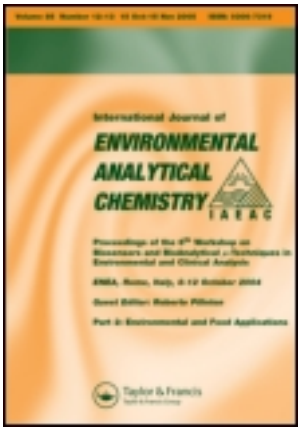

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A new spectrofluorometric method for the determination of total arsenic in sediments and its application to kinetic speciation

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A new spectrofluorometric method for the determination of total arsenic in sediments and its application to kinetic speciation

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A simple and sensitive spectrofluorometric method has been developed for the determination of arsenic (As) using rhodamine-B as a fluorescent agent. This method is based on the reaction of As(III) with potassium iodate (KIO_3) in acid medium to liberate iodine, which decreases the fluorescence intensity of rhodamine-B. This decrease in intensity was used to quantify As(III). A linear decrease in the response was observed with the increasing As(III) concentrations. An R^2 value of 0.995 was obtained. As(III) in the concentration range of 0.4 μg mL^{-1} to 12.5 μg mL^{-1} showed linearity and reproducibility by this method. The limit of quantitation was found to be 0.4 μg mL^{-1} of As(III) was the limit of quantitation. This method was successfully used to determine the total concentration of As in coastal and estuarine sediments. This study suggests that the estuarine sediments were more contaminated with As than the coastal sediments and the probable source of high As content in estuarine sediment is agricultural sewage in the study area. The concentrations of dynamic (non-residual) As species in sediments which can be subsequently released to the overlying water column as a result of either physical or biogeochemical disturbances was determined by using this method. It was observed that total As content does not correlate with the dynamic fraction of As in the sediments. Total organic carbon present in the sediments played a crucial role in controlling its bioavailability. Dissociation rate constants of As-sediment complexes were successfully determined by using this newly developed spectrofluorometric method.

Keywords: arsenic determination; rhodamine-B; spectrofluorometry; non-residual arsenic; coastal sediment; kinetic speciation

1. Introduction

Arsenic (As) is a ubiquitous trace element, classed as a semi-metal or metalloid. As can be found in different oxidation states in nature and each of the forms vary in toxicity and occurrence.

The concentration of this carcinogenic metalloid is increasing in different environmental compartments mainly for the following reasons. First, erosion of As containing surface rocks probably accounts for a significant amount of As in water supplies [1]. Secondly, the addition of waste products into rivers and estuaries, especially those in agricultural, industrial and population centres may lead to a significant increase in As contamination in water column and sediments.

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Estuarine and coastal sediments are generally considered a sink for metals and metalloids. In a survey of 19 estuaries in the UK, Burt *et al.* [2] reported that As concentration in estuarine sediments was in the range of 5–1740 mg kg^{-1}. The exponential growth of the human population along the sea coast and estuarine areas around the world has caused deterioration in the environmental quality of the coastal and estuarine sediments. As is being widely used in glass manufacture, pigment production, rodent poisons, insecticides, fungicides, medicines, printing, tanning etc. Thus, industrial effluent, municipal and agricultural sewage can be an important source of increasing concentration of As in estuarine and coastal sediments. Oxidation of volatile arsine in air, and dust from the burning fossil fuels [3] can increase the amount of accumulation of this metalloid in different environmental compartments. Due to its toxicity, determination of As is of critical importance in protecting the population from the health hazards it poses [4]. The toxicity, bioavailability and environmental mobility of As are very much dependent on its chemical speciation [5,6].

Mobility and bioavailability of As depends on several physicochemical and biological parameters of the system. The bioavailability of As in estuarine and coastal sediments is a consequence of complex interactions between As, sediments, planktons and the microbial community.

It is well known that As exists in −3, 0, +3 and +5 oxidation states. Environmental forms include arsenous acids ($As(OH)_3$), arsenic acids (H_3AsO_4), arsenites ($AsO(OH)_2^-$), arsenates ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}), methylarsenic acid ($CH_3AsO(OH)_2$), dimethylarsinic acid ($(CH_3)_2AsO(OH)$), arsine (AsH_3), etc. The degree of protonation of these protonated oxyanions of As(III) and As(V) depends on pH of the system. As(III) and As(V) can form organic complexes (by reacting with natural organic ligands, such as amino acids, fulvic acids, humic acids), or it can get adsorbed on particle surfaces (Fe-oxides, biological material, sediments) in natural waters and sediments. Most of these As species are not directly taken up by the organisms and only a fraction of the total As concentration is bioavailable, and interacts with organisms. The bioavailability of As is controlled by its speciation in the system. Thus, it is extremely important to determine the total As concentrations and its speciation in different environmental systems.

Various techniques and methodologies such as, flow injection analysis with hydride generation, atomic absorption spectroscopy, gas fluorometry-atomic absorption spectroscopy, inductively couple plasma-atomic emission spectroscopy, X-ray fluorescence, neutron activation analysis, atomic fluorescence spectroscopy, etc. are reported in the literature [7–11]. All these techniques are sensitive but are time consuming and expensive and require highly trained personnel.

