An investigation on suspended solids sources in urban stormwater runoff using ^7Be and ^{210}Pb as tracers

Chengqing Yin and Liqing Li

ABSTRACT

Radionuclides ^7Be and ^{210}Pb were used as tracers to identify suspended solid sources and transport pathways in the storm runoff events from urban catchments. Water samples were collected in runoff of storm events in Wuhan City, China. Suspended solids, COD, TN, TP, and the ^7Be and ^{210}Pb activities in the suspended solids were analyzed. Following the pathway of urban runoff pollution, the rain precipitation, urban ground dust, gutter sediments, and sewer deposit samples were analyzed for ^7Be and ^{210}Pb activities. The results show that the $^7\text{Be}/^{210}\text{Pb}$ ratio decreased through the system from a value of 0.86 ± 0.44 in ground dust, to 0.63 ± 0.18 in suspended solids in storm runoff from the sewer outlet, to 0.55 ± 0.31 in gutter sediments, and to 0.41 ± 0.13 in combined sewer deposits. The $^7\text{Be}/^{210}\text{Pb}$ ratio decrease suggests that $60 \pm 12\%$ of suspended solids at sewer outlet originated from the drainage system sediments, the rest was from the wash-off of urban ground dust during the rainfall events. The ^7Be and ^{210}Pb trace approach can give insight into the short-term source and transport of pollutant during storm runoff in urban drainage systems and it can help to develop management strategies.

Key words | beryllium-7, combined sewer, lead-210, suspended solid sources, urban runoff

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INTRODUCTION

Identification of sediment transport and source in a watershed is fundamental to developing management strategies for sediments and sediment-bound nutrients and contaminants. A discrimination of sediment sources can be achieved from mass balancing tracers (Wallbrink *et al.* 1998).

Beryllium-7, cesium-137, and lead-210 are deposited on the earth's surface through wet and dry fallout. However, because of differences in the decay-rate and delivery history, each radionuclide is distributed differently in the soil (Matisoff *et al.* 2002a). Therefore, sediments derived from a soil will have a unique radionuclide signature corresponding to the land use and the depth of erosion (Whiting *et al.* 2001). Several studies used the above radionuclides as tracers to identify the fingerprint characteristics in sediment erosion sources from agricultural watersheds (Walling *et al.* 1999; Matisoff *et al.* 2005; Whiting *et al.* 2005).

In urban area, suspended solids are major pollutants in storm runoff, and they are identified as one of the major causes of the deterioration of receiving waters (Novotny & Olem 1994). In the most polluted first flush, it was found that many pollutants are in the particulate forms and are associated with suspended solids. In urban areas with combined sewer system, the storm runoff contains large amounts of suspended solids and adsorbed pollutants, and can have a significant oxygen demand or toxic impact on water ecosystems (Skipworth *et al.* 2000). There is a fundamental need to identify the main sources of suspended solids and associated pollutants in storm runoff from urban areas and to develop management strategies for receiving waters. The re-suspension of sediments in the combined sewer systems plays an important role in transport of storm runoff pollution (Chebbo *et al.* 2001, 2003; Gromaire *et al.* 2001). However, little was known about the transport paths

and sources of suspended solids in storm runoff from urban areas because of the limitation of study methods.

The objective of this study is trying to use ^7Be and ^{210}Pb as tracers to identify the sources and transport pathways of suspended solids in storm runoff from urban catchments with combined sewer systems.

The principle of ^7Be and ^{210}Pb as a tracer of sediments in urban area

Beryllium-7 is a naturally occurring radionuclide and it is produced continuously in the upper atmosphere by cosmic ray spallation of nitrogen and oxygen. Beryllium-7 is a short-lived radionuclide with $t_{1/2}$ of 53.3 d. It reaches the earth's surface mostly through wet fallout, especially from thunderstorms that scrub ^7Be from the stratosphere. In the precipitation and runoff process, ^7Be is adsorbed to particulates with K_d approximately $10^4 \sim 10^6$ (Hawley *et al.* 1986; Matisoff *et al.* 2002a,b).

Lead-210 is a long-lived radionuclide with $t_{1/2}$ of 22.3 years. It is naturally produced as a decay product of ^{238}U ($t_{1/2} = 4.5 \times 10^5$ years). Uranium-238 decays through a series of short-lived nuclides to ^{226}Ra ($t_{1/2} = 1,600$ years), and ^{226}Ra in turn decays to the noble gas ^{222}Rn ($t_{1/2} = 3.83$ days). Some ^{222}Rn escapes to the atmosphere, where it decays through a series of short-lived nuclides to ^{210}Pb . A portion of ^{222}Rn produced from the decay of ^{238}U does not escape to the atmosphere and it results in an *in situ* produced level of ^{210}Pb , referred to as 'supported' ^{210}Pb . The atmospherically derived ^{210}Pb , or 'excess' ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$), is washed from the atmosphere and delivered to the earth's surface through both wet and dry fallout and sorbs strongly to particulate matter. Thus the total activity of ^{210}Pb in soils $= ^{210}\text{Pb}_{\text{xs}} + \text{supported } ^{210}\text{Pb}$, where supported $^{210}\text{Pb} = ^{226}\text{Ra}$.

