



## Research papers

## Arsenic in solution, colloidal and particulate phases of East-Hainan estuaries

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## ABSTRACT

During two nominal dry seasons (December 2006, March 2009) and two wet seasons (July 2007, July/August 2008) the estuarine distribution and size speciation of arsenic was studied in the Wanquan river and the Wenchang/Wenjiao river estuaries, located in tropical East-Hainan (China). Arsenic in solution and in colloidal fractions was analyzed by anodic stripping voltammetry after oxidative UV digestion thereby including inorganic As(III) and As(V) as well as organic As forms. Particulate As was determined by high-resolution ICP-MS after a microwave assisted total decomposition protocol. Taking the two relatively similar estuaries and the two expeditions for each season together, the average concentrations of total dissolved As ( $< 0.4 \mu\text{m}$ ; td-As) of the freshwater endmember were 4.4 nM and 7.6 nM during the dry and the wet seasons, respectively, which suggests a low – if ever – level of contamination. With one exception (uptake by phytoplankton in the lower estuary), during the dry season td-As increased essentially conservatively along the salinity gradient to 14.4 nM as the mean value for salinities of about  $S=30$ . During the wet seasons, however, td-As only showed a tendency for a conservative increase; scatter in the data was attributed primarily to heavy rain and side inputs of variable As concentrations from overflowing aquaculture ponds and piles of excavated soil. The separation of colloidal fractions revealed that on average 82% of td-As remains in solution ( $< 5 \text{ kDa}$ ), followed by 13% in small colloids (5 kDa to 30 kDa) and 5% in large colloids (30 kDa– $0.4 \mu\text{m}$ ). Particulate As ( $0.24 \pm 0.06 \mu\text{mol/g}$ ) showed no dependence on either salinity, suspended particles, estuary or season. Relatively high distribution coefficients ( $\log K_D=4.48\text{--}4.81$  in the freshwater;  $\log K_D \sim 4.18$  at high salinities) arose primarily from the very low td-As. Except for certain impacts from aquaculture ponds, the two estuaries might be considered uncontaminated with respect to As.

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## 1. Introduction

Due to widespread pollution of drinking and groundwater by arsenic in several countries, especially in South and Southeast Asia (see for a review: Fendorf et al., 2010; Henke, 2009), and due to the toxicity of As (e.g., Sharma and Sohn, 2009), its distribution and behaviour has recently been investigated in numerous studies. However, there is no generally accepted explanation scheme for the controlling processes. In oxic natural waters total dissolved As (td-As) occurs primarily in inorganic forms, with pentavalent As being the most stable form (at  $\text{pH} \sim 8$ :  $\text{HAsO}_4^{2-}$ ) but with significant contributions from metastable As(III); organic

forms comprise predominantly monomethylarsonic acid and dimethylarsinic acid, which are likely produced by phytoplankton to mitigate toxicity stress (Andreae, 1978; Henke and Hutchinson, 2009; Sharma and Sohn, 2009).

Size speciation of a trace constituent in natural waters and the distinction between the solution, colloids and particles is important to various environmental questions, including those concerning the cycling of vital or toxic trace chemicals and especially their transport properties (Doucet et al., 2007). In addition, for essential elements like e.g., Fe in marine waters, considerable differences may exist in the bioavailability of soluble versus colloidal forms (Wang and Die, 2003). For transport processes in estuaries, one may anticipate that dissolved and colloid-bound molecules are carried with the moving fluid, while the particles may settle out of a mixed water body to the sediments below (Gustafsson and Gschwend, 1997). Aside from the IUPAC

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definition, that the colloidal size range typically has at least one dimension in the 1 nm to 1  $\mu\text{m}$  size range, while particles are defined as material whose dimensions are  $> 1 \mu\text{m}$ , many other size-based definitions are currently in use, which are essentially operational. At the lower end of the size scale, colloids differ from true solution in that solid-phase materials (1–1000 nm) are dominated by surface properties including surface area and electrical charge (rather than bulk properties such as the chemical composition), while at the upper end (ca. 1  $\mu\text{m}$ ) surface properties become less relevant and gravitational forces begin to exceed forces due to Brownian motion, eventually leading to the settlement of the particles (Lead and Wilkinson, 2007).

Traditionally, physical speciation schemes are operationally defined and separate dissolved ( $< 0.4 \mu\text{m}$ ) and particulate ( $> 0.4 \mu\text{m}$ ) phases by filtration. More recent work has further divided the dissolved phase into soluble ( $< 1 \text{ kDa}$  or  $< 10 \text{ kDa}$  or even  $< 200 \text{ kDa}$ ) and colloidal (from 1 kDa or from 10 kDa or from 200 kDa to 0.4  $\mu\text{m}$ ) components (de Bettencourt and Andreae, 1991; Bauer and Blodau, 2009; Guo et al., 2011; Pokrovsky and Schott, 2002; Schlosser et al., 2008; and literature therein). To calculate the fluvial input of As to the ocean, it is important to understand the behaviour of As in the estuaries, where the net result of the reactions decides whether truly dissolved and colloidal forms may reach the ocean or whether the aqueous constituent is converted to particulate forms with may settle to the sediment. Thus, estuarine biogeochemical processes may act as a filter for fluvial components on their way to the coastal sea (Chester, 2000).

While coastal ocean waters have a relatively constant concentration of total dissolved As (13–25 nM: Cullen and Reimer, 1989; Cutter and Cutter, 1998; Matschullat, 2000), riverine As globally and in China (Ren et al., 2007, 2010) exhibits widely different concentrations ranging from about 0.5 nM (Huron, Tasmania; Featherstone et al., 2004) or 1.7 nM (Krka, Croatia; Seyler and Martin, 1991) in pristine rivers, over 9–21 nM in large European and American rivers, up to 60–600 nM in European rivers with significant pollution (e.g., Andreae et al., 1983; Seyler and Martin, 1990).

Although dissolved As may be influenced by a number of processes (Smedley and Kinniburgh, 2002), including coprecipitation with Fe oxo-hydroxides, diffusion from sediment pore waters, uptake/release due to biological activity, Martin and

Windom (1991) state that conservative mixing between the fluvial and the marine end-member is the most prominent behaviour of As in estuarine systems when summarizing earlier findings in eight estuaries at moderate latitudes. Meanwhile, however, there are numerous studies showing some reactivity of As in the estuarine zone and non-conservative behaviour. Especially seasonal observations or studies of whole annual cycles (e.g., Masson et al., 2009; Vandenhecke et al., 2010) revealed not only that arsenic addition to or removal from solution predominate in a given system, but also that both opposing processes may occur simultaneously, possibly with varying relative intensities along the estuarine salinity range and between different parts of the year. Thus, a high probability of conservative behaviour with small effects of estuarine reactions may not only be restricted to estuaries where relatively uncontaminated river water mixes with seawater of much higher As concentration (Martin et al., 1993); it may be further required that the following processes are low or absent: dissolved iron flocculation, phytoplankton production, high turbidity and/or release of As from sediment pore water.

In the present study we investigate the distribution of td-As, particulate As and colloidal As in two shallow estuarine systems of tropical East-Hainan (19.4°N, 110.7°E) in order to contribute to our knowledge about the size speciation and distribution of As in tropical estuaries, where data are scarce, and to examine the pollution state of these two estuaries with respect to arsenic.