Thus there is a need to develop a new simple, reliable, sensitive and inexpensive method which would overcome the existing inadequacies in the determination of trace amount of As in environmental systems. The first objective of this study was to develop a spectrofluorometric method for the determination of total concentration of As in sediments.

It is well known that accumulated As in sediments can be subsequently released to the overlying water column as a result of either physical disturbance or diagenesis and the sediments may persist as a source of As long after the cessation of direct pollution events.

Hence, for the study of As pollution in coastal sediments, analysis of the dynamic As fractions (which can be bioavailable) in sediment is of prime importance. In addition, the sediments can act as a useful indicator to improve management strategies.

Competeting ligand exchange method was applied to study the As speciation in coastal sediments. In order to perform this study a suitable complexing agent that was capable of extracting dynamic As fractions from sediments was required. It has been reported that ethylenediaminetetraacetate (EDTA) can extract principally organically bound and carbonate bound fractions of As by forming strong soluble complexes. This reagent can also extract As occluded in Fe amorphous oxides [12,13]. Quevauviller *et al*. [14] proposed the extraction of trace metalloids contents in calcareous sediments with EDTA solutions, relating the extracted fraction with those bioavailable to plants. Moreover, some authors have used solutions of EDTA to extract As and Sb from industrial contaminated sediments, since these metalloids can react with different carboxylic acids [12,15,16].

On the basis of this current state of knowledge, a kinetic based speciation study was performed using EDTA as a competing ligand to understand the rate of release of dynamic As species from coastal sediments of Bay of Bengal and the percentage of dynamic As species present in sediments. As concentrations was determined by spectrofluorometry method. It is important to note that the extractable dynamic As complexes do not represent only those As complexes which dissociate on sediments and bind to EDTA in solution but also those As complexes which do not interact with EDTA but leach out from sediment and can become available in solution. The second objective of this study was to determine the dynamic As complexes in sediments which will help us to understand the bioavailability of As and the amount of As which can be released to the overlying water column as a result of either physical or biogeochemical disturbances [17,18].

2. Experimental

2.1 *Reagents*

In the proposed method, As(III) is reacted with acidified potassium iodate (KIO_3) to liberate iodine (I_2). The liberated I_2 bleaches the pinkish red colour of rhodamine-B which is measured at 574.9 nm by spectrofluorometric technique. This methodology has been used for the determination of total concentration of As in sediments.

Stock solution of As (1.0 mg mL^{-1}) was supplied from Merck. Working standard was prepared by appropriate dilution of stock solution: Rhodamine-B (Molychem Pvt, India), 0.05% aqueous solution; Potassium iodate (KIO_3) (Fischer Scientific Pvt), 2%, aqueous solution; Hydrochloric acid (HCl) (Merck Pvt), 0.4 M aqueous solution. All the reagents used were of A.R. grade or the best quality available. All solutions were prepared in ultrapure water from a Milli-Q-Plus water purification system (resistivity 18.2 ΩM.cm).

2.2 *Methods*

Kinetic fractionation experiments to find out the dynamic As species were conducted for silt- and clay-sized (<0.063 mm) sediment samples. Two grams of sediments were added to 200 mL of 0.05 M EDTA (Merck Pvt) solution (at pH 6.0) in a 300 mL Teflon bottle, and the mixture was continually stirred with a Teflon-coated magnetic stirring bar throughout the experiment. The ratio of the mass of sediment to the volume of EDTA solution (mass/volume) was set at 0.01, as this ratio provided sufficiently high metalloid concentrations in the extract to be accurately quantified, while requiring a minimum amount of sediment, which was only available in limited quantities. A special effort was made to maintain a homogeneous suspension in order to avoid changing the mass/

volume ratio during sampling. Larger mass/volume ratios would be undesirable, as they could cause problems with filtration. At set time intervals, 2.0 mL of the suspension were filtered through a 0.2 μm syringe filter. Sample aliquots were collected over a 36 h period. The initial time for the kinetic measurement (i.e. $t = 0$) was taken as the time just before the sediment was added to the EDTA solution. The filtrate samples were then analysed spectrofluorometrically as described above to monitor the concentration of As in the extract solution as a function of time. A reagent blank and procedure blank were also collected and analysed for each experiment. Each sample was analysed three times to ensure that the fluorescence readings were reproducible, and the kinetic experiments were performed in triplicate for all samples to ensure repeatability of results. To account for sensitivity of the instrument was monitored throughout each experiment by analysing a standard solution followed by a reagent blank between every five samples. If the sensitivity changed more than 10% during an experiment, a correction factor was applied to compensate for the drift.

2.3 *Apparatus*

Varian Cary Eclipse Fluorescence Spectrophotometer has been used in this study to measure fluorescence of rhodamine-B. The Cary Eclipse is a computer-controlled, scanning fluorescence spectrophotometer with dual monochromators and measurement modes for fluorescence.

