due to microbial limitations by drought stress and acidification by drought-induced oxidation processes. On the other hand, the measured low pH (< 4.5 pH), in all pore water samples at our site might indicate that the drought acidification effect is not pronounced here, as pH in our peat is generally low. Moreover, due to the low Fe concentrations in our peat, the effect of DOC immobilization through binding to Fe-(hydr)oxides during drought and aeration as proposed elsewhere (Riedel et al., 2013) is probably low at our study site. Accordingly, due to the low pH and the low amount of Fe-(hydr)oxides at our site suppression of DOC production by drought events seems to be of low importance here and probably in ombotrophic peatlands in general.

Pore water As and Pb concentrations in the Odersprung bog ranged from 1.2 µg L^{-1} to 3.8 µg L^{-1} and 0.5 µg L^{-1} to 8.4 µg L^{-1}, respectively (Fig. 5). Both, As and Pb concentrations were highest in the uppermost sample at 20 cm depth. While As was steadily decreasing and leveled out in 70 cm depth, Pb concentrations peaked again around 60 cm depth with 4-5 µg L^{-1} Pb before it leveled out in about 120 cm depth. Concentration profiles throughout the year show only small changes in the uppermost samples. Lowest As pore water concentrations at 20 cm and 40 cm depth occurred at the first sampling in spring (Fig. 6, doy 136) with 2.5 µg L^{-1} and 2.1 µg L^{-1}, respectively. At the end of the summer drought As concentrations remained at around 3 µg L^{-1} (doy 203), while Pb pore water concentrations decreased from about 6 µg L^{-1} (20 cm depth) and 3 µg L^{-1} (40 cm depth) to lowest annual concentrations of 3.3 µg L^{-1} and 1.7 µg L^{-1} Pb during summer drought, respectively. While highest Pb concentrations (8.4 µg L^{-1}) were measured at the beginning of fall, (Fig. 6, doy 236) when the water level had not yet fully recovered, highest As concentrations occurred after the complete rewetting of the bog in September congruently with DOC concentrations (doy 254). Pb concentrations at 40 cm depth were constant with exception of a slight decrease during summer drought (doy 311: ~3 µg L^{-1}). The very high Pb concentrations measured during water table recovery might be due to mobilization of a Pb pool, which built up during drought in the most reactive surface-near peat layer by microbial decomposition or mineralization processes. This assumption might also explain the decoupling of DOC and Pb export apparent at discharge events after dry preconditions, as a readily solubilized Pb pool is easily flushed. Moreover, it explains the absence of the initial dilution effect as seen in DOC stream concentrations. Furthermore, the DOC pool increases after drought, when wet conditions prevail again, explaining the lag time of DOC peak concentrations in pore waters.

The decreasing Pb concentrations with depth allow a determination of the discharge water source. The hydrologic response of the bog discharge was characteristic for a rapid near-surface runoff. Comparing absolute concentrations in pore water and discharging water, the high Pb concentrations of more than 10 µg L^{-1} in runoff at the fall rain event can only be generated in the uppermost part of the bog, where Pb concentrations were highest. Following this assumption also the low flow concentrations must have been generated in the upper part of the peat profile as Pb concentrations below 1 m depth were too low to generate the observed Pb concentrations in discharge. The variable Pb concentrations at different flow conditions are attributed to different water levels, which affect variable parts of the Pb pool in the acrotelm and are thus able to mobilize different amounts of Pb. This does also indicate that, in line with the hydrologic discharge response, low flow discharge is generated from upper peat layers and not from seeping water originating from the deep peat sections.

3.6 Fluxes and inventory estimations

While DOC and As concentrations were highest in summer and seemed to be more dependent on temperature, DOC, As and Pb fluxes were not controlled by the concentration changes over the year, but mainly by discharge (Fig. 7). This dependency is valid up to a discharge of 8 L s^{-1}, while at higher discharge dilution is observed. Highest element fluxes occurred during high discharge events in spring and fall and during snowmelt. Flux calculations show that 10% of the monitoring time span, when highest discharge was recorded, contributed 39 %, 40 % and 43 % of the annual DOC, As and Pb export. Similar patterns have been described by Koehler et al. (2009) for DOC fluxes from a blanket bog in Ireland. Clark et al. (2007) calculated that 10 % of the monitoring time span including highest discharge contributed 50 % of the annual DOC export and Hinton et al. (1997) estimated 41-57 % of annual DOC export by the 10 % time of highest discharge. When separating the annual hydrograph record in storm flow and low flow conditions (boundary at 0.3 L s^{-1} by visual examination), 72 % of the record exhibited high discharge conditions, which contributed 97.6 % of total annual discharge and about 96 % of annual As, Pb and DOC export..

