PARTICLE SCAVENGING AND TIDAL EXCHANGE IN SAN DIEGO BAY, CALIFORNIA AND THEIR SIGNIFICANCE TO REDISTRIBUTION AND DILUTION OF PARTICLE-REACTIVE CONTAMINANTS

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ABSTRACT
San Diego Bay (SDB; California, USA) is a heavily urbanized and one of the most contaminated embayment in the U.S. To understand the impact of hydrological and sedimentological processes upon the fate of contaminants, we measured radioisotopes ^{210}Pb, ^{210}Po, ^{234}Th, ^{137}Cs, and ^{226}Ra and PCBs in samples collected from the sediments and water column of SDB. Radioisotope activities and water contents in the sediments indicated a highly disturbed sedimentation history. Water column ^{210}Pb and ^{210}Po activities suggested strong tidal exchange, particle scavenging, and sediment resuspension. The temporal influence of tidal exchange on the particle-reactive species was underlined by systematic variation of ^{210}Po and ^{234}Th during a tidal cycle. These patterns are compatible with a declining PCB concentration in the water column, and may have implications on the transport and fate of other particle-reactive contaminants in SDB and vicinity as well.

RESUME
La Baie de San Diego (SDB ; Californie, USA) est très urbanisée et l'une des plus contaminées des Etats-Unis. Nous avons mesuré les radio-isotopes ^{210}Pb, ^{210}Po, ^{234}Th, ^{137}Cs, ainsi que ^{226}Ra et PCB dans les échantillons de sédiments et d'eau de SDB, afin de comprendre l'impact qu'ont les processus hydrologiques et sédimentologiques sur les contaminants. Les profils des radio-isotopes et la composition de l'eau contenue dans les sédiments, ont indiqué une sédimentation extrêmement modifiée. L'activité de ^{210}Pb et ^{210}Po dans l'eau suggère un fort échange de marée, l'absorption et la réglementation de particules ainsi que la resuspension de sédiments. L'influence temporelle de l'échange de marée a été indiqué par la variation systématique de ^{210}Po et ^{234}Th pendant le cycle de marée. Ces modèles sont compatibles avec une baisse de la concentration de PCB dans l'eau et pourraient avoir des implications sur les contaminants et leur transport dans la SDB ainsi que aux alentours.

1. INTRODUCTION

San Diego Bay (SDB) is a narrow mouthed, semi-closed embayment situated at the southern corner of California near the United States-Mexican border (Figure 1). The width of the Bay ranges from 0.4 to 5.8 km and the length is about 24 km. Water depths vary from 1 to 18 m with an average of 10 m. The mean tidal range is 1.7 m but may reach as high as 3 m (Chadwick *et al.* 1999). The residence time of the bay water ranges from 1 day near the bay mouth to 40 days at the southern end of the Bay (Largier 1995).

SDB is surrounded by a number of cities, it also hosts about 9,000 commercial and military vessels, making it one of the most contaminated embayments in the United States (Fairey *et al.* 1996; Senate Committee on Toxics and Public Safety Management 1988). The contaminants include heavy metals and organic contaminants, most noticeably polychlorinated biphenyls (PCBs) (Fairey *et al.* 1996; McCain *et al.* 1992; Schroeder, 1994; San Diego Bay Interagency Water Quality Control Board, 1994). There are very limited studies on the contamination level in the water column (Zeng et al, 2002), and the extent to which oceanic processes affect the distribution and transport of these contaminants remains largely unclear.

Uranium-series radioisotopes (^{238}U, ^{235}U and their daughter nuclides ^{234}Th, ^{230}Th, ^{222}Rn, ^{226}Ra, ^{210}Pb and ^{210}Po, among others) have shown great promise as tracers to oceanic processes (Broecker and Peng, 1982, and references therein) thanks to their diverse chemical characteristics (mostly particle affinity), which produces disequilibria in the oceanic processes, and to their large range of half lives, which allows studies of oceanic processes of different time scales. The radioisotopes of our concern include (half lives are shown in brackets): ^{238}U (4.5 billion yr)→^{234}Th(24.1 day)→ ...→ ^{226}Ra (1600yr) →^{222}Rn (gaseous; 3.8day)→ ...→^{210}Pb→ ^{210}Po→. ..→^{206}Pb (stable). Among them, ^{234}Th, ^{210}Pb and ^{210}Po are very particle-reactive, being scavenged onto sediment by settling particles. ^{210}Pb in coastal oceans is mostly produced through atmospheric fallout after the decay of ^{222}Rn. The grand daughter of ^{210}Pb, ^{210}Po, generally behaves similar to ^{210}Pb. ^{137}Cs, a radioisotope produced by nuclear tests, had a peak fallout rate at 1963 A.D., which provides a time marker in recent sedimentation. Particle affinity of ^{210}Pb, ^{210}Po and ^{234}Th enables them to mimic behavior of many particle-reactive contaminants in SDB, including PCBs (*Zeng et al, 1999*). Hence, transport and redistribution of the radioisotopes are expected to approximate those of PCBs, and may provide insights into the distribution and fate of other particle-reactive contaminants as well.

