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Intra-annual variations of arsenic totals and species in tropical estuary surface sediments

Parthasarathi Chakraborty^{*1}, Saranya Jayachandran^{1,2}, P. V. Raghunadh Babu¹, Shanta Karri^{1,3}, Priyadarshini Tyadi¹, Yao Koffi Marcellin^{1,4} and Brij Mohan Sharma^{1,5}

^{*1}National Institute of Oceanography (CSIR), India, 176 Lawsons Bay Colony, Visakhapatnam, 530017, Andhra Pradesh, India, Phone-91-891-2539180 (Ext 332); Fax: 91-891-2543595, e-mail: pchak@nio.org

²Cochin University of Science and Technology, Cochin-682022, Kerala, India

³Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Hyderabad - 500 085, Andhra Pradesh, India

⁴Centre de Recherches Oceanologiques, BP V18 Abidjan, Cote d'Ivoire

⁵TERI University, 10, Institutional area, Vasant Kunj, New Delhi, India.

Abstract:

Arsenic totals and species were found to vary during a one year period in the surface sediments of Godavari estuary (the third largest river in India). This study suggests that increasing salinity of overlying water column of sediments may alter the mobility of arsenic complexes in an estuarine system. The higher salt (NaCl) concentrations result in less arsenic adsorption to the sediment due to formation of weak arsenic complexes because of competition from Cl⁻ ions or due to a reduction in interparticle attraction by the action of Na⁺. It is suggested that controlled freshwater discharge (from a dam) in an estuary influences the salinity of surface water and can have significant impact on the distribution and speciation of arsenic in sediments and water column in such system.

KEY WORDS: Arsenic speciation, Salinity, Sediments, Estuarine sediments, River discharge.

1. Introduction:

Arsenic is, a toxic metalloid, widely encountered in different environments and organisms (Ng et al., 2003; Milton and Johnson, 1999; Parsons et al., 2008). Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, use of arsenic as pesticides and additives create additional impact. Oxidation of volatile arsine in air, and dust from burning fossil fuels can also increase the accumulation of this metalloid in different environmental compartments (Rich et al., 2000; Liu et al., 2002; Berg et al., 2001; Pi et al., 2000).

Once released into the environment, arsenic moves through weathering and leaching processes to accumulate in lakes, estuaries and oceans where sediments serve as a sink (Meade, 1982). However, depending upon the total arsenic loading and overlying water chemistry, sediment can also act as a source of arsenic to overlying water column and biota (Anawar et al., 2004; Nickson et al., 2000). Ecotoxicity and mobility of arsenic in sediments strongly depends upon its specific chemical forms or way of binding in sediments.

Arsenic(III) and arsenic(V) can form organic complexes (by reacting with natural organic ligands such as amino acids, fulvic acids and humic acids), or it can get adsorbed on particle surfaces (Fe-oxides, biological material, sediments) in natural waters and sediments. Most of these arsenic species are not directly taken up by the organisms and only a fraction of total arsenic concentration is bioavailable and interacts with organisms (Maria et al., 2008). The toxicity and bioavailability of arsenic are very much depend on the chemical speciation in the system (Peshut et al., 2008; Jack et al., 2003). Non residual/dynamic complexes of arsenic are expected to have biological impacts. Thus, it is extremely important to determine the total arsenic concentrations and its speciation in different environmental systems. The distribution and speciation of arsenic in estuarine sediments of Godavari River was studied. An attempt was made to understand the influence of monsoon discharges on arsenic distribution and its speciation in the sediments of Godavari estuary (during November-09 to January 11).

The sequential extraction method has been widely used to study trace metal partitioning in soil and sediments (Chakraborty et al. 2011, Chakraborty et al. 2012^a, Chakraborty 2012. The most widely used sequential extraction methods are those recommended by Tessier et al. (1979), Kersten and Forrstner (1986) and the Community Bureau of Reference (BCR) (Quevauviller et al., 1993). Due to high reproducibility of the results obtained and applicability to different sediment matrices modified BCR method is widely used (Quevauviller et al., 1993) and applied for the speciation study of

arsenic in this research. This research aims to study the distribution and speciation of arsenic in the estuarine sediments of Godavari estuary and identify the factors of overlying water column which can remobilize sediment-bound arsenic in a tropical estuary. The relevance of this study is that remobilization of arsenic may increase its bioavailability in sediments and the overlying water column.

2. Study area

The Godavari estuarine system is located around 16°15'N and 82°5'E covering an area 330km². The Godavari is one of the major rivers in India with a basin of 3.1×10⁵km² and 25 tributaries and an annual discharge of 105km³. (Rao et al., 1994).

It has been reported earlier that the bulk chemistry of the Godavari river sediments consist mostly (75%) of four elements (Al, Si, Ca and Fe). Compared to the Indian mean value, the Godavari sediments are enriched in heavy metals. The high concentration of metals is probably because of the distribution of rock types in the main Godavari basin. The nature of the bed rock and the percentage of each rock type have been reported as follows: 20.1 % of granites and hard rock; 19.2% of sedimentary rock; 55.7% of Deccan trap and 5.1% of recent alluvium.

It is well known that basin geology is an important factor in the controlling mechanism of sediment chemistry. Tributaries of Godavari River which drain through Deccan traps have shown relatively higher concentrations of heavy metals compared to those tributaries which flow through granite rock. The range of concentrations reported for arsenic in the bed sediments of Godavari river varied from 3.0- 14 mg.kg⁻¹ (sampling was done in 1978 and 1979). These old data were used (in this study for comparison) to indicate the concentrations of arsenic in the sediments when there was no or little industrial impact on the river.

The Godavari River serves needs for local agricultural activities and domestic use. Near the town Rajamundry the river flow is regulated by a dam at Dowaleswaram. It has been reported by Sarma et al (2010) that the monsoon derived fresh water is stored in this dam reservoir and conserved for utilization during the dry seasons by the Irrigation Department. With the onset of summer monsoon runoff, the dam reservoir is first filled and the surplus water is released downstream. Downstream of the dam, the Godavari is naturally divided into Gautami and Vasishta distributaries that form respective estuarine systems (Fig. 1) and these observations were conducted in Gautami Godavari estuary as it carries the major river discharge. The river discharge data were collected from the dam authorities at Dowleswaram.

3. Sample collection

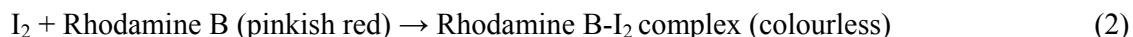
The sampling was conducted from December 2009 to February 2011. Sediment samples were collected from three different stations to represent variety of environments. For instance, Kotipalli represents upstream, Yanam represents middle of the estuary and Bhairavapalem represents downstream of the estuary. The sampling stations are shown in the Fig. 1 Yanam is surrounded by areas under the east Godavari district. There are large scale industrial units in Yanam (manufacturing ceramic wall and floor tiles, shrimp feed and feldspar power). In addition, there are medium scale units of manufacturing pharmaceutical formulations, hydrogenated oil/vanaspathi, microwave electronic items, plastic, etc. The river Gouthami Godavari forms southern boundary of Yanam and flows eastwardly to meet the Bay of Bengal. Bhairavapalem, an island on the eastern bank of the Gaderu River, is a fishing village within east Godavari district of Andhra Pradesh.