This flux calculations implicate that high discharge events contribute over-proportional to element exports in a short time period. While low flow conditions generate high element concentrations, greater discharge not primarily dilutes element concentrations, but connects additional pools to discharge, which results in higher fluxes. Concluding, as different DOC, As, and Pb pools, i.e. different peat layers, correspond to different hydrologic conditions, also different linkages to element exports are likely. If low flow discharge is generated in the lower acrotelm, not only general pool sizes are different, but also mobilization conditions, i.e. different pH, redox, DOC quality. Further insight into differences between low flow and high flow export dynamics might be gained through Pb isotope determinations (see Klaminder et al. 2008), a determination of DOC age or DOC characterization.

The importance of high discharge events to Pb, As and DOC exports gets more relevant in view of changing climate conditions with more frequent heavy rain events in this region. Furthermore, that it is crucial at which time of the year rain events will occur in the future. A data separation by season indicates that fall contributes to the largest extend to annual element export followed by spring and similar ranges in summer and snowmelt (Table 1). This pattern is in line with the assumption that higher microbial activity on the one hand, and elevated discharge, which flushes the acrotelm on the other hand favors DOC, As and Pb export.. The lower fluxes during summer are attributed to prevailing low flow, dry conditions. Figure 8 displays discharge to element loading plots separated by season and high discharge event sampling. It highlights higher loadings at the same discharge volume dependent on season by a steeper increase of the regression line. In general, element loadings are lowest at snowmelt and increase over the year with highest loadings during the fall event. At the end of the year, loadings decrease again. While this general trend is similar for DOC and As, Fig. 8 also shows that Pb loadings during snowmelt and the second spring event are quite similar and that concentrations are less dependent on discharge volume, indicated by lower R^2 values of the regression lines.

The annual DOC export from the investigated bog catchment can be estimated to 155 kg C ha^{-1} a^{-1} ±67 kg C ha^{-1} a^{-1} (Table 2) and is similar to values from other studies (Worrall et al., 2003; Koehler et al., 2009). As the upstream catchment is completely snow covered during winter, including the stream outlet at the bog, no flux quantification during winter is possible. It can be speculated though, that fluxes are probably low due to low temperatures and low flow conditions during winter season.

Aqueous exports of As and Pb were calculated to 7.8 ± 3.0 g As ha^{-1} a^{-1} and 39 ± 16 g Pb ha^{-1} a^{-1}. Annual Pb export was in the same range as values reported by Rothwell et al. (2011) with annual aqueous Pb export of 55 ± 18 g Pb ha^{-1} a^{-1} from a contaminated eroded ombrotrophic peatland. The authors also highlighted the importance of particulate Pb export for peatland systems, which needs to be considered when estimating total Pb export. The calculated aqueous As export from our site were much lower than those reported by Rothwell et al. (2011) (47.1 ± 9.9 g As ha^{-1} a^{-1}), in spite of higher As contents in our peat. This might be due to the eroded nature of their sampled bog and the prevailing post-depositional mobilization of As in peat due accelerated water table drawdowns and a consequent binding to Fe-(hydr)oxids (Rothwell et al., 2010).

As and Pb inventories were calculated based on the median element contents in the upper 30 cm of the 16 analyzed cores and were 0.91 g As m^{-2} (0.64-1.17 g m^{-2}) and 13.98 g Pb m^{-2} (7.47-24.02 g Pb m^{-2}), respectively (Table 2). Element contents in the upper 30 cm varied over a wide range pointing out the importance of a multi-core approach for calculating peatland element inventories. Rothwell et al. (2010) calculated a storage of 0.19-0.44 g As m^{-2} and 12.2-13.5 g Pb m^{-2} in another contaminated peatland. While our calculated Pb inventories are similar, As inventories are higher than those reported by Rothwell et al. (2010). When referring annual fluxes to the bog area of the catchment 0.04 kg As a^{-1} and 0.2 kg Pb a^{-1} were exported in 2013 by the bog drainage. This equals to 0.85 ‰ and 0.27 ‰ of the calculated As and Pb inventories respectively (Table 2). Even though conclusions based on a one year data set are limited and uncertainties are high, it becomes clear that As seemed to be more mobile than Pb. Neglecting future element deposition and changing export conditions it would take more than 1000 years to deplete As pools and more than 3000 years for Pb pools stored within this polluted peatland. Furthermore, the observed element content variation among all cores might also implicate differences in pore water concentration levels within the stream catchment.

4. Conclusions

Our results highlight the importance of comprehensive field studies to gain further understanding in generation and controls of element exports from peatlands. The combination of pore water and discharge data showed that As and Pb exports are not only dependent on the amount of precipitation and discharge, but on the frequency and depth of water table fluctuations, and the extend of pool connectivity in the acrotelm. This has been demonstrated by higher As and Pb concentrations and exponential increase of export at high discharge events, especially after a longer dry period and higher temperature. A distinct bog-specific discharge threshold of 8 L s^{-1} was observed, which indicates a connection of all available pools. This threshold presumably depends mainly on the size of the bog and drainage conditions. Significant correlations of annual As, Pb and DOC concentrations in discharge hints to transport of As and Pb as organic complexes with decoupling of Pb from DOC concentrations at storm events following dry preconditions. Comparing the annual bog As and Pb export with element inventories indicates that As is much stronger mobilized than Pb, with annual fluxes accounting for 0.85 ‰ and 0.27 ‰ of total As and Pb inventory, respectively. Results also point out the over-proportional contribution of high discharge events to As, Pb and DOC annual export. The challenge for prospective research is to unravel the biogeochemical effects of short term water level fluctuations on trace element and DOC mobilization processes within peatlands to further improve parameterization of peatland catchment models.