3. Theory

3.1 *The kinetic model*

The kinetic model proposed by Olson and Shuman [19] was adapted [20,21] to investigate the kinetic speciation of As in the coastal sediments of Bay of Bengal. Consider sediments samples of n different components, in which each component, M-Sediment$_i$, exists in equilibrium with its dissociation products: free metalloid ion or extractable metalloid complexes, M, and a naturally occurring, heterogeneous complexant, Sediment$_i$, such as humic acid adsorbed on sediment and binding sites on sediments' surfaces (charges have been omitted for simplicity). The subscript, i, represents different binding sites on the naturally-occurring heterogeneous complexant:

$$\text{M-Sediment}_i \underset{k_{f,i}}{\overset{k_{d,i}}{\rightleftharpoons}} \text{M} + \text{Sediment}_i \quad \text{(slow)} \tag{1}$$

$$\text{M} + \text{EDTA} \longrightarrow \text{M} - \text{EDTA} \quad \text{(fast)}, \tag{2}$$

where the formation and dissociation rate constants, $k_{f,i}$ and $k_{d,i}$, are coupled by the stability constant, $K = k_f / k_d$, through the principle of microscopic reversibility.

If each complex, M-Sediment$_i$, dissociates simultaneously and independently (at a rate that depends on the nature of the functional group, its position on the macromolecule, and the residual charge), the concentration of the free metalloid ion, c_M, or extractable metalloid complexes and the total concentration of all complexes, $c_{\text{M-Sediment}}$, at any time, t, is given by a summation of exponentials as shown in Equation (3):

$$c_{M\text{-}Sediment}(t) = \sum_{i=1}^{n} c^{\circ}_{M\text{-}Sediment_i} \cdot \exp(-k_{d,i} \cdot t), \quad (3)$$

where $c_{M\text{-}Sediment_i}$ is the initial concentration of M-Sediment$_i$ and $c_{M\text{-}Sediment_i}$, (t) is the concentration of M-Sediment$_i$ at any time, t.

The model assumes that: (a) the reactions are first-order and pseudo-first-order; (b) reaction (2) is much faster than reaction (1), so that reaction (1) is the rate-determining step, and the measured kinetics then represent the kinetics of the dissociation of the metal complex, M-Sediment$_i$; (c) M-Sediment does not directly (i.e. without predissociation) react with the EDTA; and (d) the ratio between the concentrations of complexed metal and free metal is much larger than unity:

$$(\text{i.e. } c_{M\text{-}Sediment}/c_M < 1).$$

4. Study area

Sediment samples were collected from four different environmentally significant sites of coastal Andhra Pradesh, India. These sites are located in four different regions as shown in Figure 1.

(1) Kalingapatnam is not an industrially developed city but an important minor port is close to this station.
(2) Vishakhapatnam is an industrially developed city.

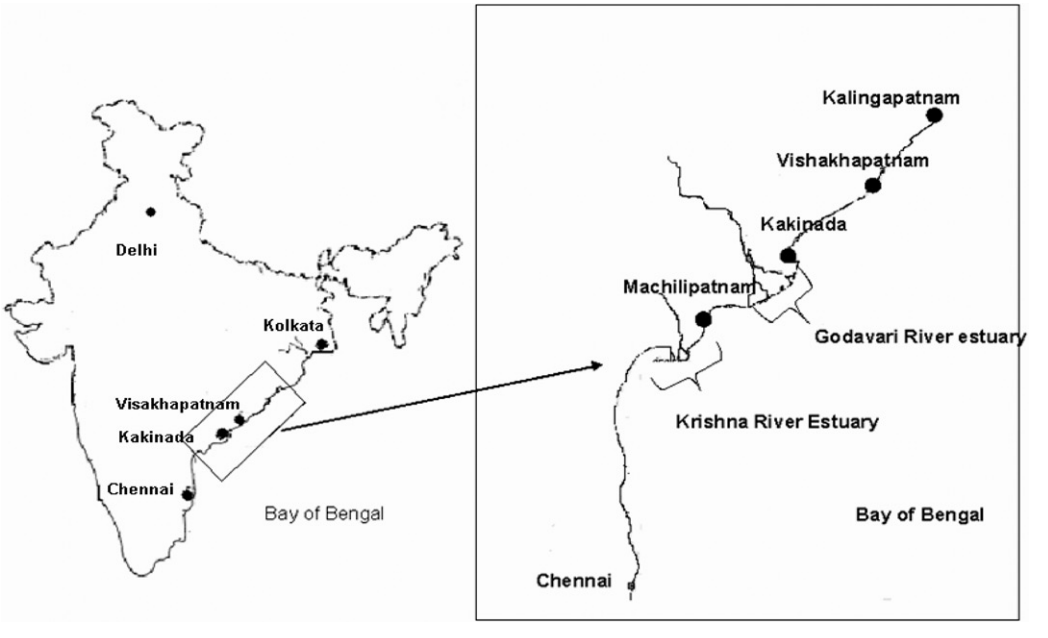

Figure 1. Map of the sampling areas along the east coast (Andhra Pradesh region) of Bay of Bengal. The filled circles within the boxes are the locations of the four environmentally significant sites.

Table 1. Geographical locations of sampling sites.

