Science of the Total Environment 449 (2013) 63–70

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Changes in catchment conditions lead to enhanced remobilization of arsenic in a water reservoir

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HIGHLIGHTS

- ► We examine increasing dissolved arsenic in water reservoirs.
- ► Arsenic release from sediments was controlled by decreasing water nitrate concentration.
- ► Basin sediment arsenic was found in ferric and humic matter.
- ► A long term trend of arsenic in water is negatively related to nitrate.

ARTICLE INFO

Article history:
Received 21 June 2012
Received in revised form 3 November 2012
Accepted 11 January 2013
Available online 13 February 2013

Keywords:
Arsenic fluxes
Iron
Metalloid
Nitrate
Sediments

ABSTRACT

Increasing arsenic concentrations in freshwater ecosystems is of global concern. Processes affecting arsenic fluxes in catchments are known. These processes are in turn controlled by the underlying geology and air pollution history. In contrast to the knowledge on catchment processes less is known about the hydrochemical processes controlling the fixation/remobilization of arsenic within lakes and artificial reservoirs. Consequently, we examined a reservoir system in the Ore Mts. (Germany) regarding its sink and source potentials affecting arsenic fluxes. This area was faced with heavy deposition inputs from coal burning based acid rain until the beginning of the 1990s. Hereafter concentrations of sulfate and nitrate in runoff waters decreased, whereas dissolved organic carbon (DOC) concentrations are still increasing. Along with this, arsenic concentrations in the water discharge from the catchments increase. Our results reveal that the sediments of the investigated reservoir system contain high inventories of arsenic in association with ferric and organic phases. A nitrate deficit dependent arsenic release is suggested. It is indicated that arsenic release from the reservoir sediments may be controlled by water nitrate concentration, which in turn is dependent on the nitrate concentration in the runoff water from the catchment.

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1. Introduction

Apart from widely known problems with arsenic contamination of aquifers, elevated arsenic concentrations in surface waters are of equal concern even on a global scale (Smedley and Kinniburgh, 2002; Smith et al., 2000). Potential sources are mining activities as well as natural bedrock weathering or atmospheric deposition with subsequent soil and sediment related accumulation and release processes. An example in Central Europe is the upper region of the Erzgebirge (Ore Mts.), Saxony, Germany. Acid deposition has been a serious problem in this region (Zimmermann et al., 2003). As a result of intensive lignite burning (notably in power plants in adjacent Northern Bohemia) not only acid deposition occurred but also a dust related arsenic deposition could be notified (Erbanova et al., 2008). Matschullat (2000) claims soil humic layers as sink for deposited arsenic.

Beginning in the 1980s but mainly from the 1990s several environmental parameters changed. Kopacek et al. (2002) reported a decrease of sulfur and nitrogen deposition since that time. Furthermore, changes in the water composition of reservoirs during this period to less acidic conditions were shown (Ulrich et al., 2006). A major trigger for this development came by the political and economical change in the states of Central and Eastern Europe since the end of the 1980s. Emission-intensive lignite based power generation in these countries dropped rapidly leading to a decreased acid deposition (Armbruster et al., 2003; Zemek et al., 2006). Additionally, large-scale forest soil liming was performed (Ulrich et al., 2006). Along with these changes a significant increase of arsenic in the Altenberg reservoir system could be observed. Such trends were also observed in other studies conducted in the Czech Republic and Sweden (Erbanova et al., 2008; Novak et al.,

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http://dx.doi.org/10.1016/j.scitotenv.2013.01.041

2010; Wallstedt et al., 2010). Regarding the source of mobilized arsenic, an elevated arsenic background of soils in the catchment areas appears as main factor. Bombach et al. (1994) report a geogenic origin for arsenic in soils and river sediments of the Ore Mts., but also a fly ash related deposition from lignite based power generation and domestic fuel as mentioned above is shown (Erbanova et al., 2008).

With the decrease of sulfate deposition the S pools in the soils decrease (Mitchell and Feger, 2004), but water pH and dissolved organic carbon (DOC) increase (Monteith et al., 2007). Novak et al. (2010) showed an increase in arsenic concentrations in a catchment runoff following a decreased input of acids and Bauer and Blodau (2006) demonstrated a mobilizing potential of DOC for arsenic. Hence higher arsenic concentrations in the tributaries may be explained as a concomitant feature of a regression in soil acidification and increased DOC abundance.

In contrast, it is not clear whether the pelagic increase of arsenic in the Altenberg reservoir system can be entirely attributed to an increase of arsenic in the tributaries, because of generally higher arsenic concentrations in pelagic and outlet water compared to the tributaries. Thus, an internal arsenic release has to be considered. The known association of arsenic to ferric minerals in sediments, and the control of their adsorption capacity by the redox conditions and alternative electron acceptor supply in the aquatic environment lead to the hypothesis that arsenic dynamics may be superimposed by the nitrogen dynamics of the site, which was a major focus of this study.

