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Lead Isotope exchange between dissolved and fluvial particulate matter: a laboratory study from the Johor River estuary

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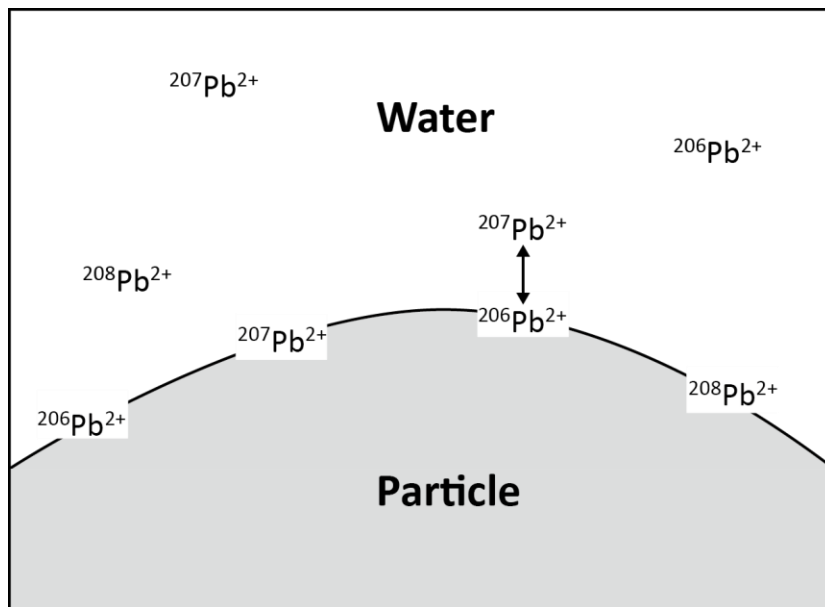
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Abstract

Atmospheric aerosols are the dominant source of Pb to the marine environment, and as a result, in most regions of the ocean the Pb isotopic composition of dissolved Pb in the surface ocean (and in corals) matches that of the regional aerosols. In the Singapore Straits, however, there is a large offset between seawater dissolved and coral Pb isotopes and that of the regional aerosols. We hypothesize that this is a result of isotope exchange between dissolved Pb from anthropogenic aerosol deposition and adsorbed particulate natural crustal Pb on particles delivered to the ocean by coastal rivers. To investigate this issue, Pb isotope exchange was assessed through a closed-system exchange experiment using estuarine waters collected at the Johor River mouth (which discharges to the Singapore Straits). During the experiment, a known amount of dissolved Pb with the isotopic composition of NBS-981 ($^{206}\text{Pb}/^{207}\text{Pb}=1.093$) was spiked into the unfiltered Johor water (dissolved and particulate $^{206}\text{Pb}/^{207}\text{Pb} = 1.199$) and the changing isotopic composition of the dissolved Pb was monitored. The mixing ratio of the estuarine and spike Pb should have produced a dissolved $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic composition of 1.161, but the first dissolved Pb sample collected shortly after the spike addition had $^{206}\text{Pb}/^{207}\text{Pb}=1.178$, reflecting the influence of the spike plus some exchange with the particulate reservoir. Within a week, the $^{206}\text{Pb}/^{207}\text{Pb}$ in the water increased to 1.190 and continued to increase to 1.197 during the next two months without significant changes of the dissolved Pb concentration. These observations in a closed-system laboratory experiment can account for the isotopic difference between Singapore aerosols and seawater/corals in our field observations. The kinetics of isotope exchange was assessed using a simple K_d model, which assumes multiple sub-reservoirs within the particulate matter with different exchange rate constants. The K_d model reproduced 56% of the observed Pb isotope variance. Both the closed-system experiment and field measurements imply that isotope exchange can be an important mechanism for controlling Pb and Pb isotopes in coastal waters. We hypothesize that a similar process may occur for other trace elements. Further investigations on the distribution of Pb and Pb isotope in estuaries and coastal waters should further assess the role of isotope exchange in ocean Pb chemistry.

Graphical abstract



Keywords: isotope exchange, Pb, Pb isotopes, estuaries, particles, Singapore

1 Introduction

Fluvial transport has long been noted as an important source for metals into the ocean [e.g. 1-2, and references therein]. The transport of metals involves direct injection of dissolved metals and transport of particulate matter that may release or exchange elements when it contacts seawater [3-6]. Through their interaction with seawater, crustally-derived particulates can affect the concentration of some elements in estuarine waters [e.g.: Ba, Cd, 6-10]; or can affect the isotopic composition of some elements without much change in concentration [11]. Such isotope exchange has been noted for Sr and Nd in both closed system experiments [12,13] and in field observations [14-16]. There is no information on whether such isotope exchange influences Pb isotope data in coastal and estuarine waters.

Pb is widely used in tracing anthropogenic emissions into the earth surface environment, as its isotopic composition can distinguish sources from different reservoirs [17]. Understanding the processes that affect Pb isotopes in different environments is of critical importance in interpreting Pb data in a dynamic environment. In the modern open ocean, aeolian input is the major source of Pb [18]. And absent an abundant supply of crustal particulates, Pb isotopes found in surface oceans are generally the same as the aerosols depositing in the sea surface [e.g.: 10,19,20]. In estuarine and coastal environments, the fluvial contribution of elemental Pb into the ocean and the potential exchanges in Pb isotopes by crustal particulates has not been clearly assessed because of the dynamic nature of estuarine environments and the overwhelming supply anthropogenic Pb into the modern environment.

As an alternative strategy, the fluvial and estuarine behavior of Pb has been investigated extensively using radiogenic ^{210}Pb . It has been found that the majority ($\geq 79\%$) of ^{210}Pb in an estuary was associated with particulate matter [e.g.: 21-25], although some exceptions have been found in rivers with high concentrations of dissolved organic matter [e.g.: 26]. These studies concluded that ^{210}Pb is scavenged within the estuaries, and by analogy it was suggested that stable Pb should be scavenged as well. However, there are significant differences between the pathways by which natural Pb and ^{210}Pb move through the environment. Much of the elemental Pb is originally contained within mineral crystals, but dissolving these unstable phases during weathering releases elemental Pb which largely adsorbs onto mineral surfaces [e.g. 27]. In contrast ^{210}Pb is produced within the ^{238}U decay series by its precursor the inert gas ^{222}Rn . Therefore there may be some differences between the elemental Pb budget compared to the ^{210}Pb budget, although this subject has never been explored in the field.

Despite very few observations of stable Pb isotope ratios in estuarine and coastal water, a few studies did imply that isotope exchange may influence Pb in coastal and estuarine regions. One example comes from coral Pb studies in the Singapore Strait. Three corals were investigated on an east-west transect of the straits, and the Pb isotopes in these corals all shown $^{206}\text{Pb}/^{207}\text{Pb} \Rightarrow 1.190$ [28,29] distinct from regional aerosols ($^{206}\text{Pb}/^{207}\text{Pb}$

$\approx 1.097\text{--}1.167$ in Southeast Asia [30]). No high $^{206}\text{Pb}/^{207}\text{Pb}$ sources in the region have been found except regional natural soil. Hence isotope exchange between seawater and natural crustal particulates is a possible explanation for why $^{206}\text{Pb}/^{207}\text{Pb}$ was higher in marine systems compared to the aerosols.

Another example is a coral Pb study [30] in the northern Persian/Arabian Gulf (Kuwait Bay). In this study, a box model was employed to quantify the relative contribution of atmospheric (mostly anthropogenic) and fluvial (mostly natural) Pb to the Kuwait Bay. In the model, if the budget was calculated from Pb concentration in the coral, anthropogenic Pb should dominate Pb in the Kuwait Bay. However, if the budget was calculated based on observed Pb isotope ratios referred from the coral, anthropogenic Pb should only contribute $\sim 50\%$ of the Pb in the Kuwait Bay. The misfit between concentration and isotope budget in the model implied that the Pb isotopes in the water might have been altered by isotope exchanged with the natural crustal particulates transported from the Euphrates and Tigris rivers.

A third example is the Japanese GEOTRACES data on dissolved Pb and Pb isotopes in Indian Ocean seawater (KH09-5, November to December 2010; [32]). 13 stations were covered including the Arabian Sea and Bay of Bengal. The $^{206}\text{Pb}/^{207}\text{Pb}$ in one profile obtained from the Bay of Bengal was 0.005–0.010 higher than in a profile obtained from the Arabian Sea, despite a concentration profile depth distribution that was almost identical. The isotopic offset could not be fully explained by different anthropogenic sources as the offset was observable throughout the water column whereas the anthropogenic dissolved Pb contamination in the northern Indian Ocean was still confined to the upper ocean. From these observations, Lee proposed that isotope exchange in the Arabian Sea and Bay of Bengal might have also contributed the isotopic offset between the two profiles.

These examples imply that isotope exchange might be an important mechanism modulating Pb isotopes in the ocean. To this end, the objective of this study is to experimentally illustrate the isotope exchange of Pb between the dissolved phase and coastal particulate matter, and investigate the kinetics of exchange using a simple K_d -type model.