In order to understand the particulate wash-off, sediment transport and sediment sources, it is very helpful if a particle-bound and radioactive tracer with a suitable half-life could be employed. Both ^7Be and ^{210}Pb are delivered continuously to the land by atmospheric fallout where they become strongly bound to particulate matter. Thus, the activities of ^7Be and ^{210}Pb in suspended sediments are a measure of the time since the surface particles were tagged by sorption of these radioactive tracers. In this study,

^7Be and ^{210}Pb were used as tracers to identify and characterize suspended solids transport and sources in storm runoff from urban area.

In urban catchments with combined sewer systems, surface and sewer sediment transport process can be depicted as in Figure 1. On wet weather days, urban ground dusts or particles are washed off by rain-runoff, and transported in the combined sewer networks. In this transport process, the sediments originally deposited in gutter drains and combined sewer systems are resuspended and eroded due to the increased flow velocities during the storm events. Thus, the sediments in the sewer outlet may have different sources, such as urban ground dusts and drainage sewer sediments.

Decreases in the $^7\text{Be}/^{210}\text{Pb}$ ratio in urban sediment transport processes are suggested by two ways (Matisoff *et al.* 2005). First, the decrease in the $^7\text{Be}/^{210}\text{Pb}$ ratio in sediments may reflect an increase in the time since the sediment was tagged with atmospherically derived ^7Be with ^7Be decaying much faster than ^{210}Pb . Alternatively, a decrease in this ratio can be caused by dilution of ^7Be -rich sediment with ^7Be -deficient sediment. For the first reason, lower values of $^7\text{Be}/^{210}\text{Pb}$ ratio can occur when the sediment gets 'older', such as in the combined sewer. Consequently, the $^7\text{Be}/^{210}\text{Pb}$ ratio is able to trace the urban sediment transport and give insight into the relative contribution of urban ground and sewer to suspended solids of stormwater runoff measured at catchment sewer outlet.

MATERIALS AND METHODS

This study was conducted on three urban catchments, i.e. Shilipu, Wulidun and Qilimiao, which drained to Moshuihu Lake in Wuhan City. More detailed research was performed on the Shilipu catchment with 130 ha urban area. It is an old residential area with some small businesses and almost no industrial activities. Around 85% of the land is impervious. The population density is 130 inhabitants per hectare. Sewage and stormwater are combined and discharged into the lake directly. The sewer network includes five circular concrete trunks. Presently, this district is planning to reconstruct the water discharge

Figure 1 | The transport process of urban ground/sewer particles or sediments.

system. Sanitary sewage is being intercepted to a wastewater treatment plant, and the storm water management is of great concern.

Four types of sediments which are likely to be the potential sources of suspended solids in stormwater runoff were sampled at the catchment. Urban ground dusts were sampled from 9 sites with different land uses by a vacuum cleaner. Sediment samples from 13 gutters were collected using a shovel. Sediment samples were collected from 5 sewage sewer sites and 6 combined sewer sites in concrete trunks. The samples were dried at 60°C , ground to a fine consistency, weighed and stored in plastic boxes for measuring ^7Be and ^{210}Pb .

Urban stormwater runoff from the catchments was monitored at the combined drainage outlet during 2003 to 2006. Two storm events of 25.5 mm precipitation on 24 June and 85.0 mm precipitation on 9 July 2006 were studied and water samples were collected for investigating the suspended solid sources. At the beginning of a rainfall, samples were collected at 10 min interval and later the sampling interval was increased to 20 min. The runoff flow rates were continuously measured through a rectangular weir constructed by the outlet of combined sewer and calculated by the velocity and cross section area.

Simultaneously, the total suspended solids samples were taken to measure the ^7Be and ^{137}Pb by collecting

abundant runoff water. Approximate 25 L of storm runoff water was taken and stored in 30 L polyethylene buckets. The water samples were settled and centrifuged to get the suspended solids. The particulate matter from the centrifuge was dried at 60°C , ground to a fine consistency, weighed and stored in plastic boxes for ^7Be and ^{210}Pb activity measurements.

Total suspended solids (TSS) and chemical oxygen demand (COD) were measured according to *Standard Methods for the Examination of Water and Wastewater* (1998). Water samples were filtered with $0.45\ \mu\text{m}$ pore-size glassfiber filters. The filtered and unfiltered water samples were digested with $\text{K}_2\text{S}_2\text{O}_7$ solution for determination of dissolved and total nitrogen and phosphorus concentrations (Ebina *et al.* 1983).