A Van Veen stainless steel grab (with an area of 0.02 m²) was used to collect sediment. Without emptying the grab, a sample was taken from the centre with a polyethylene spoon (acid washed) to avoid contamination by the metallic parts of the dredge. Multiple sampling was done at each station. The samples were stored at -20°C and then dried at 60 °C in a forced air oven (Kadavil Electro Mechanical Industry Pvt Ltd India, Model No. KOMS. 6FD). Sediments were subsequently stored at 4°C until needed.

4. Materials and methods

4.1 Spectrophotometric determination of As in sediments

This method is based on the reaction of As(III) with KIO₃ in acid medium to liberate iodine. This liberated I₂ bleaches the pinkish red colour of rhodamine-B:



The decrease in absorbance is measured at a particular wavelength, which is directly proportional to As(III) concentration. The differential absorbance of the Rhodamine-B dye with various concentration of arsenic against a reference solution shows a maximum difference at 553 nm. Therefore, this wavelength was chosen for spectral measurements.

A series of standard solutions of As(III) were prepared from a stock solution of 1000 mg mL^{-1} of As(III) in such a way that the concentration range in calibrated flasks contained $1.0\text{--}10.0 \text{ } \mu\text{g mL}^{-1}$ of As(III). An amount of 7.5 mM of KIO_3 and an amount of 1.0 mL of 0.4 M HCl was added in each calibrated flask and the mixtures were shaken gently. This was followed by addition of 62.6 mM rhodamine-B. The solution was reacted for 15 min then diluted to 25.0 mL with ultrapure water. The absorbance of each sample was measured at 553 nm against a reagent blank. A linear response was observed from the spectrophotometer with the variation of As(III) concentrations. An R^2 value of 0.987 was obtained. A few drops of 10% potassium iodide (KI) was added for the determination of total arsenic in natural samples to convert any As(V) to As(III).

In order to understand the intra-annual variability in total concentrations of arsenic in the estuarine sediments at three different sampling sites, an acid mixture of 69% (V/V) HNO_3 (8 mL) – 30% (V/V) H_2O_2 (2 mL) – 48% (V/V) HF (2 mL) was used to digest sediment samples. 10% KI solution was added to all the digested samples in order to reduce As(V) to As(III). These samples were used to determine the total concentrations of As in the sediments by following the above procedure. The Marine Sediment Reference Materials for Trace Metals and other Constituents from National Research Council, Canada (HISS 1, MESS 3, and PACS 2) were used to check the sensitivity and reliability of the method. A good recovery was obtained by using the spectrophotometric method.

4.2. Apparatus

Spectroquant UV/VIS Spectrophotometer (Model: Pharo 300) from Merck (Germany) Ltd., was used in this study to measure absorbance of Rhodamine-B. The Spectroquant® Pharo 300 UV/ VIS spectrophotometer offers a wide wavelength range from 190 to 1100 nm

4.3 Leaching procedure and Reagents

All the extraction processes were performed in Teflon containers. The reagents used in this study were of analytical grade or better (ultrapure)

4.3.1 Sequential extraction procedure

A series of batch extractions were performed on sediment samples, following BCR protocol (Quevauviller et al., 1993). In this investigation, the sum of ion-exchangeable, water soluble and carbonate/ bicarbonate fraction of arsenic (Fr.1); Arsenic bound to Fe and Mn oxides i.e., reducible fraction of arsenic (Fr 2); fraction of total arsenic bound to organic matter (Fr.3) and residual arsenic

fraction (Fr. 4) were determined. The procedure and protocols has been elaborated elsewhere (Quevauviller et al., 1993).

The extracted liquid samples (containing arsenic) in each fractions (5.0 mL) were acid digested to dryness (with a mixture of H₂O₂ (1.5 mL), HNO₃ (1.5mL) and HClO₄ (1.5mL) in Teflon vessels) on a hot plate. The residues were redissolved in 2% ultrapure HNO₃ and analyzed by spectrophotometrically to obtain the distribution of arsenic in different phases of the sediments. Each sample was analyzed in triplicates.

The application of certified reference materials (CRMs) in analytical chemistry for quality control purposes is well recognized and recommended by a wide range of international, national and professional organizations. However, the use of CRM was not necessary in the present case. Validation of the sequential extraction method was done by comparing the total arsenic concentration (determined by spectrophotometrically) with the sum of the concentrations of arsenic fractions obtained by following the sequential extraction protocols. The comparable (close to 100% recovery) values of total arsenic concentration support the reliability and validity of the sequential extraction method. The data are presented as supporting documents (Table 1SD).

5. Results and discussion

The total concentrations of arsenic and its intra-annual variation at each station are presented in Table 1. The total concentrations of arsenic in the sediments collected at Kotipalli station (upstream) were high (ranging from 76.4 to 347.4 mg.kg⁻¹) followed by Bhairavapalem (downstream) (ranging from 3.5 to 136.3 mg.kg⁻¹). The lowest concentrations of arsenic were found in the sediments collected at Yanam (middle of the estuary). The total organic carbon (TOC) content in the sediments is also presented in Table 1 (ranging from 24.7 to 150.0 mg.kg⁻¹).

Long term use of pesticides (usually organo-arsenic compound) in agricultural field, and industrial sewage are probably responsible for the high concentrations of arsenic found in the sediments collected at Kotipalli station (upstream). The increasing high concentrations of arsenic in the sediments at Kotipalli station during the time of the year (January to June) when there was very little or no river discharge indicate that the source of arsenic at Kotipalli station was probably because of anthropogenic activities around the area. It is interesting to notice that the total arsenic content in the sediments collected at this station did not decrease with the increasing river discharge (from July to October). This observation suggests that Godavari River probably contributes arsenic in the

sediments collected at Kotipalli. It has also been mentioned in our previous study that Godavari River was a major contributor of arsenic found in the sediments at Kakinada (Chakraborty et al. 2012^b). It is necessary to know the basin geology of Godavari River to identify the source of arsenic. The range of concentrations reported for arsenic in the bed sediments of Godavari river varied from 3.0-14 mg.kg⁻¹ (sampling was done in 1978 and 1979). The reported high concentrations of arsenic in the sediments collected at Kotipalli during the time of heavy river discharge period suggest that Godavari River carried arsenic and the source of arsenic was mainly anthropogenic.

The total concentrations of arsenic in the sediments collected at Yanam (middle of the estuary) (24.7 to 150 mg.kg⁻¹) were found to be much lower than the concentrations found in the sediments at Kotipalli. The lower concentration of total arsenic content in the sediments collected at Yanam was probably because of the increasing salinity of the overlying water column at this station. It has been reported that Cl⁻ ion can compete with arsenic (in the form of arsenate and arsenite) for positively charged surface binding sites on mineral oxides in sediments (Monabbati, 1999) and can reduce the adsorption processes of arsenate/arsenite on sediments. Thus, increasing salinity in the overlying water column may reduce total arsenic content in sediments. Secondly, NaCl, likely through the action of Na⁺, decreases interparticle attraction that results in the release of particles and colloids from the sediment bed, along with particle-sorbed arsenic (Monabbati, 1999). It has been reported that arsenic can be removed rapidly from sediments (80% within seven hours) by NaCl (Howard and Beck, 1993; Pilon and Howard, 1987).

Sarma et al (2010) reported that Kotipalli station, representing the upstream of Godavari River, is mostly dominated by freshwater throughout the year whereas salinity at Yanam varies from near freshwater to brackish water (~30 practical salinity unit) during no discharge period. Thus, varying salinity of the overlying water column probably increased arsenic mobility in the sediment-water systems at Yanam and decreased the total arsenic content in the sediments.