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Tables

Table 1: Seasonal distribution of discharge, DOC, As and Pb export fluxes at the Odersprung catchment.

	Record time	Q	DOC export	As export	Pb export
	%	%	%	%	%
Snowmelt	7.6	19.8	7.4	11.1	7.2
Spring	21.3	25.5	19.2	15.3	19.1
Summer	35.6	10.8	12.5	10.2	12.0
Fall	35.6	47.5	60.8	63.4	61.7

Table 2: Estimated mean DOC, As and Pb export in 2013 and element inventories in the upper 30 cm peat. Uncertainties were estimated by the standard deviation of flux calculations and element inventories calculated of each core.

	Mean annual fluxes		Peat inventory[a]		Export
	g ha^{-1} a^{-1}	kg bog^{-1} a^{-1}	g m^{-2}	kg ha^{-1}	‰ of inventory
DOC[b]	$154.79*10^3$	773.93	16,689	$166,89*10^3$	0.93
uncertainty	$88-221*10^3$	441-1107	(15,336-17,417)	($153.36*10^3$- $174.170*10^3$)	(0.89-1.01)
As	7.8	0.04	0.91	9.1	0.85
uncertainty	4.8-10.8	0.02-0.06	(0.64-1.17)	(6.4-11.7)	(0.66-1.22)
Pb	39.2	0.2	13.98	139.8	0.27
uncertainty	23.1-55.3	0.12-0.28	(7.47-24.02)	(74.7-240.2)	(0.16-0.51)

[a] upper 30 cm [b]total C for peat inventory, respectively

Figures

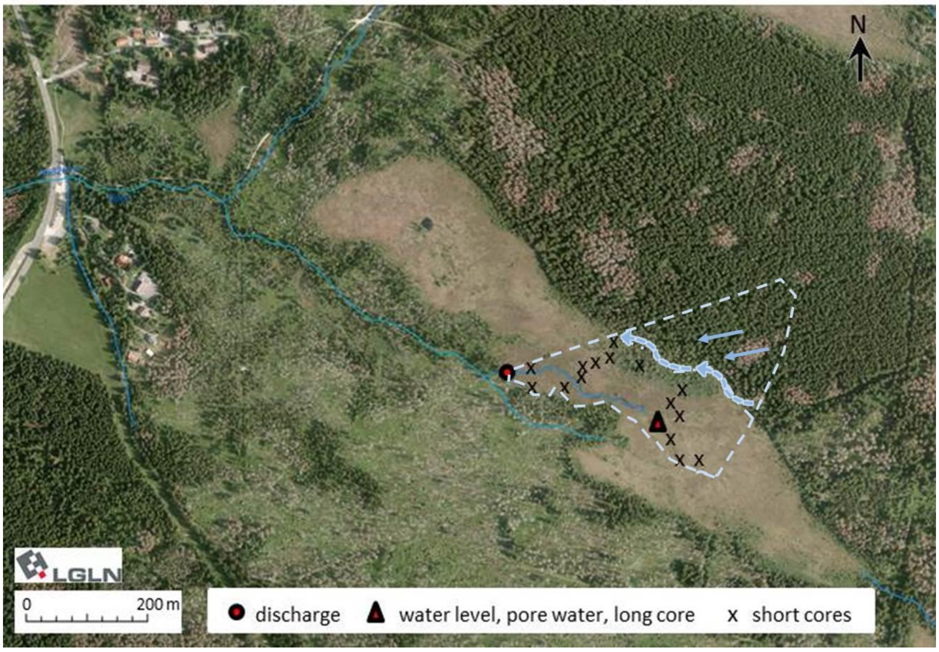

Fig. 1: Location of the study area in the Harz Mountains, northwestern Germany, with catchment boundaries indicated by the dashed light-colored line. Circle denotes discharge monitoring site, triangle marks location of pore water sampling, as well as water level monitoring and peat core retrieval. Crosses mark the location of short cores for inventory calculations. Map Source: Lower Saxony Ministry for Environment, Energy and Climate Protection.

