^{238}U removal and accumulation in Concepción bay sediments, Chile

Laura Farías

Programa Regional de Oceanografía Física y Clima, Universidad de Concepción, Casilla 160-C,
Concepción 3, Chile; lfarias@profc.udec.cl
Departamento de Oceanografía, Universidad de Concepción,
Casilla 160-C, Concepción 3, Chile

Marco A. Salamanca

Lizandro A. Chuecas

Departamento de Oceanografía, Universidad de Concepción,
Casilla 160-C, Concepción 3, Chile

ABSTRACT

Activity profiles of ^{234}U, ^{238}U and ^{210}Pb, as well as the ^{234}U/^{238}U ratio, and ^{210}Pb$_{xs}$ radiochemical parameters and macrobenthic abundance in sediments were measured and calculated at different times during a year (1991), along a transect between the head and the mouth of Concepción Bay, Chile. This bay is a semi-enclosed shallow embayment with a strong seasonality in its hydrographic and biological characteristics due to wind driven upwelling. Upwelling of oxygen-poor and nutrient-rich water occurs and organic detritus reaches the seabed, creating a sub-oxic and anoxic environment during, at least, 57% of the year. ^{238}U and ^{234}U activities in the sediments show a gradual increase from 1.57 to 6.07 dpm g^{-1} from the surface to 15 cm depth in the sediments. Under suboxic-anoxic conditions, this pattern is consistent with a reduction of U(VI) to U(IV) and its subsequent removal from pore-water. A ^{234}U/^{238}U ratio of 1.10 ±0.08 indicates an authigenic origen. The ^{238}U accumulation rate and inventory show a significant increase from Station 1 (head of the bay) to Station 3 (mouth of the bay) from 348 to 794 dpm cm^{-2} kyr^{-1} and of 14 to 32 dpm cm^{-2}, respectively. The organic-rich and highly reducing sediments also show an increase in sulphate-reduction rates, sulfur speciation and bioturbation activities of macrobenthos. These patterns suggest that the extent of U enrichment in these sediments is regulated by bacterial sulphate reduction rate and bioturbation and bioirrigation activities. The estimated ^{238}U accumulation rates are higher than those reported for other anoxic environments, representing an important U sink in marine sediments. The geochemical behaviour of U seems to be very sensitive to the redox condition and this characteristic could become an important paleoceanographic tool to identify changes in oceanographic conditions during the last millennium.

Key words: U removal and accumulation, bacterial sulphate reduction and bioperturbation, Coastal upwelling, Central Chile.

RESUMEN

Remoción y acumulación de ^{328}U en los sedimentos de la bahía de Concepción, Chile. Las actividades del ^{234}U, ^{238}U y del ^{210}Pb, los parámetros radioquímicos como la razón ^{234}U/^{238}U y el exceso de ^{210}Pb$_{xs}$ y la abundancia del macrobentos fueron medidas y estimadas en sedimentos marinos a lo largo de una transecta ubicada entre la boca y la cabeza de Bahía Concepción, durante un ciclo anual. Esta bahía es un ambiente semicerrado y somero, sujeto a una fuerte estacionalidad en sus características hidrológicas y biológicas debido a la influencia de la surgencia costera que se desarrolla en dicha región. La surgencia de aguas ricas en nutrientes y pobres en oxígeno da como resultado una alta producción de detritos orgánicos que alcanzan los sedimentos, creando condiciones subóxicas y/o anóxicas durante, al menos, el 57% del año. Los perfiles de ^{234}U, ^{234}U y ^{238}U entre la superficie y los 15 cm de profundidad muestran un

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incremento gradual de sus actividades en rangos que fluctuaron entre 1.57 y 6.07 dpm g^{-1}. Bajo condiciones subóxicas y anóxicas, esta distribución es consistente con la reducción del U(VI) a U(IV) y su consecuente remoción del agua intersticial y su acumulación en la fase sólida.La razón ^{234}U/^{238} de 1,10 ± 0,08 indica un origen autigénico. La tasa de acumulación e inventarios de ^{238}U muestran un aumento significativo desde la Estación 1 (cabeza de la bahía) hacia la Estación 3 (boca de la bahía), con rangos que fluctuaron desde 348 a 794 dpm cm^{-2} kyr^{-1} y desde 14 a 32 dpm cm^{-2}, respectivamente. Estos sedimentos, ricos en materia orgánica y altamente reductores, muestran también un incremento similar desde la cabeza hacia la boca de la bahía, en las tasas de sulfato-reducción, especiación de azufre y la actividad bioperturbadora e irrigadora del macrobentos. Estos patrones sugieren que el grado de enriquecimiento de U en estos sedimentos es el resultado de su reducción y remoción del agua intersticial, la cual está regulado por la tasa de sulfato-reducción y la bioperturbación y bio-irrigación. La tasa de acumulación de ^{238}U es mayor a las encontradas para otros ambientes o cuencas anóxicas e indican una importante área para la pérdida de U en sedimentos marinos. El comportamiento geoquímico del U parece ser muy sensible a las condiciones óxido-reductoras de los sedimentos, representando una herramienta importante para identificar cambios en las condiciones paleo-oceanográficas del último milenio.

Palabras claves: Remoción y acumulación de U, Sulfato-reducción y bioperturbación, Surgencia costera, Chile Central.

INTRODUCTION

Enhanced concentration of U in marine sediments has been well documented in deep sea systems, *e.g.*, siliceous oozes (Bloch, 1980; Cochran and Krishnaswami, 1980), metaliferous sediments (Cochran, 1982), turbidites (Colley and Thomsom, 1992), anoxic basins (Anderson, 1987; Barnes and Cochran, 1991) and coastal sediments (Mckee *et al.* 1987; Barnes and Cochran, 1991, 1993; Church *et al.*, 1996), both in ancient (Thomsom *et al.*, 1990; Colley and Thomson, 1990, 1992; Klinklammer and Palmer 1991) and recent sedimentary environments.