2 Sampling and methodology

2.1 Closed system isotope exchange experiment

A closed-system isotope exchange experiment was carried out using estuarine water from the Johor River mouth (Figure 1). The Johor River is located at the southern end of

the Malaysian Peninsula and discharges a large quantity of freshwater from the Malaysian Peninsula to the Singapore Strait [33,34]. The mean annual discharge for Johor River is $\sim 1200 \text{ km}^3/\text{year}$ [35]. At the same time, a large quantity of crustal particulates is delivered to the Singapore Strait due to the mountainous terrain, intense chemical weathering, and heavy rainfall in the region [36]. The upstream of the Johor River basin is mainly forest while the downstream is agricultural land (oil palm and rubber, [37]). On November 22, 2013, 8 liter water samples were collected from the estuarine waters near Johor River mouth ($1^\circ 25' 22'' \text{N}$ $104^\circ 00' 05'' \text{E}$, Figure 1). The samples were collected by lowering a plastic coated pole sampler near the front of the boat while the boat was slowly moving forward. A trace-metal-clean bottle was attached in the front of the pole to collect the water sample. The samples were transferred to the laboratory in a dark cooler box after collection.

In the lab, 250mL of unfiltered water and 250mL of $0.4\mu\text{m}$ filtered water were sub-sampled to provide the initial dissolved Pb and Pb isotope ratios in the water before the isotope exchange experiment. A subsample of the unfiltered was acidified to $\text{pH} \sim 2$ to determine “total dissolvable” Pb and Pb isotope ratios (95% of which was derived from the particulate fraction). The remaining samples were divided into 2 groups (A and B): For group A, $\sim 3.5\text{L}$ unfiltered sample were put into a 4L trace metal clean narrow mouth bottle (Bottle A). For group B, $\sim 3.5\text{L}$ of sample was filtered through $0.4\mu\text{m}$ Nuclepore® filters, and kept in another identical narrow mouth bottle (Bottle B) to serve as an adsorption. The Pb concentration of the filtered sample at the beginning of the experiment was 18.3 pmol/kg . At time $t=0$, both bottles were spiked with 1.75mL of $\text{pH} \sim 2$ 21 nmol/kg NBS-981 ($^{206}\text{Pb}/^{207}\text{Pb}=1.093$, [38]). The amount of spike added should result in 10.5 pmol/kg concentration increase in the sample (to 28.8 pmol/kg) if no net adsorption occurs. The bottle was vigorously shaken during spike addition to minimize the possible effects of the acidic spike on the water chemistry. After spike addition, a 250mL sample was separated and filtered from each 4L bottle at different time points up to 60 days. A schematic illustration about the isotope exchange experiment is shown in Figure 2.

2.2 Aerosol sampling

Aerosol samples were collected on the roof of building S16 of National University of Singapore (NUS) from July 2011 through September 2012. From November 2012 to April 2013, the sampling station was moved to NUS CREATE Tower building but the two buildings were within 1 km distance. The samples were collected by pumping air through a pre-cleaned $0.45\mu\text{m}$ PTFE filter using a diaphragm pump (similar to that employed by Bollhöfer et al., 1999). Most aerosol samples were collected over about 1-2 weeks (at the beginning or August 2011, the sampling duration was set to 1 weeks, then changed to 2

weeks between August 2011-January 2012, and switched back to 1 week afterwards) with two samples had longer collection periods (3-4 weeks) due to sampling logistics.

2.3 Seawater sampling

Seawater samples were collected seasonally in both Hantu and Kusu from September 2011 through November 2013. The samples were filtered (0.4 μ m) and acidified to pH~2 with ultrapure 6N HCl. The time between sample collection and filtration varies from within 1 day to 6 months due to personnel limitations. Given the variable time between sample collection and filtration, only Pb isotopes are reported as Pb concentrations could have been affected by adsorption to the bottle walls. The filtered samples were stored acidified for at least 2 months before analysis to ensure the release of Pb adsorbed onto the surface of the container.

2.4 Methods for analyzing Pb and Pb isotopes

The filtered samples were analyzed for both Pb concentration and Pb isotope ratios. The Pb concentrations were measured using isotope dilution after single batch nitrilotriacetate (NTA) resin extraction [32]. In brief, 1.3mL of seawater samples were spiked with a known amount of ²⁰⁴Pb enriched spike (Oak Ridge National Laboratories) and then adjusted to pH=5.3 by adding an ammonium acetate buffer. ~2400 NTA superflow resin beads were added to each sample. After 4 days on a shaker table to allow the resin beads to bind Pb, the sample and resins were rinsed several times with ultrapure water and then eluted using 0.1M high purity nitric acid. The eluted samples were then analyzed on a Quadrupole ICP-MS (VG PlasmaQuad 2+). All samples were run in triplicate and accepted only if at least two out of three replicates agreed.

Pb isotope ratios in the seawater were measured using an IsoProbe multi-collector ICP-MS after Mg(OH)₂ co-precipitation and HCl-HBr ion exchange chromatography as described in [40,41]. The seawater sample was spiked with a minimum dose of ammonia solution to induce Mg(OH)₂ precipitation that scavenges the Pb from the seawater. The precipitates were redissolved by a minimum amount of high purity HCl and the Mg(OH)₂ precipitation method was repeated for a second time to further concentrate the Pb. The final precipitates were redissolved in 200 μ L of ultrapure 1.1M HBr and loaded onto an Eichrom AG-1X8 (chloride form, 200 – 400 mesh) anion exchange resin column, and then eluted with 1M and 6M HCl to separate the Pb from the sample matrices. After ion exchange, the samples were dried in a class 100 clean environment and redissolved in ultrapure 0.2M HNO₃ for GV IsoProbe multicollector sector ICP-MS analysis. Standardization and corrections were handled as discussed in Boyle et al [2012]. Although the expected precision and accuracy of the measurement depends on the

concentration of the sample (limited by Johnson resistor noise), this $^{206}\text{Pb}/^{207}\text{Pb}$ data should be good to at least ± 0.001 (2σ).

Pb isotope ratios in aerosols were measured using the MC-ICP-MS in the same way as seawater samples after leaching the filter in 6M high purity HCl, drying down, loading with 1.1N HBr, and passing the leachates through the anion exchange columns.

3 Results

The Pb isotope ratios in aerosols and seawater samples are shown in Figure 3. $^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore seawater was consistently ~ 1.195 with no evident seasonal cycle. Additionally, no spatial difference for Pb isotopes was observed. The $^{206}\text{Pb}/^{207}\text{Pb}$ in Singapore aerosols was ~ 1.147 , with $^{206}\text{Pb}/^{207}\text{Pb}$ in the northeast monsoon season (November to March) being slightly higher (~ 0.005) than in southwest monsoon season (April to September). However, the Pb isotopes in Singapore aerosols are clearly distinct from Singapore Strait' seawater at all times.

The change in Pb concentration during the isotope exchange experiment is shown in Figure 4. The Pb concentration in the collected water was 18.3 pmol/kg (before any manipulation); the unfiltered "total dissolvable" Pb concentration was 371 pmol/kg, indicating a large reservoir of particulate Pb (353 pmol/kg). After spike addition, the Pb concentration in unfiltered Bottle A increased to 25.4 pmol/kg; and then fluctuated between ~ 20 -30 pmol/kg within next 2 days. Afterwards, the Pb concentration increased from ~ 21 pmol/kg to ~ 35 pmol/kg within 7 days and remained there at the end of 2 months. The detailed concentration variability can be found in Table 1.

The Pb concentration in the filtered Bottle B was fairly stable at ~ 46.3 pmol/kg within 7 days and gradually decreased to ~ 36.4 pmol/kg during 2 months. We did not expect to see the Pb concentration increased by 28 pmol/kg (from 18.3 pmol/kg to 46.3 pmol/kg) from added spike, that should only have caused a 10.5 pmol/kg increase in the Pb concentration. We suspect that the higher Pb concentration in Bottle B was introduced during the large-volume filtration process involved in filling up Bottle B (this filtration took up to 3 hours and some Pb from the particles might have been released into the water during the filtration process. The high Pb concentration could also have been caused by contamination during the filtration process. However, neither cause of the high Pb concentration affects the interpretation of Pb variability during the 2 months. It was encouraging to see the Pb concentration in Bottle B decrease by only $\sim 20\%$ from 2 days to 2 months suggesting that the effect of bottle wall uptake should be minimal in the particle-buffered unfiltered experiment.