Station	Longitude (East)	Latitude (North)	Sampling date	Distance from shore (KM)	Depth (metres)
Kalingapatnam	84°10.36′	18°19.36′	21.12.08	5	23
Visakhapatnam	83°19.11′	17°38.94′	24.12.08	5	35
Kakinada	84°10.85′	16°58.96′	22.12.08	5	31
Machilipatnam	84°10.25′	16°09.16′	23.12.08	5	9

(3) Kakinada is an industrially developing city, and a branch of Godavari River joins the coastal waters through a canal that carries mostly agricultural and municipal sewage to Bay of Bengal; and
(4) Machilipatnam is not industrially developed but Krishna River estuary is very close to this place.

The general description of sampling sites is presented in Table 1. The geographic location of sites, the distance from the shore and depth from where sediment samples were collected are shown in Table 1.

5. Results and discussions

This method is based on the reaction of As(III) with KIO_3 in acid medium to liberate iodine. This liberated I_2 bleaches the pinkish red colour of rhodamine-B:

$$2HAsO_2 + 2IO_3^- + 8H^+ \rightarrow 2HAsO_3 + I_2 + 4H_2O, \quad (4)$$

$$I_2 + \text{Rhodamine B (pinkish red)} \rightarrow \text{Rhodamine B} - I_2 \text{ complex (colourless)}. \quad (5)$$

The decrease in fluorescence is measured at a particular wavelength, which is directly proportional to As(III) concentration. The fluorescence spectrum of rhodamine-B in aqueous medium is shown in Figure 2. The fluorescence peak of rhodamine-B was found at 574.9 nm (an excitation and emission wavelengths of 540 and 625 nM was used) and this wavelength was used throughout the study. The similar wavelength was also reported by Onishi for rhodamine-B in aqueous solution [22].

5.1 *Optimisation of experimental parameters to determine total As concentrations in sediments*

In order to obtain optimal experimental conditions, a systematic investigation was performed to determine the influence of KIO_3 and rhodamine-B concentrations on the sensitivity of the method. Effect of concentration of rhodamine-B in the reaction system is presented in Figure 3. A stock solution of 0.04 M rhodamine-B were made and different concentrations (20.0 μM to 125.0 μM) of rhodamine-B were added to a standard As(III) solution of 1 μg mL^{-1} with 7.5 mM of KIO_3 in acid medium and fluorescence intensities were determined as presented in Figure 3. Highest sensitivity was obtained in the presence of 62.6 μM of rhodamine-B.

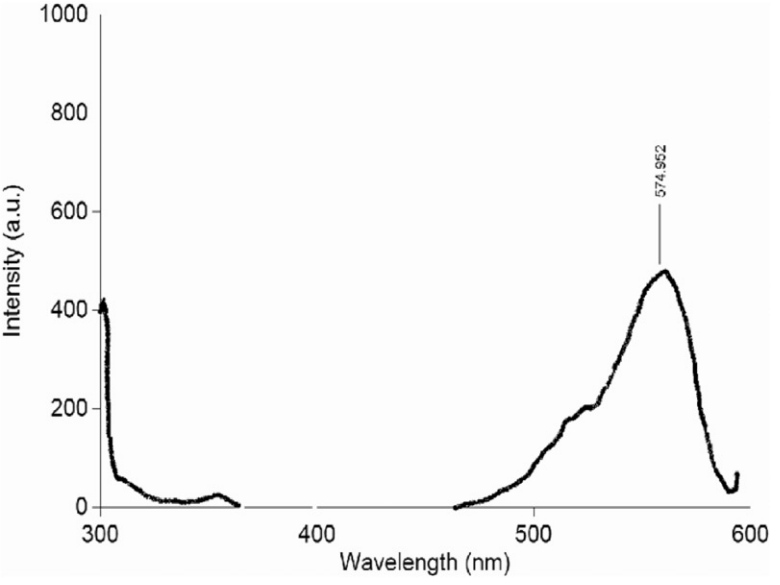

Figure 2. Fluoroscence spectrum of rhodamine-B in aqueous solution.

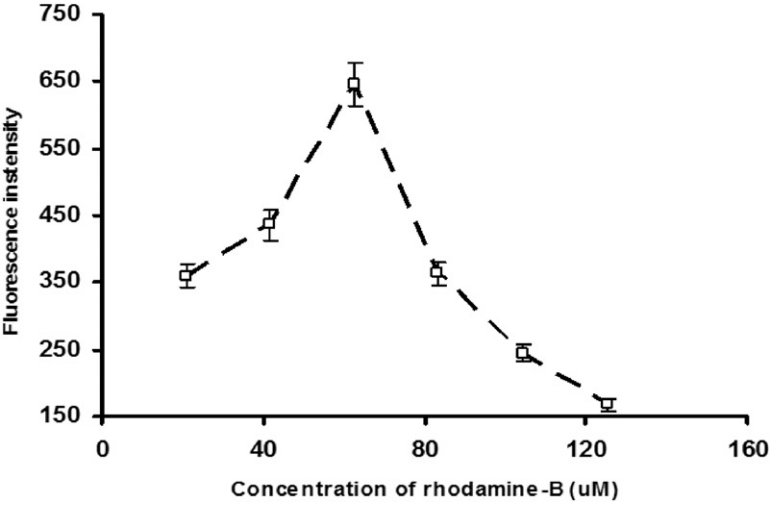

Figure 3. Effect of rhodamine-B concentrations on fluorescence intensity of rhodamine-B in model solutions. $C_{As,T} = 1.00 \pm 0.01\,\mu g\,mL^{-1}$, $C_{KIO3} = 7.5 \times 10^{-3}\,M$ $_{Rhodamine\ B} = 2.0 \times 10^{-6}\,M$ to $1.25 \times 10^{-4}\,M$, pH 6.0 ± 0.1, $T = 23 \pm 2°C$.

