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Dissolved Mo and U in rivers and estuaries of India: Implication to geochemistry of redox sensitive elements and their marine budgets

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ABSTRACT

Dissolved molybdenum (Mo) and uranium (U) concentrations were measured in five Indian estuaries; the Narmada, Tapi, Mandovi and the Mahi fall into the Arabian Sea and the Hooghly falling into the Bay of Bengal. Riverine Mo and U vary significantly, in the range of 1 to 90 and 0.02 to 19 nmol/kg respectively. The lowest Mo and U were observed in the Mandovi river, consistent with lateritic lithology exposed in its drainage, higher runoff and lower water-rock interaction. The Sabarmati has the highest U, 19 nmol/kg and sources from the groundwater having very high U concentration. The highest Mo (90 nmol/kg) is observed in the Mahi river and probably results from anthropogenic sources. Hooghly river seems to have high concentrations of Mo (14 nmol/kg) and U (8 nmol/kg) and are possibly derived from weathering of black shales of the Himalaya. Behaviour of Mo and U in all the estuaries analysed in this study is highly variable. Both Mo and U in the Narmada estuary during pre-monsoon and monsoon seasons and U in the Tapi estuary behave conservatively. Mo in the Tapi shows its addition in the mid salinity ranges (~4 to 12‰) and is sourced from anthropogenic activity probably related to effluent from industries situated along the estuary in this salinity range. Both dissolved Mo and U show their removal at lower salinity ranges in the Hooghly and the Mandovi estuaries. These estuaries are net sink of Mo in which significant amount of oceanic Mo along with riverine Mo is being lost. About 1.6×10^6 and 2×10^5 mol of Mo are being removed annually in the Hooghly and the Mandovi estuaries. Uranium removal is order of magnitude lower compared to Mo in both the Hooghly and the Mandovi estuaries. The loss of Mo and U in the estuaries are associated with mangrove swamps present in the estuaries which seems to be an important sink of the oceanic Mo and could represent its significant sink in oceanic budget of Mo.

The Gulf of Cambay has high dissolved Mo concentration compared to that of global average seawater value which is attributed to its supply from anthropogenic sources. Industrial effluent waste waters along with polluted rivers supply ~5×10^6 mol of Mo annually to the Gulf of Cambay which could be derived from petrochemicals and pharmaceutical industries situated along the Gulf coast.

1. Introduction

Estuaries represent transition zone between river and ocean where geochemical, biological and sedimentological processes are highly variable both spatially and temporally (Colodner et al., 1993; Dalai et al., 2005; Dellwig et al., 2007; Scheiderich et al., 2010). These processes determine the riverine contribution of various elements to the oceans. The study of the behaviour of various elements in the estuary therefore becomes important not only to understand their geochemistry but also to evaluate their marine budgets. Among the various groups of elements that are being investigated, one is the redox sensitive group that include U, Mo and Re. This group of elements finds applications in studies of marine paleoenvironmental conditions because of their property to be sequestered with the organic rich marine sediments (Ravizza et al., 1991; Colodner et al., 1992; Morford and Emerson, 1999; Dalai et al., 2002; Jaffe et al., 2002).

The dominant source of all these elements to the ocean is river input (Martin and Meybeck, 1979). In rivers these elements are derived from chemical weathering of various lithologies, an important one being organic rich sediments, black shales (Colodner et al., 1993; Jaffe et al., 2002; Singh et al., 2003). Recent studies, however, have shown that in some rivers anthropogenic sources can also be significant (Colodner et al., 1993, 1995; Peucker-Ehrenbrink et al., 2006; Rahaman and Singh, 2010). Available studies showed that the behaviour of these elements is complex (Emerson and Hausted, 1991; Colodner et al., 1993, 1995) and seem to depend on the regional environmental chemistry. For example both uranium and rhenium exhibit conservative and non-conservative behaviour in estuaries (McKee, 2008 and references there in; Colodner et al., 1993; Rahaman and Singh, 2010). Studies of Mo in estuaries are sparse (Colodner et al., 1993; Helz et al., 1996; Dalai et al., 2005; Audry

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et al., 2007; Archer and Vance, 2008; Scheiderich et al., 2010). In sea water, Mo and U occur as oxyanions, $(MoO_4)^{2-}$ and $UO_2(CO_3)_3^{4-}$ and their geochemistry are similar to that of Re present as perrhenate oxyanion ReO_4^- (Colodner et al., 1993, 1995). All these elements have long residence times in the oceans, orders of magnitude longer than ocean mixing times. As a result these elements have uniform concentration in the ocean. Despite its biological involvement (Dellwig et al., 2007), Mo displays conservative behaviour in ocean and is the most abundant transition element in the sea with average dissolved concentration of 110 ± 10 nM (Morris, 1975; Collier, 1985; Quiby-Hunt and Turekian, 1983). Analogous to Mo, U is also a conservative element in the ocean, with very uniform dissolved concentration of 13.6 nM (Ku et al., 1977; McKee, 2008). The major sink for these elements is removal to particulate phases in redox conditions (Colodner et al., 1995), however their sensitivity to redox condition which determines their removal from dissolved phase to solid phase is different, with rhenium being the most sensitive (Colodner et al., 1993; Morford and Emerson, 1999). The association of these elements with reducing conditions makes their concentrations high both in modern and ancient organic rich marine sediments, (Ravizza et al., 1991; Peucker-Ehrenbrink et al., 1995; Morford and Emerson, 1999; Singh et al., 1999; McManus et al., 2006).

This study focuses on the distribution of the redox sensitive elements U and Mo and the processes regulating their concentrations in rivers and estuaries draining into the Bay of Bengal, the Arabian Sea and the Gulf of Cambay and compare them with that of Re in the same rivers/estuaries (Rahaman and Singh, 2010). Such a study, in addition to characterizing their behaviour in estuaries also provides data to constrain their inputs to the open ocean and therefore their marine budgets. Available data suggest that the present supply of Mo to the global ocean is significantly higher compared to its known sinks (Martin and Meybeck, 1979; Morford and Emerson, 1999; McManus et al., 2006; Archer and Vance, 2008). Attempts are being made to look for the additional sink of marine Mo. In this study, Mo measurements have been carried out for the first time in Indian rivers and estuaries whereas in some of these estuaries particularly the Narmada, Tapi, and the Hooghly U measurements have been reported earlier (Borole et al., 1982; Somayajulu, 1994). In this study, however, U has been measured along with Mo and Re to assess their relative behaviour and seasonal variations.

2. Study area

The estuaries sampled for U and Mo are the Narmada, Tapi, Mahi and the Mandovi along the coast of the Arabian Sea and the Hooghly in the Bay of Bengal (Fig. 1a and b). These samples were also analyzed for Re, the results of which are published separately (Rahaman and Singh, 2010). The Narmada, Tapi and the Mahi estuaries open to the Gulf of Cambay near Bharuch, Surat and Dhuvaran cities respectively (Fig. 1b).

The Hooghly is one of the distributaries of the Ganga which bifurcates at Farakka. It flows to the Bay of Bengal near Kolkata (Fig. 1a). The Ganga originates in the Himalaya, drains various lithologies that include granite/gneisses, carbonates, shales, black shales and slates in the Himalaya and the alluvium in the Ganga plain. The average fresh water discharges of the Hooghly is 3000 m^3/s during the monsoon season (June–September) and 1000 m^3/s during dry season (November–May) (Sadhuram et al., 2005). Normally, the water discharge in the Hooghly river is regulated from the Farakka barrage to maintain water levels.

The Narmada originates from Amarkantak in the Vindhyan Mountains in Madhya Pradesh (MP) and flows through the Vindhyan sediments, the Deccan basalts and alluvium. The Tapi originates at Multai in Betal district of MP. It drains the Deccan basalts and alluvial deposits before draining into the Gulf of Cambay. The average annual rainfall in the Narmada and the Tapi drainage basins are 1250 and 830 mm respectively, of this ~90% is received during monsoon (Sharma

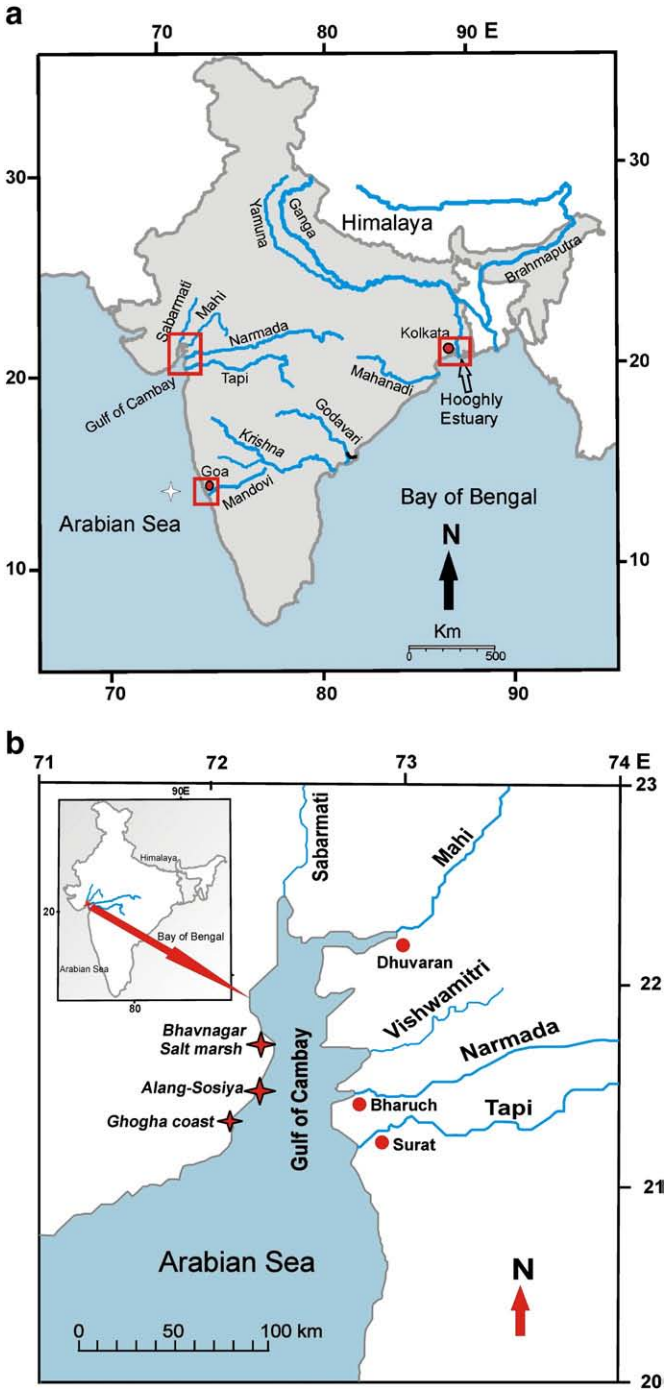

Fig. 1. (a) Map showing the locations of the estuaries studied in this work. The Narmada, Tapi, Mandovi and the Mahi estuaries fall in the Arabian Sea and the Hooghly, in the Bay of Bengal. (b) Location of the Gulf of Cambay receiving the Mahi, Narmada and the Tapi rivers.

et al., 2007). The annual discharge of the Narmada ~47.3×10^9 m^3 is 2–3 times of the Tapi ~18.9×10^9 m^3 (Alagarsamy and Zhang, 2005). Both these rivers have dams/reservoirs along their course. Large scale industries such as chemical, pharmaceutical, petrochemical and steel are situated along the Narmada and the Tapi rivers and near their mouth in the Gulf of Cambay.

