Heavy Metals Speciation of Size-fractionated Sediments Collected from Combined Sewer System Using Sequential Extraction Method

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Abstract: Sediments deposited in sewer pipes have been concerned as one of the main pollution loads from combined sewer overflow (CSO). Since the toxicity, mobility and bioavailability of heavy metals depend on their speciation, it is necessary to consider not only their amounts but also their speciation to evaluate the adverse effects on aquatic organisms in receiving waters. Sequential extraction method was applied to the size-fractionated sediments to evaluate heavy metal speciation. Although the speciation of Cr, Ni, Cu, Zn and Pb differed among sampling points as well as their contents, the content of easily exchangeable fraction was strongly correlated with total content for all the metals except for Cu. The result of heavy metals speciation revealed that Ni, Zn and Pb in combined sewer sediments could have high mobility potential. The result of size-fractionated sediments indicated that the contents and mobility potential of the heavy metals were larger as particle size was finer. Thus, it is important to control fine sediments in combined sewer to reduce the impact of CSO pollution.

Keywords: Combined sewer overflow (CSO), heavy metal, sequential extraction, sewer sediment, speciation

INTRODUCTION

Most of urban area in Tokyo is served by combined sewer system which collects both domestic wastewater and stormwater through a single piping system. In case of heavy rain, a part of untreated sewage water diluted with rain water is discharged into receiving water, resulting in the deterioration of water environment. This phenomenon is called combined sewer overflow (CSO). The most of CSO pollution is suspected to come from resuspension of combined sewer sediments which have accumulated during dry weather periods(Gromaire et al., 2000, Chebbo et al., 2001, Samrani et al., 2004). Combined sewer sediments contain trace toxic chemical compounds including heavy metals and polycyclic aromatic hydrocarbons, and they may cause ecological damage for aquatic organisms in receiving water(Rocher et al., 2004a). Until now, behaviors of these toxic chemicals have not yet been well known, while a lot of investigations were conducted on basic water quality such as SS, BOD and nutrients(J. Suárez and J. Puertas, 2005, Nagaiwa et al., 2007). Moreover, there are only few studies about heavy metal speciation in combined sewer sediments, though it is well known that the toxicity, mobility and bioavailability of heavy metals were mainly governed by their speciation(Florence et al., 1992, Seidl et al., 1998). It is necessary to investigate heavy metal speciation of combined sewer sediments for assessing the impact of CSO pollution on the aquatic environment. Houhou et al. (2009) evaluated heavy metal speciation of sewer sediments by using TEM-EDX, SEM-EDX and XRD. Although these analyses are powerful tools for evaluating heavy metal speciation, they can not directly estimate how much amounts of heavy metals are eluted. On the other hand, sequential extraction method is useful for evaluating the potential of heavy metal elution since it can determine heavy metal speciation based on its solubility in different chemical solutions.

The purpose of this study was to identify what heavy metals in combined sewer sediments were likely to be mobile by using sequential extraction method. The sediment samples fractionated by particle size were analyzed because wash-off behaviors and heavy metal contents in sewer pipes could depend on their particle sizes.
METHODS

Sampling
The samples were collected on 14th-16th November 2007 at multiple catchment areas in Tokyo. We sampled combined sewer sediments at 16 different locations (Points C1-C16) in the drainage area of combined sewer system. The Points C1-C12 were at branch sewer. Although these points were located within small area, they were not influenced by each other because they entered different trunk sewer lines independently. The Points C13-C16 were at trunk sewer. Interaction among these points was also negligible because they entered different larger trunk sewer lines independently. Thirty two mm of precipitation (9 mm of maximum hourly precipitation) was observed three to five days before the sampling dates.

Particle size distribution, water content and ignition loss
The sewer sediments were mixed well to make them homogeneous in advance of analysis. A part of the sewer sediment was used for measuring particle size distribution. The sediments were fractionated into four size-fractions (A: 250-2000, B: 106-250, C: 63-106, and D: less than 63 µm) by wet sieving method using wastewater collected at the same points. The water contents of each fraction were measured by drying at 105°C for 2 hrs. Ignition loss of each fraction was determined by drying at 600°C for 1 hr.

Total heavy metals
Total heavy metal content was analyzed according to microwave digestion method (EPA 3051). Size fractionated samples corresponding to approximately 200 mg dry weight were soaked in 10 mL of concentrated HNO₃ for 6 hrs to degrade the organic matter. They were digested in a microwave digester thereafter. Cr, Ni, Cu, Zn and Pb contents were determined with an ICP-MS (HP 4500, Yokogawa analytical systems, Tokyo).

Sequential extraction of heavy metals
The sequential extraction procedure described by Yann and Christina(2007) was employed with slight modifications in order to evaluate heavy metal speciation of size-fractionated sediments. In this study, heavy metals were classified into four types of speciation based on extractability. All extractions were conducted in triplicate. Cr, Ni, Cu, Zn and Pb contents of each fraction were determined with an ICP-MS.