## 2. Material and methods

### 2.1. Study area

The estuarine parts of the Wanquan River and the Wenchang/Wenjiao River (Fig. 1) are important estuaries of East-Hainan. They are both located at the northern part of the tropical zone with a humid warm climate. About 80% of the annual rainfall in this region occurs in the period from May to November (Ma et al., 2007). Occasionally, typhoons with heavy rainfall hit the island with dramatic consequences for the input of soil erosion products, and for the levels of nutrients and suspended particles in the estuarine systems (Herbeck et al., 2011). The Wanquan River with a drainage area of 3693 km<sup>2</sup>, a total length of 157 km and a mean annual

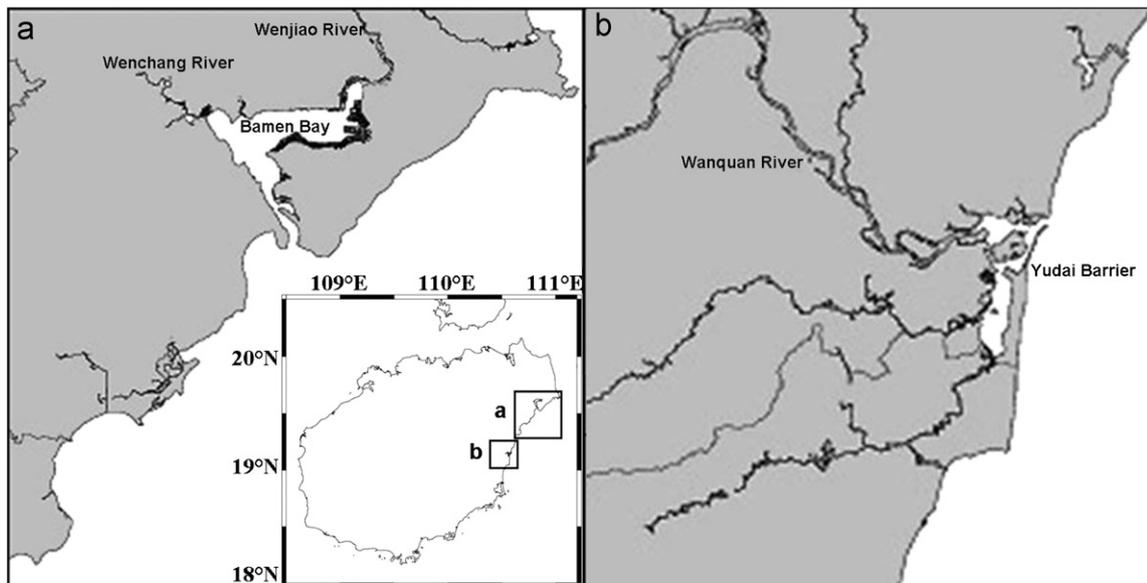


Fig. 1. Estuaries of East Hainan under investigation: (a) Wenchang/Wenjiao river estuary (WWR) and (b) Wanquan river estuary (WR).

discharge of 163.9 m<sup>3</sup>/s, is the third largest river in Hainan Island (Ge et al., 2003; Zhu et al., 2005) and forms the Wanquan River/Boao estuary (in the following: WR). Both the Wenchang River (drainage area 381 km<sup>2</sup>, total length 37 km, mean annual discharge 9.1 m<sup>3</sup>/s) and the Wenjiao River (drainage area 522 km<sup>2</sup>, total length 56 km, mean annual discharge 11.6 m<sup>3</sup>/s) empty into the Bamen Bay (Zeng and Zeng, 1989; Ye, 1988) and form the Wenchang/Wenjiao River estuary (in the following: WWR). Both estuaries have a micro-tidal, irregular diurnal tidal regime with mean range of about 0.7–0.8 m. The salinity intrusion may extend up to 5 km upstream of the Yudai Sand Barrier for the WR and upstream of the entrance to Bamen Bay for the WWR, respectively. The WWR/Bamen Bay is a shallow lagoon region (<2 m; except for the ship channel) with a low flow rate. In the also shallow WR the occurrence and extension of the mixing zone is very dynamic and its position is highly variable due to changes of river discharge, tides and wind. The nutrient regime of the WWR system is characterized by an enrichment of dissolved inorganic nitrogen, a depletion of phosphate and relatively high percentages of organic forms on the total dissolved nitrogen and phosphorus, respectively (Liu et al., 2011). A large part of the whole study area is covered by shrimp and fish ponds with high exports of nutrients and dissolved organic matter to the estuaries (Herbeck et al., this issue).

To cover the main seasonal variability in the estuarine distribution of As and its size speciation, the different forms of arsenic were studied during two nominal dry seasons (December 2006 and March 2009) and during two wet seasons (July 2007, July/August 2008) both in the Wanquan River (WR) and in the Wenchang/Wenjiao River estuary (WWR). While td-As was analyzed for all four expeditions, data on particulate and colloidal arsenic are only available for the dry season 2006 and the wet season 2007.

## 2.2. Sampling and filtration

Directly from the ship, surface water samples were filled by hand into acid-cleaned 1 L polyethylene bottles (Nalgene). Within 20 h they were filtered through 0.4 μm acid-cleaned and pre-weighed polycarbonate membranes (Nuclepore) in the laboratory. A part of this filtrate was acidified with sub-boiled conc. HNO<sub>3</sub> to pH 2, wrapped in plastic bags and stored cold (~8 °C) until analysis.

## 2.3. Ultrafiltration and colloid fractions

After filtration through 0.4 μm pore size, an aliquot (ca. 1 l) of the filtered non-acidified sample was further separated sequentially into different colloidal fractions (of about 130 mL) by cross-flow ultrafiltration at a pressure of ~2 bar (Masterflex peristaltic pump). By using polyethersulfone membrane cartridges (Vivaflow 200 cross flow system; surface area: 200 cm<sup>2</sup>; Sartorius, Göttingen, Germany) with nominal pore sizes of 30,000 Da and 5000 Da, two retentates and one permeate were obtained representing the size fractions (i) large colloids (0.4 μm to 30 kDa), (ii) small colloids (30 kDa to 5 kDa), and (iii) solution (permeate < 5 kDa), respectively. Employing the membrane cartridge with the 30 kDa cut-off firstly, the filtrate <0.4 μm was separated into ca. 870 mL permeate (< 30 kDa) and ca. 130 mL retentate (> 30 kDa). Then, by using the membrane cartridge with the 5 kDa cut-off, the permeate < 30 kDa was separated into a new permeate < 5 kDa and a retentate (ca. 130 mL) containing the fraction from 30 kDa to 5 kDa. The colloidal fractions were collected in acid-cleaned polyethylene bottles and were treated as described before for the filtrate < 0.4 μm. During the expedition in 2007 an additional fraction was obtained: by using a membrane with nominal pore sizes of 10,000 Da the fraction of the small colloids (30 kDa to 5 kDa) was

further separated (sequentially) into a fraction from 30 kDa to 10 kDa and an additional fraction from 10 kDa to 5 kDa. Before initial use the ultrafiltration membrane cartridges were cleaned by flushing with 1% hydrochloric acid (30 min), 20 mM EDTA solution (30 min) and Milli-Q water (in between and at the end), at a pressure of ~2 bar.

The ultrafiltration procedure was conducted within 20 hours after sampling. During a companion project in tropical blackwaters (in Indonesia), four samples from the same station were filtered and separated by this ultrafiltration method into a permeate (< 5 kDa) and a retentate (> 5 kDa and < 0.4 μm). The relative standard deviations for the groups (n=4) of the original filtrates, of the permeates and of the retentates, respectively, were all below 7%. The sum of the permeate and the retentate concentration corresponded to 92.4% of the original sample (relative standard deviation: 6.2%). In the Hainan samples of this study, however, two or even three (in 2007) sequential ultrafiltration steps were performed with cumulating errors (see below).

The analytical ultrafiltration protocols of de Bettencourt and Andrae (1991), Guo et al. (2011) and Pokrovsky and Schott (2002) employing several ultrafiltration membranes with progressively smaller pore sizes are similar in principle. They differ, however, in the choice of the number, the nominal molecular weight cut-offs, the composition and brand of the ultrafiltration membranes, in the ratios of permeate to retentate and in the application of frontal (or dead-end) vs. cross-flow filtration. Thus, direct comparability of results from these studies including the present one cannot be expected.