We measured ^{210}Pb, ^{234}Th, ^{137}Cs, and ^{226}Ra in sediment columns to study sedimentation history, sedimentation rate and mixing. We also measured ^{210}Pb, ^{210}Po, and ^{234}Th in water columns to study short-term hydrological and particle scavenging processes (Baskaran et al, 1992; Baskaran and Santschi, 1993; Fuller, 1982; Fisher et al, 1988).

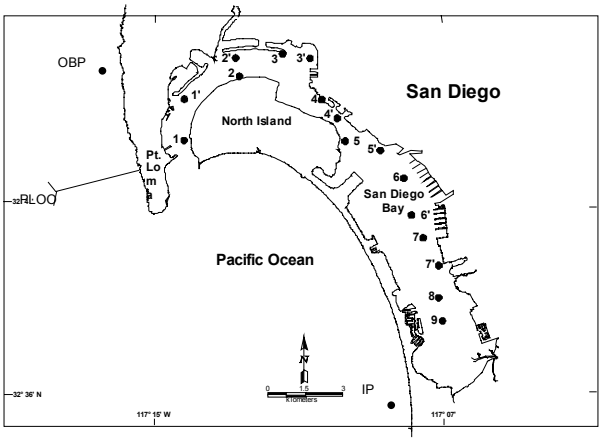

Figure 1. Map showing the study area in San Diego Bay. The first set of stations comprised stations 1-9 and the second set of stations included stations 1' to 7' Stations IP and OBP are located outside SDB.

2. METHODS

2.1 Sample Collection

Field sampling was conducted during June-July 1999 and July 2002. In 1999, water and sediment samplings were carried out at stations 1-9 and only water samples were collected at stations 1' to 7'(Figure 1). These samples were collected during the lower flood tides. In 2002 sampling season, stations IP (Imperial Pier) and OBP (Ocean Beach Pier) outside SDB were sampled on July 6. Stations 1', 2', 3 and 4' in North SDB were sampled during high ebb tide on July 11 2002. On July 26-27 multiple water samples were collected from station 2' during a 13-hour ebb-flood tidal cycle.

Water samples for radioisotope analysis were collected using 30 L Niskin bottles. Samples were transferred to 5 or 10 gallon plastic bottles pre-cleaned with hydrochloric acid and deionized water, acidified to pH $\approx$ 1, and spiked with ^{230}Th, ^{209}Po, and ^{206}Pb. About 50 mg of $FeCl_3$ were added to the samples for co-precipitation of the radionuclides.

Sediment cores for both chemical and isotope analyses were collected using a box corer. Sampling and analyses for TOC and PCB are described elsewhere (Zeng et al, 2002). Subcores were taken using precleaned acrylic plastic cylinders (9.5 cm i.d.). A small amount of overlying water was kept on all subcores, which were sealed, preserved in boxes refrigerated with dry ice, and transported to the University of Southern California (USC), where they were kept at 4^{o}C until analysis.

2.2 Radioisotope Analysis

The water samples were analyzed for ^{210}Pb, ^{210}Po, and ^{234}Th with the methods described previously (Aller and Cochran 1976; Benninger 1976). ^{210}Pb activity measurements require sufficient time for ^{210}Po ingrowth and they are not done for July 2002 samples as of the preparation of this manuscript. Sediment cores were sliced into 0.5-cm or 1-cm intervals. Each sample was dried at 60^{o}C and the water content was measured from the weight loss. Dry sediment was pulverized and loaded into plastic tubes for γ-counting using high-resolution, well-type intrinsic germanium detectors for determination of ^{210}Pb, ^{226}Ra, ^{234}Th, and ^{137}Cs activities.