Constant and minimum fluorescence value was obtained when 7.5 mM of KIO_3, 1.0 mL of 0.4 M HCl and 62.6 μM of rhodamine-B was added to a standard As(III) solution of $1\,\mu g\,mL^{-1}$ in the described order. The determination was carried out at room temperature. An amount of 7.5 mM of KIO_3 was used throughout the study (Figure 4).

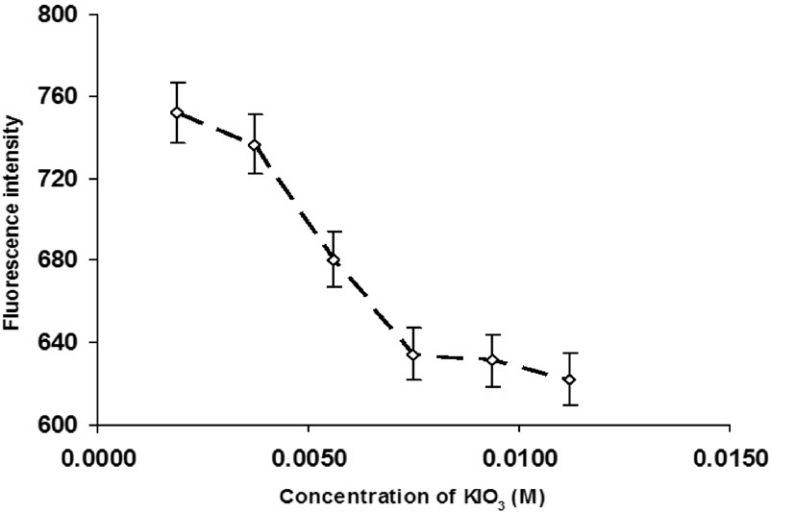

Figure 4. Effect of KIO_3 concentrations on fluorescence intensity of rhodamine-B in model solutions. $C_{As,T} = 1.00 \pm 0.01 \mu g\,mL^{-1}$, $C_{KIO_3} = 2 \times 10^{-3}$ M to 11.2×10^{-3} M; $C_{Rhodamine\ B} = 6.2 \times 10^{-5}$ M, pH 6.0 ± 0.1, $T = 23 \pm 2°C$.

A series of standard solutions of As(III) were prepared from a stock solution of $1000\,\mu g\,mL^{-1}$ of As(III) in such a way that the concentration range in calibrated flasks contained 0.4–$12.5\,\mu g\,mL^{-1}$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 μM rhodamine-B. The solution was reacted for 15 min then diluted to 25 mL with ultrapure water. The fluorescence of each sample was measured at 574.9 nm against a reagent blank. A linear response was observed from the instrument with the variation of As(III) concentrations. An R^2 value of 0.995 was obtained. A few drops of 10% potassium iodide (KI) was added for the analysis of natural samples to convert any As(V) to As(III).

As(III) in the concentration range of $0.4\,\mu g\,mL^{-1}$ to $12.5\,\mu g\,mL^{-1}$ shows linearity and reproducibility by this method. An amount of $0.4\,\mu g\,mL^{-1}$ of As is the smallest quantity that is significantly different from the blank and has been considered as the limit of quantitation. Quality control was constructed by making known additions of As to the blank matrix and by analysing certified reference material. Spike recovery within a specified interval was around 100%. Two marine sediment reference materials for trace metals (MESS-3 and PACS-2 from National Research Council, Canada) were used to validate the method and the recovery was virtually quantitative. All the data presented with 95.5% confidence interval.

In order to determine the total concentration of metalloid in the sediments, 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. All the samples from four different stations were first digested with acid mixtures and 10% KI solution was used to reduce As(V) to As(III) and the samples were used to determine the total concentrations of As in the sediments by following the above procedure. The total concentration of As and total organic carbon (TOC) and their ratio at four different sampling stations are presented in Table 2.

Table 2. Total arsenic ($mg\,kg^{-1}$) concentration determined by Spectrofluorometric method and Total Organic Carbon (TOC) concentrations in sediments in wt %.

Station	$[As]_{Total}$ $mg\,kg^{-1}$	TOC (% Wt.)	[As]/[TOC]
Kalingapatnam	21.9 ± 1.0	1.8	0.013
Visakhapatnam	51.8 ± 2.6	1.7	0.030
Kakinada	138.5 ± 7.0	14.6	0.009
Machilipatnam	50.9 ± 3.0	6.6	0.007

Notes: Values presented as the means $\pm 2 \times$ standard deviation, $n = 3$.