2. Material and methods

2.1. Study site

The Altenberg drinking water reservoir system is located in the eastern part of the Ore Mts. (Erzgebirge) (50°45′48.67″N, 13°44′5.00″E) (Fig. 1). Typical site and catchment properties of the reservoir system are given by Ulrich et al. (2006). In short: The reservoir and catchment area are situated on the quite flat top of the mountain range. The dominant bedrock is a base-poor rhyolite (Nebe and Abiy, 2002). Elevated contents of heavy metals and arsenic in the bedrock are typical for this area (Kasper, 1986). The catchment area is covered with ombrotrophic peatbogs as well as spruce stands with raw humus layers. The investigated system contains two reservoirs: the Galgenteich established in the Middle Ages and enlarged in the 1940s and the Altenberg reservoir completed in 1993. At present, the Altenberg reservoir is used for drinking water supply whereby the Galgenteich pond is operated as a predam. In addition to regular water transfer, dam seepage waters of the Galgenteich reservoir flow into the Altenberg reservoir. To avoid oxygen depletion of water withdrawn for drinking water preparation an artificial re-aeration was established close to the dam of the Altenberg reservoir using pure oxygen gas. Nutrient supply (median total P: 0,02 mg L^{-1} and median total inorganic N: 0,5 mg L^{-1}), productivity and allochthonous DOC influence indicate an oligotrophic and dystrophic character of the reservoir system. The Altenberg reservoir is dimictic, whereas its predam acts as a discontinuous cold polymictic system.

2.2. Sampling and monitoring

Water samples were taken biweekly from the tributaries as well as from the water column of the sub-basins of the reservoir system and the basin outlet according to APHA (1992). Simultaneously, the water dissolved oxygen was measured with a TA 197-Oxi WTW-sensor-device (WTW, Weilheim). The Altenberg reservoir system is subjected to a long term monitoring starting in 1993 where the detailed sampling for water arsenic analysis started in May 2008. Daily discharge values were obtained at channel control sections equipped with continuous water-level recorders with remote data transmission (OTT-Hydromet, Kempten, Germany) as well as pre-calibrated v-notch weirs established for the hydrological monitoring by the State Reservoir Administration (LTV Sachsen). Furthermore, the sediment of the Altenberg reservoir system was sampled using a Ghilardi Freefall Corer KGH 94 (with a diameter of 60 mm). Core sampling was done in January 2009 using the frozen reservoir surface for access to the sampling points. In case of a low sediment thickness an Ekman grabber (Hydro-Bios, Kiel, Germany) was used. The sampling sites are shown in Fig. 1.

2.3. Sample preparation and analysis

Water samples were filtered immediately after sampling using 0.45 μm cellulose-acetate filters and divided into subsamples. An aliquot for trace element analysis was acidified with HNO$_3$. A second sample aliquot was used unchanged for analysis of nitrate, phosphorus and DOC. Samples for arsenic speciation analysis were stabilized with phosphoric acid (10 mM) according to Daus et al. (2006). Nitrate analysis was made with an ion chromatograph (Shimadzu LC-10 AD). Phosphate was determined with a Specord 200 photometer (Analytik Jena, Germany) using the molybdenum blue method. DOC in water samples was determined with a total organic carbon analyzer (Shimadzu TOC-V; Germany). The elemental analysis was performed with an inductively coupled plasma mass spectrometer (PQ exCell, Thermo Fisher Scientific Inc, UK) according to DIN-EN-ISO-17294-2 (2004). Calibration functions

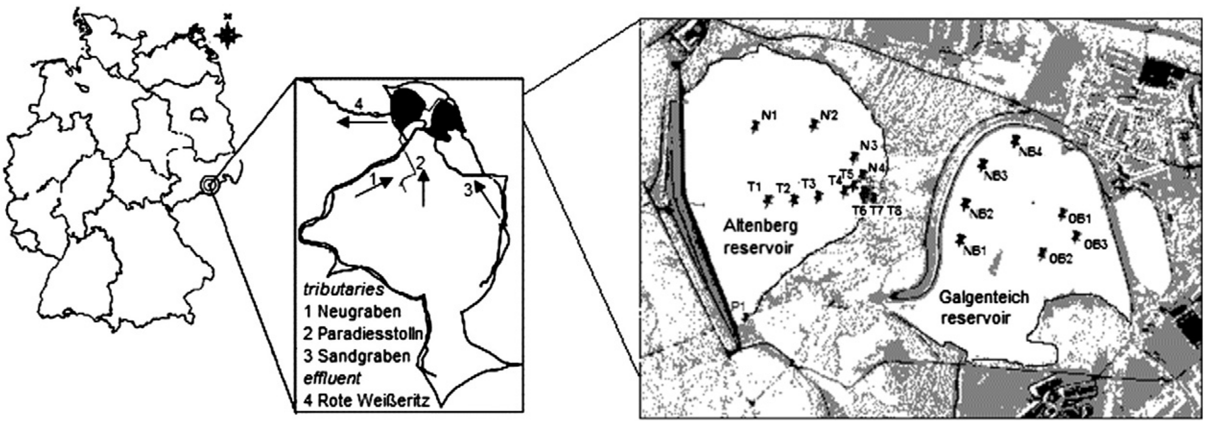

Fig. 1. Location of the Altenberg reservoir system in the Eastern Ore Mts. (Saxony, Germany) with catchment area and sub-basins. Basin left: Altenberg Reservoir, basin right: Galgenteich Reservoir. Markers in the graphic right are sediment sampling sites: T1–T8 = transect, N1–4 = Northern part, NB1–4 = Galgenteich new part, OB1–3 = old part, P1 = Paradiesstollen inflow.