3. RESULTS

3.1 Sediment Characterization

The sediments were generally dark and odorous sandy mud or muddy silt. They had more muddy components from North SDB toward the South SDB. Ubiquitous occurrence of *Siliqua patula* (razor clam) was observed in sediment samples down to 25 cm depth, suggesting bioturbation. Water content ranged from 25 to 50 % (wt %) and decreased with depth but irregularities were observed (Figure 2).

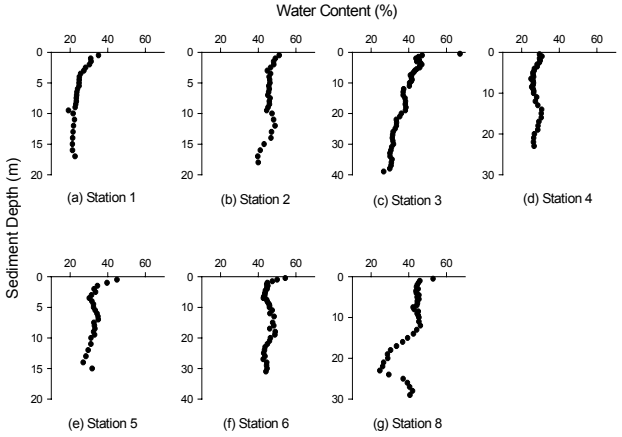

Figure 2. Water contents in sediment cores collected from stations 1-6 and 8. No sediment cores were collected from stations 7 (because it was a trash dumpsite) and 9 (because it was too shallow for the sampling cruise to access).

3.2 Radioisotopes Profiles of Sediment

Profiles of ^{210}Pb, ^{234}Th, ^{226}Ra, and ^{137}Cs are shown in figure 3. Absence of decrease of $^{234}Th_{ex}$ in 4 out of 7 sediment samples suggested strong mixing, and large spikes of $^{210}Pb_{ex}$ and $^{234}Th_{ex}$ at depths again indicated heterogeneity in sediment column. Excess ^{210}Pb profiles were used to

calculate sedimentation rates (Table 1), which were generally high but show large variations.

Table 1. Sedimentation rates (S) estimated based on a linear least-square (r^2) regression analysis of $^{210}Pb_{ex}$ profiles (Robbins 1978).

Station	1	2	3	4	5	6	8
S(cm/y)	0.39	NC*	1.54	NC*	0.34	0.92	NC*
r^2	0.52	NC*	0.66	NC*	0.50	0.33	NC*

NC: Not computable.

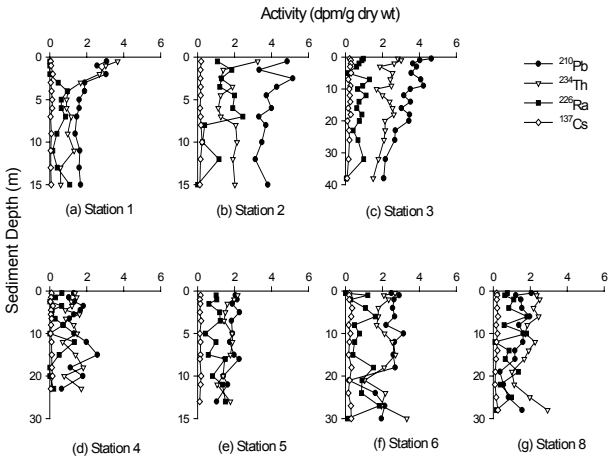

Figure 3. Profiles of $^{210}Pb_{ex}$, $^{234}Th_{ex}$, ^{226}Ra and ^{137}Cs in sediment cores collected from stations 1-6 and 8 in summer 1999.

3.3 Radioisotopes in the Water Column

The profiles of ^{210}Pb and ^{210}Po activities in water samples collected across SDB in summer 1999 showed clear spatial variability (Figure 4). Central Bay from station 3 to station 7' had relatively low ^{210}Pb activities with an average of 0.0123 dpm/g, while the stations in the North Bay and South Bay (stations 1, 1', 2, and 2' in the North Bay; stations 8 and 9 in the South Bay) had much higher ^{210}Pb and ^{210}Po activities with an average of 0.0262 dpm/g. ^{210}Po activities closely follow those of ^{210}Pb and have no statistically significant difference with those of ^{210}Pb.

Water samples collected on July 11, 2002 across North SDB showed a more distinct trend of decreasing activities of ^{210}Po and a higher proportion of particulate ^{210}Po towards the inner bay (Figure 5). ^{210}Po activities of unfiltered water increased steadily from inner bay to bay mouth (Figure 5).