Under oxic condition and pH greater than 6, U exists as U(VI) and forms the stable (3.3 µg L^{-1} or 2.4 dpm L^{-1} at salinity of 35) and soluble uranyl-carbonate (UO2(CO$_3$)$_3^{4-}$) species, in which natural occuring ^{238}U isotope represents 99.27% of the total concentration. Under reducing condition, U(VI) is reduced to much less soluble and particle reactive U(IV) species, which, like Th(IV), can be removed from solution onto particles (Cochran, 1982). In marine surface sediments, the U is mobile only over a short distance, as it is released by the oxidation of organic matter via the dissolved oxygen that penetrates through the sediment surface from seawater. Subsequently, U is immobilized by the reduction to U(IV), leading to substantial U enrichment in reducing zones (Santschi *et al.*, 1988; Barnes and Cochran, 1993). Thus, the main mechanism controlling U accumulation rates in sediments is consistent with a balance between the diagenetic release of U oxide coatings to the pore-water and the reduction and removal of U from pore-water solution to the solid phase (McKee *et al.*, 1987; Santschi *et al.*, 1988; Colley and Thomson, 1990; Barnes and Cochran, 1993).

The microbially mediated degradation of organic material in near-shore sediments controls many important biogeochemical processes. These include organic carbon remineralization of metabolizable fractions and other elements and the regulation of the chemical distributions controlled by redox conditions (Berner, 1980). The oxidation state of U exerts a strong control on its geochemical behaviour. There is a correlation between U removal rates and diagenetic redox conditions associated with organic carbon oxidation processes, *e.g.*, sulphate reduction (Barnes and Cochran, 1990, 1993). In fact, sulphate in coastal marine sediments appears to be the quantitatively most important electron acceptor, accounting for 50-70 % or more of the total sediment respiration (Howarth and Jorgensen, 1984).

There is evidence that bacteria play a role in U reduction, but whether the mechanism of dissolved U removal by bacteria is a passive or active mechanism, or both, has not been clarified yet. The microbial activity can generate HS$^-$ which could act as a reducing agent, but this is only possible at high sulphide concentration (Reynolds and Goldhaber, 1983; Mohagheghi *et al.*, 1985). It is becoming increasingly clear that U reduction in anoxic environments is often the result of a direct enzymatic process by Fe-reducing and sulphate-reducing bacteria, as has been observed both in culture experiments and under natural conditions (Lovley *et al.*, 1991; Lovley and Phillips, 1992; Lovley *et al.*, 1993; McKee and Todd, 1993).

Accordingly, the sediments of Concepción Bay represent an appropriate substrate wherein the distribution of solutes and other processes, related either directly or indirectly to the decomposition of organic matter, shows a natural gradient useful for studying the mechanisms of removal of U from sediments. Concepción bay is the largest, protected and relatively shallow coastal area located in central Chile and, is also surrounded by one of the most industrialised and urbanised areas of Chile. It is characterised by an orientation that enhances the influence of the wind and, therefore, the fertilising effect associated with coastal upwelling of Subsurface Equatorial Water (SSEW). Thus, the nutrient cycle in Concepción Bay shows a strong complexity due to the combined effects of **i-** a pronounced O_2 minimum layer and nutrient supplied by the SSEW, which on the continental shelf at 36°S are present at 80-280 m, but during the coastal upwelling it can be elevated to 20 m depth bathing the shelf and bay sediments; **ii-** high rate of nutrient recycling from sediment and **iii-** high nutrient load from domestic sewage (Farías *et al.*, 1996).

The ^{238}U solid phase distribution in the nearshore sediments of Concepción Bay provides an index of the extent to which the U geochemical behaviour is linked to organic carbon oxidation. Thus, a relationship between the accumulation of U in organic-rich sediments and the intensity of the diagenetic redox reactions (*e.g.,* bacterial sulphate-reduction) could be expected to occur in Concepción Bay sediments, where biogeochemical processes in the water column and sediments occur at different rates, both temporal and spatial scales (Ahumada *et al.*, 1983; Arcos and Navarro, 1986; Peterson *et al.*, 1988).

STUDY AREA

Concepción Bay (36°40'S;73°01'W) (Fig. 1) is a semi-enclosed (167.4 km^2) and shallow (maximum depth 45 m) embayment with a strong seasonality in hydrographic processes and high biological productivity of the water column due to wind driven upwelling (Ahumada *et al.*, 1983). The hydrographic parameters of the bay are affected by local wind variability producing the following hydrographic regimes (Ahumada *et al.*, 1983): **a-** wintertime (*ca.*, 43% of the year) is dominated by northerly winds that drive strong and efficient vertical mixing in the water column. Sub-Antarctic Surface Water (SASW) is present within the bay, associated with a high dissolved oxygen content and low nutrient concentrations; **b-** late spring, summer and early autumn (*ca.* 57% of the year), when southerly winds dominate, the combined effect of these winds, the orientation of the coast and the Coriolis force give rise to the upwelling of SSEW, characterised by higher salinity, oxygen-poor (< 40 μM) and nutrient-rich (> 25 μM N-NO_3^-) water.

The upwelled water produces an increase in phytoplankton biomass and high levels of primary productivity (Ahumada, 1989; Ahumada, 1991; Bernal *et al.*, 1989). Maximum *chlorophyll-a* concentration with values of of about 50 mg **Chl-a m^{-3}**and primary production of 5.76 g C m^{-2} d^{-1}and up to 9.6 g C m^{-2} d^{-1}, have been reported for the shelf waters, among the highest values in the literature (Fossing *et al.*, 1995). A carbon balance (Bernal *et al.*, 1989) and sediment trap data (Ahumada, 1991; Farías *et al.*, 1994) indicate that *ca.* 25-50% of the primary production generated during the upwelling season settles onto the bay sediments. Thus, oxygen-poor upwelled water and organic-rich detritus reaching the seabed, create a sub-oxic and anoxic environment during at least 57% of the year.