The Mandovi river originates in the Western Ghats of the Indian peninsula and flows east to west over a length of 75 km through the rocky terrains of Goa, before draining into the Arabian Sea (Upadhyay and Gupta, 1995). The average annual rainfall in this basin is 3000 mm, of which about 90% occurs during the southwest monsoon

(June–September). The average water discharge of the Mandovi is 16×10^9 m^3/y (Upadhyay and Gupta, 1995). A large part of the drainage basin of the Mandovi consists of basalts, phyllites, meta-greywacke/metabasalts and schists/gneisses. Most of the lithologies in the basin are capped by laterite deposits that contain bauxites (Sastry and Gopinath, 1985).

3. Methods

3.1. Sampling

Water and suspended particulate matter were collected from each of above estuaries during one tidal cycle (low tide) along the salinity gradient. Salinity, pH and temperature were measured at site. Water samples for the analysis of Re, U and Mo were collected in precleaned high density polypropylene bottles. In addition to estuaries, samples were also collected from the rivers upstream, (including samples up and down streams of major dams in the Narmada and the Tapi) coastal areas of the Gulf of Cambay and the Arabian Sea off the Goa coast (Fig. 1a). The Narmada estuary was sampled during both monsoon and nonmonsoon seasons whereas Tapi was sampled only in monsoon. The Hooghly and the Mandovi were sampled during non-monsoon. A few samples were also collected from the Mahi estuary near its mouth, water from the Sabarmati and the Vishwamitri rivers draining into the Gulf of Cambay and from a salt marsh near Bhavnagar (Fig. 1b). Open Arabian Sea samples were collected on-board FORV Sagar Sampada (Cruise # SS 256). All samples were filtered through 0.2 μm nylon filters, filtered waters were acidified to pH ~2 using high purity HNO_3 and stored in precleaned high density polypropylene bottles till time of measurement. Separate aliquot of samples were collected for alkalinity measurement and kept in air-tight cleaned bottles. This measurement was carried out in the laboratory within 2–3 days of sampling. Alkalinity was measured by acid titration with known strength (~0.01 M) of diluted HCl using auto-titrator (Metrohm 702 SM Titrino) following end point titration method.

For suspended particulate matter 10 ℓ water samples from different salinities were collected in carbouys and brought to laboratory. The suspended matters were separated from water by settling and decanting the supernatant clear water. The slurry containing suspended matter was transferred to suitable containers. Bed-loads were collected from some of the estuaries from exposed sand bars. These samples were analysed for U, Mo and Re, the U and Mo data are presented in this paper, the Re data is published in Rahaman and Singh (2010).

3.2. Analysis of U and Mo in waters

Dissolved U and Mo concentrations were measured in the water samples using a quadrapole ICP-MS (Thermo-X series) following the procedure of Rodushkin and Ruth (1997). As the samples were collected from different salinities, to minimize the matrix effect during ICP-MS measurements, they were diluted suitably to bring the salt content in the diluted waters roughly the same. This required about 30 times dilution for samples collected close to sea water end member whereas the river waters were analysed as such. Mo and U concentrations were determined by measuring their most abundant isotopes, ^{98}Mo and ^{238}U, respectively. In addition, other prominent isotopes ^{95}Mo and ^{235}U were also monitored during the analysis. The sample introducing system (tubings and nebuliser) were cleaned repeatedly with mili-Q water between measurements to minimize memory effects for Mo. Seawater and estuarine reference material (NASS-5 and SLEW-1) from the National Research Council, Canada were also analyzed along with the samples. The measured U and Mo in these reference materials are within ±20% of "information only" values for SLEW-3 and within ±10% for NASS-5 (Table 1a). Precision of measurements was determined based on replicate analyses of samples (Table 1b). This was ±4% and ±5% respectively for U and Mo.

4. Results

The dissolved Mo, and U concentrations measured in the estuaries along with salinity, pH and temperature are given in Tables 2 and 3. Re data measured in these estuaries were also given in Tables 2 and 3 and are taken from Rahaman and Singh (2010). In the Narmada estuary, the pH remains nearly constant at ~8 from fresh water to seawater (Table 2), unlike in the Tapi and the Mandovi estuaries which show significant variations between 7.5 to 8.0 and 6.6 to 8.2 respectively. Alkalinity lies between 2000 and 3000 μeq/ℓ in all the estuaries except in the Mandovi where it varies from 384 to 2236 μeq/ℓ (Table 2). Lower pH and alkalinity in the Mandovi river indicates the dominance of rainwater and limited water rock interaction. Alkalinity shows an increase in the 4–12‰ salinity range in the Tapi estuary.

4.1. Molybdenum, Uranium and Rhenium in river water, seawater and salt marsh

Mo in river water end members of the Narmada, Tapi, Mandovi and the Hooghly ranges between 1.0 to 14 nmol/kg with the Mandovi and the Hooghly having the lowest and the highest concentrations respectively (Table 2). Mo in the Narmada, Tapi and the Mandovi rivers can be accounted from weathering of lithologies exposed in their drainage basins. Basalts, the major lithology of the Narmada and the Tapi basins contain ~1 ppm Mo (Yamaguchi, 2002), similar to average crustal abundance (Manheim and Landergren, 1978). Therefore, release of Mo from a few hundred milligrams of these rocks can sustain its measured concentration. Mo concentration for the Hooghly river is not measured, however, considering that the sample with 0.5‰ salinity has 14 nmol/kg it is expected that the Hooghly river water would have Mo concentration ~14 nmol/kg. Concentration of ~14 nmol/kg is difficult to be explained in terms of silicate/carbonate weathering in the Ganga basin. Dissolved load in

Table 1a
U and Mo in reference materials and in seawater from the Arabian Sea.

Sample	Measured				Reported			
	U		Mo		U		Mo	
	ppb	nmol/kg	ppb	nmol/kg	ppb	nmol/kg	ppb	nmol/kg
SLEW-3 For n = 12	1.40 ± 0.03	5.9 ± 0.1	4.02 ± 0.02	41.9 ± 0.2	1.8[a]	7.6[a]	5.1[a]	53.2[a]
NASS-5 For n = 15	2.60 ± 0.10	10.9 ± 0.4	8.6 ± 0.3	89.6 ± 3.1	2.6[a]	10.9[a]	9.6 ± 1.0	100.1 ± 10.4
Seawater For n = 5	3.03 ± 0.05	12.7 ± 0.2	9.7 ± 0.1	101.1 ± 1.0				

Reference materials from National Research Council Canada.
[a] These are "information only" values.

Table 1b
Replicate analyses of dissolved U and Mo in estuary samples.

Sample	Salinity	[Mo]	[U]
	‰	nmol/kg	
NE-5	18.2	54.0 ± 0.6	7.8 ± 0.03
NE-5R		54.3 ± 1.1	7.8 ± 0.1
NE-10	25.3	75.0 ± 0.7	10.3 ± 0.04
NE-10R		71.8 ± 1.1	10.2 ± 0.1
NEM-5	3.4	16.2 ± 0.3	2.7 ± 0.02
NEM-5R		17.1 ± 0.4	2.8 ± 0.03
NEM-14	0	2.9 ± 0.05	1.2 ± 0.01
NEM-14R		2.9 ± 0.1	1.2 ± 0.01
MD-5	16.1	47.1 ± 0.7	4.6 ± 0.1
MD-5R		50.0 ± 0.6	4.7 ± 0.1
TPM-12	17.4	61.2 ± 1.1	6.8 ± 0.1
TPM-12R		59.5 ± 1.2	6.8 ± 0.1
W-5	14.7	50.0 ± 0.7	8.4 ± 0.1
W-5R		49.1 ± 1.3	8.3 ± 0.04
KOH-15	25.6	132.2 ± 1.9	15.2 ± 0.1
KOH-15R		135.0 ± 1.7	15.3 ± 0.1

R: replicate.

the Ganga from the weathering of silicate/carbonate rocks having average Mo abundance ~1 ppm (Manheim and Landergren, 1978) can support only 15% of dissolved Mo of the Ganga. Therefore, the high Mo in the Hooghly has to be derived from lithologies rich in Mo, such as organic rich sediments. For example, black shales are known to be rich in Mo with concentration in the range of 10–1000 ppm (Yamaguchi, 2002), orders of magnitude higher than that in average continental crust. Therefore, if such Mo rich black shales are present in the basin of the Ganga; they can serve as its source. In this context, Dalai et al. (2002) and Singh et al. (2003) have suggested weathering of black shales as a potential source of high Re and U in the Himalayan rivers.