The isotopic variability during the isotope exchange experiment is illustrated in Table 1. During the 2 months of the experiment, the $^{206}\text{Pb}/^{207}\text{Pb}$ of the filtered and spiked bottle “B” was 1.168 ± 0.002 (2σ), indicating no isotope exchange happened in this bottle. On the other hand, the Pb isotopic variability in the unfiltered “A” during isotope exchange experiment is shown in Figure 5. Before the spike addition, the $^{206}\text{Pb}/^{207}\text{Pb}$ in both filtered and acidified unfiltered samples was 1.199, showing that the dissolved and acid-soluble particulate have the same isotopic composition. Assuming that the filtered (dissolved) concentration of this water was 18.3 pmol/kg, the spike addition (1.75 mL of 21 nmol/kg) should have lowered the dissolved $^{206}\text{Pb}/^{207}\text{Pb}$ in the bottle to 1.161 (calculated $T = 0$). Filtering a subsample soon after the spike addition (within 5 minutes), the $^{206}\text{Pb}/^{207}\text{Pb}$ in Bottle A was 1.178 and further increased to 1.189 by 3 hours. From 3 hours to 1 day, the $^{206}\text{Pb}/^{207}\text{Pb}$ in Bottle A decreased from 1.189 to 1.181. After that brief drop, $^{206}\text{Pb}/^{207}\text{Pb}$ increased steadily from 1.181 to 1.197 at 2 months (Figure 5).

4 Discussion

4.1 Pb isotopes in Singapore seawater and aerosols

Pb isotope ratios in Singapore seawaters were generally stable during our 2-year sampling period, with $^{206}\text{Pb}/^{207}\text{Pb} = 1.195 \pm 0.004$ (2σ) and $^{208}\text{Pb}/^{207}\text{Pb} = 2.479 \pm 0.006$ (2σ). The steady Pb isotope ratios in Singapore seawater indicates that the Straits’ Pb was dominated by a consistent Pb reservoir with high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio. This consistency is at odds with the oceanographic setting of the Singapore Strait. The Singapore Strait is dominated by seasonal monsoon-driven currents [42]. It is flushed mainly by South China Sea water during the Northeast Monsoon (November to March) and mainly by the Malacca Straits and Java Sea water during Southwest Monsoon (April to September) [43]. There is almost no Pb isotope data in either of these regions, but neither South China Sea water (one surface sample collected near Taiwan in 2000 had $^{206}\text{Pb}/^{207}\text{Pb} = 1.156 \pm 0.015$, 2σ , $^{208}\text{Pb}/^{207}\text{Pb} = 2.444 \pm 0.017$, 2σ , [29]) nor Indian Ocean water (eight samples of Central Indian Ocean surface water had $^{206}\text{Pb}/^{207}\text{Pb} = 1.144 \pm 0.006$, 2σ , $^{208}\text{Pb}/^{207}\text{Pb} = 2.426 \pm 0.009$, 2σ [44]) can account for the isotope ratios of Pb in Singapore seawater.

The high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Singapore seawater is clearly distinct from Pb isotope ratios of Singapore aerosols. Singapore aerosol $^{206}\text{Pb}/^{207}\text{Pb}$ averaged 1.150 in northeast monsoon season and 1.145 in southwest monsoon season (Figure 3). Atmospheric deposition appears to be the main source of Pb to the Singapore region as suggested by the sedimentary record from the central catchment reserve [45]. However, none of the $^{206}\text{Pb}/^{207}\text{Pb}$ in aerosols comes close the 1.195 ± 0.004 (2σ) observed in Singapore Strait seawater. Instead of reflecting the aerosol Pb isotope value, the high $^{206}\text{Pb}/^{207}\text{Pb}$ in

Singapore water is similar to the 100-year old natural soil we observe in this region [45]. In this case, the isotope differences between Singapore seawater and aerosols, together with the near-constancy of Pb isotopes in Straits seawater all suggest that the Pb isotope ratios in Singapore seawater have been converted from their primary aerosol values into more 'crustal-like' values by exchanging with crustal particulates.

4.2 Mechanisms inferred from the closed-system isotope exchange experiment

Total dissolvable Pb in the Johor River mouth sample was 371 pmol/kg, but only 18.3 pmol/kg was dissolved at the natural pH. These data indicate that less than 5% of Pb was in the dissolved form. The fraction of dissolved Pb is similar to that observed for ^{210}Pb in many estuaries [e.g.: 21-25]. Soon after spike addition, the Pb concentration in unfiltered Bottle A increased to 25.4 ± 1.4 pmol/kg, which was nearly that expected for the amount of Pb added. Within the first 3 hours, the Pb concentration increased from 25.4 pmol/kg to 32.7 pmol/kg, and then decreased steadily to 20.9 pmol/kg from 3 hours to 2 days. It is difficult to be confident that the high Pb concentration at $T = 3$ hr was a real signal as it was only a single sample that must be considered in view of Pb's contamination-prone character. The decreased Pb concentration from 3 hours to 2 days was more prominent as the decreasing trend was visible at $T = 5$ hr, 24 hr and 47.5 hr. The decrease in Pb concentration implied that Pb was scavenged from the water from 3 hours to 2 days. In the following 2 days to 2 months, the Pb concentration increased to 33.9 pmol/kg at $T = 7$ days and remained at ~ 33 pmol/kg. The increase in Pb concentration from 2 days to 2 months suggested that processes other than scavenging removal can release Pb from particulate matter into the water. The release of Pb from particles has been suggested in some estuaries [e.g.: 46]. The dissolution and scavenging of Pb might function at different rates that result in the observed fluctuations of Pb concentration in Bottle A. We cannot specify which processes account for these Pb removal/addition observations, but some possibilities are ion exchange with particle surfaces (+ or -), biological uptake (-), biological decomposition (+), scavenging onto mineral or biological surfaces (-), mineral dissolution (+), mineral precipitation (-). The time dependence of these processes may differ substantially, i.e., some may occur quickly and others slowly.

Pb isotope ratios in the unfiltered Bottle A show large changes during the experiment. Soon after spike addition, the $^{206}\text{Pb}/^{207}\text{Pb}$ decreased from 1.199 to 1.178, reflecting the effect of the low $^{206}\text{Pb}/^{207}\text{Pb}$ from the NBS-981 spike (1.093). It should be noted that by simply adding 1.75mL of 21nmol/kg NBS-981 into the 18.3 pmol/kg of sample, the resulting $^{206}\text{Pb}/^{207}\text{Pb}$ should be 1.161 (calculated from mass balance assuming simple mixing of dissolved Pb), which is lower than the observed first sample $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.178). The higher observed $^{206}\text{Pb}/^{207}\text{Pb}$ from simple mixing indicates that some isotope

exchange happened within minutes so the $^{206}\text{Pb}/^{207}\text{Pb}$ in the bottle has already been altered to higher value within a few minutes (our filtration would generally take ~5 minutes). The $^{206}\text{Pb}/^{207}\text{Pb}$ increased to 1.190 within 7 days while the Pb concentration only increased by 9.8 pmol/kg. If the increase in $^{206}\text{Pb}/^{207}\text{Pb}$ was purely due to release from particulate Pb ($^{206}\text{Pb}/^{207}\text{Pb} = 1.199$), the resulting $^{206}\text{Pb}/^{207}\text{Pb}$ at $T = 7$ days should be 1.184 by mass balance, which was again lower than the observed 1.190. The disproportional increase in $^{206}\text{Pb}/^{207}\text{Pb}$ also indicates that the particulates exchanged Pb isotopes and altered the $^{206}\text{Pb}/^{207}\text{Pb}$ to higher values. From 7 days to 2 months, the $^{206}\text{Pb}/^{207}\text{Pb}$ further increased to 1.197 without obvious change in Pb concentration, that further supports an isotope exchange mechanism. It is difficult to explain the $^{206}\text{Pb}/^{207}\text{Pb}$ data for $T = 3$ hr and $T = 1$ day (Figure 5) given the coarse temporal resolution we have in this study. However, despite these uncertainties our closed-system experiment clearly demonstrates a rapid Pb isotope exchange process (within 1 week for the majority of isotope change, Figure 5).

4.3 A model for Pb isotope exchange

It has been previously suggested that isotope exchange without net element transfer occurs for Sr and Nd isotopes. The mechanism for this isotope exchange was proposed as contemporaneous dissolution and precipitation into secondary minerals [4,12-14]. That suggested mechanism for Sr isotopes might not be plausible for Pb as the concentration for Pb in seawater was generally in pico-molar region [e.g.: 47], in which the formation of secondary minerals by precipitation is not likely.

We suggest that the Pb isotope exchange happens between multiple distinct exchangeable sub-reservoirs. We make this assumption following the modifying premises proposed by [48,49]: “the radioisotopes and their natural stable counterparts may not be exchanged rapidly especially with those not in the surface sorption sites. Sorption of certain cations may not follow the reaction, but may involve oxidation and precipitation, ion exchange inside crystal lattices through diffusion, and adsorption of radiotracers on colloids <followed by> coagulation of colloids on larger particles etc.” Hence we assume that there are multiple Pb reservoirs with different exchange rate time constants. As discussed in section 4.2, there must be at least one rapid exchange reservoir operating within a few minutes and one slow exchange reservoir that operates over days to months.