Table 2 shows that sediment collected from Kakinada station contained highest concentration of As ($138.5 \pm 7.0\,mg\,kg^{-1}$), whereas sediments collected from Visakhapatnam and Machilipatnam were found to contain high concentration of 51.8 ± 2.6 and $50.9 \pm 3.0\,mg\,kg^{-1}$ of As, respectively. The sediment collected at Kalingapatnam was found to be less contaminated with As ($21.9 \pm 1.0\,mg\,kg^{-1}$).

Concentration of As was expected to be high in the sediment samples collected from Kakinada station because of the fact that Kakinada bay is a shallow water marginal environment with the main land on the west, mangrove swamps on the south and a narrow sand bar running northward from the mangrove, roughly parallel to the coast line at a distance of about 11 km, on the east. In addition to numerous creeks and mangrove swamps and a branch of Gautami Godavari, it receives farm drainage mixed with agricultural sewage through the Kakinada canal. Agricultural sewage is expected to have a high concentration of As because of its use as insecticides, fungicides in agriculture. Thus, it can be assumed that the sediments collected at Kakinada bay can have a high concentration of As compared to the sediments collected at other three stations. Secondly, Godavari River may be another major contributor of As found in the sediment at Kakinada.

Under the conditions of large fresh water discharge into the estuary, As is carried to the estuary. Coagulation or precipitation of As complexes can take place which can result in an increased concentration of As as observed in the sediment collected at Kakinada. However, further study is required to identify the major source for this high concentration of As in sediment found in Kakinada.

Visakhapatnam city is located on the east coast of Bay of Bengal. It is an industrial city in India and several industrial plants have been established in Visakhapatnam. Atmospheric emissions/industrial effluent from these industries can also enhance the concentration of As in sediments. However, sediment collected at Kalingapatnam was found to be less contaminated by As. This is because of the fact that Kalingapatnam is neither industrially developed like Visakhapatnam nor very close to the estuary.

Total As content in the sediments was determined by the spectrofluorometric method. The interference of major cations and other trace metals was studied and found to have negligible effect in As determination. However, total As concentrations cannot represent the bioavailability of As in sediments. Further speciation studies were performed to determine the concentrations of dynamic and extractable As species in the sediments.

5.2 *Optimisation of experimental parameters to determine dynamic As in sediments*

In order to obtain optimal experimental conditions, a systematic investigation was performed to determine the influence of pH and EDTA concentration on the efficiency of As extraction from the sediment samples. The optimisation experiments were performed on each sample.

5.2.1 *pH*

The pH dependence of trace metal/metalloid extraction by EDTA is due to competitive extraction by H^+ [23–25]. It is therefore necessary to determine at what pH this competition is minimised. In addition, major cations (e.g. Na^+, K^+, Mn^{2+}, Fe^{2+}, Mg^{2+}, and Ca^{2+}) compete with As for complexation by EDTA. This competition changes with pH due to the pH-dependence of major cation solubility [23,26]. The optimum pH must also minimise two undesirable effects at low and high pH conditions. At very low pH, the complexation efficiency of EDTA is reduced due to protonation of the EDTA molecule. Under very high pH conditions, there is an increasing tendency for the metal ions to combine with OH^- to form insoluble hydroxides [24]

The pH range studied was from 4 to 8. EDTA precipitated at pH 3. It was found that within a pH range of approximately 6–8, there was no significant change in the concentration of As extracted, suggesting that As was predominantly released into the solution because of the presence of EDTA. No significant pH changes were observed after 24 h of extraction for any of the pH values studied. The optimal pH was chosen to be pH 6 due to the fact that this value is acidic enough to prevent precipitation of metal hydroxides (mainly iron-hydroxide, which can adsorb As species and significantly interfere in our experiment), and was demonstrated to be alkaline enough to minimise competitive extraction by H^+. pH 6 also optimises EDTA buffering capacity, as pKa, 3 of EDTA is 6.16, which ensures minimal variations in pH throughout the kinetic extraction experiments.

5.2.2 *Concentration of EDTA*

It is well known that EDTA is a non-specific complexing agent; it extracts a wide variety of cations from the sediment. Hence, an important parameter to consider is the ratio, R, between the EDTA concentration and the total concentration of all extracted cations:

$$R = \frac{[\mathrm{EDTA}]}{\sum [\mathrm{M}_i^{n+}]},$$

where M^{n+}, is any major cation (e.g. Fe^{3+}, Mg^{2+}, Ca^{2+}, K^+, Na^+ etc.). When $R \ll 1$, there is a lack of EDTA, and increasing concentrations of EDTA will extract greater concentrations of cations. However, when $R \gg 1$, EDTA is in excess and has attained maximum extraction efficiency; hence, any further increases in EDTA concentration will not increase extracted cation concentrations [23,26,27]. An excess of EDTA is a necessary condition in order for the kinetic model to be valid, as it minimises suppression of trace metal solubilisation due to competition by other major cations for complexation by EDTA [23–25]. The results for the EDTA concentration optimisation experiments, suggested that 0.05 mol/L represents an excess of EDTA.

The total concentrations of As, total organic carbon (TOC) and [As]/[TOC] ratios in the samples are presented in Table 2. Complexation of As with humics on the surface

of sediments and adsorption of As on sediments, iron oxide or iron hydroxide can influence and change the concentration of dynamic As species in sediment.

