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Distribution of Selenium, Molybdenum and Uranium in Sediment Cores from the Colorado River Delta, Baja California, Mexico

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Abstract The distribution of selenium, molybdenum and uranium was studied in ~1.5 m sediment cores from the Colorado River delta, at the Colorado (CR) and Hardy (HR) riverbeds. Core HR2 showed highest Se, Mo and U concentrations at its bottom (2.3, 0.95 and 1.8 μg g^{-1}) within a sandy-silt layer deposited prior to dam construction. In CR5 the highest concentrations of these elements (0.9, 1.4 and 1.7 μg g^{-1} respectively) were located at the top of the core within a surface layer enriched in organic carbon. A few samples from HR2 had Se above the probable toxic effect level guidelines.

Keywords Sediment · Selenium · Molybdenum · Uranium

The natural flow of the Colorado River (CR) toward the Gulf of California has been significantly reduced by the construction of dams since 1935. During the last 40 years flood flows have occurred only occasionally due to extreme rainfall and increased meltdown in the upper Colorado Basin. Both, modern and pre-dam flows transported particulate and dissolved components from the riverbed itself, but also from human activities such as agriculture and mining along the basin. Molybdenum and U are among the potential contaminants in the sediments from the Colorado delta that have not been studied previously and Se has only been reported for modern sediment in some areas (García-Hernández et al. 2001). These elements are of concern not only because of their particular geochemistry, but also because they have potential contaminant sources in the CR basin, such as the seleniferous shales in the upper basin (Engberg 1999), as well as the mining of U and Mo at the CR basin in Arizona and New Mexico (Ludington and Plumlee 2009). Near the US-Mexico border, high Se concentrations (15 μg g^{-1}) have been reported for Salton Sea sediment (Schroeder and Orem 2000). The present study describes the downcore distribution of Se, Mo and U in sediments from two distinctive channels in the estuarine CR delta. These distributions are discussed in terms of past sedimentological changes, as well as known flood-flows that may have affected their concentrations in the sediment record. The aim is to assess changes in element distribution prior and after water flow was interrupted toward the CR delta.

Materials and Methods

Two ~1.5 m long sediment push cores were sampled in 2007 and 2008 at the deeper waters (2.5 m depth) of the CR and Hardy River (HR) respectively (Fig. 1). For the analyses of Se, Mo and U, sediment subsamples (0.5 g) were digested with aqua regia (1:3 HNO_3:HCl) at 95°C for 2 h. Element concentrations were determined with a Perkin Elmer Sciex ELAN 6100 ICP-MS. Reference samples GXR-1 and GRX-4 (USGS Geochemical Exploration Reference Materials) indicate recoveries of Se = 100%; Mo = 95% and U = 82%. In addition, grain size and organic carbon analyses were carried out for core HR2 using a Horiba LA910 laser grain size analyzer and a LECO CHNS932 elemental analyzer after pretreatment with 1 N HCl. Grain size and carbon results for core CR5 are taken for comparison from Daessle et al. (2009) and

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Lugo-Ibarra et al. (2011). Detection limits (μg g^{-1}) are: Se = 0.1, Mo = 0.01 and U = 0.1.

Results and Discussion

Sediment type varied downcore with alternating silty, clayey-silt and silty-clay facies. Sandy silt was only found at the bottom of core HR2 and clay-dominant layers were mainly found in the lower sections of both cores indicating a predominant clay deposition in the past. The downcore distributions of Se, Mo y U in cores HR2 and CR5 are shown in Fig. 2. The highest concentrations of these elements (Se = 2.3, Mo = 0.95 and U = 1.8 μg g^{-1}) were found near the base of core HR2 within a sandy-silt layer. More recently (at 40–80 cm), a second enrichment occurred in this core. The covariation of these elements was probably controlled by their similar redox chemistries, in that all are insoluble under reducing conditions but soluble in oxic environments (Lemly 1999). Cluster and principal components analyses (using Ca, Sc, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Cs, La, Au, Tl, Pb, Th and U as variables) confirmed that Se, Mo and U co-varied and could be grouped as one single geochemical component in both cores. The concentrations of Se, Mo and U were low compared to other sites (Table 1), but potential contaminant sources couldn′t be disregarded. Weathering of tailings from U mining in the Colorado basin may have also increased the abundance of dissolved species of Mo and Se into rivers and groundwater (Ludington and Plumlee 2009). Another likely source for these elements was agriculture, where Se and Mo are used as additives of fertilizers, and U is enriched in many superphosphates. A significant enrichment of these elements derived from agriculture drains was reported for the Salton Sea (Schroeder and Orem 2000). Core CR5 had highest Se = 0.9 μg g^{-1}, Mo = 1.4 μg g^{-1} and U = 1.7 μg g^{-1} concentrations in the upper section (0–25 cm). At this depth, Mo had the highest concentrations of both cores. In deeper sediments of core CR5 the element concentrations decreased even below detection limits. The maximum element concentrations at the surface of CR5 mirrored enrichment in organic carbon of 1.7% at 13 cm (Lugo-Ibarra et al. 2011) signaling the role that organic matter played in absorbing Mo and U in these sediments. In core HR2 organic carbon ranged 0.3%–1.5% and the maximum didn′t mirror Se, Mo or U distributions.