In modeling this process, we assume that Pb on the surface of suspended particulate matter approaches distribution coefficient (K_d) equilibrium with dissolved Pb with a time constant that is characteristic of sub-reservoirs within the particulate matter:

$$K_d = \frac{\text{particulate Pb per gram of suspended particulate matter}}{\text{dissolved Pb per gram of water}} \quad (1)$$

We estimate $K_d = 2 \times 10^6$ from the total (acid) dissolvable Pb in the water sample compared to the 0.4 μm filtered dissolved Pb at the initiation of the experiment with the assumption that the total particulate concentration is 10 mg/kg (average particulate concentration measured in the Singapore Straits, [50]). It is possible that not all of the acid soluble Pb participates in exchange equilibrium at the higher natural pH, but the total exchangeable Pb must be close to this number in order to be consistent with the high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio at the end of the exchange experiment.

In the model, we assume Pb ions move in and out from each reservoir to dissolved pool at the same rate for all of its isotopes. We treat each Pb isotope separately assuming the same K_d for each, and then calculate the isotope ratios (note – it is known that small stable isotope ratio fractionations can occur during ion exchange – e.g. [51] – but these fractionations are generally a few permil compared to the 110% radiogenic Pb isotope signature differences in nature and in this experiment). Taking ^{206}Pb as an example, the instantaneous concentration of ^{206}Pb in the reservoir R_i at time point t can be calculated from equation 2:

$$[^{206}\text{Pb}]_{R_i,t} = [^{206}\text{Pb}]_{R_i,t-1} + \frac{\Delta t}{T_i} \times \{ [^{206}\text{Pb}]_{R_i,\text{equilibrium}} - [^{206}\text{Pb}]_{R_i,t-1} \} \quad (2)$$

where T_i is the time constant for reservoir i ; and Δt is the time step. The equilibrium concentration for reservoir i can be calculated from the instantaneous concentration in the dissolved seawater as equation 3:

$$[^{206}\text{Pb}]_{R_i,\text{equilibrium}} = K_d \times [^{206}\text{Pb}]_{\text{sw},t-1} \times PM \times \frac{[^{206}\text{Pb}]_{R_i,t_0}}{\sum_{i=1}^t [^{206}\text{Pb}]_{R_i,t_0}} \quad (3)$$

where the PM is the concentration of particulate matter (assumed 10 mg/kg). The same equation can be applied for the other isotopes, and then the isotope ratios can be calculated by taking ratios of the concentrations of each Pb isotope in each reservoir.

The model was initiated based on the initial 18.3 pmol/kg concentration ($[Pb]_{\text{sw},t_0} = 18.3 \text{ pmol/kg}$) and measured isotopic composition before spike. And then the dissolved concentration is augmented by an 10.5 pmol/kg NBS-981 addition. This increases the concentrations of all the dissolved Pb isotopes, which then approach K_d equilibrium given assumed reservoir sizes and kinetic time constants. The size of each reservoir and its kinetic time constant was established by trial and error; but at least two reservoirs and time constants are necessary to explain our results. The model proceeds by time steps with rate constant-based transfer of Pb to the particulate phases (which is determined by the difference between the equilibrium adsorbed Pb for each isotope based on the

dissolved concentration from the previous time step, equation 2 and 3) and the calculated adsorbed Pb from the previous time step.

We began with a single reservoir that accounts for the long-term time evolution of the isotope ratios in the experiment, adjusting the time constant (69 days) to fit the later stages of the experiment (23 days to 2 months). Then we added a second reservoir that exchanges more rapidly (1.7 days), and used trial and error variations of the time constant and reservoir size to fit the intermediate stages of the experiment. Finally, we added a third reservoir with very rapid exchange constant (5 hours) and approximated the earlier portion of the experiment. With the 3 exchangeable reservoirs, our simple model could reproduce the fast increase in $^{206}\text{Pb}/^{207}\text{Pb}$ as we observed in the close-system experiment with $R^2 = 0.56$ (excluding the $T=3$ & $T=24$ hr ratios, R^2 rises to 0.89).

4.4 Comparison between the batch experiment and field measurements in the Singapore Strait water

The change in $^{206}\text{Pb}/^{207}\text{Pb}$ during the experiment provides a direct evidence for isotope exchange between dissolved and particulate Pb and can explain the field observations for Singapore Straits seawater. Investigations in Singapore seawater indicated the $^{206}\text{Pb}/^{207}\text{Pb}$ in the seawater was >1.190 (Figure 3), different from either regional aerosols ($^{206}\text{Pb}/^{207}\text{Pb} = \sim 1.140$) or the open-ocean seawater feeding the Singapore Strait ($^{206}\text{Pb}/^{207}\text{Pb} = 1.144\text{--}1.156$ [29,51]). In the isotope exchange experiment, $^{206}\text{Pb}/^{207}\text{Pb}$ increased from 1.178 to >1.190 . The magnitude of the increase in $^{206}\text{Pb}/^{207}\text{Pb}$ during the experiment was comparable to the difference between Singapore seawater and aerosols.

Besides the magnitude of increase, the timescale of the isotope exchange in the close-system experiment also supports the consistent isotopic departure between Singapore seawater and aerosols. In the experiment, the major change in Pb isotopes occurred within a week. If the timescale of isotope exchange is much shorter than the residence time of Pb in Singapore water, the isotope exchange could maintain a consistent isotopic difference between Singapore seawater and aerosol (Figure 3), which agrees well with what has been observed in Singapore. The residence time of Pb in the Singapore Straits has not been directly investigated but the temporal variation of Pb/Ca in Singapore corals seem to correlate with the local rainfall with a lag of 2-3 years [28]. The 2 to 3-year-lag agrees with the ^{210}Pb -derived residence time in the surface oceans feeding water to the Singapore Strait (1.8 year in South China Sea [53], 4 years in eastern Indian Ocean, [54]) and could be taken as a preliminary estimate of the residence time of Pb in Singapore water. In this case, the timescale of isotope exchange (hours to days) should be significantly shorter than the residence time of Pb in Singapore water and the isotope

exchange could maintain the observed isotopic difference between anthropogenically-sourced Pb and Singapore Straits seawater.

4.5 The potential role of Pb isotope exchange in ocean chemistry

Crustal particulates transported by rivers have been proposed as an important factor regulating the chemistry of marine trace elements [4]. The global suspended riverine flux has been estimated as 15-20 Gt/year [55,56]; among which, rivers in South Asia and maritime continent transport disproportionately high amount of particulates to the Pacific and Indian Ocean (~2/3 of the global suspended particle flux, [36]). These fluvial particulates provide abundant materials for isotope exchange happening in these regions, changing the Pb isotope in the water to more 'crustal-like' ratios. The influence of isotope exchange on the geochemistry of Pb, and the extent of this influence is still poorly understood because of sparse seawater Pb isotope data in estuaries, coastal areas and near continental margins. Despite this paucity of observational data, the batch isotope exchange experiment imply that isotope exchange can significantly influence the isotopic composition of Pb in coastal environments, and illuminate the fate of particulate material upon its arrival to oceans. Further experimental investigations, including sterilized systems that cannot have biological uptake or decay, targeted exchange experiments using waters from other rivers (especially in regions where the geological Pb source is extreme); some simple single well-characterized phase experiments to illuminate the exchange process in a simple system, and better evidence on the spatial distributions of Pb isotope in estuaries and coastal environments could provide important insights for the processes affecting Pb in the ocean.

This evidence has implications for the natural oceanic Pb cycle as well as the anthropogenic impact. Before extensive Pb contamination of the atmosphere, Pb would have weathered from unstable natural crustal materials and then adsorb back onto the residual stable weathered phases. When rivers carried this particulate matter into the ocean, particles that had experienced a relatively high-Pb (suspended particulate) environment would have encountered very low-Pb ocean waters (resulting from efficient internal ocean scavenging) and released some of the adsorbed Pb into the ocean in a dissolved form, that would then mix out into the open ocean. This fluvial source (supplemented by the same process occurring on wind-blown dust deposited into the ocean) would have been the source of lead to the ancient ocean as represented ferromanganese nodule records [e.g. 57].

5 Implications for the use of ^{210}Pb as a proxy for elemental Pb (and similar implications for other radioisotope systems)

We have shown that Pb with a different isotope composition added to the coastal marine environment takes on the natural crustal ratio of the regional continental crust, equilibrating the isotope ratios in the dissolved and particulate phases. It is clear that the same process would also occur for the uranium series radioisotope ^{210}Pb , i.e. the $^{210}\text{Pb}/\text{Pb}$ ratio of the crustal particles and the impinging open ocean waters should be equilibrated. But crustal materials should have a very low $^{210}\text{Pb}/\text{Pb}$ ratio. Taylor and McLennan [58] estimate that the average continental crust has 2.8 ppm U and 20 ppm Pb; left undisturbed until radiochemical equilibrium was attained, that would result in a $^{210}\text{Pb}/\text{Pb}$ ratio of 3.6×10^{-6} Bq/mol of Pb. The actual ratio will be lower for materials involved in the active weathering process because a lot of the ^{222}Rn produced in the ^{238}U series will be lost to the atmosphere, and a significant fraction of the daughter ^{210}Pb is deposited in the ocean [e.g. 59]. Observations near Bermuda during the 1980's (even when anthropogenic Pb contamination was high) suggest that the $^{210}\text{Pb}/\text{Pb}$ ratio of ocean waters was high (2.6×10^{-7} Bq/mol of Pb, [60]) compared to crustal materials, and it must have been much higher before anthropogenic elemental Pb contamination. Hence in the natural system, adsorbed Pb on weathered crustal material would have a low $^{210}\text{Pb}/\text{Pb}$ ratio that would have encountered dissolved marine lead with a much higher $^{210}\text{Pb}/\text{Pb}$ ratio. Isotope equilibration would have ensued, and because on an atom per atom basis there is much more stable elemental lead on the crustal material than ^{210}Pb dissolved in the seawater, most of the marine ^{210}Pb would be taken up onto the particles, releasing an immeasurably small amount of stable Pb in its place. Therefore in this situation, it would appear that ^{210}Pb was scavenged and lost from solution whereas elemental Pb could have been at least slightly released into the low-Pb dissolved phase, just by the operation of the K_d adsorption equilibration. In other words, as we noted in our introduction "there may be some differences between the elemental Pb budget compared to the ^{210}Pb budget".