Water samples collected during the July 26-27, 2002 tidal cycle showed systematic variation of ^{210}Po and ^{234}Th activities with tidal phases. High (0.06~0.08 dpm/L) and low (~0.02 dpm/L) ^{210}Po activities were close to those of outer sea/station 2', and inner bay, respectively.

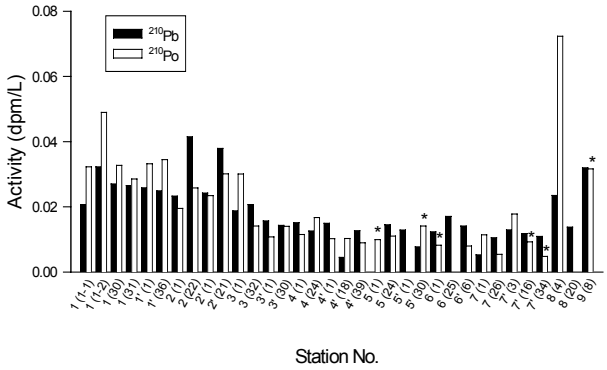

Figure 4. Distribution of ^{210}Pb and ^{210}Po activities in the water column of San Diego Bay. The numbers in the parentheses after station numbers are distance from the sediment-water interface. Measurements error were <5% except ~30% for those marked by *.

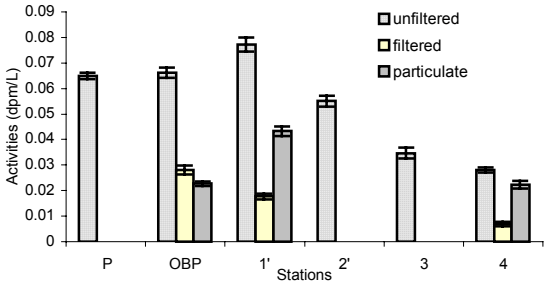

Figure 5. Unfiltered, filtered (dissolved) and particulate ^{210}Po activities in water collected on July 6 (IP and OBP) and 11, 2002 (other samples). Refer to figure 1 for station locations.

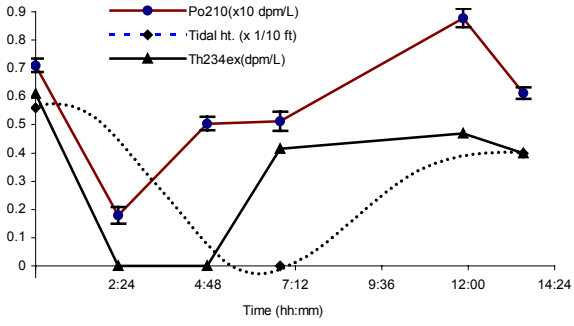

Figure 6. Variations of ^{210}Po and ^{234}Th activities with tidal phase for station 2' during an ebb-flood tidal cycle on July 26-27, 2002. Errors for ^{234}Th activities are estimated to be ~15% (not shown).

4. DISCUSSION

4.1 Sediment Heterogeneity and Sedimentation Rate

Sediment heterogeneity in SDB, reflected by the irregularities in the profiles of water and radioisotope activities (Figures 2 and 3), can be attributed to strong tidal currents (up to 100cm/s), heavy shipping traffic, and frequent dredging activities inside SDB. It was reported that docking of large vessels could stir up as much as 41.7 metric tons surface sediments per day at the Naval Station (located at central SDB) alone (Chadwick *et al.* 1999). Subsequently, tidal currents will redistribute the resuspended sediments across the bay. Dredging can produce discontinuities in sediment column and stir up a mixture of old and new sediments into the water column. In the past 50 years, there have been 11 major dredging events and 5 smaller ones (Chadwick et al, 1999). The irregularities in sediment isotope profiles (Figure 3) undermined the use of ^{210}Pb to estimate sedimentation rates (Robbins, 1978). Sedimentation rates at 3 out of 7 stations could not be calculated by the excess ^{210}Pb method (Figures 3b, d, g; Table 1). Additional information about sedimentation history is provided by ^{137}Cs. The absence of the 1963 spike in all profiles provided further constraints on sedimentation rates. High sedimentation rates across SDB were the chief reason for frequent dredging activities (Chadwick et al, 1999).