were recorded from mixed calibration samples which were prepared from single and multi-element solutions (Bernd Kraft, Duisburg, Germany). Calibration validity was confirmed with digests of standard reference material (GBW7604, poplar leaves, China). Water samples were measured directly, and solid samples were subjected to a digestion procedure. Sediment samples were digested in a closed vessel microwave system (MARS5 CEM Corp., Matthews, United States) using nitric and hydrochloric acids according to DIN-EN-13346 (2001). Limit of detection (LOD) was calculated as the threefold standard deviation of instrument blank (acidified water). LOD for arsenic was 1 μg L^{-1}. Arsenic speciation analysis was done in a HPLC-ICPMS setup according to Francesconi et al. (2002) with a PRP-X100 anion-exchange column, a 20 mM $NH_4H_2PO_4$ mobile phase at pH 5.6 and an ICPMS as an arsenic detector. Carbon contents in the solid samples were analyzed using an Elementar vario el III (Hanau, Germany) according to DIN-ISO-10694 (1995). All results for solids are given for samples dried at 105 °C.

2.4. Arsenic load calculation within the system

The matter load L in a certain space of time in each flowing system compartment is described with the basic equation

$$L = \int_t C(t)Q(t)dt \quad [\mathrm{kg}]$$

where Q [L s^{-1}] is the water flow rate at a certain point of the flow cross section, C [μg L^{-1}] the belonging matter concentration, and t the considered time span (t = one year).

This basic coherency was applied to the study's data base, which consists of biweekly determined arsenic concentrations and daily water flow data at all decisive input and output passages of the reservoir system. According to Hebbel (2009) a non-model based load estimator calculation is suited for that data structure. The annual load L is calculated according to

$$L = |Y|\overline{CQ} - |Y|\overline{C}\left(\overline{Q} - \mu_Q\right) \quad [\mathrm{kg}].$$

The first term in the equation is the standard estimator, calculated as the annual mean of the biweekly concentration-flow-products (discrete concentration (C) and according flow (Q) values), and multiplied with the time span (Y) of one year for our experiment. The second term is a continuity correction, which is the product of the time span with the annual mean of biweekly concentration values and the difference between the mean biweekly (Q) and the mean daily (μ_Q) flow values.

2.5. Statistical analyses

Trends in time series of chemical parameters were calculated using the non-parametric seasonal Kendall test (Hirsch et al., 1982; McLeod, 2011). To estimate the slope of an existing trend the Sen's non-parametric method was used (Sen, 1968). The computations for trend analysis were performed using the R system for statistical computing.

3. Results and discussion

3.1. Arsenic interactions and long-term trends in the water body

The pelagic arsenic concentration of the Altenberg reservoir system increased during the last 20 years (Fig. 2c). Simultaneously since the beginning of the 1990s, the nitrate concentrations in both parts of the