A series of model experiments were performed in the laboratory to understand the effects of varying concentrations of NaCl (in overlying aqueous solution) on the total arsenic content in the estuarine sediments. It has been reported in literature that arsenic can be removed rapidly from sediments (80% within seven hours) by NaCl (Howard and Beck, 1993; Pilon and Howard, 1987). An equilibrium time of 24 hours was set in this experiment. Three sediment samples from three different stations were chosen (containing high concentration of arsenic) for this experiment. The salinity of the overlying water column was adjusted by adding different concentrations of NaCl. It was found that removal of arsenic was gradually increased with increasing NaCl concentrations in the overlying

water column (Fig. 2). It is interesting to note that the maximum loss of arsenic was observed from the sediments collected at Kotipalli station (where the overlying water column is mainly non-brackish). The lowest amount of arsenic was released from the sediment collected at Bhairavapalem (where the overlying water column is mainly sea water with high salinity). This study suggests that Cl^- ion does compete with arsenic (in the form of arsenate and arsenite) for positively charged surface binding sites on mineral oxides in sediments and increases the release processes of arsenate/arsenite from sediments. Thus, increasing salinity in the overlying water column may reduce total arsenic content of the sediments in natural system.

However, the total concentrations of arsenic were found to be slightly higher in the sediments collected at Bhairavapalem (downstream of the estuary) compared to the concentrations of arsenic found in the sediments collected at Yanam. The higher salinity of the overlying water column at Bhairavapalem compared to Yanam should have reduced the total arsenic content in the sediments at Bhairavapalem compared to Yanam. This contradictory result can be justified by considering the less competing effects of dissolved organic carbon (negatively charged species) with arsenate/arsenite for the same binding sites on the sediments at Bhairavapalem. The decrease in total organic carbon content in the sediments at Bhairavapalem might have slightly increased the arsenic sorption process in the sediments (Balzile and Tessier, 1990; Aggett and Kriegman, 1988; Masscheleyn et al., 1991). Further investigation was carried out to understand the impact of river discharge on the salinity of overlying water column and total arsenic content in the sediments. .

5.1. Effects of river discharge on the salinity, pH of the overlying water column and total arsenic content in the sediments

The distribution of total arsenic concentrations in the estuarine sediments (collected at three different environmentally significant sampling sites) has been discussed in the previous section. It has also been shown that NaCl concentrations (salinity) of the overlying water column may play a key role in controlling total arsenic content in the studied sediments in Godavari estuary.

Thus, one could understand that river discharge from Dowleswaram dam (which was built on the Godavari River in 1842 at Dowleiswaram, approximately 60 km upstream from the mouth of the river) which controls the salinity of the water column probably plays an important role in controlling arsenic speciation in Godavari estuary.

An attempt was made to correlate the dam controlled freshwater discharge with the salinity of the overlying water column at the three sampling stations in the Godavari estuary. Figures 3 a and b

show the impact of river discharge on the salinity and pH of the overlying water column at the three stations. The salinity and pH data of the water column are presented in Table 1. In general, there is virtually no discharge between January and May due to drying of the river in the upstream. The dam controls summer monsoon freshwater discharge into the estuary. Usually the discharge starts from June reached its maximal in August. In the October – December discharge is usually low. However, it depends upon the local rainfall (the data on the average rainfall in this region is presented as supporting documents, Table 2SD). The data on rainfall were obtained from the websites of the Indian Institute of Tropical Meteorology (www.tropmet.res.in) and the Climate Diagnostics Bulletin of India (www.imdpune.gov.in). It was difficult to identify any direct the relationship (if any) between local rainfall, river discharge and arsenic distribution in the estuarine sediments.

Figure 4 shows the variation of total arsenic content in the studied sediments against the salinity of the overlying water column. A good correlation was obtained with $R^2=0.76$. This observation suggests that higher salinity of overlying water column may increase arsenic mobility in estuarine sediments.

The total arsenic content in the sediments collected from Kotipalli (upstream of the river) were found to increase from Jan-June 2010 when there was low or no river discharge from the dam. This increasing accumulation of arsenic in the sediments at Kotipalli at no river discharge period suggest that agricultural activities and industrial sewage from the local areas were probably responsible for the high concentrations of arsenic found in the sediments collected at Kotipalli station. The concentration of arsenic was found to increase with the increase in river discharge at Kotipalli station. It must be noted that river discharge in summer (June-September) is associated with water and sediment discharges. The increasing concentration of arsenic in the sediments at Kotipalli station suggest that Godavari river also contribute to the total concentrations of arsenic found in the estuarine sediments. The sources of arsenic in Godavari River are mainly anthropogenic (as discussed above on the basis of the composition of the basin of Godavari and its tributaries).

Figure 5 shows that the total arsenic content in the sediments collected at Yanam (typical estuarine system) were found to decrease from January 2010 to June 2010 when there was low or no river discharge from the dam. It has been reported that the salinity of water column at Yanam varies from near freshwater to brackish water (~ 30 practical salinity units) during no discharge period. Thus, one could expect that increasing salinity of the water column reduces the arsenic concentrations in the sediments as shown in the Fig. 5 However, the total arsenic content was found to increase with the increasing discharge (which decreases the salinity of the water column at Yanam) as shown in Fig. 5

Figure 5 shows that the variation of total arsenic concentrations in sediments at Bhairavapalem was not significantly influenced by the river discharge. Thus, one could expect a small variation in the total arsenic content in the sediments collected at Bhairavapalem. Further speciation studies were performed in order to understand the distribution and speciation of arsenic in the estuarine sediments.

5.2. Chemical fractionations of arsenic in the estuarine sediments by sequential extraction method:

A modified sequential extraction protocol proposed by Community Bureau of Reference (BCR) was applied to understand the chemical distributions and speciation of arsenic in the estuarine sediments.

Figure 6a shows the variation of different fractions of arsenic in the estuarine sediments collected at Kotipalli station. The concentrations of Fr. 1 of arsenic (which include water soluble arsenic complexes + arsenic in exchangeable form + carbonate/bicarbonate complexes of arsenic) were found to vary from 1 to 90% of the total arsenic content of the sediments.

It was found that the concentrations of arsenic as Fr. 1 gradually increased with the increasing total arsenic concentrations in the sediments at Kotipalli station. This finding is environmentally significant as this arsenic complexes (present as Fr. 1) can be easily leached to the water column and may become available to biota.

The concentrations of arsenic as Fr. 1 was found to increase in the sediments during no river discharge period (from Dec-2009 to July-2010) collected at Yanam. This is probably because of the fact that salinity (i.e. Cl^- ion concentrations) of the overlying water column gradually increased during this period at Yanam (Table 1).

It is also shown in Fig 6b that the concentrations of arsenic as Fr. 1 became negligible during the time of high river water discharge (July-2010 to Oct-2010). The concentration of Fr. 1 of arsenic gradually increased with the decreasing river discharge and increasing salinity of the overlying water column at Yanam during (Nov-10 to Feb 2011). This result revealed that Cl^- ion probably outcompeted arsenic (in the form of arsenate and arsenite) to get adsorbed at different binding and adsorbing sites of mineral oxides in the sediments at Yanam. This competition forces arsenic to form thermodynamically less stable complexes (Fr. 1). The concentrations of arsenic as Fr 1 in the sediments at Bhairavapalem did not show any trend throughout the year (Fig. 6c). During high to moderate river discharge period (from July-2010 to Nov-2010), the concentration of arsenic in the

sediments was found to increase at Bhairavapalem. However, there was no trend was found during the period from December 2009 to June-2010.