In contrast to the above rivers, the Mahi and the Sabarmati have very high Mo, 90 and 48 nmol/kg respectively. The source(s) for such high Mo is unlikely to be various lithologies present in their basins; instead it seems to be supplied by anthropogenic sources. The drainage basins of the Mahi and the Sabarmati are heavily industrialized and these industries could be an important source of dissolved Mo to these rivers as has been proposed for Re (Rahaman and Singh, 2010). Mo is used in pharmaceutical and steel industries as a catalyst and hardening agent (Goth, 1977) respectively and effluent discharges from these industries can be a source of Mo to rivers (Krupadam et al., 2006). This hypothesis draws support from the observation that industrial effluents (salinity of 10.8 to 11.6‰) analyzed in this study have very high Mo (560 and 820 nmol/kg; Table 3).

Uranium concentrations analysed in this study vary from a very low value of 0.02 nmol/kg in the Mandovi (Table 2) to 19 nmol/kg in the Sabarmati river (Table 3) and seem to depend on the lithology present in the basin and the intensity of weathering the basin is undergoing. The Narmada and the Tapi rivers have U in the range of 1 to 3 nmol/kg similar to the global average riverine U concentration, ~1.3 nmol/kg (Palmer and Edmond, 1993; Dunk et al., 2002; McKee, 2008). U in the Narmada and the Tapi measured in this study overlaps with those reported by Borole et al. (1977, 1982). The sources of U seem to be the weathering of basalts and alluvium in the basin (Borole et al., 1982). U in the Sabarmati measured in this study at Vatman bridge is higher than that reported in its upper reaches (3.4 to 15.8 nM; Borole et al., 1979) underscoring the importance of temporal and spatial variability. High U in the Sabarmati can result from the uraniferous granites present in the Aravalli mountains (Pradeepkumar et al., 2008), the source regions of the Sabarmati river and/ or ground water contribution to the river which have U content as high as 91 nmol/ℓ (Hussain and Krishnaswami, 1980).

The impact of anthropogenic activity in contributing to the higher U seems unlikely though this basin supports widespread agricultural activities and is significantly industrialized. The low concentration of U in industrial effluents, 1.4–2.8 nmol/kg (Table 3) supports this hypothesis.

In the Mandovi river, U concentration is among the lowest of the world rivers (Bertine and Turekian, 1973; Palmer and Edmond, 1993; Windom et al., 2000; Dunk et al., 2002) consistent with the low concentration observed for Mo and Re. The low U in the Mandovi River associated with lower alkalinity and TDS is due to dominance of laterites in the basin and high rainfall. Singh et al. (2003) suggested that the high U in the Ganga source water can be from weathering of black shales and/or uraniferous granites of the Himalaya. The high U in the Hooghly may also be a result of contribution from the Himalayan tributaries (Sarin et al., 1990).

Re in the Narmada river collected upstream of its estuary, average 14 ± 1 pmol/kg (Table 2; Rahaman and Singh, 2010). Re in the Tapi river near the Ukai dam is ~4 pmol/kg (Table 2). Mandovi river flowing through the Western Ghats of the Indian peninsula has the lowest range of Re concentration, 1.4 pmol/kg. Re is not measured in Hooghly river, however Re concentration of 6.6 pmol/kg measured at 0.5‰ salinity in its estuary could be close to its riverine value. Mahi river has the highest concentration of Re, 41 pmol/kg among the rivers analysed in this study. As discussed earlier, it also has the highest Mo.

Five seawater samples from the Arabian Sea off Goa have dissolved Mo 101 ± 1 nmol/kg (Table 3), within the range reported for seawater 110 ± 10 nmol/ℓ from other locations (Morris, 1975; Quiby-Hunt and Turekian, 1983; Collier, 1985). Seawater from the Gulf of Cambay, collected off the Ghogha coast, has ~12.6 nmol/kg U (Table 3), nearly same to those reported for U in the open Arabian Sea 13.44 ± 0.84 nmol/kg (Rengarajan et al., 2003) and to those measured in this study in samples off Goa coast 12.4 to 13.0 nmol/kg (Table 3). Re concentration in three open ocean surface water samples collected off the Goa coast vary within a narrow range of 40.4 to 41.0 pmol/kg (Rahaman and Singh, 2010), nearly identical to those reported for the open Pacific Ocean (Anbar et al., 1992).

Water samples from a salt marsh on the western coast of the Gulf of Cambay near Bhavnagar were analysed for Mo, U and Re concentrations. This water with a salinity of 120‰ has very high Mo, 655 nmol/kg compared to ~111 nmol/kg (Table 3) for seawater (32.5‰) from nearby regions (near the Ghogha coast). Mo/salinity ratio in the seawater near the Ghogha coast is 3.4 nmol/kg/‰ whereas for the salt marsh sample it is ~5.5 nmol/kg/‰, suggesting that the Mo in the salt marsh sample is "in excess" of what would be expected for evaporitic enrichment of seawater for the region. The presence of "excess" Mo in the salt marsh indicates that it can act as a source of Mo to adjoining sea water. This is unlike that reported for the Sapelo Island salt marsh, USA (Roychoudhury, 2006) where Mo is sequestered from dissolved to particulate phase. In contrast to Mo, Re, another redox sensitive element, behaves conservatively in the Bhavnagar salt marsh (Rahaman and Singh, 2010). In this salt marsh (salinity 120‰), dissolved U is only 27.9 nmol/kg (Table 3) about ~35% lower than that expected for evaporitic enrichment of seawater for adjacent regions. This deficiency indicates U loss in the salt marsh, similar to earlier observation in the Delaware Bay salt marsh (Maeda and Windom, 1982; Church et al., 1996). The available results of Mo, Re and U in the salt marsh sample analyzed in this study show very contrasting behavior; gain and loss of Mo and U respectively with Re behaving conservatively.

5. Mo, U and Re in Estuaries

Available results on Mo in estuaries show both conservative and non-conservative behaviour, for example; in the Southampton estuary (Head and Burton, 1970) removal of Mo was observed during spring season which was attributed to its biological utilization and/or sequestration by organic matter. Similarly, loss of Mo was reported

Table 2
Dissolved U and Mo in the Indian Estuaries.

Sample	Latitude	Longitude	Salinity (‰)	Temp (°C)	Alkalinity (μEq/ℓ)	pH	[U]	[Mo]	[Re][a]
							nmol/kg		pmol/kg
Narmada (Pre-monsoon, March 2007)									
NE07-1	21°40.81′	72°54.57′	4.8	25.4	2947	8.08	3.7	20.9	27.4
NE07-2	21°41.26′	72°52.60′	9.3	25.6	2962	7.92	5.7	36.9	43.6
NE07-3	21°40.58′	72°50.39′	11.8	25.8	2909	7.98	6.2	40.0	47.8
NE07-4	21°39.20′	72°47.42′	15.9	26.5	2814	7.93	7.3	50.1	60.5
NE07-5	21°38.80′	72°45.34′	18.2	27.1	2807	7.96	7.8	54.0	64.7
NE07-6	21°40.75′	72°42.05′	20.0	27.4	2754	8.00	8.5	60.7	71.1
NE07-7	21°40.71′	72°49.83′	21.3	27	2744	7.95	8.7	62.7	75.0
NE07-8	21°39.46′	72°35.89′	22.1	28.2	277	8.03	9.3	66.9	76.8
NE07-9	21°39.36′	72°34.51′	23.9	27.7	2738	8.02	9.8	70.2	82.3
NE07-10	21°39.62′	72°33.28′	25.3	27.8	2668	7.98	10.3	75.0	88.8
NE07-11	21°38.73′	72°33.02′	25.5	28.1	2686	8.11	10.1	73.6	85.2
NE07-12	21°38.04′	72°32.70′	27.2	27.1	2699	7.90	10.8	78.3	89.7
NE07-13	21°38.0′	72°32.7′	29.0	26.6	2653	8.08	11.3	82.9	94.0
NE07-14	21°37.94′	72°32.05′	30.2	26.4	2654	8.10	11.7	86.6	98.2
NE07-15	21°37.94′	72°32.05′	31.1	26.6	2635	8.08	12.0	89.6	103.0
Narmada (Monsoon, July 2007)									
NEM07-1	21°40.59′	72°55.58′	0	30.3	2395	8.83	1.5	4.3	10.0
NEM07-2	21°39.08′	72°46.64′	0.1	30.6	2385	7.98	1.9	8.7	11.1
NEM07-3	21°40.07′	72°37.12′	1.3	30.6	2410	8.06	2.0	10.7	16.8
NEM07-4	21°39.58′	72°36.34′	2.2	31.3	2405	7.99	2.2	12.9	20.8
NEM07-5	21°39.42′	72°35.49′	3.4	30.8	2309	8.00	2.7	16.2	26.7
NEM07-6	21°39.15′	72°34.28′	5.1	31.3	2270	8.03	3.3	21.6	37.4
NEM07-7	21°38.55′	72°33.18′	6.0	30.5	2322	8.04	3.5	23.7	39.6
NEM07-8	21°38.39′	72°33.26′	8.0	30.8	2259	8.00	4.0	28.9	48.3
NEM07-9	21°39.27′	72°35.26′	9.8	30.6	2219	8.00	4.7	34.2	59.9
NEM07-10	21°38.52′	72°33.2′	12.1	30.8	2222	8.03	5.9	46.9	84.6
NEM07-11	21°38.81′	72°33.94′	14.1	30.8	2180	8.03	6.1	51.2	80.0
NEM07-12	21°38.05′	72°33.19′	15.5	30	2155	8.02	6.3	49.6	87.6
NEM07-13	21°38.55′	72°32.93′	17.2	32.3	2146	8.25	7.0	53.8	97.4
Tapi (Monsoon, July2007)									
TPM07-1	21°10.56′	72°46.74′	0-0.2	30.6	2848	7.57	1.4	6.1	7.6
TPM07-2	21°8.9′	72°45.8′	1.1	30.5	2942	7.66	1.8	9.6	7.4
TPM07-3	21°8.52′	72°43.61′	2.1	30.6	2937	7.73	2.0	12.4	8.8
TPM07-4	21°8.86′	72°42.26′	3.9	30.5	3008	7.80	2.6	20.3	12.8
TPM07-5	21°9.15′	72°4.73′	4.9	30.2	3085	7.74	3.1	25.1	17.1
TPM07-6	21°9.3′	72°40.19′	5.8	30.3	3030	7.84	3.4	31.8	19.1
TPM07-7	21°7.97′	72°39.58′	7.8	29.9	2941	7.90	4.1	37.9	25.0
TPM07-8	21°7.05′	72°39.74′	9.8	29.6	2809	7.92	4.6	42.4	27.5
TPM07-9	21°5.79′	72°39.98′	11.5	29.6	2700	7.35	5.1	44.0	32.3
TPM07-10	21°4.97′	72°40.64′	13.1	29.6	2710	8.02	5.4	47.2	34.6
TPM07-11	21°4.41′	72°40.71′	14.9	29.6	2685	8.01	6.1	54.3	39.6
TPM07-12	21°3.6′	72°40.68′	17.4	29.8	2715	7.99	6.8	61.2	45.3
TPM07-13	21°3.16′	72°40.35′	20.3	29.7	2530	8.02	7.7	70.5	51.3
Mandovi (Post-Monsoon, October 2007)									
MD07-1	15°32.56′	73°57.69′	0.1	27.8	384	6.61	0.02	1.0	1.4
MD07-2	15°32.39′	73°55.95′	2.7	27.8	515	6.95	0.1	7.4	4.3
MD07-3	15°31.55′	73°55.60′	6.0	28.2	672	6.90	0.7	7.3	7.5
MD07-4	15°31.33′	73°55.38′	13.5	28	1113	7.43	4.2	42.0	16.1
MD07-5	15°30.33′	73°54.82′	16.1	28.9	1363	7.53	4.6	47.1	19.1
MD07-6	15°30.27′	73°54.16′	19.7	29	1512	7.72	6.2	58.0	23.2
MD07-7	15°30.11′	73°52.88′	26.9	28.9	1902	7.92	9.3	84.0	30.8
MD07-8	15°30.34′	73°50.63′	31.3	29	2131	7.98	11.2	100.0	36.9
MD07-9	15°29.29′	73°48.40′	33.7	28.5	2233	8.00	12.1	109.0	39.1
MD07-10	15°29.07′	73°41.09′	33.6	28.9	2236	8.18	11.9	109.1	39.3
Hooghly (Post-monsoon, December 2006)									
W-1	22.01°	88.19°	0.5	–	–	–	8.0	13.8	6.6
W-2	21.9°	88.09°	2.6	–	–	–	7.2	20.3	7.8
W-3	21.77°	88.02°	7.7	–	–	–	6.8	24.4	12.6
W-4	21.65°	88.02°	11.8	–	–	–	8.1	25.8	16.4
W-5	21.58°	88.08°	14.7	–	–	–	8.4	50.0	19.4
W-6	21.49°	88.13°	16.7	–	–	–	8.9	58.1	21.3
W-7	21.33°	88.19°	20.5	–	–	–	9.9	63.6	25.2
W-8	21.06°	88.2°	22.5	–	–	–	10.5	76.0	27.5
W-9	20.69°	88.21°	30.0	–	–	–	12.2	102.4	35.1
W-10	20.0°	88.2°	32.0	–	–	–	13.0	112.3	37.2