Benninger [22] quantified the ^{210}Pb budget for Long Island Sound (U.S.A) and concluded that ^{210}Pb was scavenged in estuaries, and by extension argued that elemental Pb should also be scavenged in estuaries, therefore rivers would not be a source of Pb into the ocean. As we have noted above, we show that ^{210}Pb should be removed from solution by isotope equilibration even when there is a net release of elemental Pb from crustal particles. We believe that a rethinking of some of the conclusions based on ^{210}Pb is warranted, and we suggest that the process of isotope equilibration should be quantified in other coastal marine environments to determine its generality.

Finally, we suggest that a similar process may occur for other radionuclide systems. For example, most of the thorium in crustal materials is long-lived ^{232}Th with a minor contribution of ^{230}Th from the ^{238}U series, whereas the ocean contains a higher ratio

$^{230}\text{Th}/^{232}\text{Th}$ because dissolved U is enriched in seawater and produces a steady supply of ^{230}Th to the ocean. Therefore there may be situations when net scavenging of Th is inferred from ^{230}Th data, when instead exchange with crustal ^{232}Th is the cause of the lost ^{230}Th .

Finally, these considerations should remind us that K_d -style equilibration may be an important factor in the elemental cycles of elements that don't have the strong isotope ratio contrasts that allowed us to deduce this process for Pb.

6 Conclusions

Isotope exchange of Pb in coastal waters has been investigated through a closed-system exchange experiment using estuarine waters sampled from the Johor River mouth. During the experiment, the $^{206}\text{Pb}/^{207}\text{Pb}$ in the sample changed from 1.178 to >1.190 within 7 days with disproportional changes in Pb concentration. The change in Pb isotope ratios in the batch experiment was significantly larger than the measurement error. With a timescale of isotope exchange much shorter than the residence time of Pb in a water environment, isotope exchange could maintain a consistent isotope departure from the Pb source feeding the water, which has been observed in the Singapore Strait. In addition to our closed-system experiment and field observations, a simple mathematical model was employed to simulate the kinetics of isotope exchange. Using a K_d -type exchange model, >50% of the observed $^{206}\text{Pb}/^{207}\text{Pb}$ variance can be simulated. The observations in both closed-system experiment and field measurements provide a compelling evidence for rapid (days-months) Pb isotope exchange between seawater and suspended particulate materials. Further investigation of the distributions of Pb and Pb isotopes around estuaries and coastal areas could enhance our understanding on the role of isotope exchange in marine Pb geochemistry. Finally, we suggest in some situations, isotope equilibration might need to be considered in interpreting data from ^{210}Pb and other radioisotope systems.

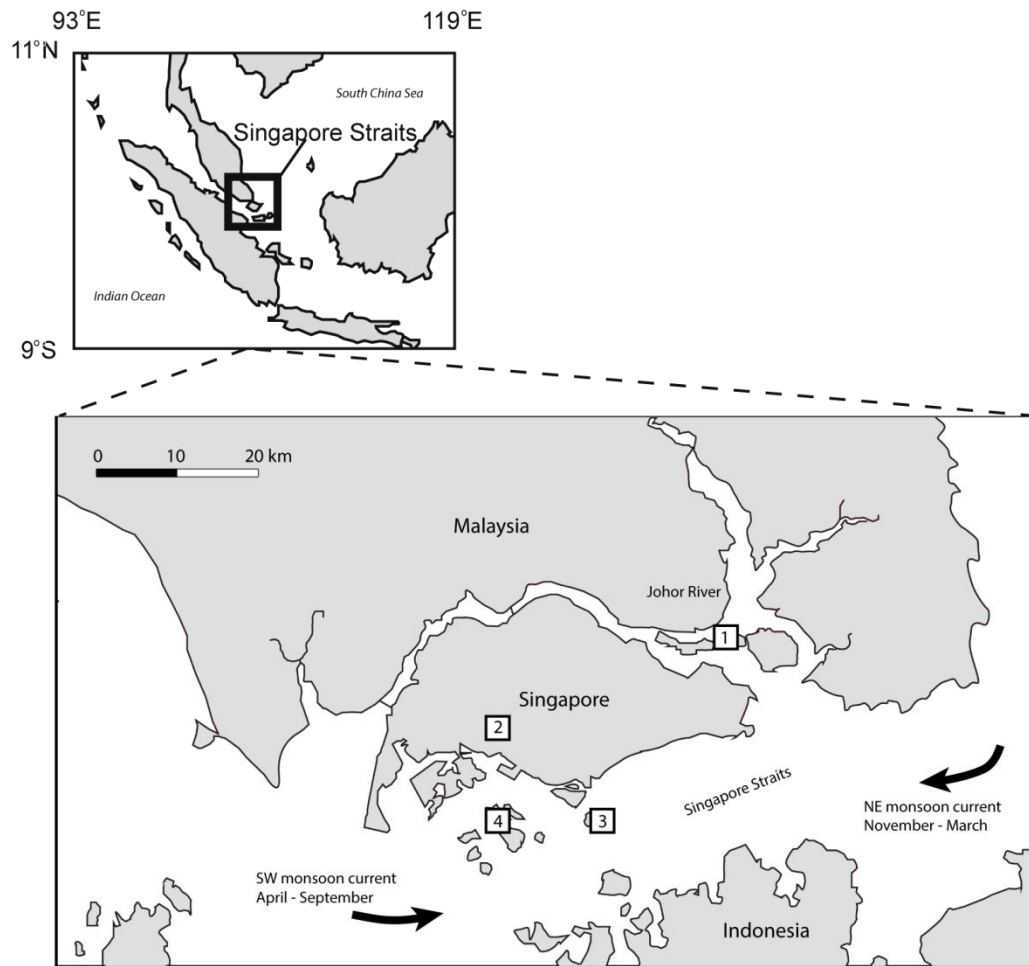


Figure 1: Map of the Singapore Strait and the Johor River. The sampling sites are illustrated in numbered boxes. The sampling sites include: 1. Johor River mouth for isotope exchange water samples; 2. National University of Singapore for aerosol samples; 3. Kusu for seasonal seawater samples; 4. Hantu for seasonal seawater samples.