The concentrations of arsenic associated with Fe and Mn-oxides were found to be high at all the three station in the Godavari estuary. The higher concentration of arsenic in this phase of the sediments is because of the fact that hydrous Fe and Mn oxides are important host phases for arsenic due to their high adsorptive capacities and low degrees of crystallinity (Fendorf et al., 1997; Raven et al., 1998). The high concentrations of total Fe was determined in all the sediments collected at three different stations. The intra annual variation of total Fe content (in terms of weight percentage) is presented in Table 1. The percentage of total arsenic associated with iron and manganese-oxide in the sediments at Kotipalli station was found to be lowest compared to the sediments collected at Bhairavapalem and Yanam. The highest percentage of total arsenic was found to associate with Fe and Mn-oxide at Yanam (up to 92% of the total arsenic). This is because of the availability of more Fe and Mn-oxide in the sediments at Yanam station. The total Fe content was also found to be highest in all the sediments collected at Yanam.

The concentrations of arsenic bound to organics (Fr 3) in the sediments collected at Kotipalli were found to increase with the increasing river discharge (during the time from June 2010 to October 2010). Table 2 shows that the concentration of total arsenic associated with organic fraction gradually increased with the increasing total organic carbon content in the studied sediments. Thus, one can infer that TOC plays one of the key roles in controlling arsenic distribution in an estuary.

The strong correlations (presented in Fig 7) exist between Fr 3 of arsenic and the TOC content of the sediments (Fig. 7). A strong correlation coefficient (R^2) value of 0.98 (for Kotipalli), 0.79 (for Yanam) and 0.73 (for Bhairavapalem) were found between the concentration of arsenic associated with organics and the TOC content of the sediment. This observation suggests that total organic carbon present in the sediments also play a crucial role in the distribution and speciation of arsenic in the estuary. The residual arsenic concentration was found to be low at almost all the stations and suggest that the arsenic found in the studied sediments were probably mainly because of anthropogenic activities.

6. Conclusions

This study suggests that increasing salinity of overlying water column may result in greater mobility of arsenic complexes in sediment. Potential arsenic release from sediments into the water column

due to change in salinity of overlying water column can be a serious cause of concern. Salinity may reduce arsenic sorption at sediment surface. However, organic matter also found to be an important controlling factor in determining the distribution and speciation of arsenic in estuarine sediment. This research demonstrated that river water discharge in an estuary may have serious impact on arsenic speciation in the estuary. It is necessary to mention that an estuarine system is very dynamic and complex in nature. The distribution and speciation of arsenic in estuarine sediments are controlled by several factors and environmental conditions. This study identified salinity as one of the factors which may play a key role in controlling arsenic distribution in estuarine system. However, further investigation is required to understand the mechanism of sediment-water exchange and cycling of processes of arsenic in a tropical estuarine system.

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Table 1: Intra-annual variability of total arsenic concentrations (mg.kg^{-1}), total organic carbon (TOC) (wt%) Fe content (wt. %) in sediments. Salinity, pH (of the water column) at three different significant sites and river water discharge ($\text{m}^3 \text{s}^{-1}$) data in Godavari estuary during Jan 10 of Dec 10.

Station	Date	Total arsenic (mg.kg^{-1})	TOC (%)	Fe(%)	Date	Salinity(PSU)	pH	River discharge
Kotipalli	9-Dec	79.2 ± 1.2	0.25	-	10-Jan	1.2	8.0	0.0
	10-Feb	87.9 ± 3.5	0.16	-	10-Feb	8.3	7.9	0.0
	10-Mar	218.4 ± 4.2	0.25	6.3	10-Mar	9.7	8.1	0.0
	10-Apr	252.7 ± 7.8	0.19	5.7	10-Apr	9.6	8.0	0.0
	10-May	314.0 ± 9.2	0.25	4.9	10-May	0.2	6.9	14.1
	10-Oct	347.4 ± 5.2	0.51	4.2	10-Jun	0.3	6.6	35.6
	10-Nov	309.3 ± 9.9	0.47	2.7	10-Jul	0.1	6.8	1515.4
	10-Dec	282.5 ± 7.2	0.48	6.1	10-Aug	0.1	6.5	4785.2
	11-Jan	163.1 ± 3.2	0.19	5.1	10-sep	0.1	7.0	5838.9
	11-Feb	76.4 ± 4.2	0.51	6.2	10-Oct	0.1	6.5	818.4
					10-Nov	0.2	6.7	248.3
				10-Dec	1.4	7.9	0.0	
Yanam	9-Dec	98.0 ± 2.1	0.25	7.8	10-Jan	22.6	8.0	0.0
	10-Feb	69.6 ± 1.7	0.25	6.9	10-Feb	26.3	7.9	0.0
	10-Apr	60.6 ± 2.3	0.31	6.0	10-Mar	28.1	7.9	0.0
	10-May	35.9 ± 3.2	0.35	4.3	10-Apr	29.7	8.0	0.0
	10-Jul	24.7 ± 2.2	0.41	5.5	10-May	20.0	7.9	14.1
	10-Aug	36.8 ± 1.4	0.48	5.6	10-Jun	14.1	7.8	35.6
	10-Oct	57.7 ± 4.2	0.38	5.3	10-Jul	15.2	7.6	1515.4
	10-Nov	87.3 ± 5.4	0.51	6.1	10-Aug	0.1	6.4	4785.2
	11-Jan	112.2 ± 7.2	0.63	6.9	10-sep	0.1	7.4	5838.9
	11-Feb	150.0 ± 9.8	0.7	7.2	10-Oct	3.7	7.4	818.4
					10-Nov	9.4	7.7	248.3
				10-Dec	18.9	7.9	0.0	
Bhairavapalem	9-Dec	53.2 ± 4.2	0.03	7.2	10-Jan	25.3	8.0	0.0
	10-Feb	71.3 ± 1.7	0.03	7.0	10-Feb	33.3	8.0	0.0
	10-Mar	41.3 ± 4.8	0.07	7.4	10-Mar	30.6	7.9	0.0
	10-Apr	80.3 ± 6.4	0.06	5.0	10-Apr	34.1	8.1	0.0
	10-May	34 ± 2.2	0.25	7.0	10-May	24.2	7.7	14.1
	10-Jul	78.5 ± 6.2	0.13	8.2	10-Jun	28.5	7.2	35.6
	10-Aug	89.3 ± 3.4	0.16	2.0	10-Jul	22.1	7.6	1515.4
	10-Oct	136.3 ± 7.2	0.25	6.7	10-Aug	1.5	7.1	4785.2
	10-Nov	31.6 ± 4.2	0.09	7.7	10-sep	17.9	6.5	5838.9
	10-Jan	107.4 ± 8.9	0.28	4.4	10-Oct	20.2	-	818.4
					10-Nov	23.4	8.0	248.3
				10-Dec	24.8	7.9	0.0	

Table 1: Intra-annual variability of total arsenic concentrations (mg.kg^{-1}), total organic carbon (TOC) (wt%) and arsenic speciation at three different estuarine sites in Godavari estuary.