–: not measured.
[a] Rahaman and Singh, 2010.

Table 3
Dissolved U and Mo in miscellaneous samples.

Sample	River/Location	Salinity	Temp	pH	[U]	[Mo]	[Re][a]
		‰	°C		nmol/kg		pmol/kg
River waters							
NE07-21	Narmada, Sardar Sarovar dam	0	27	8.34	1.4	2.3	13.9
NE07-22	Narmada, Sardar Sarovar dam	0	30.1	8.03	1.4	2.6	13.1
NEM-14	Narmada, Sardar Sarovar dam	0	30.4	8.49	1.2	2.9	8.5
TPM-14	Tapi, Ukai dam	0	–	–	0.9	3.6	4.1
KOH-08-13	Vishwamitri	0.1	30.6	7.90	5.3	23	18.0
KOH-08-17	Sabarmati, Vatman bridge	1.2	32.5	7.92	19.0	48	37.0
KOH-08-16	Mahi, Mahisagar bridge	0	29.1	8.57	7.9	90	41.0
Estuary and coastal waters							
KOH-08-14	Mahi, Dhuvaran	27	31.9	7.93	12.2	118	208.0
KOH-08-15	Mahi, Badalpur	25.6	28.9	8.40	15.2	132	118.0
KOH-08-19	Off Ghogha coast	32.4	29.8	7.79	12.5	110	171.0
KOH-08-20	Off Ghogha coast	32.5	29.6	7.95	12.7	111	129.0
Salt marsh water							
KOH-08-18	Near Bhavnagar	120	35.1	7.11	27.9	655	695.0
Open ocean water							
GA 07-1	Off Goa	–	–	–	12.4	99	–
GA 07-2	Off Goa	–	–	–	12.6	101	–
GA 07-3	Off Goa	–	–	–	12.8	101	41.0
GA 07-4	Off Goa	–	–	–	12.9	100	40.4
GA 07-5	Off Goa	–	–	–	13.0	103	40.9
Waste waters							
KOH-08-11	Pipe-line waste water, Hansot	10.8	28.3	7.70	2.8	569	178
KOH-08-12	Pipe-line waste water, Hansot	11.6	28.9	7.60	1.4	828	175

–: not measured.
[a] Rahaman and Singh, 2010.

from the coastal waters of Wadden Sea (Dellwig et al., 2007) which was ascribed to its incorporation into sediment aggregates formed in the oxygen depleted zone. In contrast, in the Chao Phraya estuary (Dalai et al., 2005) and near shore surface seawaters of the North Wales (Jones, 1974) show addition of Mo in mid salinity waters resulting either from its desorption from particulate material (Jones, 1974) or to its supply due to interaction of bottom reducing sediments with overlying oxic water (Dalai et al., 2005). Oxygen from bottom oxic water penetrates the sediments causing release of Mo and other redox sensitive trace elements (U and Re) to the pore water and subsequently to the bottom water (Morford et al., 2007). The bottom waters upwell to the surface causing an addition of Mo (Dalai et al., 2005).

The distribution of U in estuaries has been extensively studied. The available data suggest its complex nature in different estuaries. It is difficult to generalise the behaviour of U in all the estuaries (see Windom et al., 2000; Swarzenski et al., 2003; McKee, 2008 for reviews). The processes that regulate the temporal and spatial variations in the behaviour of uranium in estuaries are not well understood. Various mechanisms have been suggested for the removal or addition of uranium in estuaries. Adsorption by sediment plumes, precipitation with iron and manganese, flocculation with organic matter and reduction in organic matter rich sediments are some of the processes suggested for its removal whereas release from bottom sediments under oxic conditions and desorption from particulates are some of the processes proposed as additive processes of uranium.

In the following sections, Mo and U results obtained in the Indian estuaries along the Arabian Sea and the Bay of Bengal are discussed and compared with available Re data for the same samples (Rahaman and Singh, 2010).

5.1. Dissolved phase

The results of Mo distribution in the Narmada estuary during both pre-monsoon (March 2007) and monsoon (September 2007) are

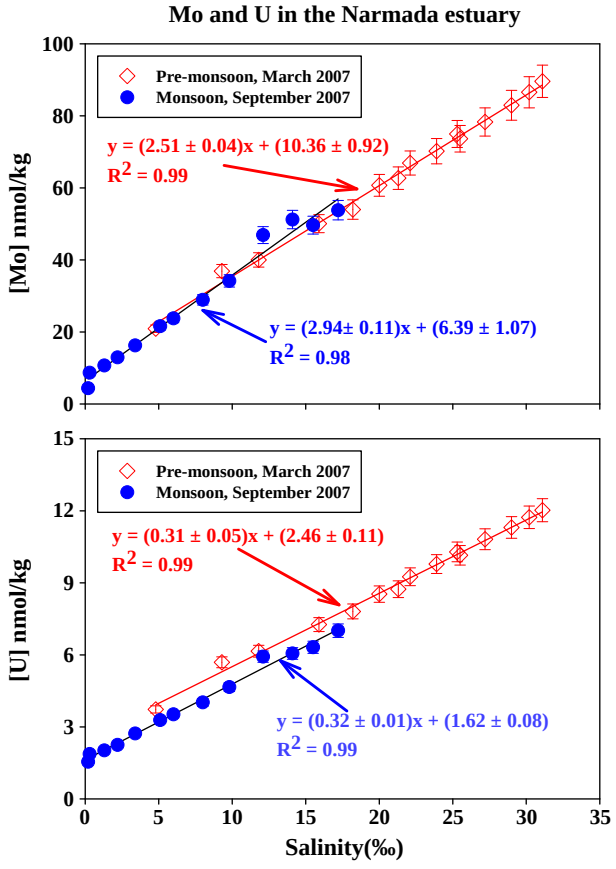

Fig. 2. Molybdenum and Uranium vs. salinity plots in the Narmada estuary for monsoon and pre-monsoon seasons. Both Mo and U show conservative behaviour in this estuary. Seawater endmember concentrations of U and Mo in this estuary obtained from the best fit lines of the data are nearly the same as those reported and measured in the Arabian Sea.

given in Table 2 and Fig. 2. Monsoon sampling could be done only upto salinity of ~17% due to highly turbulent sea. Dissolved Mo distribution shows conservative mixing of sea water and river water end members ($r^2 = 0.99$) during both these seasons. In monsoon season, two samples at salinities 12.1 and 14.1‰ lie above the mixing line (Table 2, Fig. 2). The sample with salinity 12.1‰ also has unusually high concentrations of Mo, U (in this study) and Re (Rahaman and Singh, 2010). The Mo vs. salinity lines (Fig. 2) provide Mo concentration of 109 ± 4 and 98 ± 2 nmol/kg for 35‰ salinity seawater end member during monsoon and pre-monsoon respectively. These values are within the range measured for the Arabian Sea in this study 101 ± 1 (Table 3) and reported for other ocean basins (Morris, 1975; Collier, 1985; Quiby-Hunt and Turekian, 1983). The conservative nature of Mo in the Narmada estuary is also consistent with distribution of Mo/Al in suspended phase with salinity as discussed later.