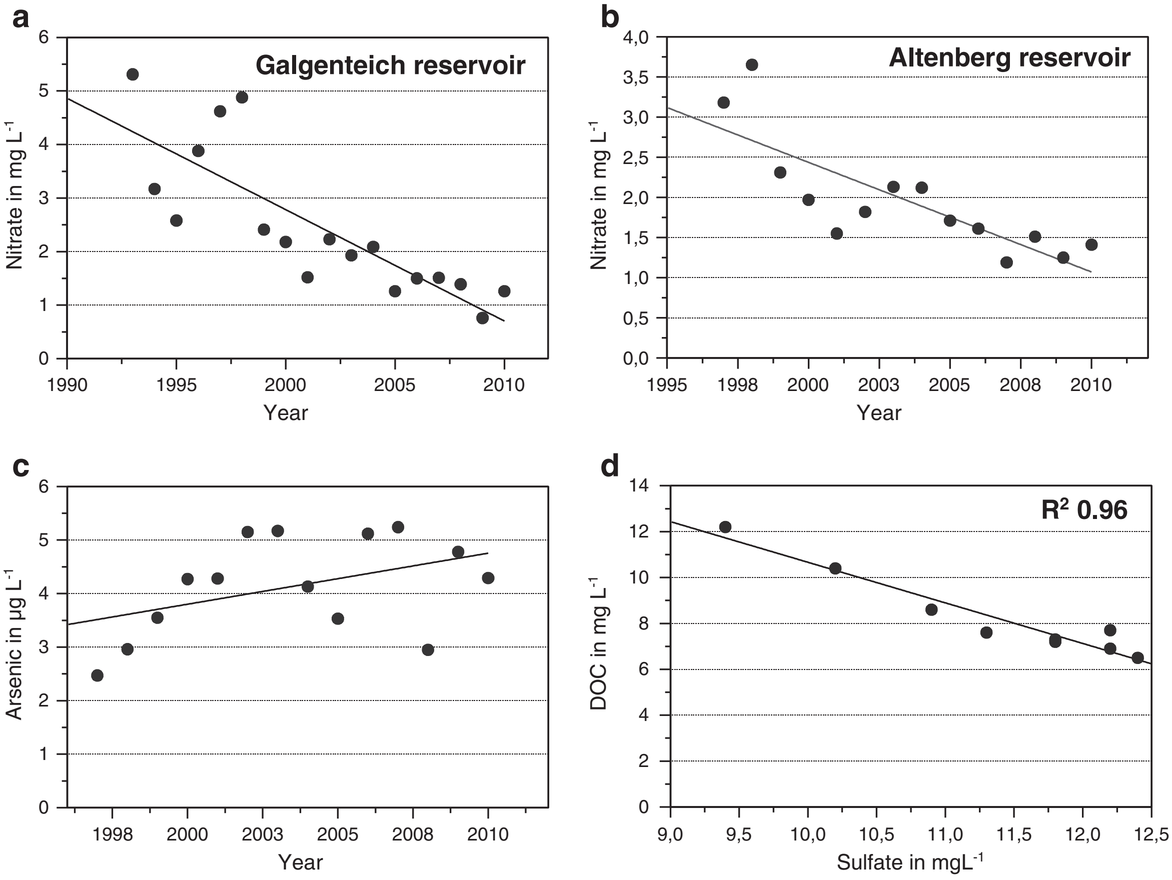

Fig. 2. (a) and (b) mean annual trend of nitrate (the lines representing the Sen's trend slope estimator based on Seasonal Kendall Test statistics) shown for the two different parts of the Altenberg reservoir system. (c) Arsenic trend in the reservoir system and (d) correlation between SO_4^{2-} and DOC in Galgenteich reservoir between the years 1997–2007 (all values as annual mean concentrations).

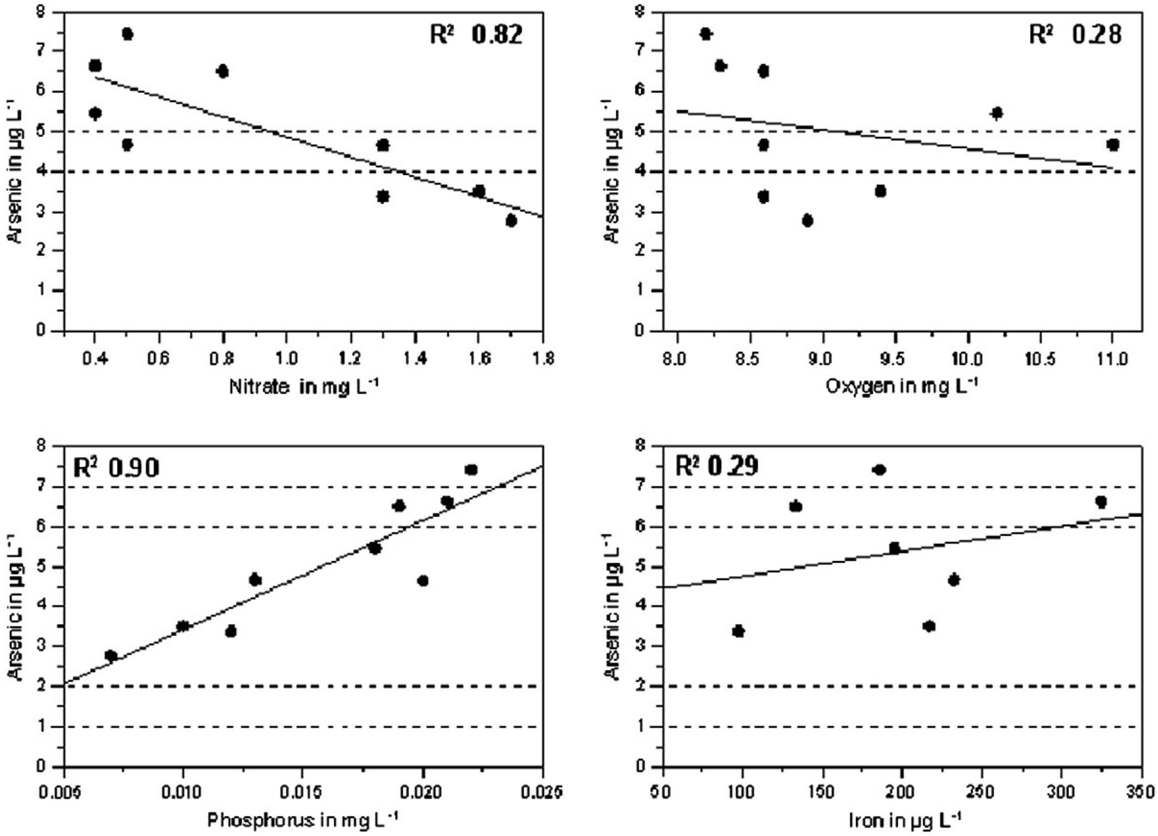

Fig. 3. Relationship between arsenic and nitrate, oxygen, phosphorus and iron in the water of the Galgenteich reservoir during 2009.