Station	Date	Total arsenic (mg.kg^{-1})	BCR sequential extraction method			
			Fr 1 (%)	Fr 2 (%)	Fr 3 (%)	Fr 4 (%)
Kotipalli	9-Dec	79.2 \pm 1.2	30.2	43.8	25.4	0.8
	10-Feb	87.9 \pm 3.5	1.3	13.2	4.6	81.0
	10-Mar	218.4 \pm 4.2	31.4	31.4	11.3	26.0
	10-Apr	252.7 \pm 7.8	26.9	26.8	29.1	17.2
	10-May	314.0 \pm 9.2	27.0	27.4	36.0	0.0
	10-Oct	347.4 \pm 5.2	14.2	22.4	35.3	0.0
	10-Nov	309.3 \pm 9.9	33.6	30.6	35.7	0.0
	10-Dec	282.5 \pm 7.2	8.7	20.7	30.7	20.1
	11-Jan	163.1 \pm 3.2	93.6	6.3	0.0	0.0
	11-Feb	76.4 \pm 4.2	0.0	0.0	57.5	42.5
Yanam	9-Dec	98.0 \pm 2.1	17.8	52.1	12.6	17.6
	10-Feb	69.6 \pm 1.7	46.3	20.5	27.0	6.3
	10-Apr	60.6 \pm 2.3	17.7	44.4	4.0	34.0
	10-May	35.9 \pm 3.2	21.2	6.1	2.2	70.5
	10-Jul	24.7 \pm 2.2	25.1	16.2	46.2	12.6
	10-Aug	36.8 \pm 1.4	1.6	1.6	41.8	19.8
	10-Oct	57.7 \pm 4.2	0.3	92.0	7.6	0.0
	10-Nov	87.3 \pm 5.4	26.1	17.9	14.1	42.0
	11-Jan	112.2 \pm 7.2	35.3	8.6	7.1	49.1
	11-Feb	150.0 \pm 9.8	21.7	12.8	41.8	23.7
Bhairavapalem	9-Dec	53.2 \pm 4.2	46.2	36.1	15.6	2.1
	10-Feb	71.3 \pm 1.7	70.0	4.1	11.6	14.2
	10-Mar	41.3 \pm 4.8	11.4	0.0	55.2	33.4
	10-Apr	80.3 \pm 6.4	3.6	28.4	10.3	57.7
	10-May	34 \pm 2.2	35.3	0.0	120.6	3.2
	10-Jul	78.5 \pm 6.2	12.9	33.6	47.4	6.0
	10-Aug	89.3 \pm 3.4	25.5	47.7	19.5	7.3
	10-Oct	136.3 \pm 7.2	31.3	36.6	7.4	24.7
	10-Nov	31.6 \pm 4.2	55.1	26.3	9.2	9.2
	10-Jan	107.4 \pm 8.9	4.4	48.1	41.3	6.1

Caption and Legends for Figures

Figure 1. Map of the sampling sites along the Godavari estuary (Andhra Pradesh region) of India, The filled circles are the locations of the five environmentally significant sites.

Figure 2. Release of arsenic from estuarine sediments: (●) Kotipalli; (○) Yanam; (▼) Bhairavapalem, as a function of varying concentrations of NaCl.

Figure 3. (a) Intra-annual variation in salinity of the water column at three sampling station: (●) Kotipalli; (○) Yanam; (▼) Bhairavapalem, with varying river discharge from Dawleshwaram dam (b) Intra-annual variation in pH of the water column at three sampling station: (●) Kotipalli; (○) Yanam; (▼) Bhairavapalem, with varying river discharge from Dawleshwaram dam.

Figure 4. The variation of total arsenic content in the studied sediments as a function of salinity of the overlying water column

Figure 5: Intra-annual variation of total arsenic content of the sediments collected at three different stations at Godavari estuary with varying river discharge and salinity of the overlaying water column.

Figure 6: Intra-annual variability of arsenic speciation (different fraction of arsenic associated with different phases of the sediments) at three different stations in Godavari estuary (a) Kotipalli; (b) Yanam; (c) Bhairabapalem.

Figure 7: Correlation between the concentrations of arsenic associated with organic matter in the sediments and the total organic carbon content of the sediments.