Mixing in surface sediment is also evident from the ^{234}Th profiles (Figure 2). Due to its short half-life, ^{234}Th can exist only in the very surficial sediment if there is no mixing. Otherwise, it can penetrate into deeper sediment. Following the simplified model of Aller and Cochran (1976) we can calculate an average mixing rate coefficient by equation: $D_b=W_a*Z$, where W_a is sedimentation rate in cm/yr, and Z is the maximum depth (cm) of excess ^{234}Th. If we use 1cm/y as the average sedimentation rate (W_a) and 5cm as the mixing depth (Z), D_b is estimated to be 5cm^2/yr or 1.6x10^{-7}cm^2/sec. Individual stations can have a much higher mixing rate coefficient, e.g. D_b for station 3 is about 2x10 $^{-6}$ cm^2/sec, about 12 times higher than average mixing rate. Mixing usually result in overestimate of sedimentation rate based on excess ^{210}Pb. In our case, however, with the help of ^{137}Cs constraints, we are confident that sedimentation rates shown in table 1 are in reasonable range.

4.2 Tidal Exchange in San Diego Bay

Figures 4 and 5 show a clear gradient of water column ^{210}Pb and ^{210}Po activities between outer sea and bay water. The apparent difference in the ^{210}Pb activities in north SDB for summer 1999 and summer 2002 samplings is most probably due to the different tidal patterns during sampling. Figure 5 showed that outer sea (i.e. stations IP and ODB) has distinctly higher ^{210}Po activities (0.06-0.08dpm/L) than inner bay water (stations 4-7; 0.01-0.03dpm/L). The outer sea ^{210}Po activities correspond well with results from other studies in adjacent areas (Bruland et al, 1974) and typical coastal oceans (Broecker and Peng, 1982). Very low ^{210}Pb and ^{210}Po activities of inner SDB suggest stronger particle scavenging process due to higher primary productivity and particle resuspension from boating activities or tidal currents. The clear gradient in north SDB (figure 5) indicate a tidal exchange between waters across the bay mouth, and this pattern is more clearly revealed by figure 5, where samples were collected at about the same time so there is no differential tidal effect on individual samples.

The effect of tidal exchange on the particle-reactive radionuclides is also shown in figure 6, where a systematic variation of activities of ^{210}Po and ^{234}Th in water column at station 2' located at north SDB is shown. Sampling started at high high tide, when the north SDB was filled with water from outer sea with high ^{210}Po and ^{234}Th activities. When tide ebbed and tidal current moved outside, north SDB was replaced by inner bay water with high particle load and low overall ^{210}Po and ^{234}Th activities until the tide reached minimum level. Then a smaller flood tide rose and filled north Bay again with outer sea water with higher ^{210}Po and ^{234}Th activities.

A mass balance consideration on the excess ^{210}Pb activities in sediments from station 1-3 (Figure 3a-c) suggested that ^{210}Pb activities in the sediment column (~20- 45 dpm/cm^2) could not be solely attributed to atmosphere fallout of only about 4 dpm/cm^2 within the upper 40-cm sediment if we adopted Fuller's (1982) estimate of 0.15 dpm/cm^2 fallout rate. Input of ^{210}Pb from river runoff was deemed insignificant in this area due to low flow volumes. Sediment focusing, a process in which abnormally high sedimentation occurs at the expense of erosion in adjacent sediments, should not be a key factor in north SDB due to strong tidal currents. Rather, strong tidal exchange, as radioisotope patterns shown in figures 4-6, may well be responsible for the large excess ^{210}Pb activities in the North Bay sediments through ^{210}Pb stripping, a process observed by Carpenter *et al.* (1981) in Washington coast. ^{210}Pb stripping is a process in which dissolved ^{210}Pb continuously brought into SDB through tidal exchange is scavenged by particles in the bay water and thus is preferentially retained in the north SDB, as shown in figure 7.

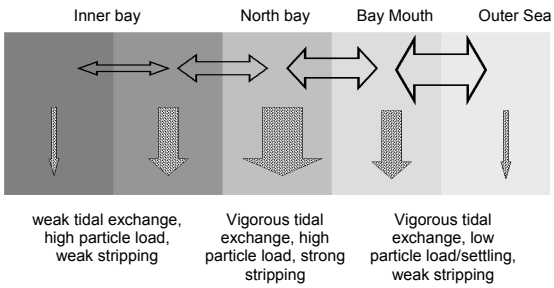

Figure 7 A simple model depicting relationship among tidal exchange, particle settling and ^{210}Pb stripping.