## 2.4. As determination in solution

All cleaning procedures of filters and sample containers as well as the voltammetric determinations were performed in a clean-air environment of class-100. Unless otherwise stated all chemicals were of "suprapur" grade (Merck) or sub-boiled in our lab. Rinsing and all dilutions were made with Milli-Q water.

### 2.4.1. UV-digestion

To convert methylated As species to inorganic As forms and to destroy organic compounds which may interfere with the voltammetric determination of As (especially in samples possibly enriched with organic colloids), 10 mL sub-samples were treated with UV-radiation (500 W; UV-digester 705, Metrohm) for 135 min, after the addition of 10 μL 5 M hydrochloric acid and 50 μL 30% hydrogen peroxide following Kolb et al. (1992). The quartz tubes for UV-digestion were cleaned in a supersonic bath first with detergent and afterwards with 0.5 M nitric acid for several hours; between uses the tubes were again sonicated and stored in nitric acid. Based on the UV decomposition step preceding all voltammetric measurements, the total dissolved arsenic (td-As) as used in the text is considered to represent the sum of inorganic and organic As species.

### 2.4.2. Voltammetry

Arsenic was determined by anodic stripping voltammetry (DP-ASV) at a rotating gold electrode (2000 rpm; 6.1204.150, Metrohm) following the recommendations of the manufacturer (Metrohm Application Bulletin 226/2e, 2011) of the voltammetric equipment that was used for this study (Metrohm unit VA 694/693). The method (similar to: Prakash et al., 2003) allows to differentiate between the total arsenic concentration (tri- and pentavalent inorganic As) and the As(III) concentration alone by appropriate selection of the deposition potential. Before the first use the working electrode was soaked in 0.1 M NaOH solution and

washed with ethanol and water. The reference electrode was a Ag/AgCl electrode and the auxiliary electrode was a glassy carbon bar. Every day before starting measurements the working electrode was conditioned in 5 M hydrochloric acid. The potential was changed sixteen times between  $-1500$  mV for 30 s and  $+400$  mV for 60 s. When the baseline was higher than  $1 \mu\text{A}$ , the conditioning was repeated. If this was not successful, the gold disc was polished with aluminium oxide. The electrodes which were used for voltammetry were rinsed with Milli-Q water after each measurement. The working electrode and the counter electrode were stored in dilute sub-boiled nitric acid over night. The reference electrode was stored in 3 M potassium chloride.

About 10 g of the samples were weighted into a quartz bin and 10 mL 5 M hydrochloric acid were added. After flushing with nitrogen for 300 s the reductive deposition comprised 60 s at a potential of  $-1200$  mV and 10 s at a potential of 0 mV; this procedure was repeated one time. The current vs. potential graph was recorded with a velocity of 20 mV/s. During standard addition a  $1.3 \mu\text{M}$  arsenic solution was used to approximately double or to triple the sample concentration and the times for reductive deposition were reduced to the half or to one-third of the first measurement, respectively.

To evaluate the merits of the method, firstly, the recovery of both As(III) and As(V) was successfully assured using standard spikes in pure water, in seawater and at three intermediate salinities, including analyses with and without prior digestion (relative standard deviations  $< 6.4\%$ ). Three sample sets of freshwater ( $n=22$ ), estuarine water ( $n=10$ ) and deep open ocean water ( $n=5$ ) revealed precisions between 6.4% and 6.8%. The limit of detection ( $3\sigma$ ) was 0.44 nM, as derived from the standard deviation (0.15 nM,  $n=15$ ) of Milli-Q water, which was subjected to the UV-digestion as described before.

Three Certified Reference Materials (CRM) from the National Research Council of Canada were analyzed at least in triplicate: the river water SLRS-5, the estuarine water SLEW-3 (salinity  $S=15$ ) and the coastal water sample CASS-4 ( $S=30.7$ ). The average values for SLEW-3 and CASS-4 (with and without prior digestion) were all within the certified ranges. The results for the river standard SLRS-5, however, were outside the certified range. The deviation is probably due to the high concentration of copper in SLRS-5 ( $17.4 \pm 1.3 \mu\text{g/L}$ ), because Cu at higher levels is well known to interfere with voltammetric measurement of arsenic (e.g., Salaün et al., 2007; Xiao et al., 2008). Since the Cu concentration of the riverine, estuarine and coastal samples from Hainan were much lower (between  $0.2 \mu\text{g/L}$  and  $2.5 \mu\text{g/L}$ ; see: Fu et al., submitted), the use of the river CRM SLRS-5 was considered inappropriate for this study.

### 2.5. As determination in suspended particles

Suspended particles were collected on  $0.4 \mu\text{m}$  polycarbonate filters (47 mm; Nuclepore), which were pre-cleaned by immersion in diluted sub-boiled  $\text{HNO}_3$  for several days and multiple rinsing with Milli-Q water. Both empty and loaded filters were dried under a clean bench and over conc.  $\text{H}_2\text{SO}_4$  for several days. The weight was determined at least threefold with one day storage over conc.  $\text{H}_2\text{SO}_4$  in between. After weighing, the filters with the suspended particles from the  $0.4 \mu\text{m}$  filtration were subjected to a microwave-assisted total decomposition technique in sealed PTFE vessels (MWS-1200 mega microwave digestion system with HPR1000-6 rotor; MLS, Leutkirch, Germany). The main destruction step involved a radiation power of up to 600 W after adding a mixture of concentrated nitric, hydrochloric, perchloric and hydrofluoric acid (sub-boiled or suprapure grade). This step was preceded by a treatment with only nitric acid under modest microwave radiation in order to largely destroy the polycarbonate

matrix of the filters (for further details, see Schüssler et al., 2005). The arsenic concentrations were determined by high resolution ICP-MS (Element 2; Thermo Scientific) in the high resolution mode. To ensure the validity of the method, the certified reference material MESS-1 (marine sediment) from the NRCC was analyzed for As; all results ( $n=3$ ) were found to be in the recommended range.

## 3. Results and discussion

### 3.1. Environmental settings of the Wanquan and Wenchang/Wenjiao estuary

The concentrations of the suspended particulate matter (SPM) were similar in the two estuaries and were essentially constant over the whole salinity profile. However, they differed considerably between the seasons: taking the two estuaries together, average values of the SPM for the wet seasons 2007 and 2008 and for the dry season 2006 were 2.3 mg/g, 2.0 mg/g and 9.8 mg/g, respectively (Fu et al., submitted). It is not clear to what extent the higher values during the dry season resulted from reduced dilution or from enhanced resuspension in these relatively shallow estuaries.

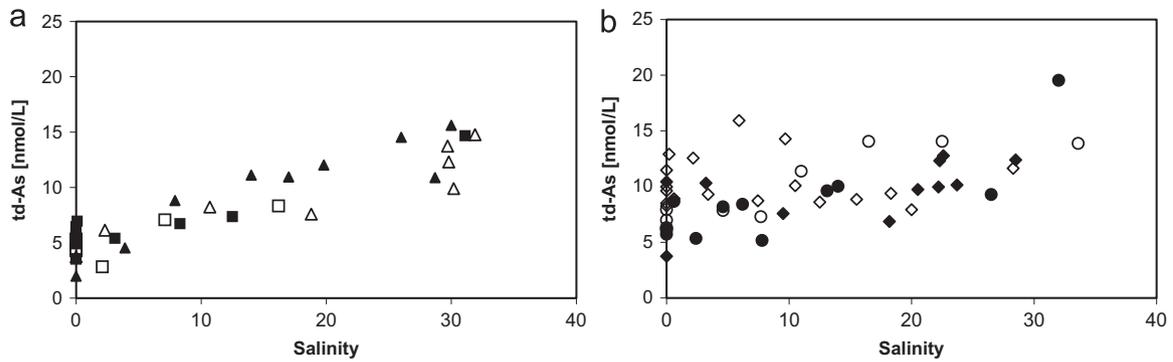
The dissolved organic carbon (DOC) content generally showed a slight decrease with salinity from mostly 2–4 mg/L in the freshwater region to about 1 mg/L at salinities of ca.  $S=30$ . The only exception from these observations in the two estuaries (Fu et al., submitted) was the considerably higher concentration of 4–7 mg/L during the wet season 2008 in WWR, possibly being due to side inputs from the banks, including overflows from adjacent aquaculture ponds via small channels (Herbeck et al., this issue; see: below).