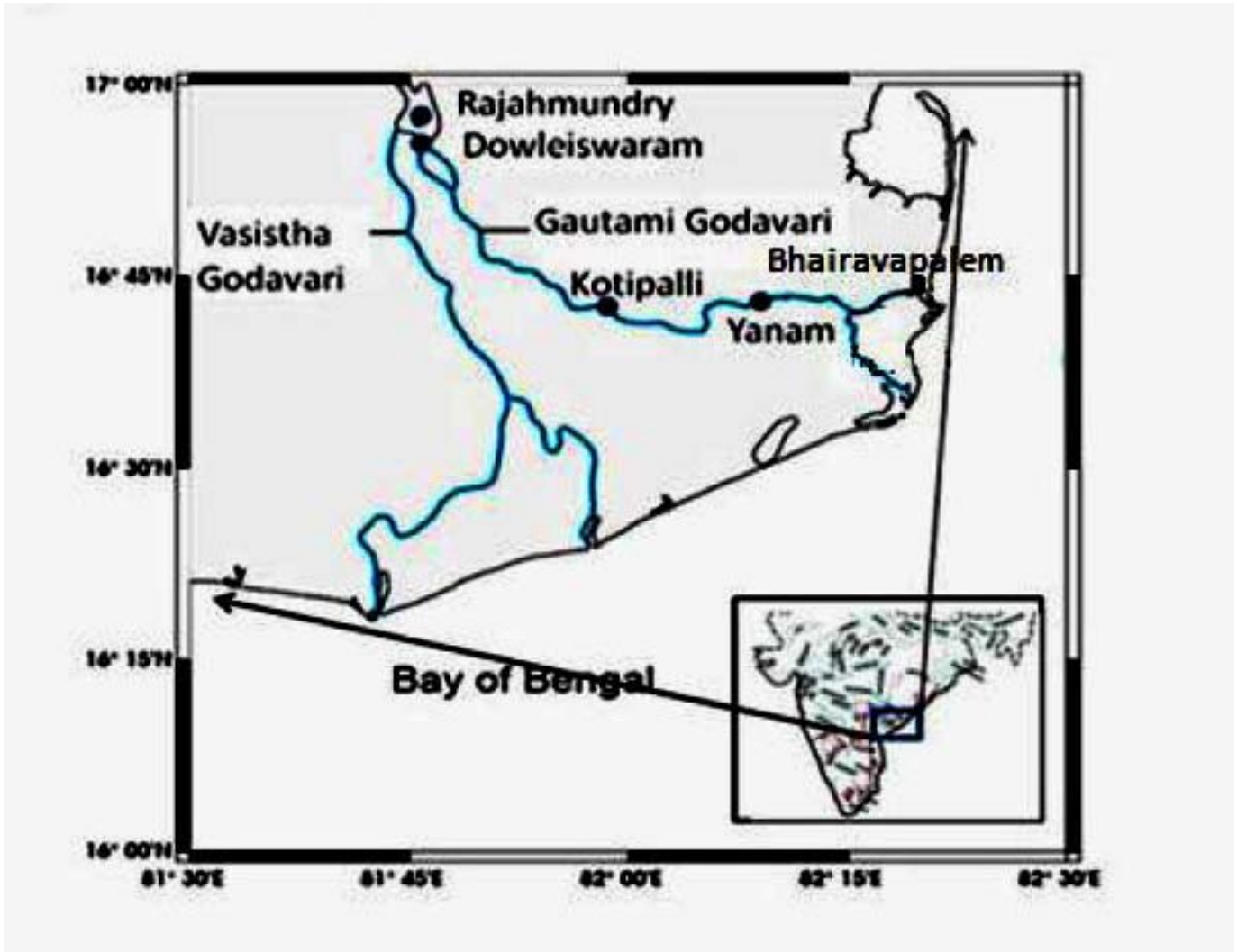


Figure 1

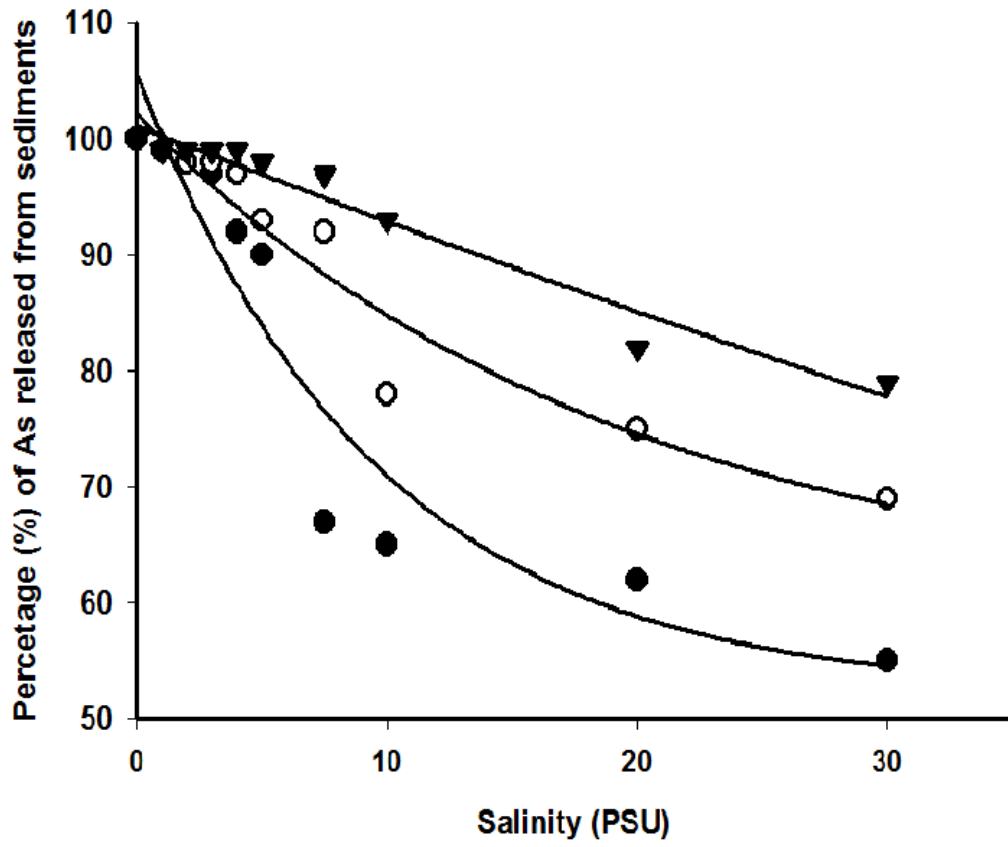