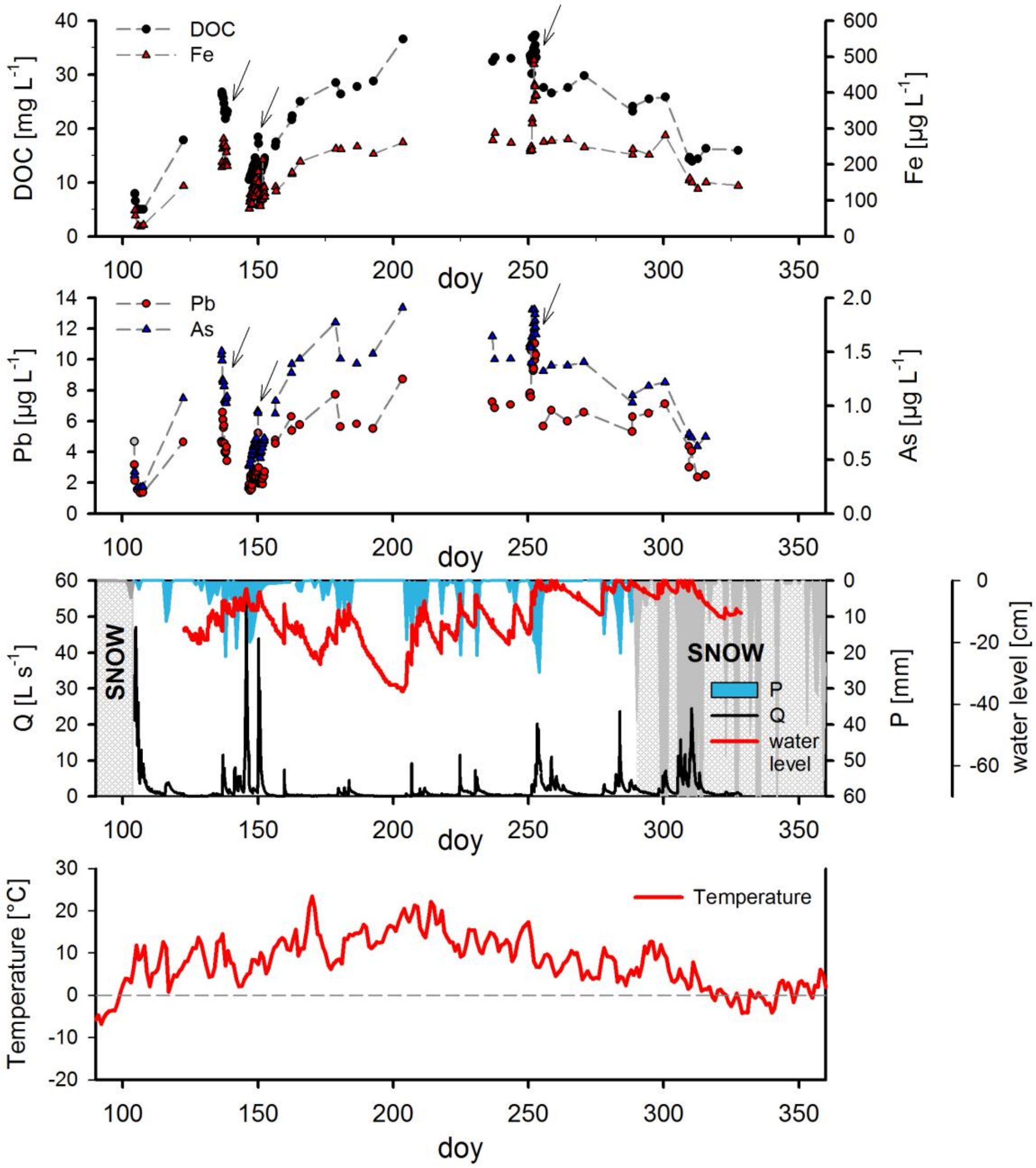

Fig. 2: Annual concentration record of DOC, Fe, Pb and As (top) at the bog outlet. Annual records of bog water level, daily precipitation, discharge and temperature (low). Sampled discharge events are highlighted by black arrows. Note that winter precipitation as snow cannot be quantified.