During both wet seasons and in both study areas dissolved Fe decreased from about  $5 \mu\text{mol/L}$  in the riverine water to typically  $0.1\text{--}0.2 \mu\text{mol/L}$  close to the coast with  $S\sim 30$ , except for the two times higher concentration of riverine and low salinity dissolved Fe in the WWR in 2008. Although the concentration of dissolved Fe in both estuaries during the dry season in 2006 was much lower than during both wet seasons, the same pattern was observed: a decrease from  $0.24 \mu\text{mol/L}$  to  $0.01 \mu\text{mol/L}$  in the WR and from  $0.44 \mu\text{mol/L}$  to  $0.04 \mu\text{mol/L}$  in the WWR (Fu et al., submitted). Being nearly identical during both seasons particulate Fe in WR decreased from about  $1.2 \mu\text{mol/g}$  in the freshwater to  $0.7 \mu\text{mol/g}$  at high salinities, while WWR showed two times higher values at lower salinities ( $S=0\text{--}20$ ), respectively.

During the four expeditions the pH in the two estuaries increased from  $\text{pH } 7.4 \pm 0.5$  in the freshwater region with increasing salinity (especially in the zone  $S=0\text{--}10$ ) to about 8.0 at salinities of  $S\sim 30$ .

### 3.2. Dissolved As in the Wanquan and Wenchang/Wenjiao estuary

The average freshwater td-As concentration (including some upstream river samples) of the two estuaries during the dry seasons (Fig. 2(a)) was  $4.8 \pm 1.3 \text{ nM}$  ( $n=11$ ) and during the wet seasons  $7.6 \pm 2.2 \text{ nM}$  ( $n=17$ ), respectively, with about 23% higher values in WWR as compared to WR. The mean td-As concentration of all samples with zero salinity was  $6.3 \pm 2.3 \text{ nM}$  ( $n=28$ ). Depending on the geological settings of the hinterland, rivers having 11 nM (Andreae et al., 1983) or 27 nM in the Huang He draining loess deposits (Huang et al., 1988) were considered uncontaminated; river concentrations of only 1.7 nM Arsenic as found in the Krka estuary (Yugoslavia; Seyler and Martin, 1991) or even 0.31–0.76 nM in the Huon estuary (Featherstone et al., 2004) suggest pristine environmental conditions. By comparison



**Fig. 2.** Dissolved arsenic ( $0.4 \mu\text{m}$ ) vs. salinity: (a) dry season: Wanquan river estuary, 2006 (open squares) and 2009 (solid squares); Wenchang/Wenjiao river estuary, 2006 (open triangles) and 2009 (solid triangles), (b) wet season: Wanquan river estuary, 2008 (open circles) and 2007 (solid circles), Wenchang/Wenjiao river estuary, 2008 (open diamonds) and 2007 (solid diamonds).

with large contaminated estuaries of e.g., France (8.8–50 nM; Seyler and Martin, 1990), or in England (e.g., 175–208 nM in the Humber river, Kitts et al., 1994; 28–98 nM in the Thames plume, Millward et al., 1997b), the td-As values of the WR and WWR suggest a small – if ever – anthropogenic impact. The td-As in the three Hainan rivers are also lower than the concentration of the numerous Chinese river/estuary systems which were compiled by Ren et al. (2007; 2010).

The average of all coastal and estuarine samples with a salinity  $S \sim 30$  was  $14.4 \pm 2.8 \text{ nM}$  ( $n=7$ ) and are at the lower end of the typical uncontaminated world seawater concentration (13 nM to 25 nM; Cullen and Reimer, 1989; Matschullat, 2000; Smedley and Kinniburgh, 2002), although Santosa et al. (1994) reported for the sum of inorganic and organic As species in the China Sea a lower average conc. of only 8.2 nM.

During the dry season, td-As shows a similar and essentially conservative distribution at least to mid-salinities in both estuaries and during both expeditions (Fig. 2(a)) thereby excluding significant contributions from addition or removal processes in the upper estuaries. The only exception from the dilution line is the behaviour of As in WWR during the dry season 2006. This depletion of td-As in the lower estuary closely resembles the distribution in the lower Huon estuary during summer which was ascribed to biological activity, i.e., to phytoplankton uptake (Featherstone et al., 2004). It is likely that also the As removal at high salinities in WWR resulted from biological uptake with the inflowing seawater.

During the rainy season, however, there was only a tendency for an increase towards the sea. Instead, considerable scatter in the td-As data is seen along the salinity profile of the estuarine mixing zone (Fig. 2(b)) which might arise from chemical reactivity and/or from advection. In comparison to the dry seasons there was no indication for enhanced addition due to desorption from inorganic particles or due to increased pore water fluxes originating from (shallow) surface sediments turning to suboxic or anoxic conditions. Because the scatter in the data is spread over the whole salinity range from  $S=0$  to 30, also removal by concomitant Fe(III) oxo-hydroxide flocculation or precipitation at elevated levels is not likely, which occurs predominantly at very low salinities (Fu et al., submitted). The only internal reaction which cannot be ruled out, but is unlikely to show such variability on short distances over the whole salinity range, is biological activity which is known to remove As from solution during phytoplankton primary production (e.g., Featherstone et al., 2004) or to release As during organic matter degradation (Michel et al., 2001).

On the other hand, several factors may contribute to variable advection of dissolved As: firstly, as indicated by higher and more variable freshwater concentrations during the wet seasons, the higher rain rate enables more contact with adjacent soil and with