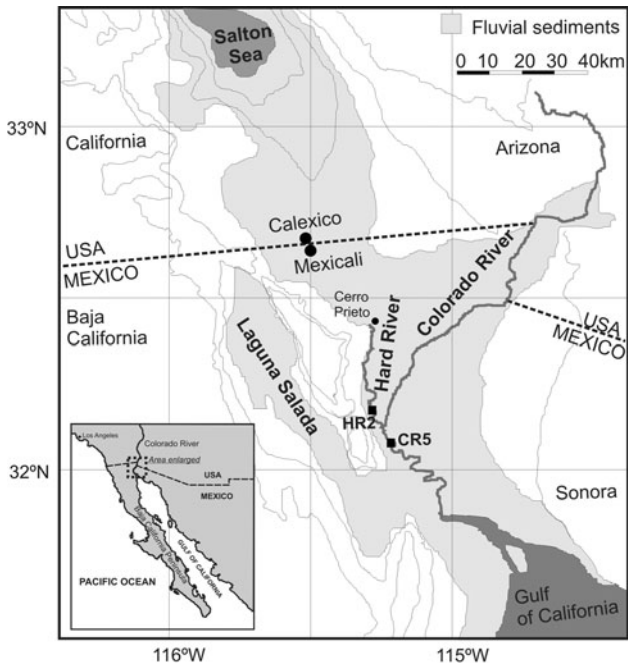

Fig. 1 Lower basin of the Colorado River and sampling sites of cores HR2 and CR5 (modified from Lugo-Ibarra et al. 2011)

Selenium, Mo and U in CR5 and HR2 were compared with average baseline concentrations using the composition of world soils and Sc as a normalizer (Sc = 7 μg g^{-1}, Se = 0.3 μg g^{-1}, Mo = 1.2 μg g^{-1} and U = 2 μg g^{-1}; (Martin and Whitfield 1983; Reimann and Caritat 1998). The resulting enrichment factors (EF) showed that at the surface layer of core CR5 shows EF < 4 for Se and EF < 1.6 for Mo. In core HR2 only Se had a significant EF throughout (EF = 1–8). The EF were highest at the surface and near the base of core HR2.

The concentrations of Se, Mo and U were compared with sediment quality guidelines for ecological risk assessment (Table 1). All except Se in core HR2 were below the published guidelines. Maximum Se concentration in core HR2 was above the low effect level (LEL), but far below the severe effect level (SEL) described by Thompson et al. (2005).

The approximate age of the sediments in the HR and CR was estimated using particulate organic pollutants as time markers (Lugo-Ibarra et al. 2011). This suggests that the date at the base of core CR5 and one core adjacent to HR2 (core HR1) must be ~1935. The base of HR1 was stratigraphically correlated with core HR2 at 135 cm. Thus it can be concluded that the enrichment of Se, Mo and U at the base of core HR2 pre-dated damming of the CR and represented natural river input to the delta. Not so the enrichments near the surface of CR5 and HR2, and the middle section of HR2, which may have derived from river flooding-erosion and/or farmland runoff after first dam construction in 1935.