In the Tapi estuary, Mo increases with salinity (Table 3, Fig. 3) with a 'bulge' in the 3.9 to 11.5‰ salinity range. This 'bulge' represents gain of Mo and suggests that it has an additional source in this salinity range. The gain ranges from 4 to 32% with respect to conservative mixing (Fig. 3). The additional source for Mo can be (i) its desorption from particles in the estuary as has been suggested for the Southampton river (Jones, 1974) or (ii) supply of Mo from bottom sediments (Dalai et al., 2005; Morford et al., 2007). Development of seasonal oxygen minimum zone along the western Indian continental shelf (Naqvi et al., 2000) can sequester Mo into sediments which can be later released to bottom water as the sediments come in contact with oxic waters (Morford et al., 2007). Intense upwelling during the

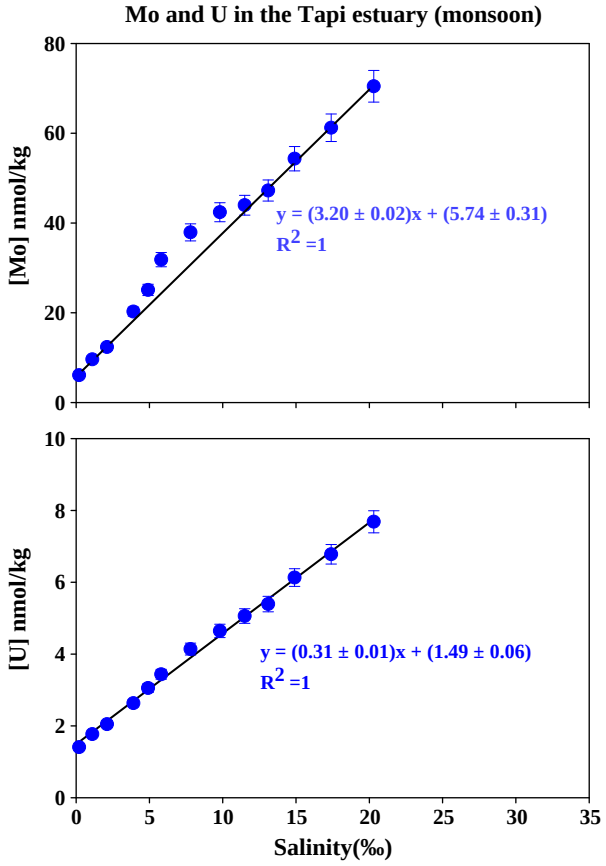

Fig. 3. Mo and U in the Tapi estuary. The sampling done during monsoons was limited to 20.3‰ salinity due to turbulent sea condition. Mo shows a gain in the salinity range of ~4 to 12‰ in this estuary. Effluent discharge from a steel plant situated in the vicinity of this estuary seems to be the source for Mo "bulge". The best fit line for Mo is based on data in the 0.0–1.1 and 13.1–20.3‰ (i.e. excluding the bulge). U shows conservative behaviour in this estuary.

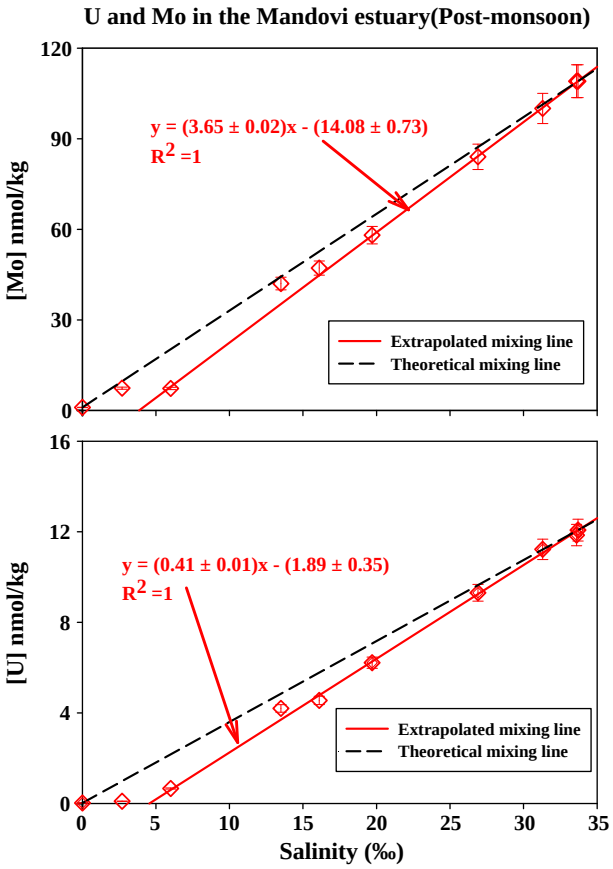

Fig. 4. Mo and U distribution in the Mandovi estuary. Two lines are shown, the theoretical mixing line is drawn by joining the river and sea water end member assuming conservative mixing and the 'extrapolated mixing line' drawn by extrapolating of the linear segment of the higher salinity data points to river end members. Both these elements show non-conservative behaviour in this estuary with loss in the lower salinity range. The removal of U and Mo in this estuary is much more than their riverine supply indicating significant loss of marine U and Mo along with their riverine supply. The equations of the extrapolated mixing lines of Mo and U are based on five data points from 19.7–33.7‰. See the text for more details.

southwest monsoon in this region can bring high Mo from the bottom water to the surface causing the observed hump. Interestingly the Mo bulge coincides with an increase in alkalinity which seems to be associated with steel plant present nearby. The likely cause for the increase in both Mo and alkalinity in this salinity range is their supply from a major steel plant along with a lime plant situated in the vicinity of this salinity range. Mo is used in steel manufacturing as a hardening agent. Discharge from these steel and lime plants can explain the increase in both Mo and alkalinity in the Tapi estuary. Increase in Mo in low salinity range in the Tapi estuary is independent of U and Re concentrations as plant does not use U and Re.

On the Mo vs. salinity plot for the Hooghly and the Mandovi data fall below the theoretical mixing line defined by riverine and marine endmembers (Figs. 4 and 5) indicating significant loss of Mo in the Hooghly and the Mandovi estuaries in the lower salinity ranges (Figs. 4 and 5) in contrast to the Narmada and the Tapi estuaries data. A number of factors can contribute to the observed loss of Mo in these two estuaries which has been discussed in Section 6.1.

U versus salinity plots for both the seasons in the Narmada estuary (Fig. 2) show conservative mixing ($R^2 = 0.99$) with nearly identical slopes 0.31 ± 0.11 and 0.32 ± 0.1. The conservative mixing of U in the Narmada estuary is consistent with the results of Borole et al. (1982). However, their study hinted at a slight removal of U in the lower salinity region of this estuary, which is not observed in this work. The conservative behaviour of U in the Narmada estuary is similar to that of

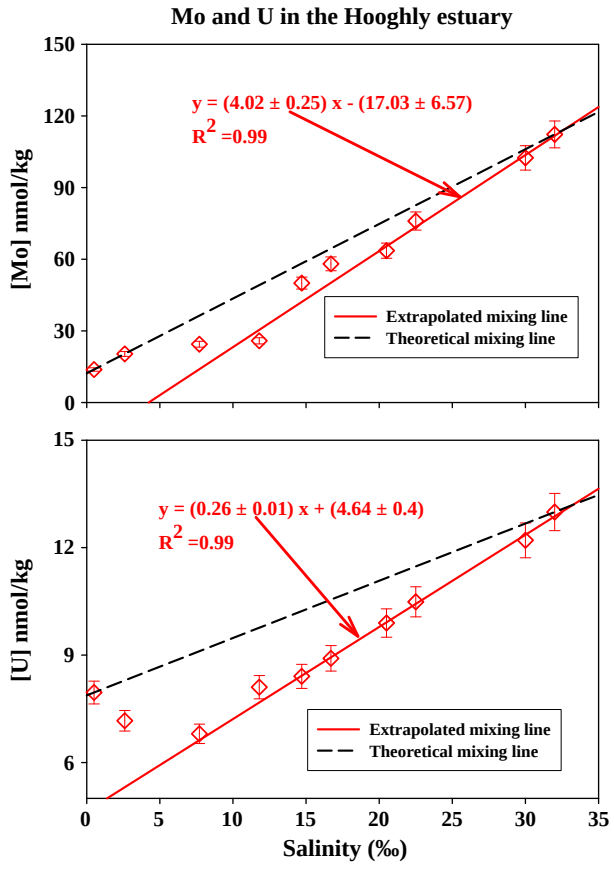

Fig. 5. Mo and U in the Hooghly estuary. Both these elements show removal in the low and mid salinity range, analogous to that in the Mandovi (Fig. 4). About 40% of riverine U is removed in this estuary similar to that reported for the Meghna (combined Ganga-Brahmaputra) estuary in Bangladesh (Caroll and Moore, 1993). Mo loss is much higher compared to its riverine supply. The equations are based on four data points beyond 20‰ salinity.

other redox sensitive elements, Re (Rahaman and Singh, 2010) and Mo (this study) measured in this estuary. Based on the best fit lines of Fig. 2 the extrapolated dissolved uranium concentration at 35‰ salinity corresponds to 13.2 ± 0.4 and 12.8 ± 1.8 nmol/kg, for the two seasons are within the range for average global sea water ~13.6 nmol/kg (Ku et al., 1977), the Arabian Sea 13.44 ± 0.84 nmol/kg (Rengarajan et al., 2003) and measured in this study offshore Goa 12.8 ± 0.2 nmol/kg (Table 3).

Uranium in the Tapi estuary is also conservative as evident from the U-salinity plot (Fig. 3). Re behaves conservatively (Rahaman and Singh, 2010) but significant amount of additional Mo gets incorporated in this estuary. The riverine and seawater uranium in the Tapi estuary estimated based on the Fig. 3 are 1.5 ± 0.1 and 12.3 ± 0.4 nmol/kg respectively. The marine U of the Tapi estimated from the mixing line is nearly same as that measured directly in the sea water endmember and with that of the Arabian Sea water off Goa.