The binding capacity and affinity of sediment for As is dependent on the number and type of ligands, on their position in the structure of the complexants, on the As to binding sites (present in sediment) ratio, pH, ionic strength and other factors. Benjamin and Leckie reported that the surfaces of some metal oxyhydroxides in sediment comprise various binding sites, the binding energy of which can vary more than one order of magnitude [28,29]. Humic substances, which are ubiquitous in the sediments, are known to possess strong binding sites accounting for approximately 1–10% of the total sites and weak binding sites accounting for about 90–99% of the total sites [30].

Kinetic speciation of As was performed by competing ligand exchange method in conjunction with spectrofluorometric determination. The kinetic data of As species extraction from the sediment samples are presented in Figure 5. The fluorescence signal in CLEM/spectrofluorometry was measured in the intensity mode. The relative concentration of As(III) species extracted during the reaction is given by the quotient $I_{As\ t}/\ I_{As\ Total}$ where, $I_{As\ t}$ represents the intensity observed with the sample at time t, and $I_{As\ Total}$ represents the intensity observed for a reference solution of As(III) with no complexation. The dynamic fraction of As(III) can be calculated by using this quotient:

$$\text{Percentage (\%) of dynamic As(III) species} = (I_{As\,t} \times 100)/I_{As\,Total}\,.$$

Secondly, dynamic fraction (c_l) can also be obtained by non-linear regression (NLR) analysis of the exponential rise curve (experimental curve). This analysis can also provide the corresponding dissociation rate constant (k_d) of dynamic As(III) complexes.

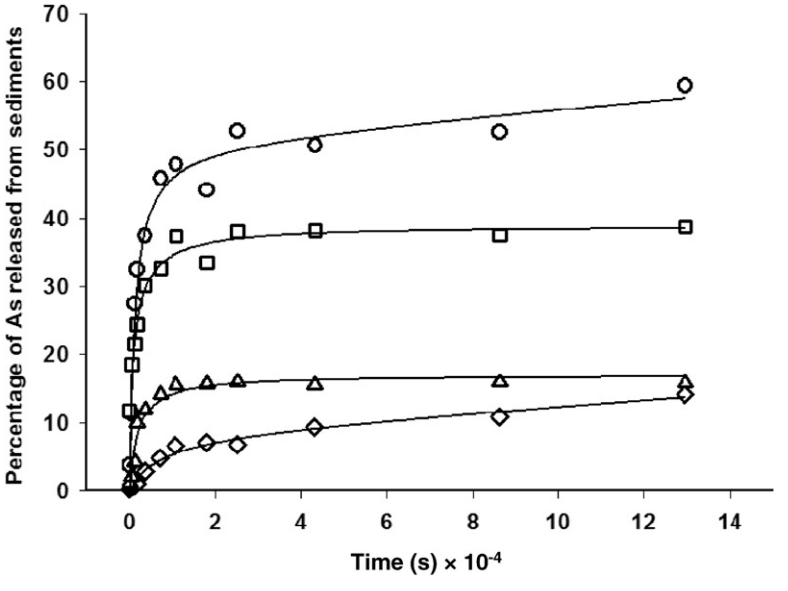

Figure 5. Release of extractable dynamic (non-residual) As species from sediments as a function of time in presence of 0.05 M EDTA at pH 6. (O): Kalingapatnam; (Δ): Machilipatnam; (□): Visakhapatnam; (◇): Kakinada.

NLR analysis was performed to obtain the dynamic fraction and their corresponding dissociation rate constants in this study.

Each curve in Figure 5 shows two distinguishable features: a quickly rising section that represents the rapid extraction of As ion or As-complexes from sediment. This part of the curve indicates a fraction of total As concentrations that are weakly bound to sediments and can be quickly released to the overlying water column as a result of any biogeochemical perturbation and may become bioavailable which can be hazardous to the environment. However, this rapid extractable As concentration from sediments varied from one station to another. A very slowly rising section of each curve lies almost parallel to the x-axis, which can be attributed to slow dissociation of strong kinetically inert As–sediment complexes (which do not undergo dissociation within the time scale of the experiment).

Each curve in Figure 5 was fitted to the kinetic model (Equation (3)) by non-linear regression analysis using the Marquardt–Levenberg algorithm and the results are presented in Table 3. Although these data were fitted to a simplified equation, it is necessary to note that the systems are complex.

The first part of all curves in Figure 5 are almost indistinguishable from one another, suggesting that they represent dissociation of one or more As complexes (As-sediment/As-humic, or adsorbed As complexes on iron oxide/hydroxide) having very similar dissociation rate constants; probably, they are all of As complexes with low thermodynamic stability and are dynamic in nature. However, stable As complexes which are weakly bound to sediments can also be leached rapidly from sediments.

The highest percentage of dynamic As species in sediment was found in Kalingapatnam, followed by Visakhapatnam, and Machlipatnam. The lowest fraction of dynamic As species was observed in Kakinada. Thus, fast extractable As concentrations in sediment samples decreased in the order; Kalingapatnam > Vishakhapatnam > Machilipatnam > Kakinada.