All the collected sediment samples were placed into plastic boxes ($\varnothing 7.5\ \text{mm}$, H7.0 mm) for analysis by gamma spectroscopy for ^{210}Pb (465.52 keV), ^7Be (477.56 keV) and ^{214}Bi (609.3 keV). An HPGe gamma detector was used for the radionuclide analysis. Samples were first counted for 8–12 hours to measure the ^7Be activities. After that samples were sealed for more than four weeks to allow secular equilibrium in growth of gaseous ^{222}Rn ($t_{1/2} = 3.83$ days) from the decay of its ^{226}Ra ($t_{1/2} = 1,600$ years) parent. The activity of this supported ^{210}Pb was determined from the activity of the ^{214}Bi parent. Samples also were counted for

8–12 hours to measure the ^{210}Pb and ^{214}Bi . Standards were prepared using the same geometries as the samples. Counting efficiencies were established using a mixed radionuclide standards and were interpolated for the energy of the ^7Be emission since these standards do not contain ^7Be . All measured counts were corrected for background levels, branching ratios and decay, and were then divided by their respective sample weights and reported as activity per gram.

RESULTS AND DISCUSSION

Activities of ^7Be and ^{210}Pb in different sediment sources from the urban catchments

The specific activities of ^7Be and ^{210}Pb in urban ground dust, gutter sediments, sewage sewer sediments, and combined sewer sediments are given in Table 1. It was found that the highest values of the ^7Be specific activities were in the urban ground dusts, followed by gutter sediments, combined sewer sediments, and that sewage sewer sediments had the lowest ^7Be specific activities. The highest values of the ^{210}Pb and $^{210}\text{Pb}_{\text{xs}}$ specific activities appeared in the gutter sediments, followed by combined sewer sediments, urban ground dusts, and that sewage sewer sediments had the lowest ^{210}Pb and $^{210}\text{Pb}_{\text{xs}}$ specific activities. The $^{210}\text{Pb}_{\text{xs}}$ activities were almost equal to the ^{210}Pb activities for the four types of urban particles or sediments.

The highest ^7Be specific activities in urban ground dusts can be interpreted as their exposure to the ^7Be atmospheric fallout. The lowest ^7Be specific activity in the sewage sediments is because of their biological origin. Compared to the other kinds of sediments, the low ^7Be and ^{210}Pb specific

activities in combined sewer sediments are as a result of the dilution of ^7Be and ^{210}Pb in the sewer.

Although there were to some extent differences among the four types of sediments, neither ^7Be nor ^{210}Pb or $^{210}\text{Pb}_{\text{xs}}$ is able to effectively differentiate the four types of sediments except the sewage sewer sediments. The reason is probably because of the preferential movement of the fine particles, which adsorb most of Be and Pb isotopes, during the flowing process. However, the $^7\text{Be}/^{210}\text{Pb}$ ratio was expected to be able to differentiate the four types of sediments (Table 1) and this ratio is less variable than either of the two isotopes individually. It can be noticed that the $^7\text{Be}/^{210}\text{Pb}$ ratio decreased through the system from a value of 0.86 in the urban ground dusts, to 0.55 in gutter sediments, to 0.41 in combined sewer sediments. Each of these groups has $^7\text{Be}/^{210}\text{Pb}$ ratios that are significantly distinct from each other. This trend can be interpreted as the combination of age increase and dilution effect in the transportation process through the system. Consequently, the $^7\text{Be}/^{210}\text{Pb}$ ratio can be employed as an indicator to differentiate the urban ground dust and combined sewer sediments which is one of the major source of suspended solids of stormwater runoff and identify their relative contribution.

The temporal pattern of the $^7\text{Be}/^{210}\text{Pb}$ ratio in suspended solids during the storm events

The temporal patterns of flow rate, suspended solids concentration, and $^7\text{Be}/^{210}\text{Pb}$ ratio are shown in Figure 2 for the 25.5 mm storm event on 24 June 2006. With the flow rate increase, the suspended solids concentration increased rapidly, and maximum measured suspended solid concentration occurred immediately prior to peak discharge.