The overall trend of U distribution in the Narmada, Tapi and the Hooghly estuaries are similar to those reported earlier in them (Borole et al., 1982; Somayajulu, 1994). The Mandovi estuary is studied for the first time which shows U removal in low salinities similar to its behaviour in the Hooghly estuary (Fig. 4).

Re shows perfectly conservative behaviour in all the four estuaries (Fig. 6; Rahaman and Singh, 2010) which were analysed for Mo and U. It is interesting to note that seawater endmember of Re in the Hooghly and the Mandovi estuaries are ~40 pmol/kg, similar to those reported for open Arabian Sea and other part of the global ocean (Anbar et al., 1992; Colodner et al., 1993), however, seawater end member of Re is 3 to 5 times higher in the Gulf of Cambay estimated based on conservative mixing of river water and seawater observed in the Narmada and the Tapi estuaries which has been attributed to its contribution from anthropogenic activity (Rahaman and Singh, 2010).

5.2. Mo and U in suspended particulate matter in the Narmada estuary

Mo in the suspended load of the Narmada estuary during pre-monsoon range from 5.7 to 9.7 nmol/g with an average of 8.1 ± 1.1 nmol/g (Table 4), twice the average continental crustal abundance of 4.2 nmol/g (Manheim and Landergren, 1978). Average uranium in these samples is 6.9 nmol/g spread over a narrow range of 6.7 to 7.2 nmol/g (Table 4) and similar to that reported earlier (Borole et al., 1982). The Al concentrations in the samples vary between 8.2% and 9.1% (Table 4).The observation that Mo and U do not show any systematic trend with salinity (Fig. 7) indicate that Mo and U are neither lost nor gained by these particles in the salinity range (4.8–28.5‰).

6. Discussions

U, Mo and Re are sensitive to redox conditions in the ocean and sediments depositing in reducing environment is one of their important sinks. However, the sensitivity of these three elements to prevailing reducing conditions differs with Re and U being more sensitive than Mo. Despite all being redox sensitive elements, their behaviour in different estuaries are different as has been shown above.

6.1. Comparative behaviour of U, Mo and Re in estuaries

The results of the present study along with that of Rahaman and Singh (2010) provide data to assess the comparative behaviour of Mo, U and Re. These results show loss of U and Mo in the Hooghly and the Mandovi estuaries whereas Re behaviour is conservative (Fig. 6; Rahaman and Singh, 2010). Fig. 8 shows plots of Mo/Re and U/Re ratios with salinity in the estuaries. In perfectly conservative environment in the estuary, both Mo/Re and U/Re should show an exponential mixing with salinity between river and seawater endmembers. Any deviation from the theoretical mixing lines could result from either the addition or removal of these elements in the estuary. Nature of the exponential mixing line will depend on the difference between river and seawater endmembers. Mo, Re and U are conservative in the ocean with long residence times (Colodner et al., 1993; Morford and Emerson, 1999), therefore the marine endmembers of U/Re and Mo/Re are expected to be the same in all the estuaries and equals to global open ocean values of 0.34×10^3 and 2.75×10^3 for U/Re and Mo/Re respectively (Ku et al., 1977; Colodner et al., 1993; McManus et al., 2006). This assumption, however, is not valid in the Gulf of Cambay and the open ocean end members of the Narmada and the Tapi estuaries (Fig. 6) because significant input of anthropogenic Re (Rahaman and Singh, 2010). In these estuaries U/Re and Mo/Re are only 0.12×10^3 and 0.87×10^3 respectively, much lower than that expected for open ocean. Their riverine endmembers however can differ depending on their concentrations in different rivers. The nature of the Mo/Re and U/Re in all the estuaries follows the same trend as Mo, U versus salinity plots, as Re behaves quite conservatively in all the estuaries, albeit its major supply from anthropogenic sources in the Gulf of Cambay (Rahaman and Singh, 2010). Though, the Mo/Re in the Tapi has a hump in low salinity region due to addition of Mo from anthropogenic activity. In the Hooghly and the Mandovi both Mo/Re and U/Re show dips in lower salinity ranges suggesting either removal of Mo and U or addition of Re, considering the conservative nature of Re in these estuaries (Rahaman and Singh, 2010), the dips in mixing lines can be interpreted in terms of the loss of Mo and U compared to Re, and thus bring out differences in the behaviour among these elements.

As has been shown Section 5.1, significant amount of Mo and U are being lost in the lower salinity ranges in the Hooghly and the Mandovi estuaries (Figs. 4 and 5) whereas Re behaves conservatively in these

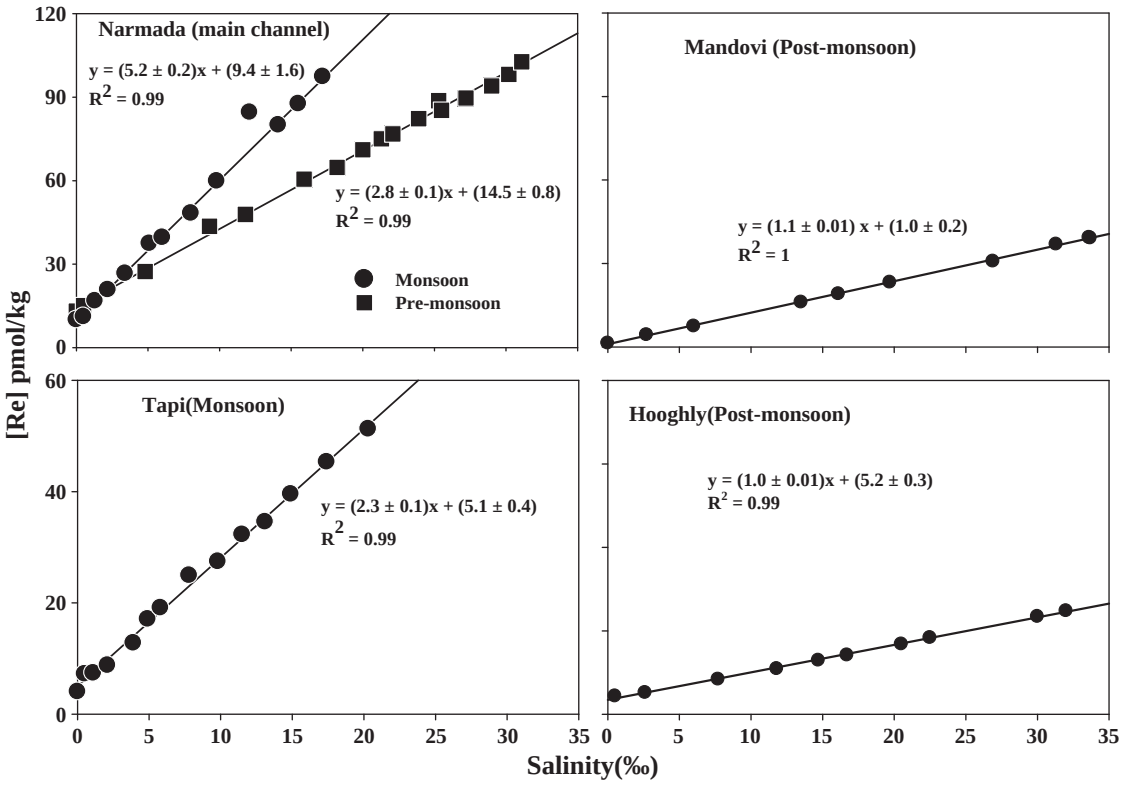

Fig. 6. Re vs. Salinity plots in the estuaries indicate that Re behaves conservatively in all the estuaries, however the seawater end-member of Re for the Narmada and the Tapi estuaries are 3 to 5 times higher compared to Arabian seawater and open ocean Re concentration. Re data of all the estuaries are taken from Rahaman and Singh (2010).

estuaries, despite the fact that all of them are sensitive to reducing condition. A number of factors can contribute to the observed loss of Mo and U in these two estuaries. These include complexation Mo and U with organic matter, development of anoxic conditions within the particulate aggregates (Dellwig et al., 2007) and their uptake from water by reducing sediments of salt marshes and mangrove forest. Such mechanisms have been reported for the loss of U in the estuaries of the lower Meghna (combined Ganga-Brahmaputra, Carroll and Moore, 1993), in the Delaware (Sarin and Church, 1994; Church et al., 1996) and in the Savannah (Windom et al., 2000). However, the observation that Re which is more susceptible to reducing condition (Colodner et al., 1993) behaves conservatively in the Hooghly and the Mandovi estuaries (Rahaman and Singh, 2010) challenges the importance of reductive removal of dissolved Mo. These results, therefore has to be explained by a mechanism that can preferentially remove U and Mo from solution without affecting the distribution of Re such as the selective incorporation of Mo and U to Fe–Mn hydroxides (Crusius et al., 1996; Morford and Emerson, 1999; Morford et al., 2005) or by utilization of Mo and U by microbial activity as Re loss is abiotic (Morford et al., 2009). As the losses of Mo and U observed in the Hooghly and the Mandovi estuaries are associated with mangrove swamps, their utilization by biological activity could be the preferred interpretation as it will contribute to loss of Mo and U but not Re. More systematic work in the sediments and waters in the mangrove area needs to be done to ascertain this hypothesis.

Table 4
Al, U and Mo in the suspended sediments of the Narmada Estuary.