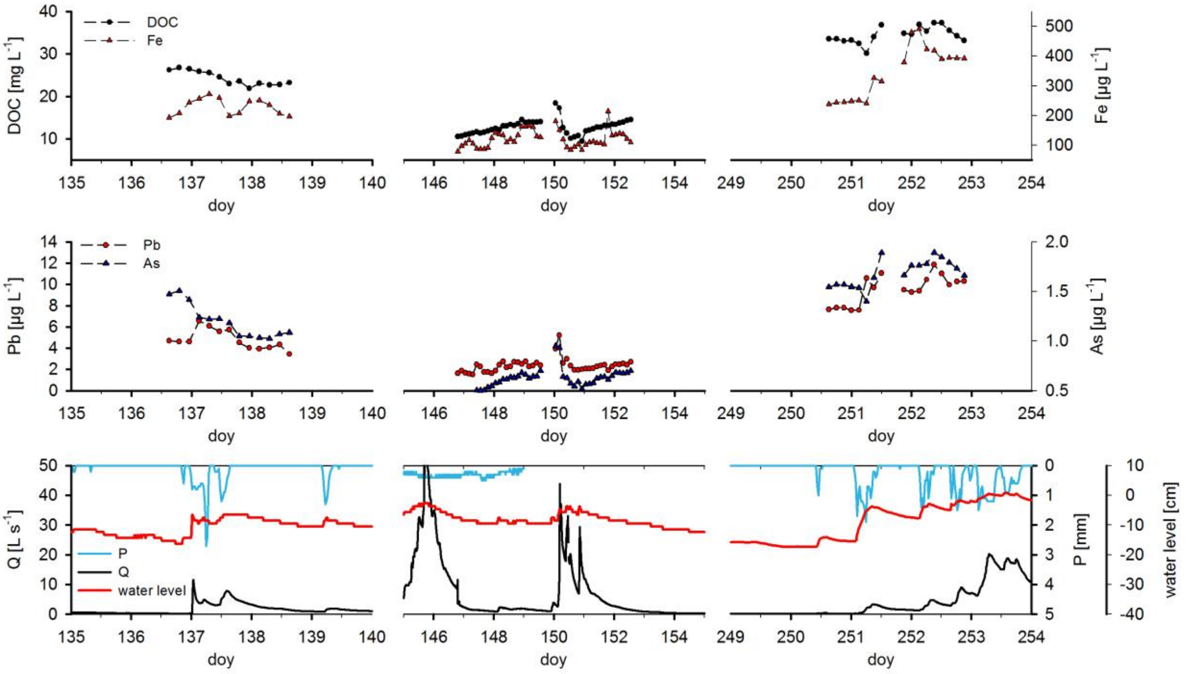

Fig. 3: High resolution DOC, As and Pb concentrations during recorded spring (doy 135-155) and fall (doy 250-260) events. Records of bog water level, precipitation (30 min resolution) and discharge (low).

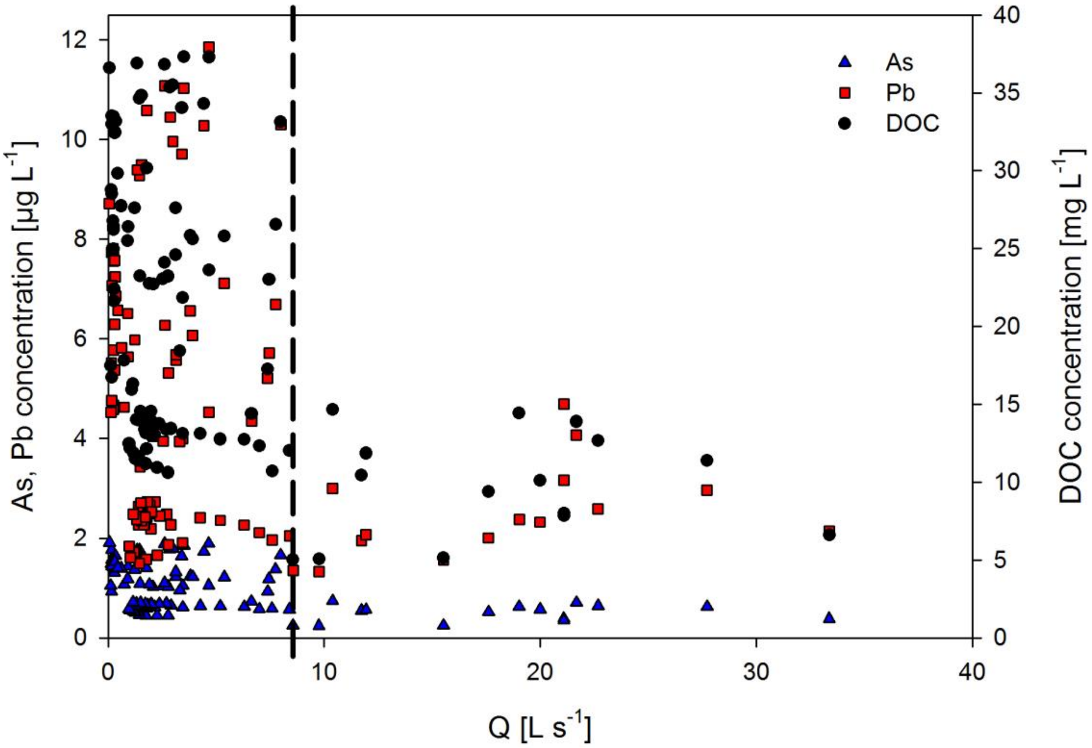

Fig. 4: DOC, Pb and As stream concentration to discharge (Q) plot (c/Q). The black dashed line indicates the threshold discharge value for a compulsive dilution effect.