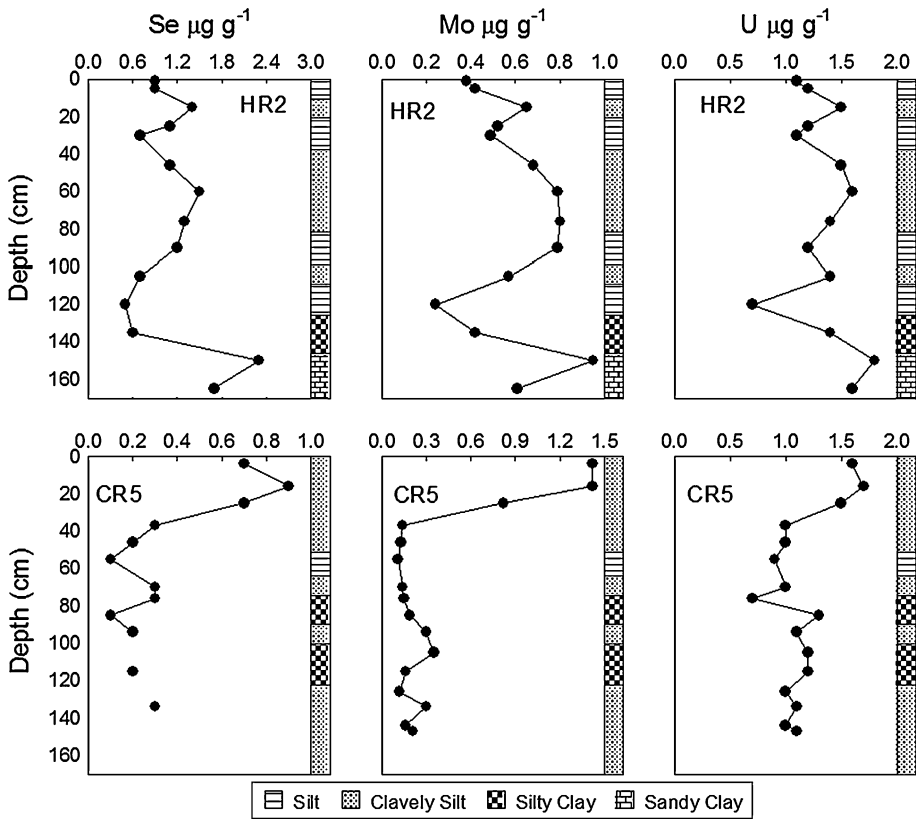

Fig. 2 Downcore distributions of selenium, molybdenum and uranium (µg g^{-1}) in cores HR2 and CR5 from the CR delta

Table 1 Comparison of the concentrations of selenium, molybdenum and uranium in sediments from the Colorado River delta, other river and coastal sediments, and with freshwater sediment quality guidelines for ecological risk assessment

Site	Se (µg g^{-1})	Mo (µg g^{-1})	U (µg g^{-1})
Cores from the CR delta[a]	<0.1–2.3	0.11–1.42	0.7–1.8
Central coast of California, USA[b]		1.34–2.38	2.99–5.47
Mazatlán continental platform, Mexico[b]		6.26–16.8	4.29–17.32
Mannering Bay, Australia[c]	0.7–16.5		
Surface sediment fom the CR delta[d]	0.6–5		
Santa Clara wetlands, Sonora, Mexico[e]	0.8–1.8		
Lowest effect level (LEL)[f]	1.9	13.8	104.4
Severe effect level (SEL)[f]	16.1	1,238.5	5,874.1

[a] Present study, [b] McManus et al. (2006), [c] Peters et al. (1999), [d] García- Hernández et al. (2001), [e] García- Hernández et al. (2000), [f] Thompson et al. (2005)

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References

Daesslé LW, Lugo-Ibarra KC, Tobschall HJ, Melo M, Gutiérrez Galindo EA, García Hernández J, Álvarez LG (2009) Accumulation of As, Pb and Cu Associated with the Recent Sedimentary Processes in the Colorado Delta, South of the United States-Mexico Boundary. Arch Environ Contam Toxicol 56:680–692

Engberg RA (1999) Selenium budgets for lake Powell and the upper Colorado river basin. J Am Water Resour Assoc 35:771–786

García-Hernández J, Glenn EP, Artiola J, Baumgartner JD (2000) Bioaccumulation of Selenium (Se) in the Cienega de Santa Clara Wetland, Sonora, Mexico. Ecotoxicol Environ Saf 46:298–304

García-Hernández J, King KA, Velasco AL, Shumilin E, Mora MA, Glenn EP (2001) Selenium, selected inorganic elements, and organochlorine pesticides in bottom material and biota from the Colorado River delta. J Arid Environ 49:65–89

Lemly AD (1999) Selenium transport and bioaccumulation in aquatic ecosystems: a proposal for water quality criteria based on hydrological units. Ecotoxicol Environ Saf 42:150–156

Ludington S, Plumlee GS (2009) Climax-type porphyry molybdenum deposits: US geological survey open-file report 2009–1215, 16 pp

Lugo-Ibarra K, Daesslé LW, Macías-Zamora V, Rámirez-Álvarez N (2011) Persistent organic pollutants associated to water fluxes and sedimentary processes in the Colorado River delta. Baja California, Mexico. Chemosphere 85:210–217

Martin JM, Whitfield M (1983) The significance of the river input of chemical elements to the ocean. In: Wong CS, Boyle EA, Bruland KW, Burton JD, Goldberg ED (eds) Trace metals in sea water. Plenum, New York, pp 265–296

McManus J, Berelson WM, Severmann S, Poulson RL, Hammond DE, Klinkhammer GP, Holm C (2006) Molybdenum and uranium geochemistry in continental margin sediments: paleoproxy potential. Geochim Cosmochim Acta 70:4643–4662

Peters GM, Maher WA, Jolley D, Carroll BI, Gomes VG, Jenkinson AV, McOrist GD (1999) Selenium contamination, redistribution and remobilization in sediments of Lake Macquarie, NSW. Org Geochem 30:1287–1300

Reimann C, Caritat P (1998) Chemical elements in the environment: factsheets for the geochemist and environmental scientist. Springer, 398 pp

Schroeder RA, Orem WH (2000) Nutrient dynamics in the Salton basin-implications from calcium, uranium, molybdenum, and selenium. Annual meeting: American geophysical union. Available at: http://pubs.usgs.gov/post/pos01-001/pdf/AGU_Poster.pdf. Accessed May 2011

Thompson PA, Kurias J, Mihok S (2005) Derivation and use of sediment quality guidelines for ecological risk assessment of metals and radionuclides released to the environment from uranium mining and milling activities in Canada. Environ Monit Assess 110:71–85