Sample	Salinity	Al (%)	[U]		[Mo]	
	‰		ppm	nmol/kg	ppm	nmol/kg
NESS-1	4.8	9.1	1.9	6.8	0.9	9.7
NESS-2	9.3	8.3	1.8	6.7	0.6	5.7
NESS-3	11.8	8.6	1.9	6.9	0.9	8.8
NESS-5	18.2	8.9	1.9	6.9	0.8	8.0
NESS-6	20	8.5	1.9	7.0	0.7	7.3
NESS-7	21.3	8.3	1.9	7.1	0.8	7.9
NESS-8	22.1	8.5	1.9	7.0	0.7	7.6
NESS-9	23.9	8.3	1.9	6.7	0.9	9.4
NESS-10	25.3	8.2	1.9	6.9	0.7	7.7
NESS-10R	25.3	8.2	1.9	6.9	0.8	8.1
NESS-11	25.5	9.0	2.0	7.2	0.9	8.9

6.2. Removal of U and Mo in the Hooghly and the Mandovi estuaries

The extent of loss of U and Mo in the Hooghly and the Mandovi estuaries are estimated following earlier approaches (Li and Chan,

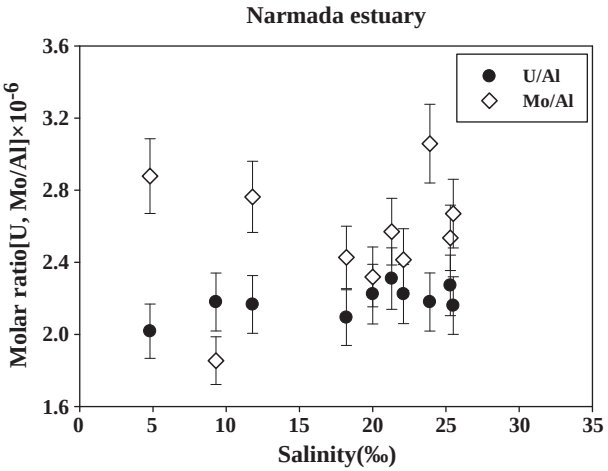

Fig. 7. Mo/Al, U/Al of suspended load vs. salinity in the Narmada estuary. The U/Al varies within narrow range, whereas Mo/Al shows large scatter. The data however do not seem to show very systematic trend suggesting that both Mo and U are not being adsorbed on or being released from these particles in this estuary.

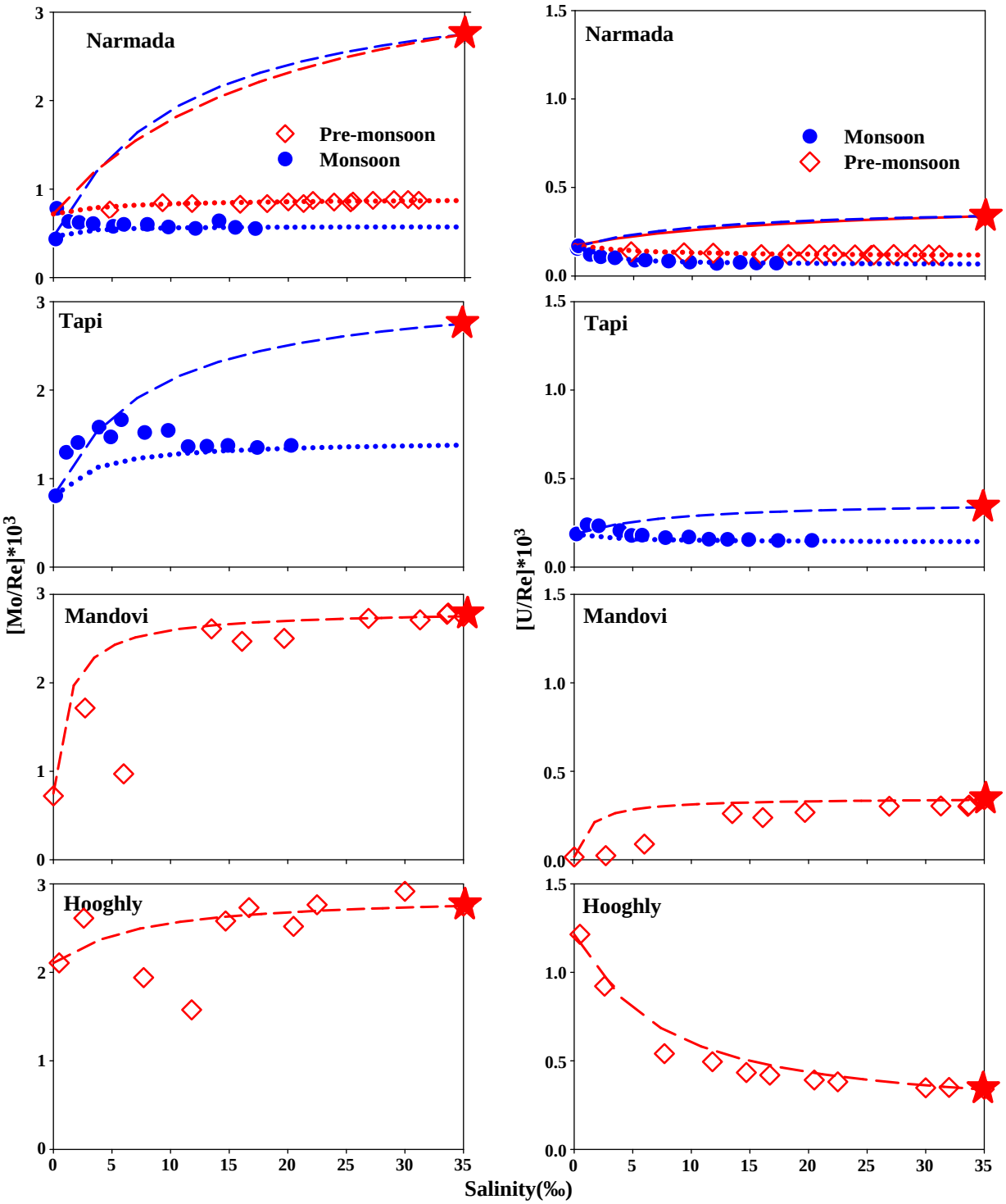

Fig. 8. Mo/Re and U/Re vs. salinity in the various estuaries studied in this work. They should represent exponential mixing curves between respective riverine and seawater endmembers. Seawater endmembers of U/Re and Mo/Re (★) is estimated based on the U, Re and Mo concentrations available for the open ocean. Theoretical mixing lines between riverine and global ocean endmembers are also shown (dashed lines). In case of the Narmada, both U/Re and Mo/Re are invariant with salinity and fall much below the theoretical mixing line. The marine U/Re and Mo/Re in the Narmada and the Tapi estuaries are lower compared to open ocean values which is due to 3–5 times higher marine Re content in the Gulf. Dotted lines show the theoretical mixing lines between riverine endmembers and the observed marine endmember in the estuaries of the Narmada and the Tapi. In the Tapi, excess Mo in the mid salinity range is due to anthropogenic supply. Marine endmembers of U/Re and Mo/Re in the Hooghly and the Tapi estuaries are, unlike the Narmada and the Tapi, similar to those reported for the global ocean. The Hooghly and Mandovi show loss of both Mo and U as they fall below the mixing lines in lower salinity ranges.

1979; Maeda and Windom, 1982; Swarzenski et al., 1995) and using the U, Mo vs. salinity relationship (Figs. 4 and 5). The relevant relation is

$$Total\ Loss = Q(I\text{–}R) \quad \text{(i)}$$

where, Q is the river water discharge, I is the y-axis intercept of the extrapolated conservative mixing lines of the samples with salinities higher than 20‰ (Figs. 4 and 5) and R is the observed riverine U and Mo concentration.

For the Hooghly estuary, both the uranium and molybdenum mixing lines in the salinity range ~20–32‰ indicate linear trend, the

extrapolation of which yield intercepts of +4.64 and −17.03 nmol/kg on the U and Mo axis respectively compared to the riverine U and Mo concentrations of 8 and 14 nmol/kg. Negative intercept denotes the removal of U and Mo "in excess" of their riverine supply and therefore includes some component of seawater. Using the relation (i) and water flux of 52 km^3/y, U loss in the Hooghly estuary is estimated to be ~1.7×10^5 mol/y and that of Mo ~1.6×10^6 mol/y. Similar calculations for the Mandovi estuary yield loss of ~3×10^4 and 2×10^5 mol/y for U and Mo respectively. In the Mandovi estuary, the removal of both U and Mo are more than their riverine supply whereas in the Hooghly only Mo removal is more than its riverine supply. Thus, both the Hooghly and the Mandovi estuaries act as sinks for Mo where its removal is much more than its riverine supply. This suggests that during river and sea water mixing part of oceanic Mo is also sequestered in these estuaries. In the Hooghly estuary, 40% of uranium supplied by the river is sequestered in the estuary and only ~60% of it is transported to the open ocean.

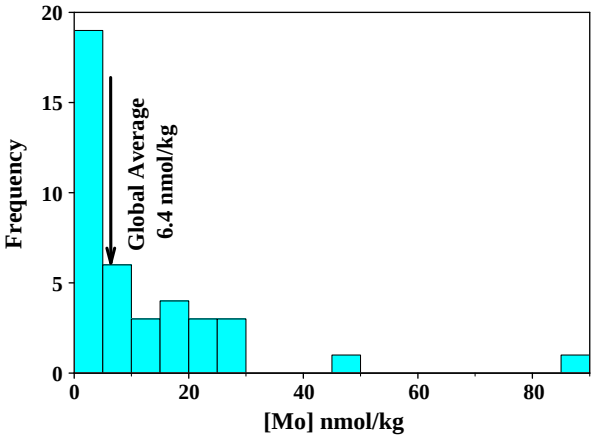

Fig. 9. Histogram of dissolved Mo concentration of the global rivers based on reported data and from this study. Discharge weighted global average riverine Mo concentration is 6.4 nmol/kg.

6.3. Loss of Mo in the estuaries: impact on global oceanic budget

Major source of Mo to the global ocean is its riverine input which supplies 1.8–2.3×10^8 mol/y (Bertine and Turekian, 1973; Morford and Emerson, 1999; McManus et al., 2006; Archer and Vance, 2008). Table 5 is a compilation of Mo concentration reported in global rivers (Martin et al., 1978; Colodner et al., 1993; Walker and Peucker-Ehrenbrink, 2004; Archer and Vance, 2008 and this study). The average global riverine concentration of dissolved Mo based on the data in Table 5 representing ~28% the fresh water discharge is ~6.2 nmol/kg (Archer and Vance, 2008). This increases marginally to 6.4 nmol/kg based on Mo data of this study (Table 5 and Fig. 9) and those reported in Walker and Peucker-Ehrenbrink (2004) and Archer and Vance (2008). This corresponds to a global riverine Mo flux of ~2.4×10^8 mol/y. Mo input flux increases to ~2.6×10^8 mol/y (Morford and Emerson, 1999; McManus et al., 2006) if Mo flux from low temperature hydrothermal weathering (0.2×10^8 mol/y) is added. The primary sinks of Mo are the oxic (0.9×10^8 mol/y) and anoxic (0.2 to 0.8×10^8 mol/y) sediments. McManus et al. (2006) estimated, based on available Mo isotope composition of the various reservoirs, sinks of 0.1×10^8 mol Mo/y in anoxic sediments and ~0.4×10^8 mol Mo/y in the continental margins. These estimates clearly indicate a significant deficit in the oceanic Mo sink if it is in steady state with respect to input/output.