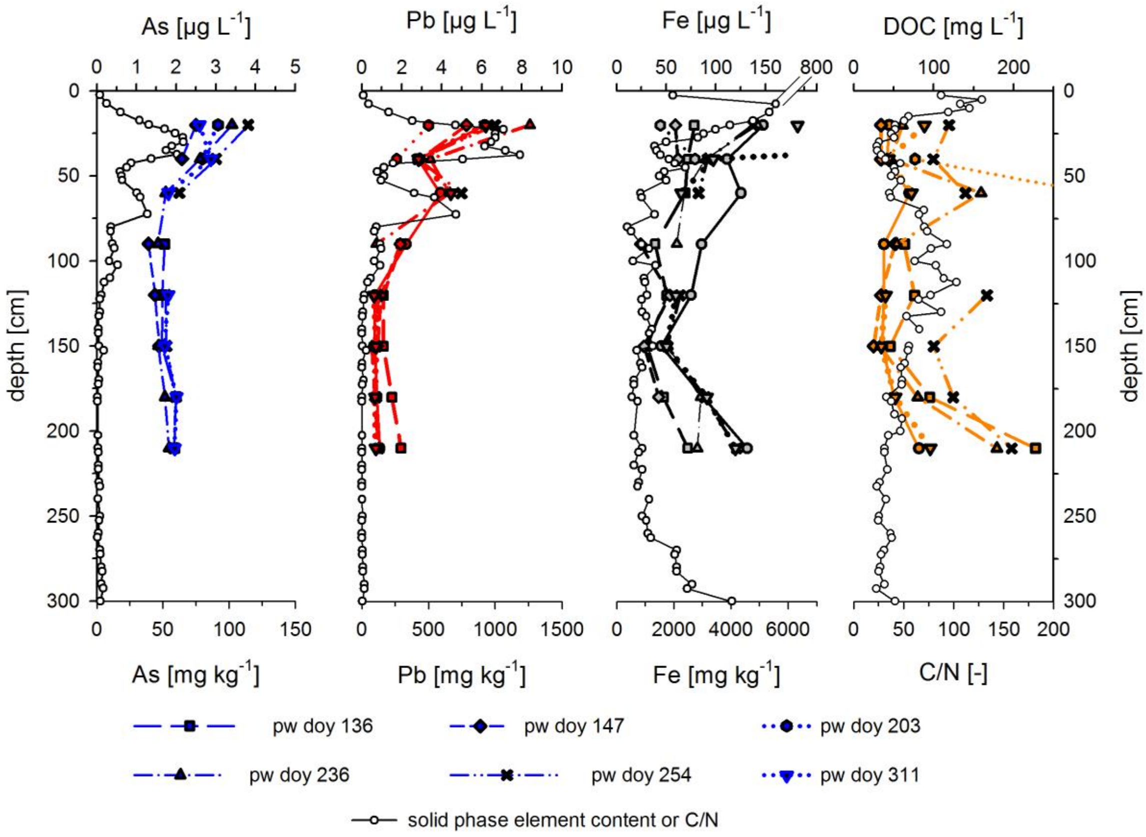

Fig. 5: A) As and Pb contents of the long peat core taken at the Odersprung bog and carbon nitrogen ratios (C/N) as indicators for peat decomposition. B) Pore water concentrations of As (left, blue), Pb (middle, red) and DOC (right, orange) along a depth profile (250 cm).