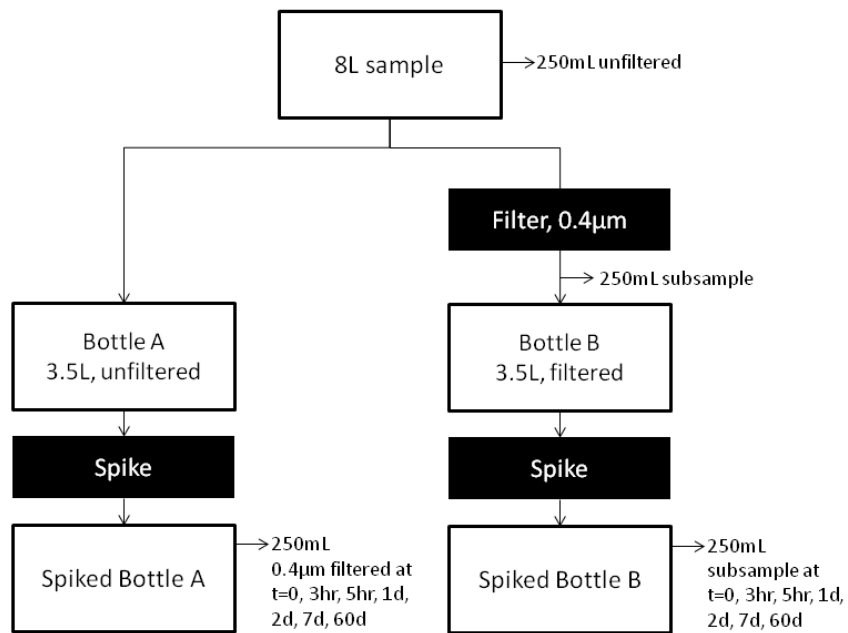


Figure 2: Schematics of the isotope exchange experiments

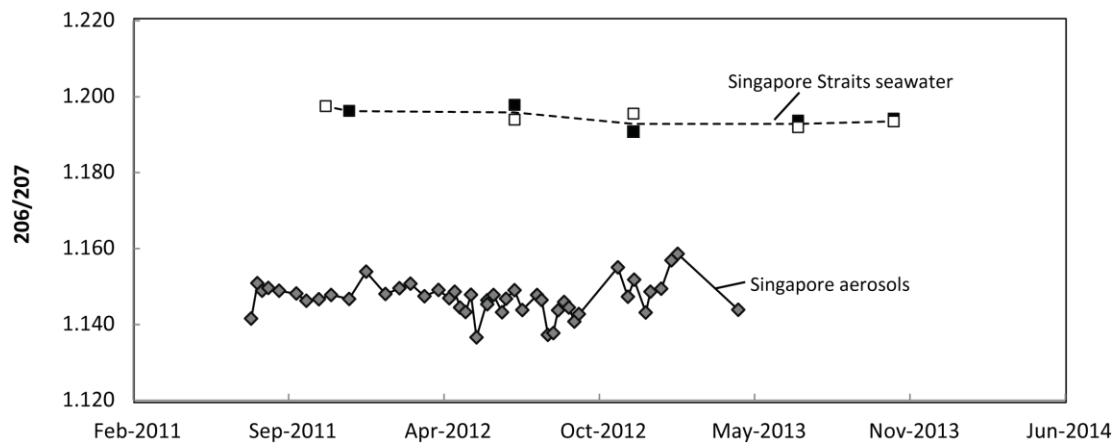


Figure 3: The Pb isotope time series in Singapore aerosols (grey filled diamonds) and seawater (squares). The seawater samples were taken from the Singapore Strait near either Hantu (black filled squares) or Kusu (open squares). The dashed line illustrates an average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Singapore Strait water. The aerosol samples were taken on top of the S16 building and CREATE building.

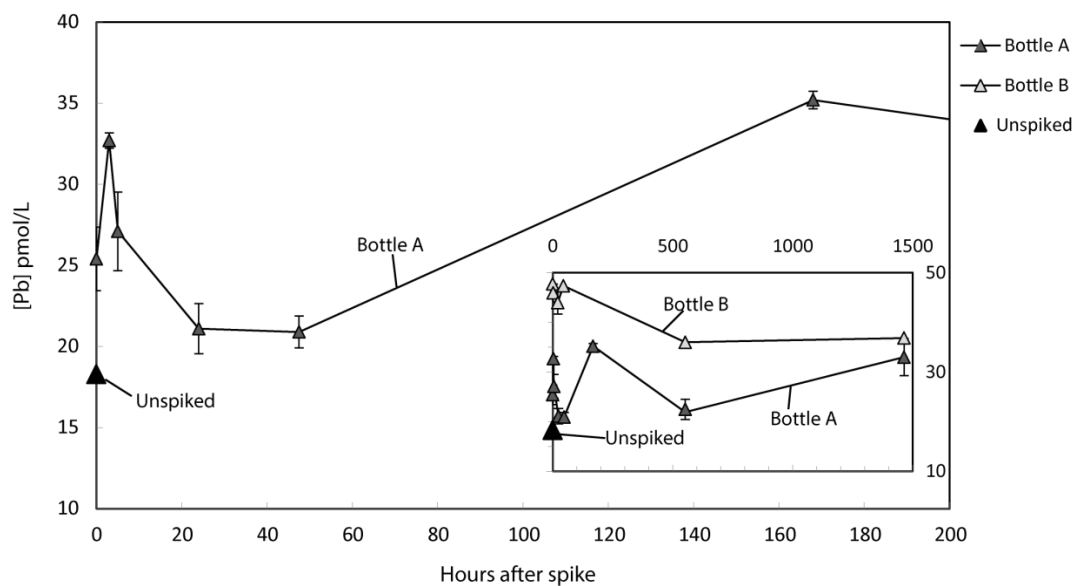


Figure 4: The measured Pb concentration in seawater after spiking with NBS-981 standard reference material. Bottle A (grey filled triangles) is the unfiltered seawater; Bottle B (open triangles) is the 0.4 μ m filtered seawater; and the unspiked sample is shown in a black filled triangle. The main figure shows the detail change in Pb concentration in Bottle A within first 200 hours and the insect figure shows the 2-month-long variation of Pb concentration in both Bottle A and B.

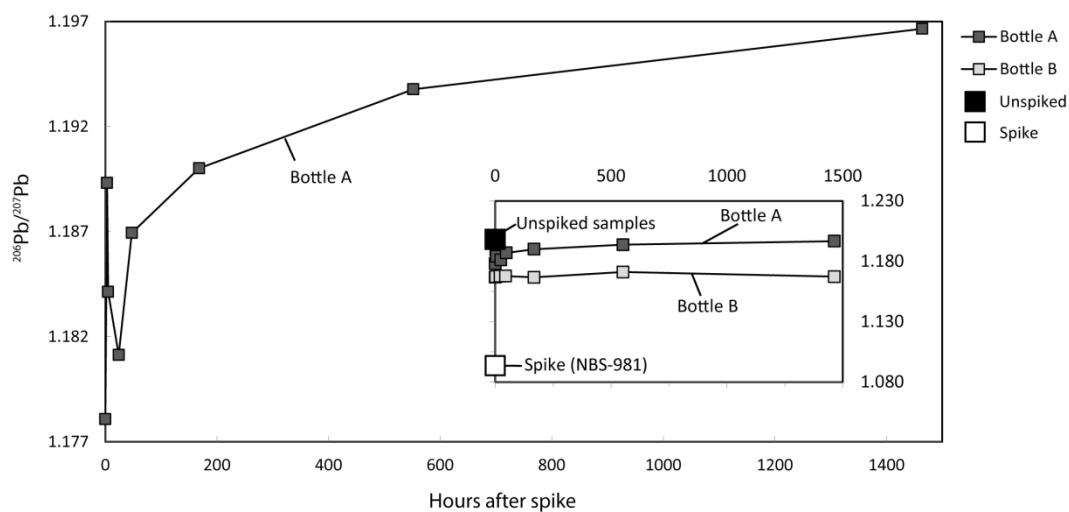


Figure 5: The measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of seawater after spiking with NBS-981 standard reference material (big open square). The main figure shows the detailed change in $^{206}\text{Pb}/^{207}\text{Pb}$ in Bottle A (grey filled squares) after spike addition. The inset figure shows the overview of the $^{206}\text{Pb}/^{207}\text{Pb}$ in unfiltered sample (big filled square); spike (big open square); the change in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in Bottle A and Bottle B (filtered at $t=0$, open squares).

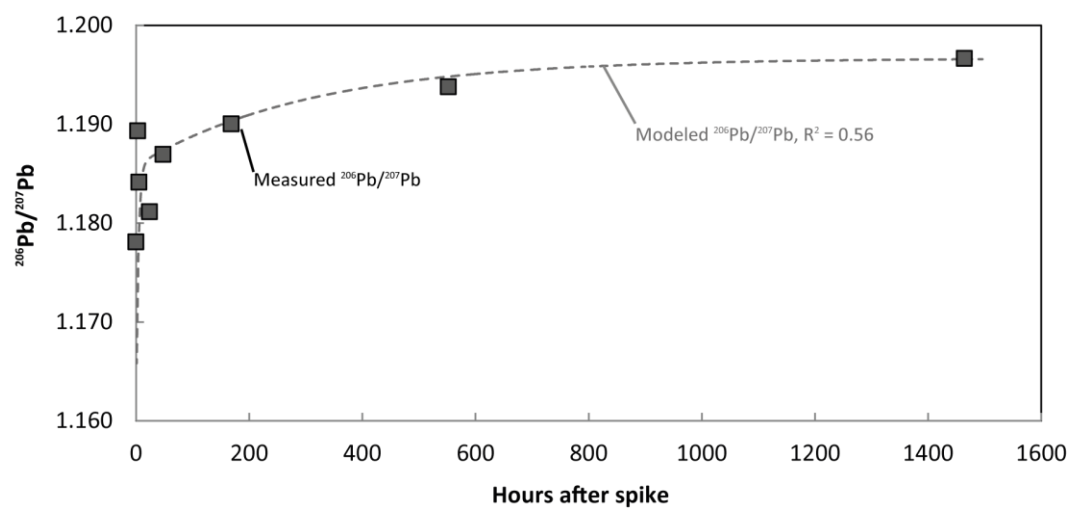


Figure 6: The modelled $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (dashed grey line) compared to measured values from the close-system experiment (filled squares).