The sediments of Concepción bay are soft, black reducing mud (mainly silty clay), rich in organic matter. The sediment surface is frequently covered by a filamentous microbial association of the genera *Thioploca* and *Beggiotoa* (Gallardo, 1977) and the upper few centimetres of the sediment column is inhabited by an abundant macrobenthic community dominated by polychaete worms, tolerant to low oxygen conditions (Carrasco, 1996). The solutes in pore-water are typical of anoxic sediments that have undergone quick remineralisation of organic matter via sulphate-reduction (Farías and Salamanca, 1990; Ferdelman *et al.*, 1997). These

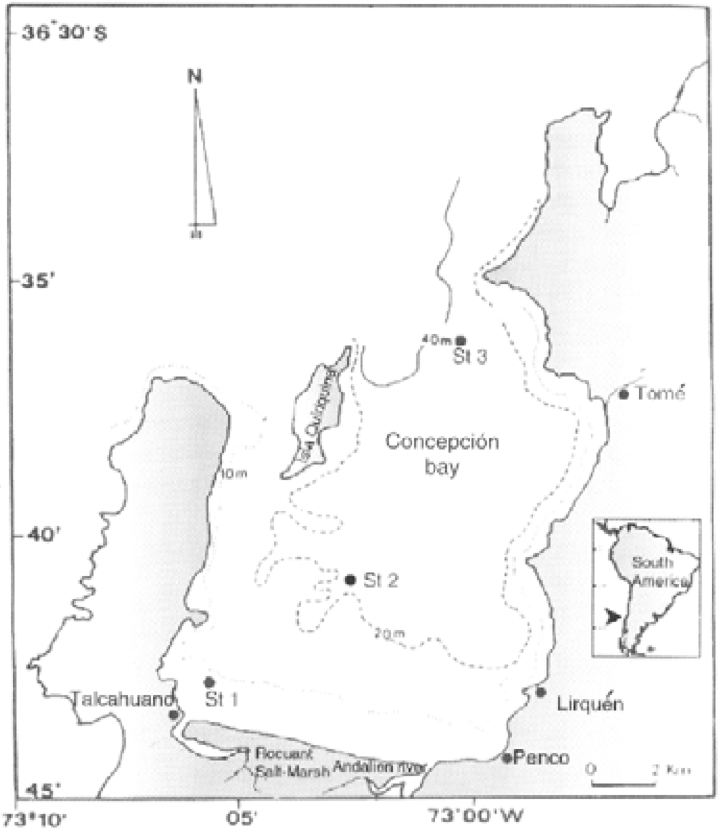


FIG. 1. Location of sampling stations in the sediments of Concepción Bay, Chile.

processes in the upper 20 cm of the sediment column are evidenced by a steep positive pore-water concentration gradient in dissolved ammonium concentration. In turn, these gradients support high ammonium fluxes to the overlying waters (up to 10 mmol m^{-2} d^{-1}) during the upwelling season (Farías *et al.*, 1996).

METHODS

SAMPLE COLLECTION

The samples were collected during January, April, August and November of 1991 on board the R.V. Kay-Kay. Rectangular Plexiglass corers, operated by divers (to recover undisturbed samples of 15-20 cm in length), and gravity cores were used to collect sediments from three stations along a transect from Talcahuano Harbour to the mouth of Concepción Bay (Fig. 1). A 212 cm^2 rectangular core was taken for radiochemical (^{238}U, ^{234}U, and ^{210}Pb) and sedimentological analyses (percentage of water, bulk density, porosity). The cores were stored at 4°C after collection and then sectioned at 1-2 cm intervals.

In order to characterise the redox conditions from each interval, a gravity core was taken to determine Eh and pH. These measurements were made under a glove bag filled with N_2, by inserting the platinum electrode directly through a sealed hole to avoid air contamination. Macrofauna samples (triplicate) were taken with a 0.1 m^2 grab. Samples were sieved through a 0.5 mm mesh and biological material was fixed with 10% water-formaline solution and stored in a Rose Bengal ethanol solution for later separation and identification.

ANALYTICAL METHODS

For U isotope determination, ashed sediment samples (4-5 g) were leached in hot 6 N HCl and spiked with a ^{232}U/^{228}Th tracer. The U was separated from Th and other interferences (Ra and Fe) using DOWEX 1x8 anion exchange columns, following a modified procedure of Bhat *et al.* (1969). The purified U fraction was electro-deposited onto a stainless steel disc from an ammonium sulphate solution of pH 2 (Talvitie, 1972). The ^{210}Pb was determined by its granddaughter ^{210}Po using the chemical procedures delineated by Flynn (1969). A sample of 1-2 g of dried sediments was digested with successive concentrated acids and then spontaneously deposited onto silver discs. ^{209}Po yield tracer was added to each sample prior to acid digestion.

The ^{238}U, ^{234}U and ^{210}Pb activities were determined using an alpha-spectrometer Canberra 35 Plus, equipped with four detectors. In order to obtain the excess of ^{210}Pb, the measured ^{210}Pb activities were then corrected for ^{226}Ra-supported ^{210}Pb activities by subtracting the stable, low-level activities at the base of the cores. In this case, it is assumed that the ^{210}Pb is in equilibrium with the ^{226}Ra activity. This relation has previously been corroborated by Salamanca (1988). The water content, porosity and dry bulk densities of each section were determined by drying at 110°C, assuming a dry weight density of 2.65 g cm^{-3}. Weight loss on ignition at 475°C, as a measure of Loss Organic Ignition (LOI) was measured in sediment samples after drying to constant weight (Dean, 1974). ^{238}U and ^{210}Pb$_{xs}$ inventories from 0 to 15 cm depth were calculated by adding from all horizons the product of isotope activity, internal width and dry bulk sediment density. The sediment apparent accumulation rates were estimated from ^{210}Pb distributions by means of a dimensional, steady-state sedimentation model (Cochran, 1982). A multivariate covariance analysis (ANCOVA) between U as the dependent variable, depth as classificatory variable, and stations and sampling periods as co-variables was carried out.