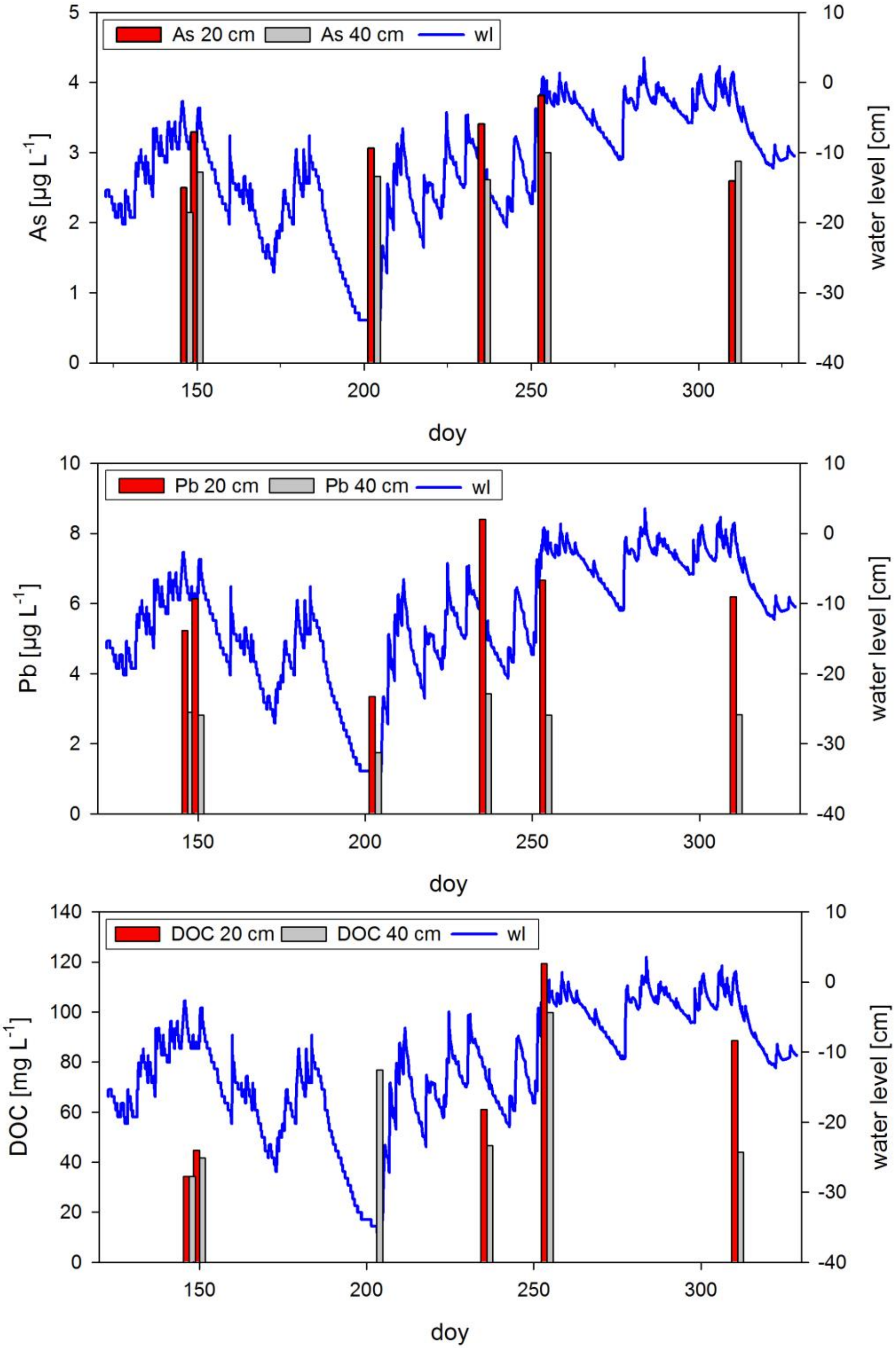

Fig. 6: Pore water concentrations of As (top), Pb (middle) and DOC (low) in 20 cm and 40 cm depth over time. The blue line indicates the recorded bog water level (wl).