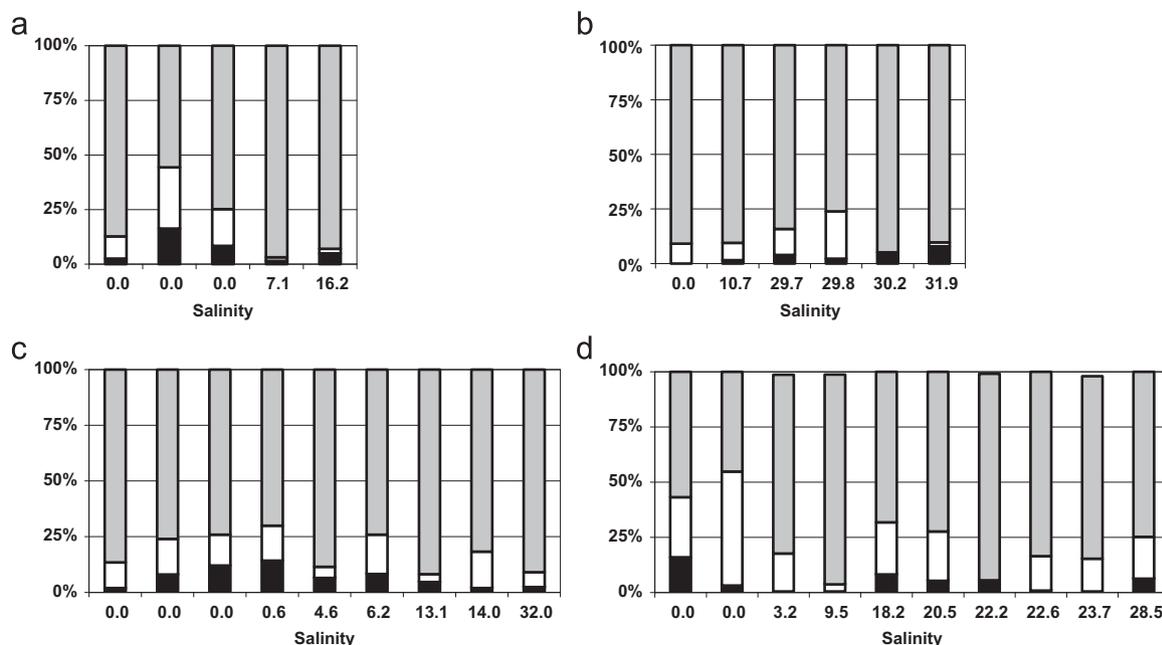
piles from excavation of the aquaculture ponds and may mobilise into solution the adsorbed As which has accumulated during previous months and the soluble As originating from the degradation of organic materials on land. Secondly, the waters of the overflowing aquaculture ponds (especially in WWR) may be enriched in As originating from high loadings of fertilizer and other materials (Herbeck et al., this issue). A sample from a shrimp pond with a salinity of  $S=21.7$  had exceptionally high values of td-As (29.1 nM) and of DOC (16.8 ppm). In addition, during the expedition in August 2008 a typhoon moved through the area and heavy rain may have washed even more As into the estuarine waters from the small side tributaries and over the aquaculture pond dikes (Herbeck et al., 2011). After a typhoon Li et al. (2002) observed largely enhanced dissolved inorganic arsenic concentrations in surface seawater of the Jiulongjiang estuary and the Xiamen Harbour lasting for at least ten days. Because both estuaries of this study are shallow and have only low volumes, the sporadic side input may entail locally relatively large concentration changes. Thus, side input from the numerous aquaculture basins and from small creeks combined with the higher fluvial concentration during the wet season (Fig. 2(a) and (b)) probably has the largest influence on the heterogeneous increase of td-As towards the coastal sea.

Except for removal of As by phytoplankton uptake in the estuarine high salinity region, it appears that As essentially behaves conservatively, which is probably due (Martin et al., 1993) to a low level of contamination in the fluvial source and the apparent absence of larger impacts from dissolved iron flocculation, high turbidity in the water and pore water release, respectively.

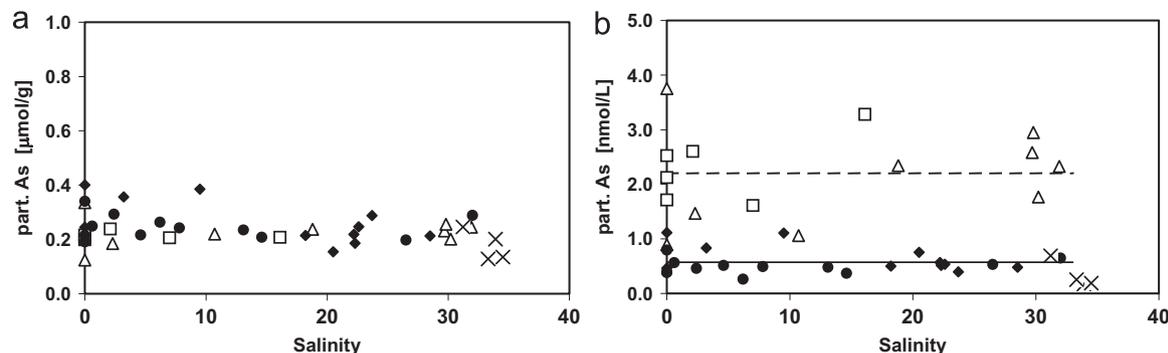
### 3.3. Colloidal As in the Wanquan and Wenchang/Wenjiao estuary

In Fig. 3 the cumulated arsenic percentages of the large colloids (nominal fraction from  $0.4 \mu\text{m}$  to 30 kDa), the small colloids (nominal fraction from 30 kDa to 5 kDa), and the solution (nominal fraction below 5 kDa) are plotted with increasing salinity on the x-axis for the dry season 2006 and the wet season 2007 in the two estuaries. In 2007 the small colloid fraction (30 kDa to 5 kDa) was further separated into two nominal fractions from 30 kDa to 10 kDa and from 10 kDa to 5 kDa, which did not provide additional information (results not shown). Because the calculation of the different fractions from sequential separation entails an accumulation of individual errors of the different fractions, only those samples are depicted in Fig. 3 in which the sum of the concentration of the individual fractions were in the range from 70 to 130% of the As concentration of the unseparated filtrate, thereby excluding 7 of the 37 samples.

Since the bar graphs of Fig. 3(a)–(d) show no tendency in either fraction percentage, salinity dependence, estuary (WR vs.



**Fig. 3.** Colloidal arsenic as cumulated percentages in three size fractions: from 0.4 μm to 30 kDa (black), from 30 kDa to 5 kDa (white) and smaller than 5 kDa (grey); (a) dry season 2006 in Wanquan river estuary, (b) dry season 2006 in Wenchang/Wenjiao river estuary, (c) wet season 2007 in Wanquan river estuary, (d) wet season 2007 in Wenchang/Wenjiao river estuary. Stations are arranged according to increasing salinity.



**Fig. 4.** Particulate arsenic vs. salinity, (a) composition (w/w) and (b) concentration (w/v); dry season: Wanquan river estuary 2006 (open squares) and Wenchang/Wenjiao river estuary 2006 (open triangles); wet season: Wanquan river estuary 2007 (solid circles) and Wenchang/Wenjiao river estuary 2007 (solid diamonds); coastal seawater (crosses). The broken and the solid lines represent the average particulate As per volume during the dry and the wet season, respectively (excluding the coastal values).

WWR) or season, the average percentages were calculated for the individual fractions. Obviously, most As resides in the solution (fraction < 5 kDa:  $81.8 \pm 4.7\%$  on average), followed by the small colloids (fraction from 5 kDa to 30 kDa:  $13.0 \pm 4.7\%$ ), and the lowest contribution was observed for the large high molecular weight colloids (fraction from 30 kDa to 0.4 μm:  $5.3 \pm 1.7\%$ ). The solution (< 5 kDa) as the most abundant fraction of td-As contains “truly dissolved” inorganic and organic As monomers as well as the arsenic in association with relatively small macromolecules. This is in close agreement with observations of Guo et al. (2011) who found that 55–80% of As in the 0.4 μm filtrates remain in the ultrafiltrates < 5 kDa, when comparing filtrates (0.4 μm) and ultrafiltrates (< 5 kDa) of groundwater of the Hetao basin (Inner Mongolia). In both the marine and freshwater end-member of the Beaulieu estuary, As appears to be in true solution passing through ultrafiltration membranes having a nominal 0.5 kDa cut-off (Howard et al., 1984). During an early study of colloidal arsenic in the Ogeechee river estuary, Waslenchuk and Windom (1978) concluded that As was partly associated with light DOC (> 2 kDa, < 10 kDa), because As was depleted (with respect to the 0.4 μm filtrate) in the ultrafiltrates which have

passed through a membrane with 2 kDa cut-off, but no depletion was observed when applying a membrane with 10 kDa cut-off. Applying ultrafiltration (< 100 kDa, < 10 kDa, < 1 kDa) to water samples from small NW Russian estuaries Pokrovsky and Schott (2002) suggested that arsenic was mainly present in the form of truly dissolved inorganic species and that it was not associated with any of the two pools of colloids composed of organic-rich and Fe-rich particles. Studying the distribution of As in different size fractions of experimental solutions, Bauer and Blodau (2009) also found the majority of total As ( $93 \pm 2\%$ ) in the dissolved size fraction < 5 kDa. Thus, despite methodological differences for the separation of colloids, residence in the size fraction < 5 kDa, as observed in this study, appears to be the predominant behaviour of dissolved As in rivers and estuaries.