RESULTS AND DISCUSSION

GENERAL SEDIMENT CHARACTERISTICS

Sediments from all stations are grey to black muds (*ca.* 80 % clay minerals with mean grain size of 7.05 phi), with high superficial sediment porosity (0.93-0.90 v v^{-1})) and high organic content (15-18 % LOI). The sediments reveal reducing characteristics (Eh< -150 mV) from the first few millimetres of depth, except during the winter period (August), when a surface oxidized layer (*ca.* 5-10 mm) is observed. The pH varies from 7.5 to 7.2. The black to green colour of the sediments can be caused by the presence of common micro-crystalline sulphide (*i.e.*, FeS and FeS$_2$), which indicate reducing conditions (Ferdelman *et al.*, 1997). The oceanographic and geochemical characteristics at the three stations are presented in table 1.

The silt-clay sediments of Concepción Bay and adjacent shelf may be considered as a record of an organic-rich, anoxic sedimentary environment where the very high superficial carbon oxidation rates (up to 3 mol cm^{-3} d^{-1}) are entirely related to sulphate reduction (Thamdrup and Canfield, 1996). Concepción Bay sediments are only comparable to those measured in highly productive water and organic carbon deposition areas (*e.g.*, enclosed bays, estuaries and salt marshes).

The sulphate reduction rates have been recently measured in a location similar to Stations 2 and 3 of this study and found to range between 50 and 1500 nmol cm^{-2} d^{-1} at the surface (Thamdrup and Canfield, 1996; Ferdelman *et al.*, 1997; Farias, 1998). The maximum values occurring at Station 3 and these values are consistent with those found in other upwelling and highly productive ecosystems (Canfield, 1989). The ammonium pore-water profiles and their fluxes across the sediment-water interface reflect also an increase in the diagenetic ammoniun production from Station 1 to Station 3 (Farías and Salamanca, 1990; Farías 1998).

Concentrations of pore-water sulphide and speciation of sulphur compounds (*e.g.*, pyrite, acid volatile sulphur 'AVS', elemental S) also exhibit a strong spatial variability in the sediments of Concepción Bay (Ferdelman *et al.*, 1997). Station 1 is one of the most polluted sites in the bay due to the

TABLE 1. STATION LOCATION, SOME GEOCHEMICAL CHARACTERISTIC OF THE SEDIMENTS AND NEAR BOTTOM WATER PARAMETERS IN CONCEPCION BAY.

Variables	**Station 1**	**Station 2**	**Station 3**
Depth (m)	5	22	36
Distance from the shore (km)	1	8.2	12.5
Bottom water ([1])			
Oxygen (ml L^{-1})	n.d	0.4	0.2
Nitrate (μM)	18.96	15.87	15.67
ammonium (μM)	18.02	10.82	10.56
Sediments			
General characteristic	Silt clay, Black Highly reducing	Silt clay Gray/black Reducing (Eh <-150 mV)	Silt clay Gray/black Reducing (Eh <-100 mV)
Water content (%)	71.73 ± 8.03	70.09 ± 13.2	68.98 ± 12.1
LOI (%)	17.73 ± 1.23	15.30 ± 1.81	15.02 ± 2.01
Sulphate reduction rates[2] n md $m^{-2}d^{-1}$	n.d	28.3	42.5
Acid Volatile Sulphur (AVS)[3] (%)	Strong smell of H_2S	76.5	52.9
Pyrite [3] (%)	n.d	0.7	42.5

[1] Average concentrations of chemical variables in bottom water measured during upwelling periods (Ahumada, 1989). [2] Data taken from Ferdelman *et al.* (1997), obtained at the same stations, but sampling were not carried out at the same time; n.d.: not determined. 3. Percentage of sulphate reduced and experimentally recovered in AVS and pyrite.

dumping of untreated sewage from fishmeal factories and the sediments have a high sulphide concentration (> 1000 μM) (Rudolph and Ahumada, 1987). The sediments at Station 2 have intermediate to high sulphide concentrations (356-1200 uM), whereas , the lowest values were observed at Station 3 (1-2 μM), despite the fact that high sulphate reduction rates have been reported (Ferdelman *et al.*, 1997). Therefore, the produced sulphide must have been rapidly reoxidized.

The differences in AVS concentration and sulphur speciation in the sediments between the intermediate (Station 2) and outer sites (*e.g.*, Station 3) can be explained by the different physiology of the bacterial mats dominating the sediments. *Beggiatoa* spp. grow in the highly-reducing sediments of the inner parts of the bay, whereas *Thioploca* spp. grow in more oxidised sediments with respect to sulphur speciation on shelf locations (Huetel *et al.*, 1996). On shelves, Fe reduction is mainly coupled to oxidation of reduced S and the precipitation of sulphides as pyrite-dominated H_2S scavenging (Thamdrup and Canfield, 1996; Ferdelman *et al.* 1997). *Thioploca* is able to oxidise a maximum of 35% of sulphide production (Ferdelmam *et al.*, 1997), revealing a potential to oxidise part of the sulphide with its intracellular nitrate (Fossing *et al.*, 1995).

The macrofauna in Concepción Bay sediments consisted of 26 taxa or species groups during the sampling period, being characterised by large numbers of polychaete deposit feeders. The Spionid *Paraprionospio pinatta* (Erlers) represented about 75.58-98.57% of the total macrofauna abundance. There are no clear patterns in the temporal abundance patterns over the seasonal cycles, but a spatial trend in the relative abundance along the organic matter gradient was observed. Station 1 was defaunated during the sampling period, while Station 3 had a maximum abundance (*ca.* 1512 individuals per 0.1 m^{-2}). The variation of total abundance of the macrobenthic community between stations and sampling periods and the relative contribution of Polychaeta are shown in table 2.

SOLID PHASE RADIOCHEMICAL DATA

The sediments of Concepción bay have a ^{238}U activity ranging from 1.57 to 6.07 dpm g^{-1} with a mean of 3.02±1.12 dpm g^{-1}. The vertical distributions of ^{238}U at the different stations are plotted in figure 2. ^{238}U activity remains relatively constant with depth at Station 1 while Stations 2 and 3 show a significant increase from 2-3 dpm g^{-1} at the surface of the sediment to 4-6 dpm g^{-1} at 15 cm depth ($p < 0.05$,

TABLE 2. ABUNDANCE OF MACROBENTHIC ORGANISMS (INDIVIDUALS PER 0.1 m^{-2}) AND THE RELATIVE IMPORTANCE OF POLYCHAETA (%) AT EACH STATION IN CONCEPCION BAY SEDIMENTS.