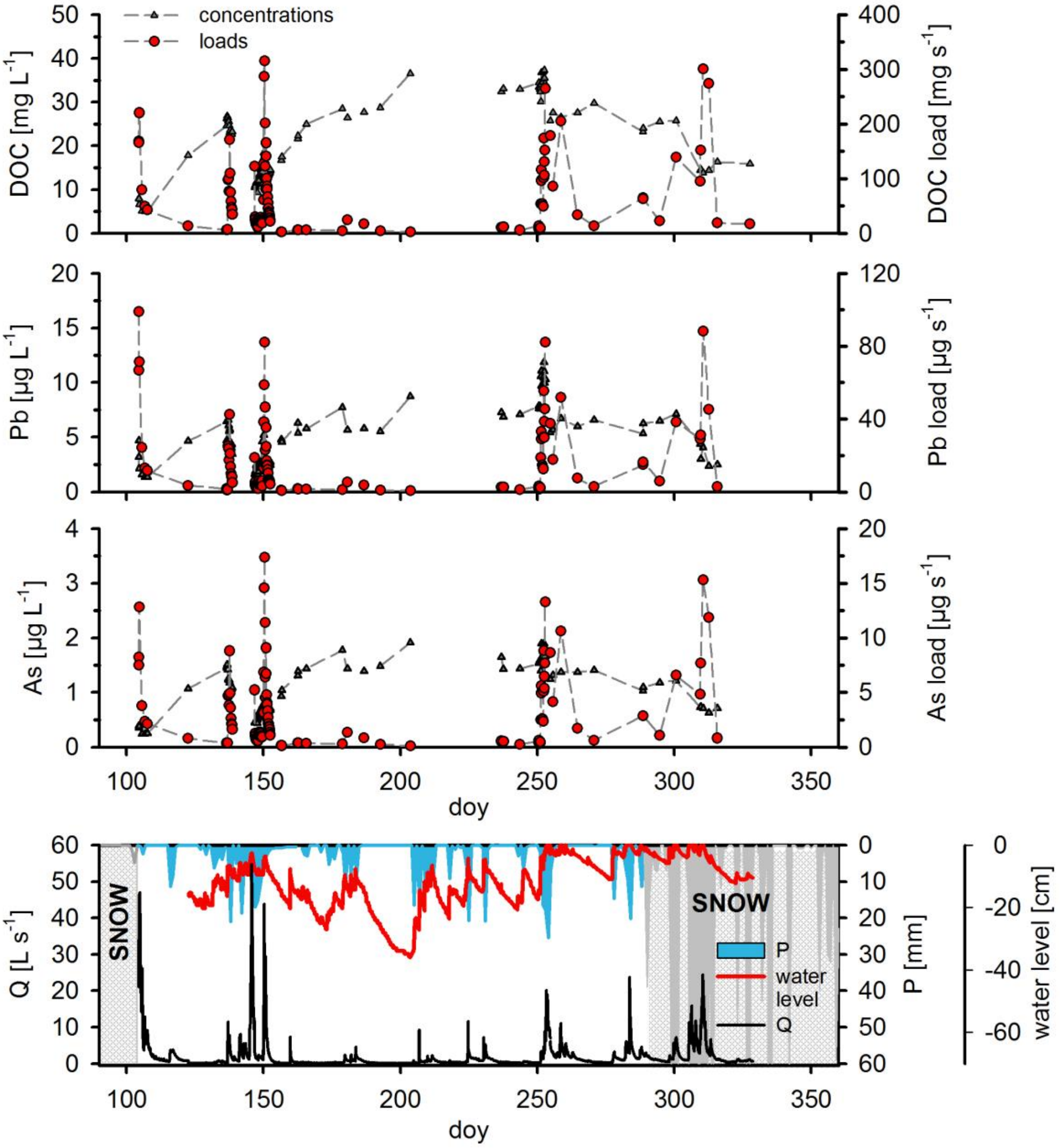

Fig. 7: Concentration record and instantaneous loads of DOC, Pb and As at the bog outlet. Annual records of bog water level, precipitation and discharge (low).

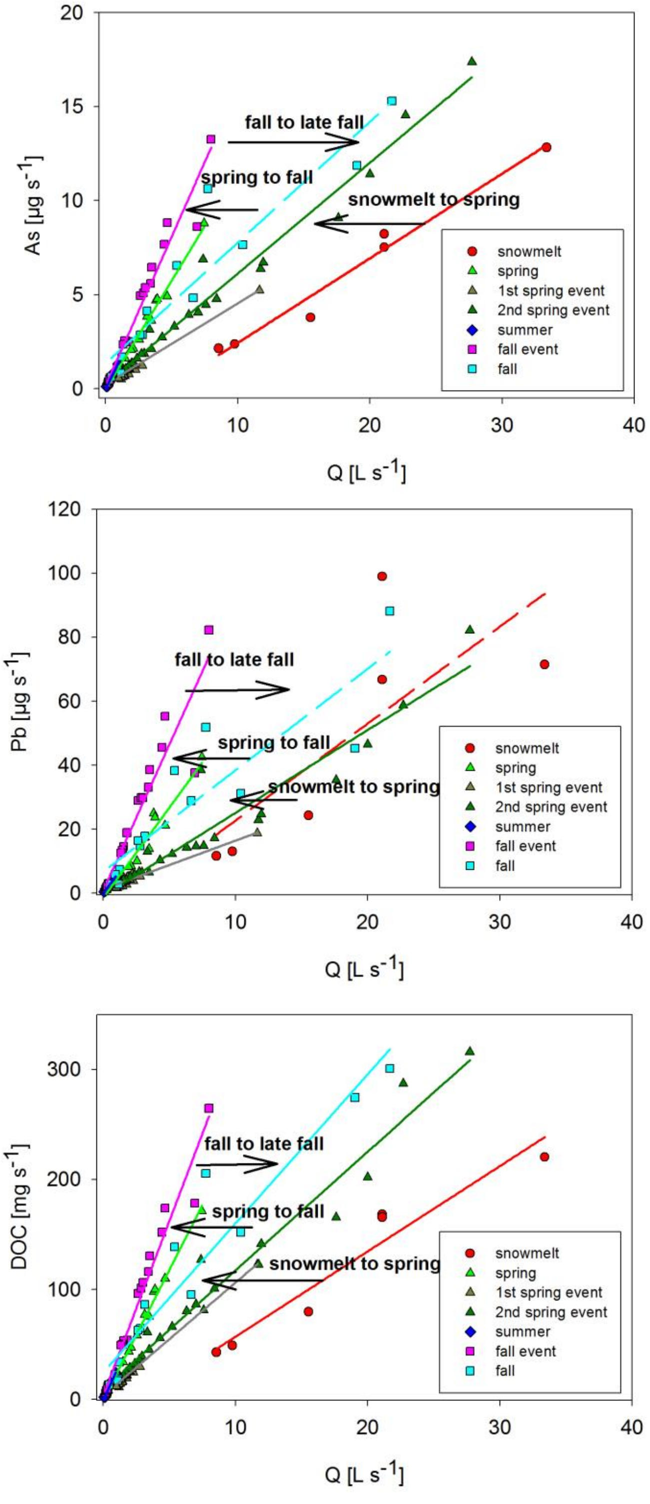

Fig. 8: As (top), Pb (middle) and DOC (low) loadings to discharge (Q) plots divided by season and event sampling. Regression lines with $R^2 > 0.90$ are plotted with a solid line, $R^2 < 0.9$ are plotted with a dashed line.