reservoir system decreased (Fig. 2a,b). A strong interaction between sulfate and DOC could be observed (Fig. 2d), which can be explained by a decrease in sulfur deposition and an increase in pH resulting in higher decomposition rate of the organic matter in the catchment (Berg and McClaugherty, 2003) and a higher DOC mobility. In turn this may have resulted in higher DOC concentrations (Kominkova et al., 2000) as had been shown previously by Ulrich et al. (2006). The strong correlation between nitrate and arsenic was also proven in both parts of the reservoir system in the year 2009 (Figs. 3 and 4). Comparing both water bodies, a higher arsenic concentration level in the Altenberg reservoir is given, compared with the Galgenteich predam (Fig. 8). This indicates a source function in the downstream reservoir. In both water bodies an arsenic control via nitrate can be expected. Furthermore, the strong correlation between arsenic and phosphorus, as found for both reservoirs (Figs. 3 and 4), appears to be due to the arsenate and phosphate similarity and particularly the same concentration controls (Manning and Goldberg, 1996; Waychunas et al., 1993). Hupfer and Lewandowski (2008) show an influence of redox status on phosphate adsorption in lakes and Kleeberg and Dudel (1997) describe a nitrate control approach for phosphate release from lake sediments where nitrate deficiency causes a decreasing phosphate adsorption to ferric minerals and its release into the pelagic zone. An application of this mechanism to our observed arsenic release and its correlation to nitrate are obvious. With respect to the source of nitrate in our system, this may depend on the nitrate load in the tributary water flows which in turn is a function of nitrogen release in the catchment area. Regarding the high deposition rates in the past (Zimmermann et al., 2003), Armbruster et al. (2003) showed nitrogen saturation (Stoddard and Traaen, 1995) for our research area in the period 1995 to 1999 followed by a decrease in nitrogen output. This was caused by reduced deposition and a recovered vitality related increased nutrient retention in the forest stands. Hence, in the past a comparable high nitrate supply of the basin waters may have had beneficial effects on arsenic retention due to elevated nitrate release from the catchment area. Starting in the late 1990s this situation changed to a lower catchment nitrate output.

The oxygen content in the Galgenteich reservoir follows a natural dynamic and shows no correlation to arsenic content (Fig. 3). Dissolved oxygen data in the Altenberg reservoir were recorded in the water column of the hypolimnion. The positive interaction between oxygen and arsenic in the Altenberg reservoir contrasts common knowledge (Rancourt et al., 2001) but can be explained by the artificial aeration (oxygenation) of the water body only in the surroundings of the raw water outlet, which was done to avoid negative redox potentials of the raw water within the water-column. This aeration was done by coarse bubbles above the sediment which results indeed in higher O_2 concentrations in the hypolimnion, but fails to stabilize the redox entirely, which is evident from findings of reduced arsenic species (see Fig. 5 below). Resulting from this, the O_2 concentration data are partially misleading by indicating the above mentioned uncommon positive correlation with arsenic. According to Senn and Hemond (2002) a strong anoxia at the sediment–water–interface is a premise for an arsenic release into the water column. So we have to assume that recorded oxygen contents in the hypolimnetic water column do not reach the sediment water interface in the Altenberg reservoir and the premise of anoxia at the sediment–water–interface is valid for the periods of arsenic concentration increase. Senn and Hemond (2002) showed for the Upper Mystic Lake that nitrate replaces oxygen, resulting in a nitrate concentration control over the iron and arsenic release from lake sediments. The negative correlation of arsenic with nitrate (Fig. 3), as well as the positive correlation with iron (Fig. 3) are indicators for this process in the Altenberg reservoir. Regarding the findings of Senn and Hemond (2004) this iron is expected to occur as colloidal hydrous ferric oxyhydroxides which form surface complexes with the arsenic of the water.