Sampling period	Total abundance			Polychaeta
	Station 1	Station 2	Station 3	(%)
January 1991	2	817 ± 72	654 ± 54	98.5
April 1991	14	133 ± 11	1512 ± 138	75.5
August 1991	4	634 ± 27	869 ± 72	88.8
November 1991	2	137 ± 11	429 ± 32	89.9
Total mean	**22**	**1727**	**3694**	

ANCOVA analysis, Table 3). The ^{238}U enrichment with depth increases by a factor of two, particularly in the cores from Station 3. The results indicate that ^{238}U increases significantly with depth and this pattern is different between sampling stations ($p.< 0.05$), but no significant differences occur between sampling periods ($p.=0.123$).

Figure 3 presents the vertical distribution of excess ^{210}Pb activity for the three sampling stations. Station 1 presents an almost uniform activity throughout the sediment column. By contrast, at Stations 2 and 3 the distribution is characterised by a break in slope, with a zone of relatively uniform activity from the sediment surface to 5-8 cm depth, due to biological mixing, followed by a decrease of ^{210}Pb activity with depth. For an explanation of the ^{238}U radiochemical profiles, chemical (reduction and removal onto particles) and physical (diffusion and mixing) mechanisms must be considered. The ^{234}U/^{238}U ratio in Concepción bay sediments presents an average value of 1.11 ± 0.08, consistent with an authigenic origin (Thomson *et al.*, 1990). The addition of authigenic ^{234}U increases the ^{234}U/^{238}U activity ratios from 0.9-1, characteristic of detrital phases, a value of 1.15, characteristic of seawater (Cochran, 1982). The ^{234}U and ^{238}U activities in Concepción Bay sediments show a very strong correlation (r^2= 0.92, DF=79), essentially identical in sediments from all depths (Fig. 4). The least squared regression gives a ratio of change in ^{234}U to change in ^{238}U of 1.043±0.04 (95% C.L.). The U/Th ratios higher than 2 (Farías, 1992), together with concentrations of Al in the sediment column (Salamanca, 1988), indicate a constant detrital-phase composition in the sediment column. Therefore, the enhancement of U in the sediments suggests authigenic enrichment.

TABLE 3. RESULT OF A MULTIVARIATE COVARIANCE ANALYSIS (ANCOVA) PERFORMED BETWEEN U, AS THE DEPENDENT VARIABLE DEPTH, AS CLASSIFICATORY VARIABLE, AND STATIONS AND SAMPLING PERIODS AS CO-VARIABLES.

Source	SS	DF	MS	F-ratio	p
Depth	35.326	6	5.887	7.566	0.000
Station	18.016	2	9.008	7.471	0.000
Period	8.023	3	2.675	1.986	0.123
Error	58.354	75	0.778		

The ^{238}U profiles in Concepción Bay sediments also seem to be affected by biological mixing (*i.e.*, particle mixing and burrow irrigation by benthic fauna). In fact, these sediments are densely inhabited (except Station 1) by macrobenthic assemblages of deposit feeder Polychaeta (Table 2). Sediment X-radiographs reveal extensive networks of burrows, which indicate an intense circulation of pore-water through the sediments (Farías, 1992). The fluid transfer may be orders of magnitude greater (volumetrically) than particle reworking (Aller and Cochran, 1976). Consequently, benthic organism activities introduce from overlying seawater about 2.45 dpm L^{-1} of dissolved ^{238}U and ^{234}U (Farías, 1992), penetrating several centimetres down into the reducing sediment column, wherein an intense remineralisation of deposited organic matter coupled with a sulphate reduction from the sediment surface are observed (Thamdrup and Canfield, 1996; Ferdelman *et al.*, 1997; Farías, 1998). Thermodynamic prediction of U reduction indicates that U in pore-water of anoxic sediments that contain dissolved Fe^{2+} and HS^{-1} should be gradually reduced and removed from solution (Barnes and Cochran, 1990, 1993).

URANIUM ACCUMULATION RATES

The ^{238}U inventories fluctuate from 14.22 dpm cm^{-2} to 32.21 dpm cm^{-2}, being considerably higher at Station 3. Also, the excess of ^{210}Pb yields average inventories which increase from Station 1 to 3 (Station 1: 8.73±1.48 dpm cm^{-2}, Station 2: 20.28±3.07 dpm cm^{-2} and Station 3: 21.62 + 3.09 dpm cm^{-2}). The apparent accumulation rates estimated from $^{210}Pb_{xs}$ vary from 0.17 to 0.28 cm yr^{-1}. The U accumulation rates can be estimated from the increase in U with depth (average value over 0-20 cm) and dry sediment accumulation rate of 0.15 g cm^{-2} yr^{-1}, derived from