Figure 2

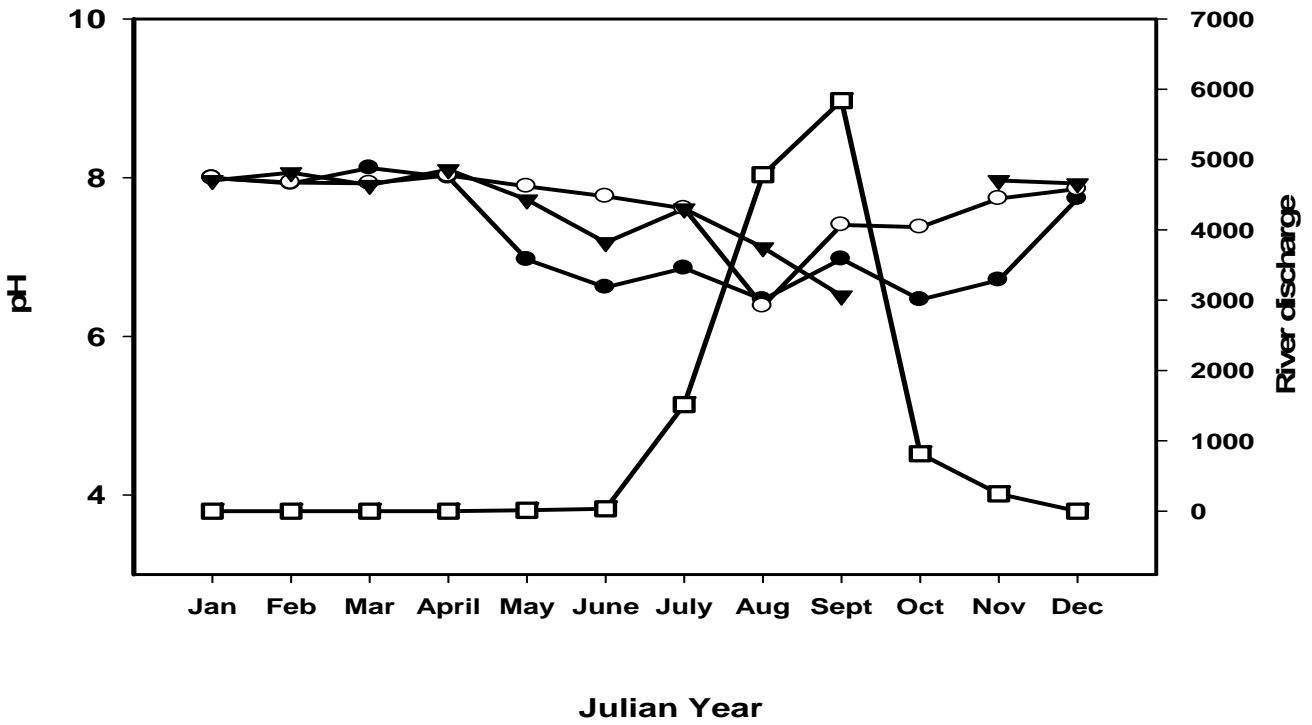
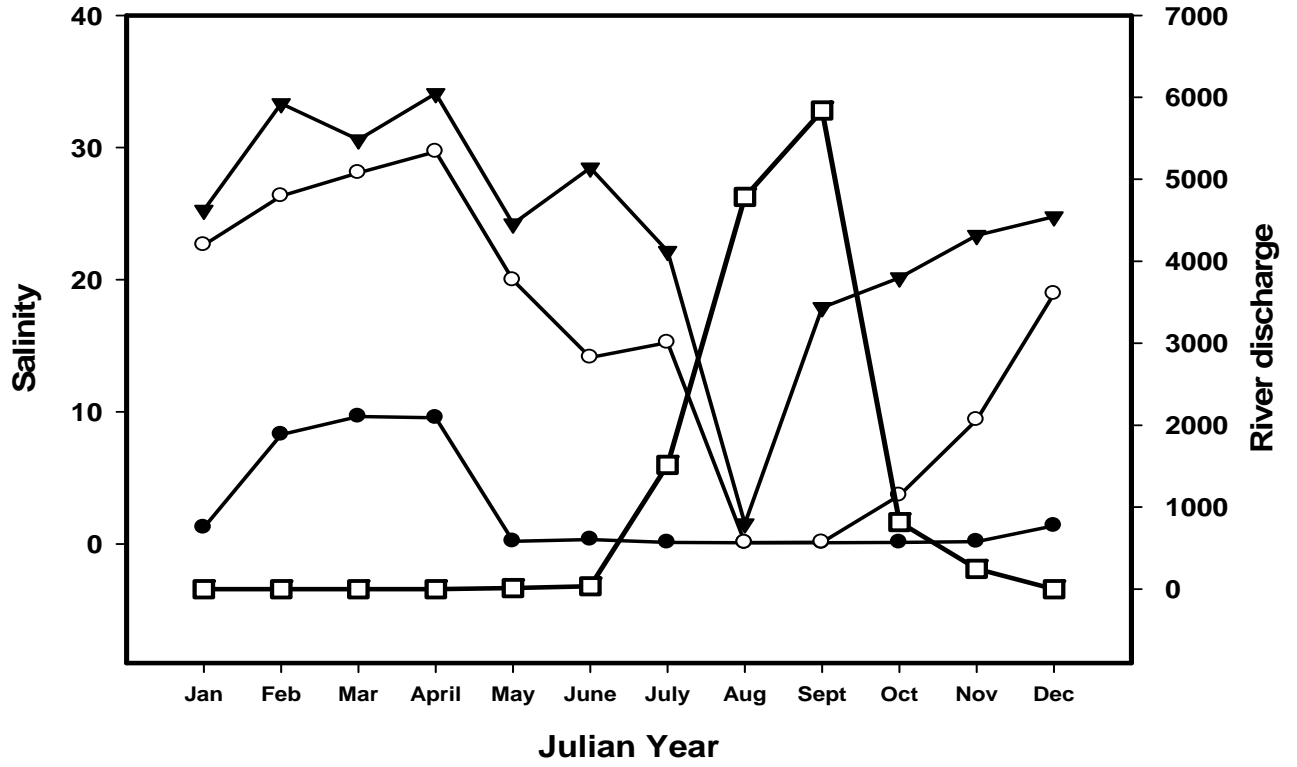