Present day mismatch between the input and output of Mo budget of seawater could be due to increase in its riverine supply during the Holocene as has been suggested in case of Sr and other elements (Vance et al., 2009) resulting from enhanced chemical weathering of fresh sediments exposed by the glaciers during the Last Glacial Maxima. The role of such a process in contributing to Mo flux is unclear, if this is significant it can contribute to the imbalance. However, if the current riverine input of Mo is not affected by glacial hangover (Vance et al., 2009), and represents its long term average its removal is certainly lower than its supply.

This study has demonstrated that Mo can be removed in the estuaries such as in the Hooghly and the Mandovi. These estuaries are associated with mangroves (Carroll and Moore, 1993; Singh et al., 2004). If Mo is being sequestered with similar efficiency in the estuaries containing the mangrove swamps in other parts of the coastal ocean, this could be an important sink for Mo. The Hooghly and the Meghna (combined Ganga and the Brahmaputra in Bangladesh) are part of the

Table 5
Mo in global rivers.

River	[Mo] nmol/kg	Ref.	River	[Mo] nmol/kg	Ref.
Mississippi	10.3	1	Brahmaputra	9.0	2
Susquehanna River	3.0	1	Amazon	4.3	2
Mad river	3.0	1	Chang Jiang River, China	16.7	2
Klamath River	14.8	1	Dnepr Kherson	18.0	3
Russian River	3.6	1	Prut at reni	29.0	3
Eel River	3.5	1	Danube at Reni	19.0	3
Wateree River	2.6	1	Danube at Vilkovo	20.0	3
Lake superior	4.3	1	Dnestr at Majaki	29.0	3
Brazos River	2.9	1	Bug at Novaja Odessa	30.0	3
Colorado River	1.1	1	Kuban at Temruk	22.0	3
Rio Maipo	1.8	1	Hudson	4.6	4
Po River	5.0	1	Houstonic	5.5	4
Congo River	1.8	1	Connecticut	7.8	4
Rhone river	21.1	1	Hooghly	13.8	5
Red River	4.9	1	Narmada	4.3	5
Itchen River, SE England	4.8	2	Tapi	6.1	5
Kalix River, Sweden	4.9	2	Mahi	90.0	5
Nile River, Sudan and Egypt	7.1	2	Sabarmati	48.0	5
Volga River, Russia	6.7	2	Mandovi	1.0	5
Ottawa River, Canada	2.2	2	Vishwamitri	23.0	5
Global average (discharge weighted)				6.4	5

1. Bertine and Turekian, 1973.
2. Archer and Vance, 2008.
3. Colodner et al., 1995.
4. Walker and Peucker–Ehrenbrink, 2004.
5. This study.

same mangrove swamp system and hence the Mo loss of Hooghly can be extended to this entire system. Similar loss of U (~40%) in both the Hooghly (this study) and the Meghna (Carroll and Moore, 1993) estuaries attest to this contention. Following the approach of Windom et al. (2000) and Dunk et al. (2002) and the annual water discharge of 1000 km^3, the Mo loss of the entire Ganga–Brahmaputra estuary can be estimated to be $\sim 31\times10^6$ mol/y. If Mo loss in the estuary occurs only during lean flow period as has been suggested for U (Carroll and Moore, 1993), Mo loss, based on the water discharge of 140 km^3/y, could be $\sim 4\times10^6$ mol/y. Considering the mangrove swamp area of the Ganga–Brahmaputra system $\sim 1.8\times10^{10}$ m^2 (Carroll and Moore, 1993) the Mo sequestration rate in these estuaries show a range of 0.2 to 1.7 mmol/m^2/y depending on Mo loss occurring during the lean flow only or during the entire year. If this rate is applicable to mangroves globally, the global Mo removal rate based on mangrove swamp area of $\sim 1.8\times10^{11}$ m^2 (Spalding, 1997) is in the range of 0.4×10^8 to 3.1×10^8 mol/y. This range corresponds to 15%–120% of Mo supply and underscores the important role of mangroves in determining the oceanic budget of Mo. This study indicates that the estuaries associated with mangrove swamps are an important sink of Mo which could serve as the reported missing sink of Mo (McManus et al., 2006).

7. Anthropogenic Input of Mo, U and Re in the Gulf of Cambay

Three of the estuaries studied, the Narmada, Tapi and the Mahi fall in the Gulf of Cambay, a semi enclosed basin at the northern end of the Arabian Sea. These rivers, as mentioned earlier, flow through highly industrialized areas and therefore, there is a potential for supply of Mo, U and Re from the industrial waters. To assess them, effluent waste waters were analysed for both Mo, U and Re. The results showed that the U contents of the Mahi river (7.9 nmol/kg) and of the effluent waste waters (1.4 and 2.8 nmol/kg) are in the range of other rivers of this region, however their Mo and Re concentrations are extremely high. The Mahi river has a Mo and Re concentrations 90 nmol/kg and 41 pmol/kg (Rahaman and Singh, 2010) respectively, where as two industrial effluent waste waters have 569 & 828 nmol/kg Mo and 175 and 178 pmol/kg Re. It is reported (Rahaman and Singh, 2010) that ~5000 million m^3 of the industrial waste water is supplied to the Gulf of Cambay annually. Using 700 nmol/kg (average of two measured values) for typical Mo concentration of the effluent waters, it can be estimated that this sources can supply 3.5×10^6 mol/y of Mo to the Gulf of Cambay. In addition to effluent waste waters which are directly discharged into the Gulf, polluted rivers such as the Mahi and the Sabarmati also supply $\sim 1.3\times10^6$ mol/y of Mo to the Gulf. Altogether the anthropogenic sources supply $\sim 5\times10^6$ mol/y of Mo to the Gulf of Cambay. The natural Mo flux supplied by the Narmada and the Tapi rivers is 0.3×10^6 mol/y. Flux of anthropogenic Mo is ~17 times higher compared to its natural sources in the Gulf of Cambay. Gulf of Cambay also receives large quantity of anthropogenic Re (Rahaman and Singh, 2010). This study coupled with the results of Rahaman and Singh (2010) suggests that industrial effluents discharged either directly or through rivers are an important source of Re and Mo to the Gulf of Cambay; in contrast, anthropogenic source does not seem to be important for U in this region.

8. Conclusions

Uranium and molybdenum concentration in the estuaries of the Hooghly in the Bay of Bengal and the Mahi, Narmada, Tapi and the Mandovi estuaries in the Arabian Sea are analysed in this study. River waters, seawaters and salt marsh samples along the Gulf of Cambay are also analysed for their U and Mo concentrations. Mo was analysed for the first time in the Indian estuaries. Both dissolved U and Mo show highly variable concentrations in the rivers analysed in this study, vary from 0.02 to 19.0 nmol/kg for U and 1 to 90 nmol/kg for Mo. The highest concentration of U is found in the Sabarmati river where as the Mahi river has the highest Mo concentration, most probably sourced from anthropogenic sources such as industrial activities in the region. The lowest U and Mo are measured in the Mandovi river resulting due to lateritic lithology, higher runoff and lower water–rock interaction in its drainage. U and Mo measured in the Arabian Sea water are similar to their average global values.

Behaviour of both U and Mo in the four estuaries analysed in this study are quite variable. In the Narmada estuary, U and Mo show conservative mixing between riverine and seawater endmember during pre-monsoon and monsoon. U is conservative in the Tapi estuary but Mo shows non-conservative behaviour (addition) in the mid salinity ranges resulting from anthropogenic activity. Both U and Mo show non-conservative behaviour (removal) in the Hooghly and the Mandovi estuaries. They get removed in the lower salinity ranges in these estuaries. This is in variance with the behaviour of Re in these estuaries showing perfectly conservative behaviour. The loss of U and Mo in these estuaries could be due to reducing condition prevailing in the Hooghly and the Mandovi estuaries caused by mangrove forest. About 40% of riverine uranium is being lost in the Hooghly estuary. Mo in the Hooghly and the Mandovi and U in the Mandovi estuary indicate their net sink. Annually $\sim 1.6\times10^6$ mol of Mo is being lost in the Hooghly estuary, which is more than double of its riverine supply. Mandovi estuary loses $\sim 2\times10^5$ mol of Mo annually. Uranium removal in both Hooghly and Mandovi estuaries are one order of magnitude lower compared to that of Mo. Such processes in the estuaries not only prevent the riverine supply of elements to enter the open ocean but also remove part of marine component and could be an important sink of such elements influencing their oceanic budget. Such removal on global scale has been estimated earlier for U. This study estimates Mo loss in the range of 0.4×10^8 to 3.1×10^8 mol/y in the global estuaries associated with mangrove swamp. This could be a significant sink of Mo and could be important for global Mo budget (McManus et al., 2006).

Mo concentration in the Gulf of Cambay is much higher compared to that of the Arabian Sea and that of global average seawater value. Higher value of Mo in the Gulf is attributed to its supply from anthropogenic sources. Polluted rivers and industrial effluent waste waters supply $\sim 5\times10^6$ mol of Mo annually to the Gulf of Cambay. These rivers and waste waters also have been reported to supply significant amount of Re to the Gulf (Rahaman and Singh, 2010). Numerous petrochemicals and pharmaceutical industries situated along the coast of the Gulf of Cambay are probably supplying Mo and Re to the effluent waters and finally to the Gulf, however these anthropogenic sources do not contain U in them and that may be the reason for normal U content in the Gulf of Cambay. Further, this study indicates that salt marshes act as a sink of oceanic U and probably a source of Mo to the seawater.

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