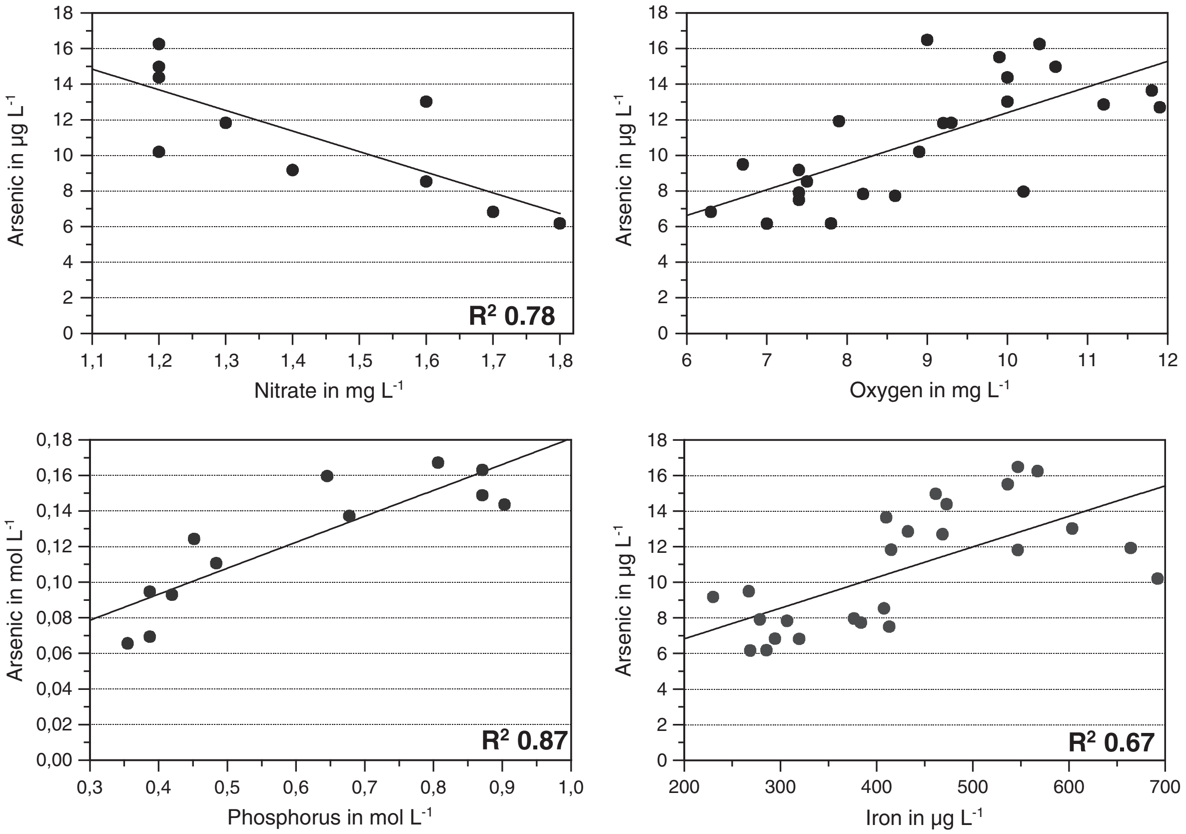

Fig. 4. Correlation between arsenic and nitrate, oxygen, phosphorus and iron in the water of the Altenberg reservoir during 2009, correlation coefficient is shown as R^2.

The speciation of pelagic arsenic of the Altenberg reservoir is presented in Fig. 5. Our results show a coexistence of reduced arsenic species as As^{3+} and dimethylic arsenic acid (DMA) and high oxygen concentrations (Figs. 4 and 5), whereas the main part of arsenic exists as As^{5+}. This is in contrast to other findings (Gao et al., 2007; Hollibaugh et al., 2005; Oremland and Stolz, 2003) showing that As^{3+} is not coexisting within higher oxygen levels. This discrepancy can be explained by a limited water residence time within the re-oxygenated area, the kinetic control of the As^{3+} oxidation process (Johnson and Pilson, 1975). Additionally, a stabilizing influence to reduced arsenic species due to the high DOC concentrations, which may be under respirative decomposition, may be proposed.

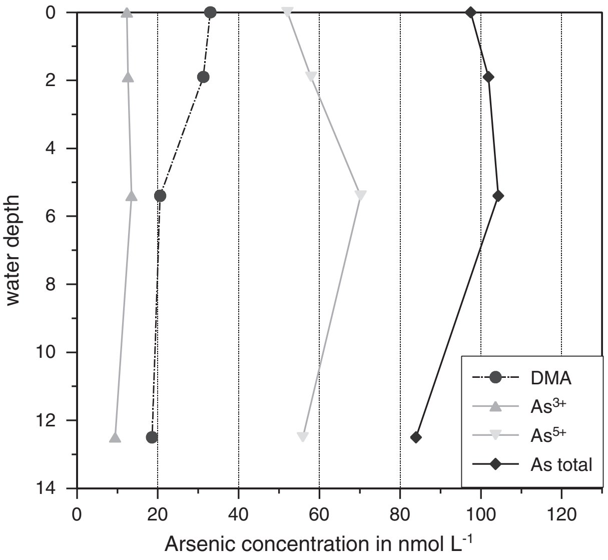

Fig. 5. The vertical distribution of arsenic species in the pelagic water of Altenberg reservoir at the end of September in 2010. DMA = dimethylarsinic acid.

A further arsenic compartment of the system is given with the seepage waters of the Galgenteich reservoir, reaching the Altenberg reservoir via dam seepage. High arsenic concentrations (max: 160 µg L^{-1}) strongly correlate with iron (R^2 0.7) in these waters. A respiratory dissolution of arsenic containing ferric oxide phases can be assumed as the source process. Along the 200 m open transfer path to the inflow into the Altenberg reservoir most of As and Fe precipitate (data not shown). The As enters the reservoir mostly bound to ferric oxide particles.

3.2. Arsenic content in the sediments of the reservoir system and the interaction with other elements

The sediments of both reservoirs were sampled considering historical (constructional) changes (Galgenteich reservoir) and the tributary inflow as well as the runoff outflow structure (Altenberg reservoir) of the reservoir system (Fig. 1). For the Galgenteich reservoir a strong difference in arsenic content between the old and the new part could be observed (Fig. 6a), with higher contents in the younger and deeper part of the basin. Furthermore, the same pattern as shown for arsenic was proven for iron, resulting in a high correlation (R^2 0.92) between both elements in the sediments (Fig. 6b,d). The common explanation for this high correlation coefficient is the strong binding of arsenic to iron (Bauer and Blodau, 2006; Islam et al., 2004). In addition, a higher carbon content in the sediments of the newer part of the Galgenteich reservoir was verified, with at the same time high correlation to arsenic (R^2 0.92) (Fig. 6c,d). This could be explained by the high adsorption capacity of the organic matter for arsenic with special focus on biofilms (Schaller et al., 2010a,b) especially at the sediment water interface. The higher carbon and iron contents in the deeper part of the reservoir