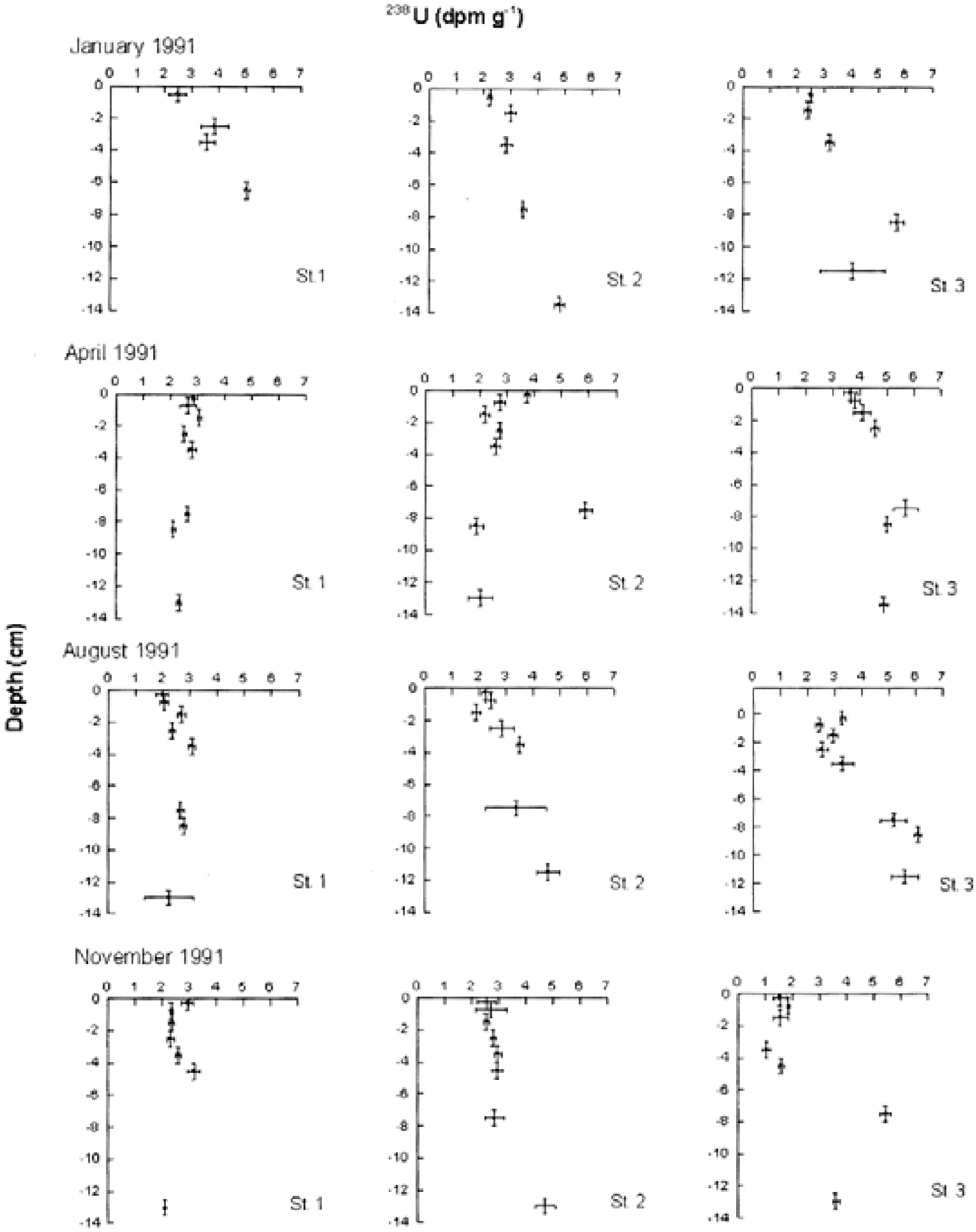


FIG. 2. Vertical distribution of ^{238}U activity (dpm g^{-1}) in the sediment cores during the different sampling periods. The sample location and water depth are given in table 1. The error bars represent one standard deviation of alpha counting.