Two processes are involved in the above scenario: 1. Tidal exchange of water across the bay mouth, with a decreasing strength towards the inner SDB. 2. Particle settling and scavenging of radioisotopes, which is proportional to the particle abundance and the availability of dissolved radioisotopes in the water column. These two closely related

processes produce a strongest stripping effect in the north SDB, where these two factors add up. Elsewhere, the stripping is not as strong due to low concentration of dissolved radioisotopes (inner SDB) or low particle abundance (outer sea). Stripping may have a similar effect on ^{234}Th activities in the sediment column (see figure 3). This is not as pronounced as that of ^{210}Pb due perhaps to the short half live of ^{234}Th, but it serves as additional evidence that stripping of particle-reactive radioisotopes takes place at SDB.

4.3 Implications of tidal exchange and Particle Scavenging to the Transport and Fate of Particle-Reactive Contaminants

In a parallel study (Zeng et al, 2002), we measured the PCB concentrations in water and sediment columns across SDB. PCB concentrations in sediment were below detection limit, and those in water column supported the notion that PCB concentration is declining over the past few decades (Chadwick *et al.* 1999; Fairey *et al.* 1996; McCain *et al.* 1992). We found higher PCB levels near bottom sediment at stations 2 and 3 for the summer 1999 sampling (Zeng et al, 2002), probably related to the stripping process discussed above.

Strong tidal exchange between the outer sea and SDB could have transported PCBs (in both the particulate and dissolved phases out of the Bay. The decreasing trend of water column PCB concentrations toward the bay mouth might suggest dilution effects due to a stronger tidal exchange in that area than inside the Bay. We have estimated that about 1 kg of PCBs could be transported out of SDB annually (*Zeng et al, 2002*). Based on Fairey's data on the total PCB concentrations in the sediment of SDB (1996), it was calculated that about 200kg of total PCBs exist in the top 10cm of sediment for the entire SDB. Therefore about 0.5% of total PCBs in the upper 10cm sediment are transported outside SDB by tidal exchange each year. But if we only consider top 5cm (i.e. mixing depth, as indicated by sediment ^{234}Th profile discussed above) sediments, which should have a considerably smaller PCB inventory due to a sharp decrease of PCB input in recent years (McCain *et al.* 1992; Schroeder, 1994), as high as 2-5% of PCBs in the surface sediment can be transported outside SDB annually, making it a significant process that produces a steady decrease of total PCB inventory in SDB.

Tidal exchange provides vigorous ventilation and beneficiary cleansing for SDB water and sediment. But there are some complications. There is a major municipal sewage outfall immediately offshore Point Loma (Point Loma Ocean Outfall, PLOO, see figure 1) that pumps annually an average of 175 million gallons treated sewage containing 15,000 tons of total suspended solid (TSS) and 24 tons of heavy metals(Cd, Cr, Cu, Pb, Hg, Ni, Ag and Zn) (CRWQCB and USEPA, 2002). Due to proximity of PLOO to the mouth of SDB and southward movement of California Current, these contaminants from the outfall may approach the bay mouth and participate in the tidal exchange with SDB water. If the contaminants are particle-reactive, as many are, tidal exchange with SDB water may result in their retention at north SDB, as in the case of ^{210}Pb and ^{234}Th stripping in this study. Hence further studies are needed to determine the adverse effect of tidal stripping in the north SDB. Stripping may also have significance on other estuaries or coastal waters that are affected by tides.

5. SUMMARY

We used the spatial and temporal distributions of ^{210}Pb, ^{210}Po and ^{234}Th in the water column across and outside SDB to disclose the significance of tidal exchange on the distribution and transport of these particle-reactive radionuclides, and discussed the implications of tidal exchange process to particle-reactive contaminants. The following conclusions are drawn: (1). Tidal exchange is an important process in SDB, especially for the north SDB, where concentration of ^{210}Po and ^{234}Th show spatial and temporal variation due to tidal exchange in conjunction with particle scavenging; (2). Natural sedimentation in SDB shows heavy signs (e.g. heterogeneity) of perturbation by anthropogenic (e.g. dredging) activities; (3). Tidal exchange in the water column results in stripping of ^{210}Pb and ^{234}Th, and presumably other particle-reactive elements, which produces abnormally high sediment inventory of these species; (4). Tidal exchange generally serves to dilute the contaminants in SDB, but the stripping process has the potential of bringing particle-reactive contaminants into SDB if the source is outside of SDB; (4). The use of naturally occurring radioisotopes such as ^{210}Pb and ^{234}Th as proxies for particle-reactive contaminants in coastal environment warrants further studies.

6. LITERATURE CITED

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California Regional Water Quality Control Board San Diego Region (CRWQCB) and U.S. Environmental Protection