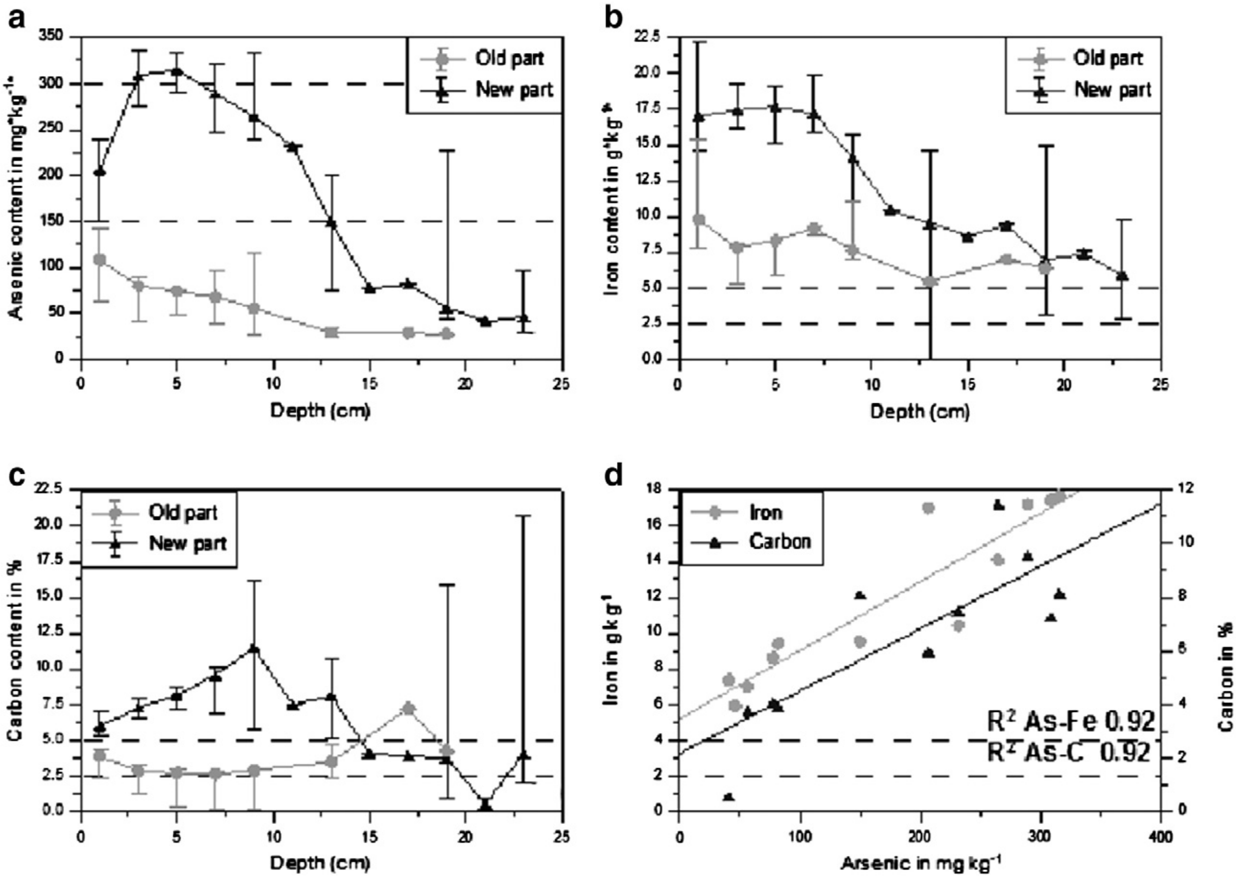

Fig. 6. Contents of arsenic, iron and carbon in the sediments of the older and the newer part of the Galgenteich reservoir. Panel d shows the correlation of iron and carbon with arsenic of the sediments of the newer part of Galgenteich reservoir.

may be due to the fine-grained character of particulate organic and ferric matter, which is formed in the water column via microbial growth and flocculation and shows a quite low sedimentation velocity. According to Håkanson and Jansson (2002) an accumulation of such fine-grained material is preferred in deep basin ranges, whereas shallow basin ranges are more dominated by quick sinking coarse mineral particles.

For the Altenberg reservoir an increasing arsenic content within the sediments was determined along a longitudinal transect (Fig. 7a) beginning from dam to the inlet of the arsenic containing seepage water (see above). The survey emphasizes the role of seepage waters as point sources with drastically elevated arsenic contents in the 'estuary' area. But outside this range the sediment arsenic content tends to follow a quite homogenous distribution, including also the northern part of the reservoir. An exceptional situation was found at the inflow area of the Paradiesstollen tributary (Fig. 7b) with a high arsenic sediment content compared to a low equilibrium concentration in the aqueous phase. This could be explained by the significant higher nitrate concentration ($p<0.01$) of the Paradiesstollen tributary, which in turn may stabilize the redox state of the upper sediment layer (Nealson and Saffarini, 1994), followed by an increased adsorption activity of ferric minerals (Kleeberg and Dudel, 1997). An arsenic stock approximation from core sampling data revealed a range of about 2 tons in Galgenteich