#### 3.4. Particulate As in the Wanquan and Wenchang/Wenjiao estuary

During both seasons (December 2006 and July 2007) particulate As (w/w) shows equal, essentially constant distribution profiles with salinity (Fig. 4(a)). The only exception are a few slightly higher values in upstream river waters and some lower values in coastal

waters. The latter is probably due to dilution with freshly produced biogenic particles (low in As) as inferred from the much higher Ca content of the coastal samples ( $S > 30$ ). The average As content of  $0.24 \pm 0.06 \mu\text{mol/g}$  ( $n=38$ ) is six times higher than the As value for the continental crust of Eastern China ( $0.04 \mu\text{mol/g}$ ; Gao et al., 1998), but well within the range for uncontaminated marine sediments ( $0.07\text{--}0.53 \mu\text{mol/g}$ ; Henke, 2009). This average is slightly higher than in the main channel of the Changjiang, where Yao et al. (2007) found particulate As in the range from  $0.09$  to  $0.24 \mu\text{mol/g}$ .

Other studies of particulate arsenic often show higher variability along the estuarine salinity gradient at widely differing concentration levels: (i) for the freshwater part of three large French rivers Seyler and Martin (1990) report highly variable particulate arsenic concentrations in the range from  $9.6 \mu\text{g/g}$  to  $47.2 \mu\text{g/g}$  ( $0.13 \mu\text{mol/g}$  to  $0.63 \mu\text{mol/g}$ ) being affected by anthropogenic inputs and a decrease along the profiles to high salinities near the coast, which is at least partly due to the admixture of marine particles with a lower As content; (ii) in contrast, the particulate arsenic concentrations in the Seine estuary were systematically higher in estuarine ( $0.4 < S < 30$ :  $0.21 \mu\text{mol/g}$ ) than in fresh waters and increased in the salinity range from  $S=0.4$  to a maximum of particulate As at  $S \sim 25$  (Michel et al., 1999); (iii) without notable differences over the seasons De Gieter et al. (2005) report average particulate As in four zones of the Scheldt estuary to continuously decrease from  $40.8$  to  $17.8 \mu\text{g/g}$  ( $0.54 \mu\text{mol/g}$  to  $0.24 \mu\text{mol/g}$ ), seemingly dominated by dilution processes; (iv) in two branches of the Gironde estuary with an overall average particulate As concentration of  $0.44 \mu\text{mol/g}$  ( $n=96$ ) Masson et al. (2009) observed considerable spatial but the absence of seasonal variability; (v) in the Penzé estuary (NW France) particulate As ranged from  $3.3$  to  $56 \mu\text{g/g}$  ( $0.04\text{--}0.75 \mu\text{mol/g}$ ) with highest values in the upper estuary ( $S=0\text{--}10$ ) and a general decrease towards the coastal sea (Vandennecke et al., 2010); and (vi) in the Humber estuary which receives contaminant input from a metal refinery, Kitts et al. (1994) found in the SPM (1 M HCl digest) a mean particulate As concentration of  $0.69 \mu\text{mol/g}$ . Thus, in contrast to these observations of predominant decreases towards the coast, the As content of the suspended particles of East-Hainan estuaries does not depend on salinity and it may be concluded that there is – if any – only a slight anthropogenic contamination.

While the As content (w/w) of the suspended particles is essentially constant in all samples, the distribution of particulate As per unit volume (w/v) shows a marked difference between the seasons (Fig. 4(b)) which pertains to both estuaries. The particulate As in the freshwater and along the salinity gradient (excluding coastal samples) was on average  $2.20 \pm 0.80 \text{ nmol/L}$  ( $n=15$ ) and  $0.57 \pm 0.22 \text{ nmol/L}$  during the dry and wet season, respectively, which originates from the distinctly different SPM concentration during the two seasons.

Thus, during the dry season the freshwater entering the estuaries contains on average 57% of the arsenic in solution ( $< 5 \text{ kDa}$ ), 13% in colloidal forms ( $> 5 \text{ kDa}$  and  $< 0.4 \mu\text{m}$ ) and 30% in particulate phases ( $> 0.4 \mu\text{m}$ ); the respective percentages for the wet season are 74%, 16% and 10%, respectively, using the same partitioning factor for solution and colloids for both seasons (see above). Because the particulate As is relatively constant over the estuarine salinity range, its percentage on the total arsenic per volume decreases continuously towards the coastal ocean, while the percentages of As in solution and in colloidal forms increase, respectively.

### 3.5. Distribution coefficient of As in the Wanquan and Wenchang/Wenjiao estuary

Defined as the ratio of the particulate concentration (w/w) to the dissolved concentration (w/v), the distribution (or partition) coefficient  $K_D$  is of fundamental significance to geochemical modelling and pollution impact assessment, since the  $K_D$  reflects

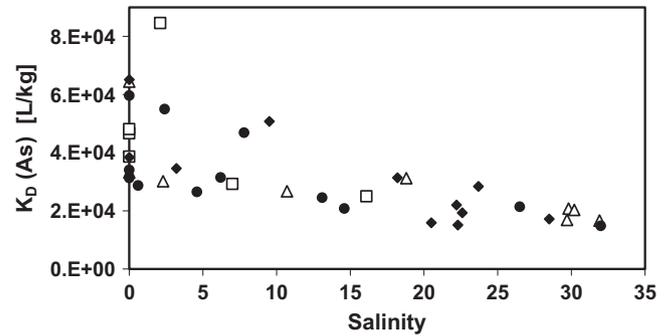


Fig. 5. Distribution coefficient of arsenic vs. salinity; dry season: Wanquan river estuary 2006 (open squares) and Wenchang/Wenjiao river estuary 2006 (open triangles); wet season: Wanquan river estuary 2007 (solid circles) and Wenchang/Wenjiao river estuary 2007 (solid diamonds).

a history of short- and long-term reactions such as adsorption, desorption and precipitation (Turner, 1996).

During the dry and the wet season all  $K_D$  values for As vs. salinity lie in the triangle spanned between ca.  $30 \times 10^3 \text{ L/kg}$  and  $65 \times 10^3 \text{ L/kg}$  in the freshwater, and  $15 \times 10^3 \text{ L/kg}$  at high salinities of  $S \sim 32$  (Fig. 5). Because the particulate As concentration is essentially constant, the  $K_D$  (As) variability results primarily from arsenic in the solution phase, especially in the freshwater influx to the estuary. In contrast to the Seine estuary, where the seasonal variability of the  $K_D$  (As) between  $\sim 8 \times 10^3$  and  $\sim 13 \times 10^3 \text{ L/kg}$  was related to seasonally varying particle composition (Michel et al., 1999), the  $K_D$  values of this study do not correlate with the SPM and in both seasons the  $K_D$  (As) covers essentially the same range. Instead, when plotted vs. SPM (not shown), the  $K_D$  (As) values form two distinct clusters around the average SPM in the two estuaries (dry season:  $9.8 \pm 2.6 \text{ mg/L}$ , wet season:  $2.3 \pm 0.9 \text{ mg/L}$ ). Thus, a “particle concentration effect” sensu Benoit et al. (1994) was not observed during this study, possibly due to the low percentage of colloidal arsenic ( $> 5 \text{ kDa}$  and  $< 0.4 \mu\text{m}$ ) in the filtrates (see above). The same was observed in a study of As in the Gironde, where in two contrasting, highly turbid fluvial branches (removal of As from solution in the Garonne, but As addition in the Dordogne) a distinct  $K_D$  (As) of  $\sim 11 \times 10^3 \text{ L/kg}$  was obtained for SPM concentrations between  $200 \text{ mg/L}$  and  $1500 \text{ mg/L}$  (Masson et al., 2009).