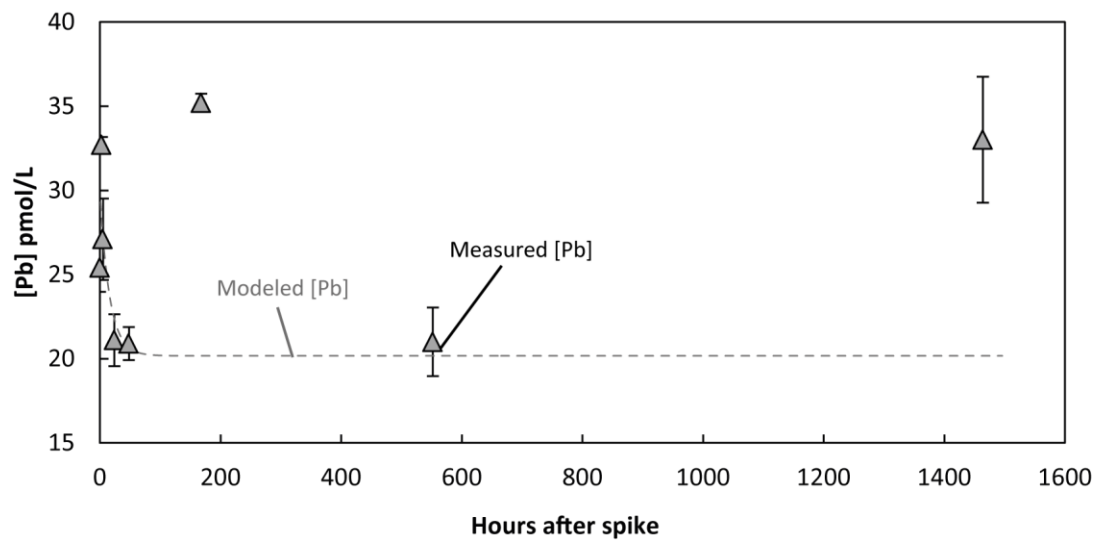


Figure 7: The modelled dissolved Pb concentration (dashed grey line) compared to measured values from the close-system experiment (filled squares).

Table 1: Variability in Pb concentration and isotopes during closed system isotope exchange experiment

<i><u>Name & Timestep</u></i>	[Pb] (pmol/L)	$\frac{^{206}\text{Pb}}{^{207}\text{Pb}}$	$\frac{^{206}\text{Pb}}{^{207}\text{Pb}}$
Johor A unfiltered	373.4 ± 5.4	1.1987	2.5438
Johor A T0 no spike	18.3 ± 2.0	1.1998	2.5239
Johor A T0	25.4 ± 1.4	1.1781	2.5085
Johor A T 3 hrs	32.7 ± 0.5	1.1893	2.5283
Johor A T 5 hrs	27.1 ± 2.4	1.1841	2.5364
Johor A T 24 hrs	21.1 ± 1.5	1.1811	2.5317
Johor A T 47.5 hrs	20.9 ± 1.0	1.1869	2.5400
Johor A T 7 days	35.2 ± 0.5	1.1900	2.5456
Johor A T 23 days	33.9 ± 2.0	1.1938	2.4788
Johor A T 2 months	33.0 ± 3.7	1.1967	2.5368
Johor B T 0	47.8 ± 1.9	1.1668	2.5210
Johor B T 2 hrs	45.9 ± 1.6	1.1671	2.5253
Johor B T 21 hrs	43.9 ± 1.1	1.1675	2.5255
Johor B T 44.5 hrs	47.4 ± 1.3	1.1678	2.5206
Johor B T 7 days	***	1.1667	2.5234
Johor B T 23 days	36.0 ± 1.8	1.1711	2.4553
Johor B T 2 months	36.8 ± 2.3	1.1673	2.5849

***ran out of sample

Table 2: New Singapore aerosol Pb isotope data. See [Lee et al, 2014] for data from July 2011-April 2012.

<u>Sampling interval</u>	<u>206Pb/207Pb</u>	<u>208Pb/207Pb</u>
April 19- 24, 2012	1.1437	2.4223
April 26 - May 1, 2012	1.1426	2.4208
May 3-8, 2012	1.1471	2.4241
May 10-15, 2012	1.1358	2.4129
May 17-24, 2012	1.1457	2.4253
May 24-29, 2012	1.1448	2.4218
June 1-6, 2012	1.1471	2.4252
June 11-18, 2012	1.1424	2.4219
June 18-22, 2012	1.1461	2.4230
June 28-July 3, 2012	1.1498	2.4287
July 5-17, 2012	1.1432	2.4222
July 27-Aug 1, 2012	1.1469	2.4265
Aug 2-7, 2012	1.1456	2.4247
Aug 10-15, 2012	1.1366	2.4162
Aug 17-23, 2012	1.1371	2.4184
Aug 23-29, 2012	1.1431	2.4219
Aug 31-Sept 5, 2012	1.1452	2.4252
Sept 6 - 11, 2012	1.1438	2.4230
Sept 13-18, 2012	1.1401	2.4192
Sept 19-24, 2012	1.1420	2.4212
Nov 7-14, 2012	1.1542	2.4350
Nov 20-28, 2012	1.1465	2.4245
Nov 29-Dec 4, 2012	1.1510	2.4277
Dec 14-19, 2012	1.1424	2.4202
Dec 20 - 26, 2012	1.1479	2.4251
Jan 3-8, 2013	1.1486	2.4252
Jan 16-21, 2013	1.1561	2.4383
Jan 24-29, 2013	1.1580	2.4418
April 12-18, 2013	1.1431	2.4224

References for Chapter 5

1. Salomons W, Förstner U. 1984. Metals in the Hydrocycle, *Metals in the hydrocycle*.
2. Turekian KK. 1977. The fate of metals in the oceans. *Geochim Cosmochim. Acta* **41**, 1139-1144.
3. Dupré B, Dessert C, Oliva P, Goddérès Y, Viers J, François L, Millot R, Gaillardet J. 2003. Rivers, chemical weathering and Earth's climate. *Comptes Rendus Geoscience* **335**, 1141-1160.
4. Jeandel C, Oelkers EH. 2015. The influence of terrigenous particulate material dissolution on ocean chemistry and global element cycles. *Chemical Geology* **395**, 50-66.
5. Viers J, Dupré B, Gaillardet J. 2009. Chemical composition of suspended sediments in World Rivers: New insights from a new database. *Sci. Tot. Environ.* **407**, 853-868.
6. Shiller AM, Boyle EA. 1991. Trace elements in the Mississippi River Delta outflow region: behavior at high discharge. *Geochim. Cosmochim. Acta* **55**, 3241-3251
7. Hanor JS, Chan LH. 1977. Non-conservative behavior of barium during mixing of Mississippi River and Gulf of Mexico Waters. *Earth Planet. Sc. Lett.* **37**, 242-250.
8. Edmond JM, Boyle EA, Drummond D, Grant B, Mislick T. 1978. Desorption of barium in the plume of the Zaire (Congo) River. *Netherlands Journal of Sea Research* **12**, 324-328.
9. Comans, RNJ, van Dijk CPJ. 1988. Role of complexation processes in cadmium mobilization during estuarine mixing. *Nature* **336**, 151-154.
10. Duce RA, Liss PS, Merrill JT, Atlas EL, Buat-Menard P, Hicks BB, Miller JM, Prospero JM, Arimoto R, Church TM, Ellis W, Galloway JN, Hansen L, Jickells TD, Knap AH, Reinhardt KH, Schneider B, Soudine A, Tokos JJ, Tsunogai S, Wollast R, Zhou M. 1991. The atmospheric input of trace species to the world ocean. *Global Biogeochem. Cycles* **5**, 193-259.
11. Jones MT, Pearce CR, Jeandel C, Gislason SR, Eiriksdottir ES, Mavromatis V, Oelkers EH. 2012. Riverine particulate material dissolution as a significant flux of strontium to the oceans. *Earth Planet. Sci. Lett.* **355-356**, 51-59.
12. Jones MT, Pearce CR, Oelkers EH. 2012. An experimental study of the interaction of basaltic riverine particulate material and seawater. *Geochimica et Cosmochimica Acta* **77**, 108-120.
13. Pearce CR, Jones MT, Oelkers EH, Pradoux C, Jeandel C. 2013. The effect of particulate dissolution on the neodymium (Nd) isotope and Rare Earth Element (REE) composition of seawater. *Earth Planet. Sci. Lett.* **369-370**, 138-147.
14. Jones MT, Gislason SR, Burton KW, Pearce CR, Mavromatis V, Pogge von Strandmann PAE, and Oelkers EH. 2014. Quantifying the impact of riverine particulate dissolution in seawater on ocean chemistry. *Earth Planet. Sci. Lett.* **395**, 91-100.
15. Lacan F, Jeandel C. 2001. Tracing Papua New Guinea imprint on the central Equatorial Pacific Ocean using neodymium isotopic compositions and Rare Earth Element patterns, *Earth Planet. Sci. Lett.*, **186**(3-4), 497-512.
16. Lacan, F, and C. Jeandel (2005), Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent-ocean interface, *Earth Planet. Sci. Lett.*, **232**(3-4), 245-257.