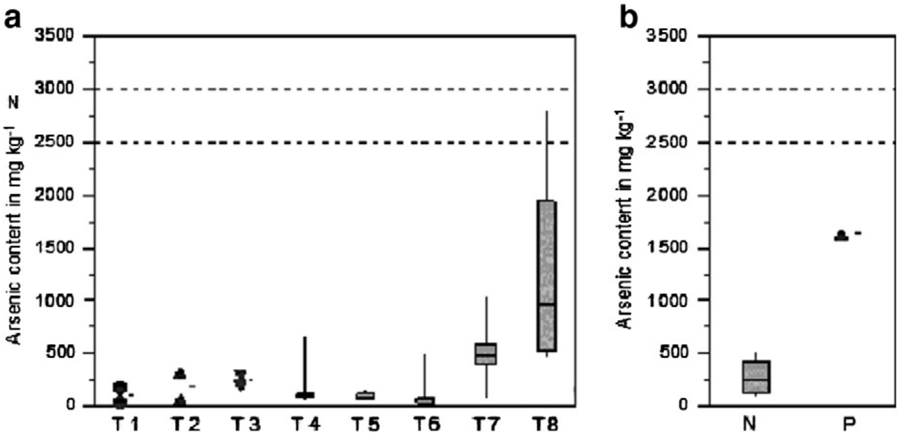

Fig. 7. Arsenic contents in sediments in the different parts of the Altenberg reservoir (T = transect, N = Northern part, P = Paradiesstollen inflow).

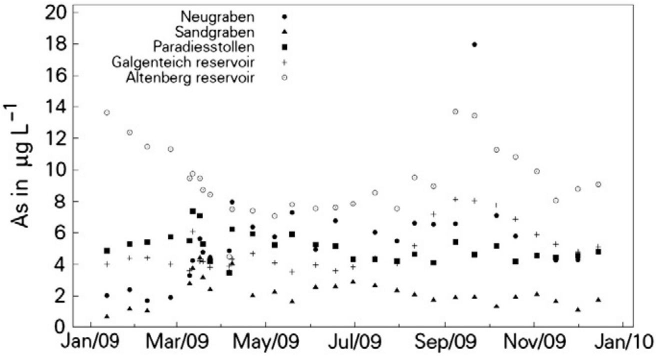

Fig. 8. Arsenic concentrations in the tributaries Neugraben, Sandgraben and Paradiesstollen, and in both parts of the Altenberg reservoir system during 2009.

reservoir and 1 ton in SPA with approximately 100 to 200 kg in the uppermost (2 cm deep) layer representing an arsenic stock near the sediment water interface.

3.3. Arsenic fluxes within the reservoir system

The arsenic concentration of the (downstream) Altenberg reservoir was nearly always higher compared to its tributaries and the Galgenteich reservoir (Fig. 8) in 2009. This implies that the Altenberg reservoir acts as a source for arsenic. The mass balance approach for the year 2009 (annual loads) revealed a clear source character for arsenic of the Altenberg reservoir system (Fig. 9). Half of the internal arsenic mobilization is explained by inflowing dam seepage waters of the predam (seepage water: 2.86 kg As, detailed data not shown). The remaining part of the internally mobilized arsenic is explained by a release from upper sediment layers, which may be remobilized by the microbial decomposition of organic matter from the sediments resulting in a lower redox potential at the sediment water interface and, thus, a destabilization of ferric sorption phases (Beck et al., 2008; Bellanger et al., 2004; Sun et al., 2002; Varsanyi and Kovacs, 2006). A redox mediated control is indicated by the negative correlation of arsenic with the nitrate content (Figs. 2, 3) as discussed above. Compared with the arsenic inventory in the sediment as shown above, such annual releases may be perpetuated for decades.

4. Conclusion

The concentration and flux patterns in the oligotrophic Altenberg reservoir system demonstrate the dependence of the arsenic storage and release behavior from hydrochemical conditions in the catchment area. In previous decades, an enhanced arsenic storage capability of the site may had been induced by nitrate availability in the tributary water fluxes due to deposition related nitrogen saturation in the watershed. As the environmental conditions of the forest ecosystems in the catchment area have been improving, the nitrate availability in the system has decreased, followed by an increasing arsenic release from sediments into water. We assume that this trend will continue with a rising arsenic load of the raw water for tap water production and rising technical efforts for the compliance of produced drinking water with threshold regulations.

Acknowledgments

The experimental studies were funded by the State Reservoir Administration of Saxony (LTV). We thank the staff of the labs at Paulsdorf and Tharandt for sampling and analysis. Special thanks go to Dr. Gunter Ilgen (BayCEER, Bayreuth, Germany) for speciation analysis.

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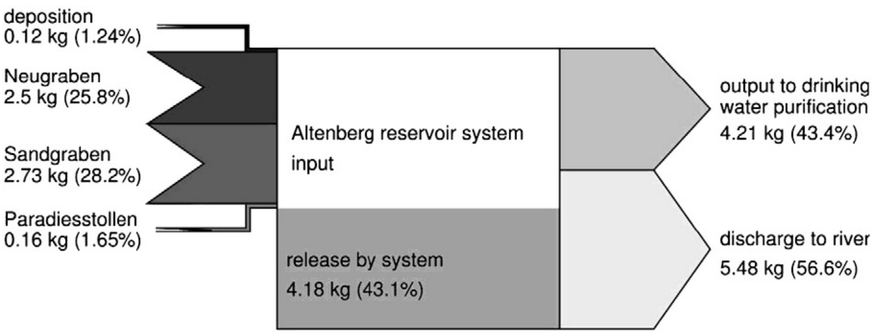

Fig. 9. Annual arsenic loads in input and output water flows of the Altenberg reservoir system during the year 2009 (as total masses in kg and % of the entire arsenic output).

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