Table 1 | The specific activities of ^7Be and ^{210}Pb in urban ground dust, gutter sediments, sewage sewer sediments, and combined sewer sediments

	^7Be (Bq/g)	^{210}Pb (Bq/g)	$^{210}\text{Pb}_{\text{ex}}$ (Bq/g)	$^7\text{Be}/^{210}\text{Pb}$	$^7\text{Be}/^{210}\text{Pb}_{\text{ex}}$
Rainfall $n = 3$	0.37 ± 0.07	0.11 ± 0.05	0.11 ± 0.05	3.75 ± 1.46	3.75 ± 1.16
Urban ground dust $n = 6$	0.19 ± 0.10	0.25 ± 0.19	0.22 ± 0.19	0.86 ± 0.44	1.41 ± 0.85
Gutter sediment $n = 7$	0.17 ± 0.24	0.34 ± 0.34	0.32 ± 0.34	0.55 ± 0.31	0.74 ± 0.53
Sewage sewer sediment $n = 3$	0.007 ± 0.004	0.12 ± 0.16	0.11 ± 0.15	0.10 ± 0.06	0.16 ± 0.11
Combined sewer sediment $n = 4$	0.13 ± 0.08	0.31 ± 0.10	0.28 ± 0.10	0.41 ± 0.13	0.45 ± 0.13
Suspended solids $n = 18$	0.18 ± 0.07	0.29 ± 0.09	0.28 ± 0.09	0.63 ± 0.18	0.66 ± 0.18

Figure 2 | Changes of $^7\text{Be}/^{210}\text{Pb}$ ratio, suspended solids, and flow rate on 24 June 2006.

Then suspended solid concentration quickly declined on the hydrograph recession limb. The high peak of suspended solids was associated with the initial runoff. The flow and suspended solid concentration relationship is ascribed to first flush effect, in which the limited supplies of readily available solids were entrained early in the storm, leaving little for transport in the later stage.

The pattern of the $^7\text{Be}/^{210}\text{Pb}$ ratio in suspended solids was characterized by the low values in the period with high suspended solid transport. The $^7\text{Be}/^{210}\text{Pb}$ ratio ranged from 0.43 to 0.81 with average of 0.65. Similar results were observed on another storm event of 7 July 2006 with 85.0 mm (Figure 3). The $^7\text{Be}/^{210}\text{Pb}$ ratio ranged from 0.31 to 0.93 with average of 0.61. The decreasing $^7\text{Be}/^{210}\text{Pb}$ ratio during solids transport from urban ground to sewer outlet could be interpreted as the addition of the low $^7\text{Be}/^{210}\text{Pb}$ ratio sediments. The results indicated that the sources of

Figure 3 | Changes of the $^7\text{Be}/^{210}\text{Pb}$ ratio, suspended solids, and flow rate on 9 July 2006.

the suspended solids were variable in time of a storm event. Significant amounts of solids in the transport were likely to originate from the combined sewer deposit typified by low values of the $^7\text{Be}/^{210}\text{Pb}$ ratio. It can be mobilized due to the increased flow velocities. Consequently, in addition to urban ground dust, drainage system deposits including gutter sediments and combined sewer sediments play a significant role as a source of pollutants in combined sewer flows during storm events.

Contribution of the different sources of sediments

Calculations were made to evaluate the contribution of urban ground dusts, gutter sediments, and combined sewer sediments to the total suspended solids output during storm events. Because the $^7\text{Be}/^{210}\text{Pb}$ ratios of gutter sediments and combined sewer sediments were close, they were merged into one new type, called drainage system sediments. Thus the contribution of urban ground dusts and drainage system sediments were calculated using the following mixing model:

$$C_s = C_1 \times f_1 + C_2 \times f_2 \quad (1)$$

$$f_1 + f_2 = 1 \quad (2)$$

where C_s is the $^7\text{Be}/^{210}\text{Pb}$ ratio in suspended solids in watershed output flow during storm events, C_1 the $^7\text{Be}/^{210}\text{Pb}$ ratio in urban ground dusts, C_2 the $^7\text{Be}/^{210}\text{Pb}$ ratio in drainage system sediments, f_1 the contribution of urban ground dusts, and f_2 the contribution of drainage system sediments.

According to the data of the two storm events, the calculated results indicated that $60 \pm 12\%$ of suspended solids at the sewer outlet originated from the drainage system deposits; the rest was from the wash-off of urban ground dust during the rainfall events.

CONCLUSION

Radionuclides ^7Be and ^{210}Pb were used as tracers to identify suspended solid sources and transport pathways in the storm runoff events from the experimental urban catchment. The $^7\text{Be}/^{210}\text{Pb}$ ratios decreased though the system from a value of 0.86 ± 0.44 in ground dust, to 0.63 ± 0.18 in suspended

solids in storm runoff from the sewer outlet, to 0.55 ± 0.31 in gutter sediments, and to 0.41 ± 0.13 in combined sewer deposits. The $^7\text{Be}/^{210}\text{Pb}$ ratio decrease suggests that $60 \pm 12\%$ of suspended solids at the combined sewer outlet originated from the drainage system sediments including combined sewer deposits and gutter sediments, the rest was from the wash-off of urban ground dust during the rainfall events. The ^7Be and ^{210}Pb trace approach can give insight into the short-term source and transport of pollutant during storm runoff in urban drainage systems.

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