In interpreting percentage (%) of As released from the sediment, the following should be considered as a general guiding principle: the absolute concentrations of As in sediment are controlling factors in determining the As–sediment stability constants; the [As]/[TOC] mole ratios in sediments are one of the contributing factors in determining the As that binds to the strong sites (<10%), forming strong As–TOC complexes, the remaining As binds to the weak sites (>90%), forming weak As–TOC complexes in sediments. For TOC, the absolute concentrations must be calculated on the basis of its As-binding

Table 3. Kinetically extractable dynamic (non-residual) As species from sediments and their dissociation rate constant.

Station	c_1 (% of fast extracted arsenic species)	k_{d1}(dissociation rate constant of fast extracted species) s^{-1}	c_2 (% of slow extracted arsenic species)	k_{d2} (dissociation rate constant of slow extracted species) s^{-1}
Kalingapatnam	45.4 ± 1.6	6.3×10^{-3}	54.5 ± 1.0	$<1 \times 10^{-6}$
Visakhapatnam	34.2 ± 1.8	8.6×10^{-3}	65.8 ± 2.5	$<1 \times 10^{-6}$
Kakinada	5.8 ± 1.0	9.5×10^{-4}	94.2 ± 6.8	$<1 \times 10^{-6}$
Machilipatnam	15.6 ± 1.5	3.5×10^{-3}	84.3 ± 5.2	$<1 \times 10^{-6}$

Notes: Values presented as the means $\pm 2 \times$ standard deviation, $n = 3$.

functional groups. The stability constants of the As–TOC complexes determine the concentrations of free As ions at chemical equilibrium. However, there are other binding and adsorbing sites also present in sediment. As species which are occluded in other metal oxides or hydroxides and adsorbs on the surface of sediments also play a crucial role in the release of As.

This extraction of As species from sediments showed that the concentration of the fast extractable dynamic As component (c_1) has a good correlation with As-to-TOC ratio. It is well known that As exists in −3, 0, +3 and +5 oxidation states [31]. Environmental forms include arsenous acids ($As(OH)_3$), arsenic acids (H_3AsO_4), arsenites ($AsO(OH)_2^-$), arsenates ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}), methylarsenic acid ($CH_3AsO(OH)_2$), dimethylarsinic acid ($(CH_3)_2AsO(OH)$), arsine (AsH_3). As(III) is a hard acid and preferentially complexes with oxygen and nitrogen. Conversely, As(V) behaves like a soft acid, forming complexes with sulfhydryl and /or amino groups. Inorganic forms of As most often exist in water supplies [32]. As is uniquely sensitive to mobilisation (pH 6.5–8.5) and under both oxidising and reducing conditions among heavy metalloids [33]. Pentavalent species predominate and are stable in oxygen rich aerobic environments. As(III) predominate in moderately reducing anaerobic environments such as groundwater and sediments. As(III), which behaves like a hard acid, is expected to undergo strong complexation reaction with oxygen containing binding sites of humics (major sites) in sediment and with oxides of iron. This indicates that speciation of As in sediment is controlled by nature of humics and metal oxide. Figure 6 shows that the concentration of fast extractable dynamic As species (c_1%) increased linearly with the As-to-TOC ratio. This indicates that TOC present in sediment play a crucial role in binding of As.

This study developed a simple inexpensive and sensitive spectrofluorometric method for the determination of total As concentration in sediments and was successfully applied for kinetic speciation of As in sediments. Dynamic As concentration (which can be related to bioavailability) in sediment which is environmentally significant and the dissociation

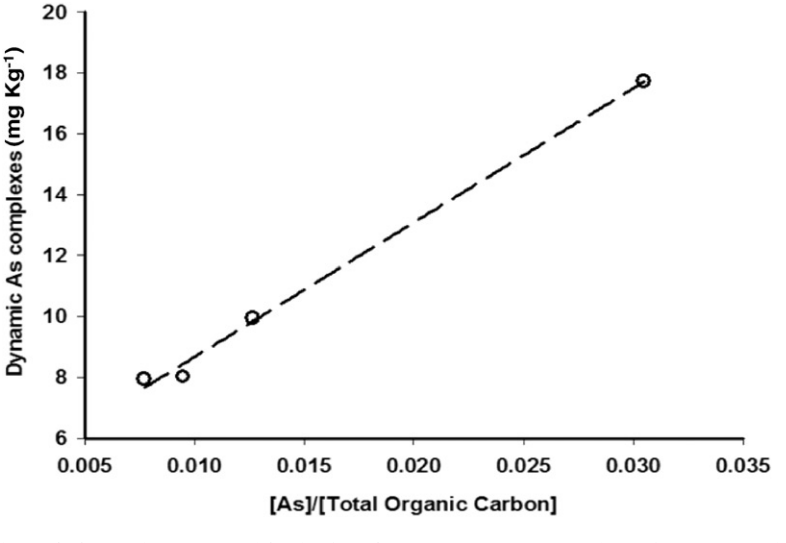

Figure 6. Plot of dynamic (non-residual) As (fast) components against As/TOC ratio found in sediments collected at four different sampling sites.

rate constant of As-sediment complexes at the coastal sediments of Bay of Bengal was also successfully determined.

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