The  $K_D$ 's (As) of this study are higher than most  $K_D$  values from the literature (e.g., Scheldt (Belgium):  $8\text{--}15 \times 10^3 \text{ L/kg}$ , De Gieter et al., 2005; Seine (France):  $6\text{--}12 \times 10^3 \text{ L/kg}$ , Michel et al., 1999; Humber Plume (England):  $2\text{--}25 \times 10^3 \text{ L/kg}$ , Millward et al., 1997a; Thames Plume (England):  $1 \times 10^3 \text{ L/kg}$ , Millward et al., 1997b), with the exception of the Humber estuary (England):  $5.9\text{--}94.3 \times 10^3 \text{ L/kg}$  (Kitts et al., 1994). The main differences to these  $K_D$  values are (i) that the prevailing SPM concentrations in the estuaries from the literature are 1–2 orders of magnitude higher than in Hainan allowing more contact during sorptive equilibration, (ii) that a clear salinity dependence is mostly lacking, thus showing reactions to occur, and (iii) that the often much higher  $K_D$  values from the freshwater zone were not included. Thus, the relatively high  $K_D$  values of this study which generally decrease with salinity appear to result from the comparably high particulate As concentration in combination with a low, more or less conservative distribution of As in solution.

## 4. Conclusions

Investigations during the dry and the wet season in the two East-Hainan estuaries Wanquan and Wenchang/Wenjiao demonstrated:

- the total dissolved As (td-As) in the freshwater with 4.4 nM on average during the dry season and 27% higher values during the wet season are at the lower end of the range observed in Chinese and other rivers of the world, suggesting a low level of contamination;
- in the estuaries td-As showed a conservative increase towards the coastal ocean during the dry season except for some depletion at higher salinities being probably due to biological uptake with the inflowing seawater. However, during the heavy rains of the wet season including a typhoon, the estuarine profile suffered from side inputs of td-As probably originating from overflowing aquaculture ponds and from enhanced leaching of excavated soil piles, which may be considered an anthropogenic impact;
- operationally defined size fractionation from the freshwater parts to the high salinity region of the estuaries showed that the overwhelming percentage of td-As resides in solution (< 5 kDa) with minor contributions of small (5–30 kDa) and larger colloids (30 kDa to 0.4  $\mu\text{m}$ );
- in contrast to most other estuaries of the world, the estuarine systems of East-Hainan revealed a nearly constant composition of the particles with respect to As (0.24  $\mu\text{mol/g}$ );
- the freshwater entering the estuaries contains on average 65% of the arsenic in solution (< 5 kDa), 15% in colloidal forms (5 kDa to < 0.4  $\mu\text{m}$ ) and 20% in particulate phases (> 0.4  $\mu\text{m}$ ); because the particulate As is relatively constant over the estuarine salinity range, its percentage on the total arsenic decreases continuously towards the coastal ocean, while the percentage of As in solution and in colloidal forms increases, respectively.

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## References

- Andreae, M.O., 1978. Distribution and speciation of arsenic in natural waters and some marine algae. *Deep Sea Research* 25, 391–402.
- Andreae, M.O., Byrd, J.T., Froehlich, P.N., 1983. Arsenic, antimony, germanium, and tin in the Tejo estuary, Portugal: modeling a polluted estuary. *Environmental Science and Technology* 17, 731–737.
- Bauer, M., Blodau, C., 2009. Arsenic distribution in the dissolved, colloidal and particulate size fraction of experimental solutions rich in dissolved organic matter and ferric ion. *Geochimica et Cosmochimica Acta* 73, 529–542.
- Benoit, G., Oktay-Marshall, S.D., Cantu, A., Hood, E.M., Coleman, C.H., Corapcioglu, M.O., Santschi, P.H., 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Marine Chemistry* 45, 307–336.
- Chester, R., 2000. *Marine Geochemistry*, 2nd edn. Unwin Hyman, London 698 pp.
- Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. *Chemical Reviews* 89, 713–764.
- Cutter, A.G., Cutter, L.S., 1998. Metalloids in the high latitude North Atlantic ocean: sources and internal cycling. *Marine Chemistry* 61, 25–36.
- de Bettencourt, A.M.M., Andreae, M.O., 1991. Refractory arsenic species in estuarine waters. *Applied Organometallic Chemistry* 5, 111–116.
- De Gieter, M., Elskens, M., Baeyens, W., 2005. Fluxes and major transport routes of arsenic in the Scheldt estuary. *Marine Chemistry* 95, 15–30.
- Doucet, F.J., Lead, J.R., Santschi, P.H., 2007. Colloid-trace element interactions in aquatic systems. In: Wilkinson, K.J., Lead, J.R. (Eds.), *Environmental Colloids And Particles: Behaviour, Separation And Characterisation*. Wiley, Chichester, pp. 95–158.
- Featherstone, A., Butler, E., O'Grady, B., 2004. Seasonal cycling of arsenic species in a stratified, microtidal estuary (Huon River, Tasmania). *Estuaries* 27, 18–35.
- Fendorf, S., Michael, H.A., van Geen, A., 2010. Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. *Science* 328, 1123–1127.
- Fu, J., Tang, X.-L., Zhang, J., Balzer, W., Estuarine modification of dissolved and particulate trace metals in major rivers of East-Hainan, China, submitted.
- Gao, S., Luo, T.-C., Zhang, B.-R., et al., 1998. Chemical composition of the continental crust as revealed by studies in East China. *Geochimica et Cosmochimica Acta* 62, 1959–1975.
- Ge, C., Slaymaker, O., Pedersen, T.F., 2003. Change in the sedimentary environment of Wanquan river estuary, Hainan island, China. *Chinese Science Bulletin* 48, 2357–2361.
- Guo, H., Zhang, B., Zhang, Y., 2011. Control of organic and iron colloids on arsenic partition and transport in high arsenic groundwaters in the Hetao basin, Inner Mongolia. *Applied Geochemistry* 26, 360–370.
- Gustafsson, Ö., Gschwend, P.M., 1997. Aquatic colloids: concepts, definitions, and current challenges. *Limnology and Oceanography* 42, 519–528.
- Henke, K.R. (Ed.), Wiley, Chichester. 569 pp.
- Henke, K.R., Hutchinson, A., 2009. Arsenic chemistry. In: Henke, K.R. (Ed.), *Arsenic: Environmental Chemistry, Health Threats And Waste Treatment*. Wiley, pp. 9–68.
- Herbeck, L.S., Unger, D., Krumme, U., Liu, S.M., Jennerjahn, T.C., 2011. Typhoon-induced precipitation impact on nutrient and suspended matter dynamics of a tropical estuary affected by human activities in Hainan, China. *Estuarine Coastal and Shelf Science* 93, 375–388.
- Herbeck, L.S., Unger, D., Wu, Y., Jennerjahn, T.C. Effluent, nutrient and organic matter export from shrimp and fish ponds causing eutrophication in coastal and back-reef waters of NE Hainan, tropical China. *Continental Shelf Research*, <http://dx.doi.org/10.1016/j.csr.2012.05.006>, this issue.
- Howard, A.G., Arbab-Zavar, S.C., Apte, S.C., 1984. The behavior of dissolved arsenic in the estuary of the river Beaulieu. *Estuarine, Coastal and Shelf Science* 19, 493–504.
- Huang, W.W., Martin, J.M., Seyler, P., Zhang, J., Zhong, X.M., 1988. Distribution and behaviour of arsenic in the Huang He (Yellow River) estuary and Bohai Sea. *Marine Chemistry* 25, 75–91.
- Kitts, H.J., Millward, G.E., Morris, A.W., Ebdon, L., 1994. Arsenic biogeochemistry in the Humber estuary, U.K. *Estuarine, Coastal and Shelf Science* 39, 157–172.
- Kolb, M., Rach, P., Schäfer, J., Wild, A., 1992. Investigations of oxidative UV photolysis I. Sample preparation for the voltammetric determination of Zn, Cd, Pb, Cu, Ni and Co in waters. *Fresenius Journal of Analytical Chemistry* 342, 341–349.
- Lead, J.R., Wilkinson, K.J., 2007. Environmental colloids and particles: current knowledge and future developments. In: Wilkinson, K.J., Lead, J.R. (Eds.), *In Environmental Colloids and Particles*, vol. 10. John Wiley & Sons, pp. 1–16.
- Li, J., Zhen, G.P., Yang, Y.P., Hu, M.H., 2002. Variation characteristics of dissolved inorganic arsenic from surface seawater in Xiamen Harbor during the typhoon 'Bilis'. *Journal of Oceanography in Taiwan Strait* 21, 404–410. (in Chinese, with English abstract).
- Liu, S.M., Li, R.H., Zhang, G.L., Wang, D.R., Du, J.Z., Herbeck, L.S., Zhang, J., Ren, J.L., 2011. The impact of anthropogenic activities on nutrient dynamics in the tropical Wenchanghe and Wenjiaohu Estuary and Lagoon system in East Hainan, China. *Marine Chemistry* 125, 49–68.
- Ma, J.-L., Wei, G.-J., Xu, Y.-G., Long, W.-G., Sun, W.-D., 2007. Mobilization and re-distribution of major and trace elements during extreme weathering of basalt in Hainan Island, South China. *Geochimica et Cosmochimica Acta* 71, 3223–3237.
- Martin, J.H., Windom, H.L., 1991. Present and future roles of ocean margins in regulating marine biogeochemical cycles of trace elements. In: Mantoura, R.F.C., Martin, J.H., Wollast, R. (Eds.), *Ocean Margin Processes in Global Change*. Wiley, Chichester, pp. 45–68.
- Martin, J.M., Guan, D.M., Elbaz-Poulichet, F., Thomas, A.J., Gordeev, V.V., 1993. Preliminary assessment of the distributions of some trace elements (As, Cd, Cu, Fe, Ni, Pb and Zn) in a pristine aquatic environment: the Lena River estuary (Russia). *Marine Chemistry* 43, 185–199.
- Masson, M., Schafer, J., Blanc, G., Dabrin, A., Castelle, S., Lavaux, G., 2009. Behavior of arsenic and antimony in the surface freshwater reaches of a highly turbid estuary, the Gironde Estuary, France. *Applied Geochemistry* 24, 1747–1756.
- Matschullat, J., 2000. Arsenic in the geosphere: a review. *Science of the Total Environment* 249, 297–312.
- Metrohm Application Bulletin 226/2e, 2011. Determination of arsenic by anodic stripping voltammetry at the rotating gold electrode. <http://products.metrohm.com/trace-analysis/prod-AB-226.aspx>.
- Michel, P., Averty, B., Chiffolleau, J.F., Romana, 2001. Biogeochemical behavior of arsenic species in the Seine Estuary in relation to successive high-amplitude primary production, anoxia, turbidity, and salinity events. *Estuaries* 24, 1066–1073.
- Michel, P., Chiffolleau, J.F., Averty, B., Auger, D., Chartier, E., 1999. High resolution profiles for arsenic in the Seine estuary. Seasonal variations and net fluxes to the english channel. *Continental Shelf Research* 19, 2041–2061.
- Millward, G.E., Kitts, H.J., Ebdon, L., Allen, J.I., Morris, A.W., 1997a. Arsenic species in the Humber Plume, U.K. *Continental Shelf Research* 17, 435–454.
- Millward, G.E., Kitts, H.J., Ebdon, L., Allen, J.I., Morris, A.W., 1997b. Arsenic species in the Thames Plume, U.K. *Marine Environmental Research* 44, 51–67.