Figure 3

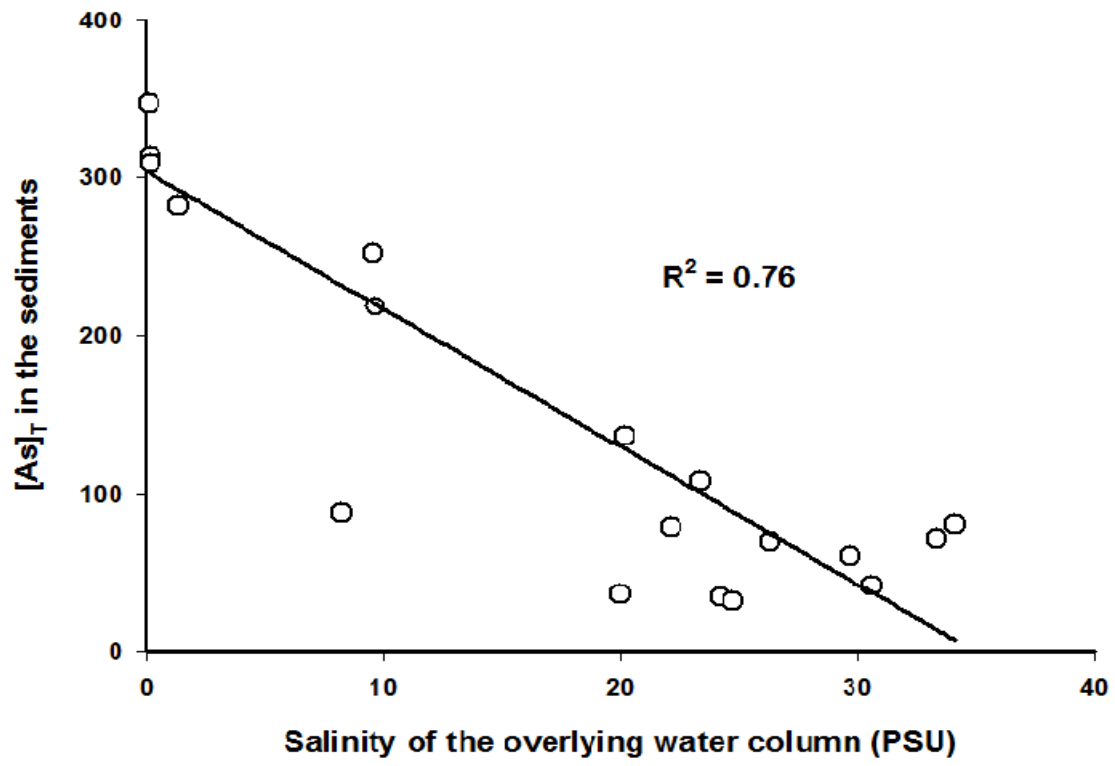


Figure 4

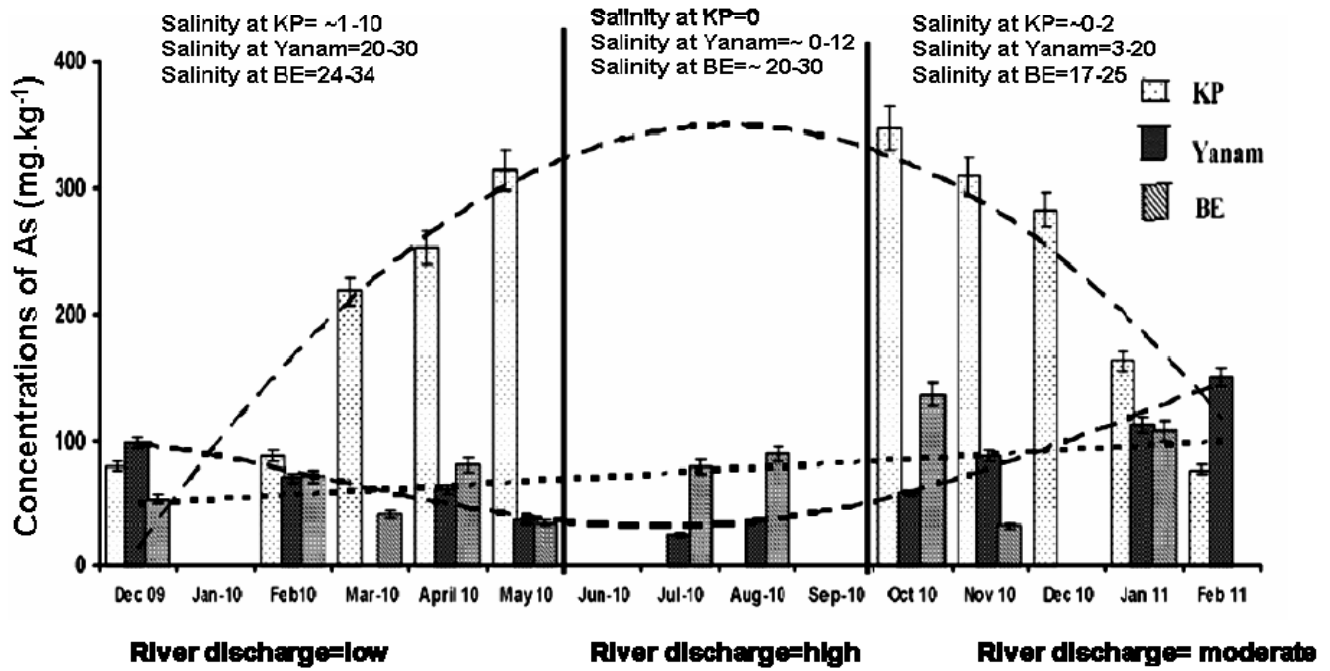


Figure 5

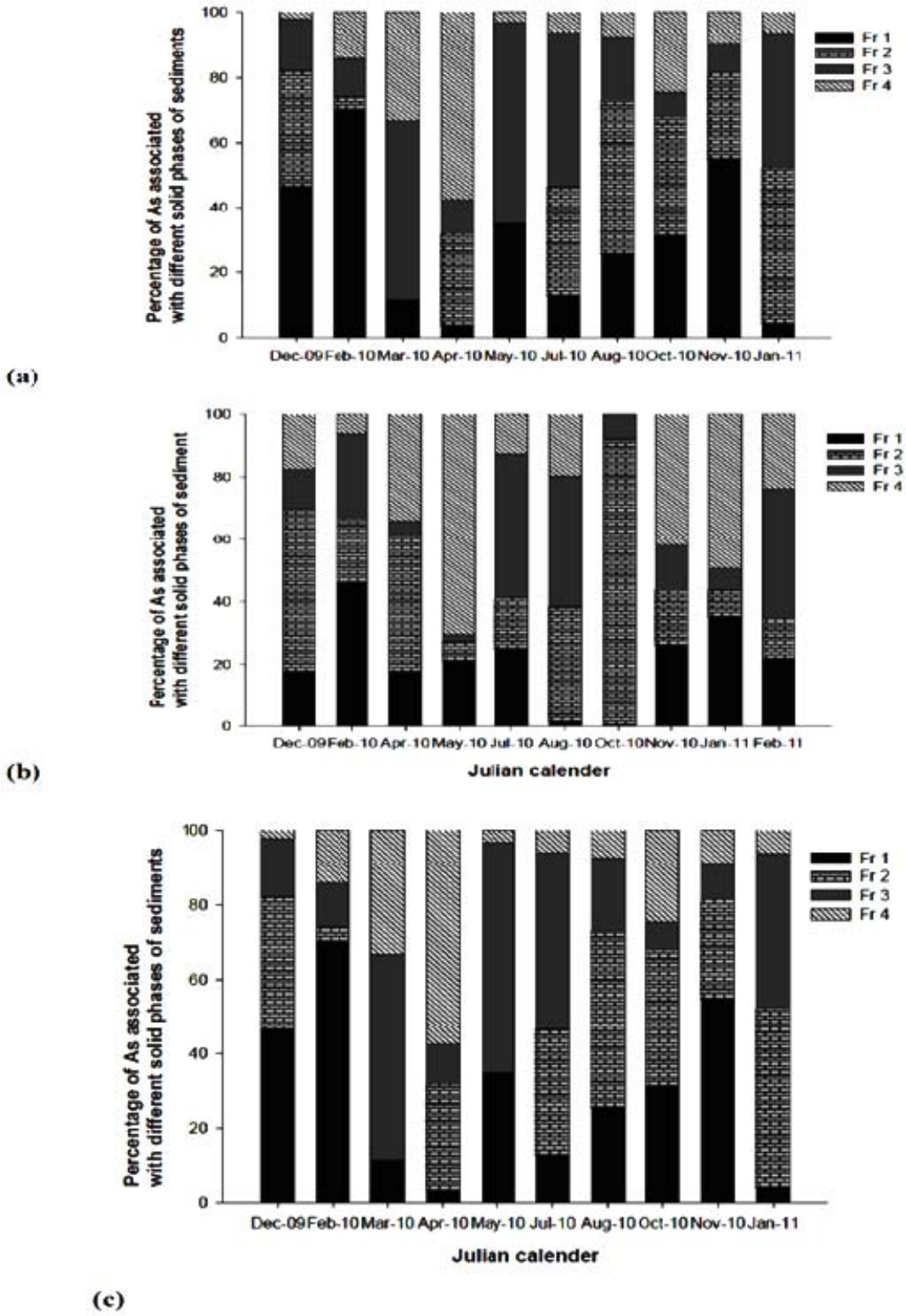


Figure 6

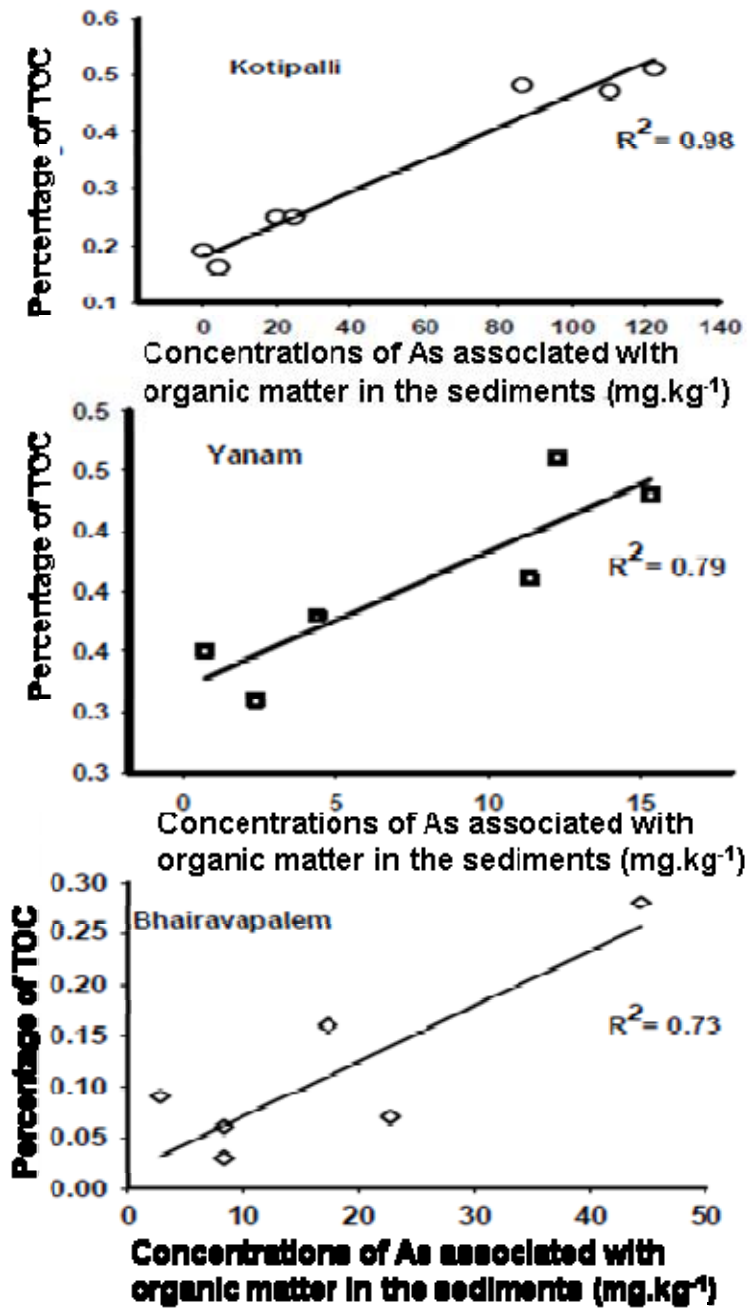


Figure 7