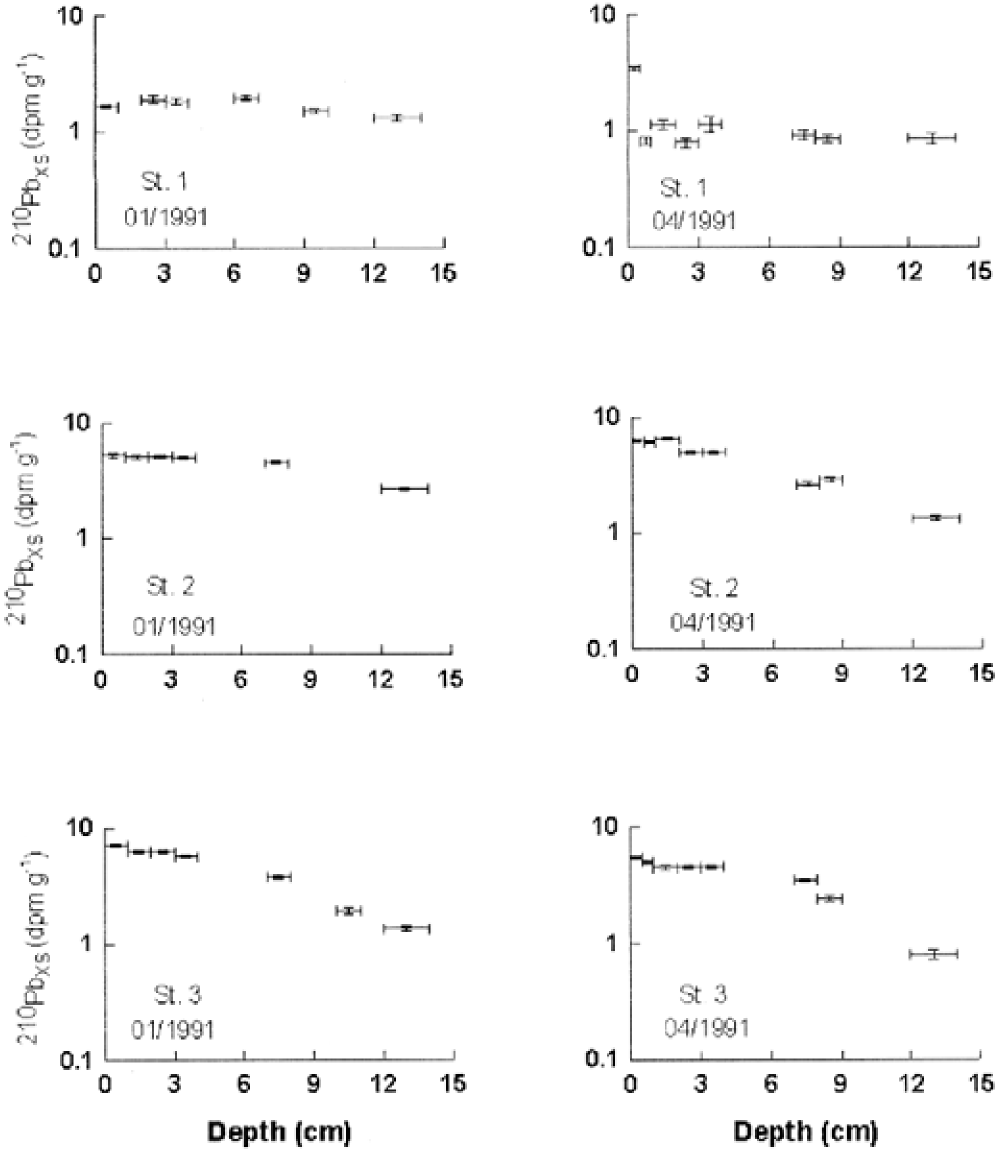
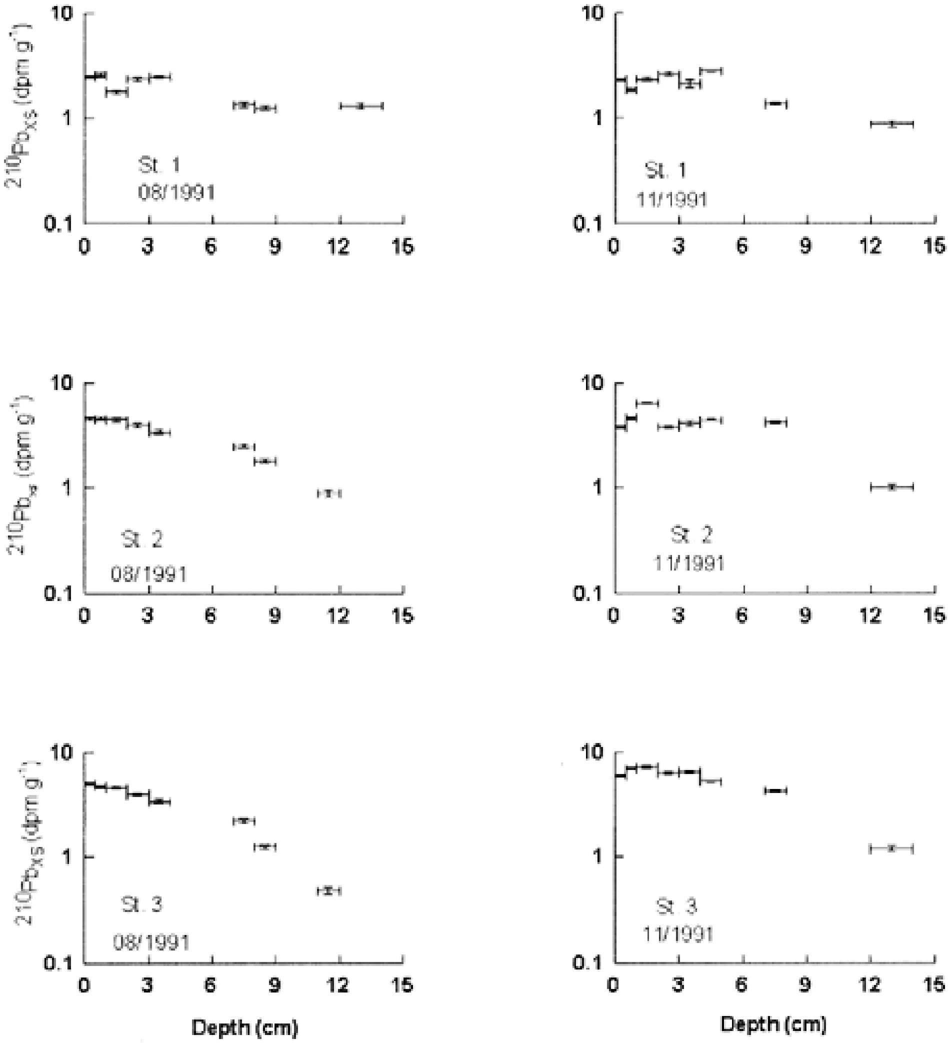


FIG. 3. Vertical distribution of Log $^{210}Pb_{xs}$ activity (dpm g^{-1}) in the sediment cores during the different sampling periods. $^{210}Pb_{xs}$ was determined by substracting the ^{210}Pb low activity at depth.

(figure 3 continued)



the $^{210}Pb_{xs}$ distribution below the bioturbation zone (Farías, 1992). The estimated U accumulation rates range from 348 to 795 dpm cm^{-2} kyr^{-1}.

The spatial and seasonal variations of total U accumulation rates and ^{210}Pb and ^{238}U inventories are presented in table 4 . A strong spatial increase of ^{238}U and $^{210}Pb_{xs}$ inventories and U accumulation rates from Station 1 to Station 3 are observed . Part of this spatial variability could be directly attributed to early diagenetic processes associated with the different intensity and mechanisms of organic carbon remineralization linked directly or indirectly to microbial activity and indirectly to the effect of bioturbation.

The processes of U removal by bacterial mechanisms are not clearly understood yet. The association of U with sulphide sediments (Reynolds and Goldhaber, 1983) and the microbial production of HS^{-1} suggest a possible role of this element as a reducing agent. It is becoming increasingly clear that bacteria may enzymatically reduce U(VI); U reduction could be coupled to the oxidation of organic matter with U acting as the electron acceptor (Cochran *et al.*, 1986; Lovley *et al.*, 1991; Lovley and Phillips, 1992;

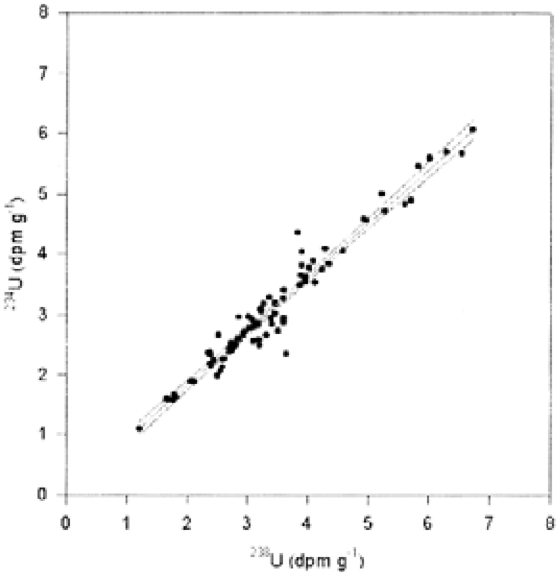


FIG. 4. Relationship of ^{234}U and ^{238}U activities from all depths in cores from Concepción bay sediments. The slope of the least squares fitted line is 1.043 ± 0.04.