- Pokrovsky, O.S., Schott, J., 2002. Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chemical Geology* 190, 141–179.
- Prakash, R., Srivastava, R.C., Seth, P.K., 2003. Direct estimation of total arsenic using a novel metal side disk rotating electrode. *Electroanalysis* 15, 1410–1414.
- Ren, J.L., Zhang, J., Li, D.D., Cheng, Y., Liu, S.M., 2007. Speciation and seasonal variations of dissolved inorganic Arsenic in Jiaozhou Bay, North China. *Water Air Soil Pollution* 7, 655–671.
- Ren, J.L., Zhang, J., Li, D.D., Cheng, Y., Liu, S.M., 2010. Behavior of dissolved inorganic arsenic in the Yellow Sea and the East China Sea. *Deep Sea Research II* 57, 1035–1046.
- Salaün, P., Planer-Friedrich, B., van den Berg, C.M.G., 2007. Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode. *Analytica Chimica Acta* 585, 312–322.
- Santosa, S.J., Wada, S., Tanaka, S., 1994. Distribution and cycle of arsenic compounds in the ocean. *Applied Organometallic Chemistry* 8, 273–283.
- Schlosser, C., Croot, P.L., 2008. Application of cross-flow filtration for determining the solubility of iron species in open ocean seawater. *Limnology and Oceanography Methods* 6, 630–642.
- Schüssler, U., Balzer, W., Deeken, A., 2005. Dissolved Al distribution, particulate Al fluxes and coupling to atmospheric Al and dust deposition in the Arabian Sea. *Deep Sea Research II* 52, 1862–1878.
- Seyler, P., Martin, J.-M., 1990. Distribution of arsenite and total dissolved arsenic in major French estuaries; dependence on biogeochemical processes and anthropogenic inputs. *Marine Chemistry* 29, 277–294.
- Seyler, P., Martin, J.-M., 1991. Arsenic and selenium in a pristine rivereestuarine system: the Krka (Yugoslavia). *Marine Chemistry* 34, 137–151.
- Sharma, V.K., Sohn, M., 2009. Aquatic arsenic: toxicity, speciation, transformations, and remediation. *Environment International* 35, 743–759.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* 17, 517–568.
- Turner, A., 1996. Trace-metal partitioning in estuaries: importance of salinity and particles concentration. *Marine Chemistry* 54, 27–39.
- Vandenhecke, J., Waeles, M., Cabon, J.-Y., Garnier, C., Riso, R.D., 2010. Inorganic arsenic speciation in the waters of the Penzé estuary (NW France): seasonal variations and fluxes to the coastal area. *Estuarine, Coastal and Shelf Science* 90, 221–230.
- Wang, W., Die, R.C.H., 2003. Bioavailability of iron complexed with organic colloids to the cyanobacteria *Synechococcus* and *Trichodesmium*. *Aquatic Microbial Ecology* 33, 247–259.
- Waslenchuk, D.G., Windom, H.L., 1978. Factors controlling the estuarine chemistry of arsenic. *Estuarine and Coastal Marine Science* 7, 455–464.
- Xiao, L., Wildgoose, G.G., Compton, R.G., 2008. Sensitive electrochemical detection of arsenic (III) using gold nanoparticle modified carbon nanotubes via anodic stripping voltammetry. *Analytica Chimica Acta* 620, 44–49.
- Yao, Q.Z., Zhang, J., Wu, Y., Xiong, H., 2007. Hydrochemical processes controlling arsenic and selenium in the Changjiang River (Yangtze River) system. *Science of the Total Environment* 377, 93–104.
- Ye, L., 1988. A typical estuary consisting of a tidal inlet and lagoon system and its engineering significance. *Estuaries* 11, 250–254.
- Zeng, Z.-X., Zeng, X.-Z., 1989. *Physicogeography of the Hainan Island*. Science Press, Beijing in Chinese.
- Zhu, D.-K., Yin, Y., Martini, I.P., 2005. Geomorphology of the Boao coastal system and potential effects of human activities — Hainan Island, South China. *Journal of Geographical Sciences* 15, 187–198.