17. Komárek M, Ettler V, Chrastný V, Mihaljevič M. 2008. Lead isotopes in environmental sciences: A review, *Environ. Int.* **34**, 562-577.
18. Patterson CC, Settle DM. 1987. Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale. *Marine Chemistry* **22**, 137-162.
19. Church TM, Véron A, Patterson CC, Settle D, Erel Y, Maring HR, and Flegal AR. 1990. Trace elements in the North Atlantic troposphere: Shipboard results of precipitation and aerosols. *Global Biogeochem. Cycles* **4**, 431-443.
20. Flegal AR. 1986. Lead in tropical marine systems: A review. *Science of the Total Environment* **58**, 1-8.
21. Baskaran M, Santschi PH. 1993. The role of particles and colloids in the transport of radionuclides in coastal environments of Texas. *Marine Chemistry* **43**, 95-114.
22. Benninger LK. 1978. ²¹⁰Pb balance in Long Island Sound. *Geochimica et Cosmochimica Acta*, **42**, 1165-1174.
23. Benninger LK, Lewis DM, Turekian KK. 1975. Use of natural lead-210 as a heavy metal tracer in the river-estuarine system, in *Marine chemistry in the coastal environment*, Chapter 12, pp 202-210.
24. Rama, Koide M, Goldberg ED. 1961. Lead-210 in natural waters. *Science* **134**, 98, 98-99.
25. Windom H, Smith Jr R, Rawlinson C, Hungspreugs M, Dharmvanij S, Wattayakorn G. 1988. Trace metal transport in a tropical estuary. *Mar. Chem.* **24**, 293-305.
26. Baskaran M, Ravichandran M, Bianchi TS. 1997. Cycling of ⁷Be and ²¹⁰Pb in a High DOC, Shallow, Turbid Estuary of South-east Texas, *Estuarine, Coastal and Shelf Science* **45**, 165-176.
27. Erel Y, Morgan JJ, Patterson CC. 1991. Natural levels of lead and cadmium in a remote mountain stream. *Geochimica et Cosmochimica Acta* **55**, 707-719.
28. Chen M, Lee JM, Nurhati IS, Switzer AD, Boyle EA. 2015. Isotopic record of lead in Singapore Strait during the last 50 years: spatial and temporal variabilities. *Marine Chemistry* **168**, 49-59.
29. Lee, J.-M, E. A. Boyle, I. Suci Nurhati, M. Pfeiffer, A. J. Meltzner, and B. Suwargadi (2014), Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century. *Earth Planet. Sci. Lett.*, **398**(0), 37-47.
30. Bollhöfer A, and Rosman KJR. 2000. Isotopic source signatures for atmospheric lead: the Southern Hemisphere. *Geochimica et Cosmochimica Acta* **64**, 3251-3262.
31. Zhao N, Boyle EA, Nurhati I, Carrasco G, Gevao B, Ghadban AN, Ali L. Submitted. Pb, Pb isotopes and Cd history in the northern Arabian Gulf seawater during the past 60 years: Anthropogenic and natural processes. *Geochim. Cosmochim. Acta*.
32. Lee J-M, Boyle EA, Echegoyen-Sanz Y, Fitzsimmons JN, Zhang R, Kayser RA. 2011. Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* **686**, 93-101.
33. Thia-Eng C, Gorre IRL, Ross SA, Bernad SR, Gervacio B, Ebarvia MC. 2000. The Malacca Straits, *Mar. Poll. Bull.* **41**, 160-178.

34. Wood AKH, Ahmad Z, Shazili NAM, Yaakob R, Carpenter R. 1997. Geochemistry of sediments in Johor Strait between Malaysia and Singapore. *Cont. Shelf Res.* **17**, 1207-1228.
35. Kia M, Pirasteh S, Pradhan B, Mahmud A, Sulaiman W, Moradi A. 2012. An artificial neural network model for flood simulation using GIS: Johor River Basin, Malaysia, *Environ. Earth Sci.* **67**, 251-264.
36. Milliman JD, Farnsworth KL. 2011. River Discharge to the Coastal Ocean: A Global Synthesis, *Cambridge University Press*.
37. Tan ML, Ibrahim AL, Yusop Z, Duan Z, Ling L. 2014. Impacts of land-use and climate variability on hydrological components in the Johor River basin, Malaysia. *Hydrological Sciences Journal* **60**, 873-889.
38. Baker J, Peate T, Waight T, Meyzen C. 2004. Pb isotopic analysis of standards and samples using a 207Pb–204Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chemical Geology* **211**, 275-303.
39. Bollhöfer A, Chisholm W, Rosman KJR. 1999. Sampling aerosols for lead isotopes on a global scale. *Analytica Chimica Acta* **390**, 227-235.
40. Boyle EA, John S, Abouchami W, Adkins JF, Echegoyen-Sanz Y, Ellwood M, Flegal AR, Fornace K, Gallon C, Galer S, Gault-Ringold M, Lacan F, Radic A, Rehkamper M, Rouxel O, Sohrin Y, Stirling C, Thompson C, Vance D, Xue Z, and Zhao Y. 2012. GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. *Limnology and Oceanography: Methods* **10**, 653-665.
41. Reuer MK, Boyle EA, Grant BC. 2003. Lead isotope analysis of marine carbonates and seawater by multiple collector ICP-MS. *Chemical Geology* **200**, 137-153.
42. Pang WC, Tkalich P. 2003. Modeling tidal and monsoon driven currents in the Singapore Strait, *Singapore Maritime & Port Journal*, 151-162.
43. Chen M, Murali K, Khoo BC, Lou J, Kumar K. 2005. Circulation Modelling in the Strait of Singapore. *Journal of Coastal Research* **21**, 960-972.
44. Lee J-M, Boyle EA, Gamo T, Obata H, Norisuye K, Echegoyen Y. 2015. Impact of anthropogenic Pb and ocean circulation on the recent distribution of Pb isotopes in the Indian Ocean. *Geochim. Cosmochim. Acta* **170**, 126-144.
45. Chen M, Boyle EA, Switzer AD, Gouramanis C. In press. A century long sedimentary record of anthropogenic lead (Pb), Pb isotopes and other trace metals in Singapore. *Environmental Pollution*.
46. Guieu C, Martin JM, Tankéré SPC, Mousty F, Trincherini P, Bazot M, Dai MH. 1998. On Trace Metal Geochemistry in the Danube River and Western Black Sea. *Estuarine, Coastal and Shelf Science* **47**, 471-485.
47. Boyle EA, Lee JM, Echegoyen Y, Noble A, Moos S, Carrasco G, Zhao N, Kayser R, Zhang J, Gamo T, Obata H, Norisuye K. 2014. Anthropogenic lead emissions in the ocean: The evolving global experiment. *Oceanography* **27**, 69-75.
48. Li YH, Burkhardt L, Teraoka H. 1984. Desorption and coagulation of trace elements during estuarine mixing. *Geochim. Cosmochim. Acta* **48**, 1879-1884.

49. Nyffeler UP, Li YH, Santschi PH. 1984. A kinetic approach to describe trace-element distribution between particles and solution in natural aquatic systems. *Geochim. Cosmochim. Acta* **48**, 1513-1522.
50. Dikou A, van Woerik R. 2006. Survival under chronic stress from sediment load: Spatial patterns of hard coral communities in the southern islands of Singapore. *Marine Pollution Bulletin* **52**, 7-21.
51. Anbar, AD, Roe JE, Barling J, Neelson KH. 2000. Non-biological fractionation of iron isotopes. *Science* **288**, 126–128.
52. Inoue M, Hata A, Suzuki A, Nohara M, Shikazono N, Yim WWS, Hantoro WS, Donghuai S, Kawahata H. 2006. Distribution and temporal changes of lead in the surface seawater in the western Pacific and adjacent seas derived from coral skeletons. *Environmental Pollution* **144**, 1045-1052.
53. Wei CL, Lin SY, Sheu DD, Chou WC, Yi MC, Santschi PH, Wen LS. 2011. Particle-reactive radionuclides (^{234}Th , ^{210}Pb , ^{210}Po) as tracers for the estimation of export production in the South China Sea. *Biogeosci.* **8**, 3793-3808.
54. Cochran, JK, Bacon MP, Krishnaswami S, Turekian KK. 1983. ^{210}Po and ^{210}Pb distributions in the central and eastern Indian Ocean. *Earth Planet. Sci. Lett.* **65**, 433-452.
55. Meybeck M, Laroche L, Dürr HH, Syvitski JPM. 2003. Global variability of daily total suspended solids and their fluxes in rivers. *Global and Planetary Change* **39**, 65-93.
56. Walling DE. 2006. Human impact on land–ocean sediment transfer by the world's rivers, *Geomorph.* **79**, 192-216.
57. Frank M, Reynolds BC, O'Nions RK. 1999. Nd and Pb isotopes in Atlantic and Pacific water masses before and after closure of the Panama gateway. *Geology* **27**, 1147–1150.
58. Taylor SR, McLennan SM. 1995. The geochemical evolution of the continental crust. *Rev. Geophys.* **33**, 241-265.
59. Nozaki Y, Thomson JJ, Turekian KK. 1976. The distribution of ^{210}Pb and ^{210}Po in the surface waters of the Pacific Ocean. *Earth Planet. Sci. Lett.* **32**, 304–312.
60. Boyle EA, Sherrell RA, Bacon MP. 1994. Lead variability in the western North Atlantic and Central Greenland: implications for the search for decadal trends in anthropogenic emissions. *Geochim. Cosmochim. Acta* **58**, 3227-3238