Gorby and Lovley, 1992; Lovley *et al.*, 1993; Barnes and Cochran, 1993; McKee and Todd, 1993).

The U accumulation rates, as well as their inventories, increase gradually from Station 1 to Station 3 (Table 4). By contrast, the pore-water sulphide tend to decrease from Station 1 to Station 3 (Table 1). Therefore, these conspicuous natural gradients in rates and mechanisms of carbon oxidation coupled with sulphate-reduction and sulphur speciation are useful in determining the mechanisms involved in U removal. If the U removal is related to general rates of bacterial oxidation of organic carbon, as defined by the rates of diagenetic redox reactions such as sulphate reduction, a more rapid U removal under conditions of higher sulphate reduction rates is expected. If the U removal is mediated by dissolved sulphide acting as a reducing agent, the most rapid U reduction under high concentrations of sulphide is expected.

Station 1 shows the lowest ^{238}U and ^{210}Pb inventories and total U accumulation rates with respect to the other two stations, but has the highest sulphide concentrations. The observed homogeneity of long-lived radionuclide and geochemical parameters, as well as the absence of biogenic structure, could also be related to physical processes that cause particle mixing during erosion and deposition associated with sediment transport events. This physical mixing as well as the high organic content and sulphide concentrations can be viewed as a local phenomenon given the shallow depth and the proximity of about 1 km to Talcahuano Harbour. By contrast, the radiochemical parameters tend to increase towards the mouth of the bay, but the sulphide concentration shows an inverse trend. Therefore, the rates of U removal have a direct relationship with bacterial sulphate reduction in the studied locations. In addition, the increase in the measured radiochemical and diagenetic parameters between the sampling stations is apparently correlated with macrofaunal abundance and its bioturbation rate. In fact, the macrobenthos stimulates the decomposition reactions and solute fluxes across the sediment-water interface (Aller, 1982).

The U accumulation rates measured in Concepción bay sediments and those found in salt marshes by Church *et al.* (1996) are higher than those reported for other anoxic basin sediments, ranging from 15 to > 300 dpm cm^{-2} ky^{-1} (Barnes and Cochran, 1993). The U accumulation in anoxic basin sediments was estimated to account for about 20% of the U input annually by rivers to oceanic U balance (Klinkhammer and Palmer, 1991; Barnes and Cochran, 1990, 1991). Therefore, the inclusion of the U re-

TABLE 4. $^{210}Pb_{xs}$ AND ^{238}U INVENTORIES AND ESTIMATED ^{238}U ACCUMULATION RATES IN CONCEPCION BAY SEDIMENTS CALCULATED FROM SOLID PHASE RADIOCHEMICAL DATA FOR EACH SAMPLING STATION.

Sampling periods	Radiochemical parameters	Station 1	Station 2	Station 3
January 1991	$^{210}Pb_{xs}$ Inventory [1]	9.37 ± 0.21	22.90 ± 0.38	20.73 ± 0.79
	^{238}U Inventory [1]	19.33 ± 0.69	21.09 ± 0.35	24.05 ± 1.24
	^{238}U Accumulation rate [2]	453 ± 20	613 ± 70	721 ± 150
April 1991	$^{210}Pb_{xs}$ Inventory	9.74 ± 0.26	19.09 ± 0.45	22.95 ± 0.48
	^{238}U Inventory	16.89 ± 0.45	19.58 ± 0.44	32.21 ± 0.41
	^{238}U Accumulation rate	348 ± 30	411 ± 60	757 ± 40
August 1991	$^{210}Pb_{xs}$ Inventory	8.66 ± 0.22	16.48 ± 0.39	17.85 ± 0.34
	^{238}U Inventory	14.24 ± 0.96	21.44 ± 1.31	28.22 ± 0.86
	^{238}U Accumulation rate	379 ± 30	598 ± 60	795 ±80
November 1991	$^{210}Pb_{xs}$ Inventory	10.20 ± 0.25	22.66 ± 0.35	15.08 ± 0.37
	^{238}U Inventory	19.84 ± 0.37	27.28 ± 0.87	24.94 ± 0.65
	^{238}U Accumulation rate	424 ± 50	558 ± 15	712 ± 20

[1] dpm cm^{-2} units. Inventories are calculated over the depth interval 0-15 cm. The error is based on counting error.

[2] dpm cm^{-2} ky^{-1} units. The error is expressed as combined error of sedimentation rate and ^{238}U solid phase measurements.

moval in shallow marine coastal sediments (*e.g.*, estuaries, salt marshes, embayments) should increase the importance of marine sediments as U sinks.

Suboxic zones also act as an important sink for certain elements, namely N, Mn, Cr, Cd, and U (Codispoti, 1995; Rosenthal and Boyle, 1995; Rue *et al.*, 1997). In the case of Cr, the Cr(VI) is partially reduced to particle reactive Cr(III), like U(IV) and Th(IV), which can then be scavenged throughout the suboxic area and removed to the sediments (Rue *et al.*, 1997). The geochemical behaviour of U seems also to be very sensitive to the redox conditions (suboxic-anoxic conditions) developed at the 0-15 cm depth of the sediment column, where intense organic carbon remineralisation through sulphate was observed. If this is so, this element could be used as a paleo-oceanographic tool to identify changes in oceanographic conditions (*e.g.*, oxygen level) during the late millennia. Presumably, U(IV) like Cr(III) is scavenged by the rain of particulate organic material through the suboxic waters (*e.g.*, SSEW) and this raises the possibility of using U: organic carbon ratios in sediments as a paleo-indicator of suboxic conditions in the overlying water column. This has been poorly reported in the scientific literature, although most recently Rosenthal and Boyle (1995) found glacial enrichments of authigenic Cd and U in sub-Antarctic sediments associated with increased accumulation rates of organic carbon.

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