Fraction 1: water soluble metals or metals associated with carbonates The 200 mg dry weight of size-fractionated sediments were extracted with 30 mL of 1 M CH₃COONH₄ (pH adjusted to 4.5). The mixture was shaken at 200 rpm for 12 hrs at room temperature followed by centrifugation at 3500 rpm for 20 min. The supernatant was filtered through a 0.45 µm PTFE filter. This extract includes water soluble metals and metals associated with carbonates which are easily exchangeable fraction and higher potential of toxicity. The remaining residue was washed twice with Milli-Q water for next extraction step.

Fraction 2: metals specifically bound to or occluded in amorphous iron The residue from the previous step was extracted with 30 mL of 0.2 M (COONH₄)₂ (pH adjusted to 3). The mixture was maintained at 80°C in a water bath for 2 hrs followed by centrifugation at 3500 rpm for 20 min.. The supernatant was filtered through a 0.45 µm PTFE filter. This extract includes the heavy metals specifically bound to or occluded in amorphous iron. The fraction is stable under oxidative condition whereas unstable and mobile under reductive condition. The remaining residue was washed twice with Milli-Q water for next extraction step.

Fraction 3: metals associated with sulfide or organic matter The residue from the previous step was extracted with 30 mL of 30% H₂O₂. The mixture was kept at 40°C in a water bath for 1 hr followed by centrifugation at 3500 rpm for 20 min. The supernatant was filtered through a 0.45 µm PTFE filter. This extract includes the heavy metals associated with sulfide or organic matter. Thus, it is chemically stable but gradually increases mobility under oxidative condition. The remaining residue was washed twice with Milli-Q water for the determination of Fraction 4.
Fraction 4: residual fraction The residue from the previous step was digested with 10 mL of concentrated HNO₃ in a microwave digester according to EPA 3051 method. The digested solution was filtered through a 0.45 µm PTFE filter. This fraction is regarded as chemically stable and inert with lower potential of environmental impact.

RESULTS AND DISCUSSIONS
Particle size distribution
Figure 1(a) shows particle size distributions of the combined sewer sediments. More than 80% of sediment particles of all samples were in the size-fraction A (250-2000 µm). The averaged particle size distributions of the sediments from branch sewers (C1-C12) and trunk sewers (C13-C16) are illustrated in Figure 1(b). The percentage of size-fraction A was 96% for the sediments from trunk sewers whereas it was 90% for the sediments from branch sewers. The statistical test also supported that the sediments from trunk sewers were composed of significantly larger particles (p<0.05).

![Particle size distributions of the combined sewer sediments.](image)

Figure 1: Particle size distributions of the combined sewer sediments. (a) Particle size distribution at each point, (b) Comparison of averaged particle size distributions between the sediments from branch sewers and those from trunk sewers.

Ignition loss
Ignition losses of the combined sewer sediments were in the range of 1.4 to 7.7% as shown in Figure 2(a). In particular, the sediments collected from C2 and C5 (branch sewers) demonstrated higher values (7.7% and 7.2%, respectively) than the others. However, no significant difference in ignition loss was observed between the sediments from trunk sewers (1.4-3.6%) and those from branch sewers (2.0-7.7%) (p<0.05). Figure 2(b) compares ignition losses of the size-fractionated sediments. Ignition losses of the size-fractions A, B, C and D were 1.1-6.3 (min-max) %, 1.4-9.6%, 4.7-25.2% and 13.8-47.0%, respectively. This indicates that finer particles contain more organic matter.

![Ignition losses of the combined sewer sediments.](image)

Figure 2: Ignition losses of the combined sewer sediments. (a) Comparison among sampling points, (b) Comparison among the different size-fractions of the sediments.
Total heavy metal contents

The total contents of Cr, Ni, Cu, Zn and Pb in the combined sewer sediments were 36(18-360) [mean (min-max)], 34(18-1100), 120(51-2100), 430(200-1200), and 60(13-610) mg kg\(^{-1}\), respectively (Figure 3). Rocher et al. (2004b) reported that the ranges of Cu, Zn and Pb contents of combined sewer sediments in Paris were 330 (150-790) [mean (10%-90%)] , 1530 (1200-2100) and 1300 (690-3180) mg kg\(^{-1}\), respectively. Though their fractionation regime was not identical to our study, on average, combined sewer sediments in Paris contained higher amounts of Cu (2.8 times), Zn (3.6 times) and Pb (20.7 times) compared with the sediments in Tokyo. The road dust samples collected from the same sampling area contained Cr(130±10), Cu(510±90), Zn (1300±40) and Pb(200±10) mg kg\(^{-1}\) (Murakami et al., 2008), which were higher than those of the sewer sediments in the present study. It suggests that there are other heavy metal sources for sewer sediments other than road dusts.

The wide range of heavy metal contents was observed among sampling points. Difference in metal content was not significant between the sediments from trunk sewers and those from branch sewers (p<0.05). The sediment from C3 contained the largest amount of Cr (360 mg kg\(^{-1}\)) while Ni contents at C5 (590 mg kg\(^{-1}\)) and C14 (1100 mg kg\(^{-1}\)) were considerably larger than the average. Cu was more abundant in the sediments from C8 (1700 mg kg\(^{-1}\)), C11 (2100 mg kg\(^{-1}\)) and C14 (850 mg kg\(^{-1}\)). The sediment from C8 also had the largest content of Zn (1200 mg kg\(^{-1}\)). High Pb contents were observed at C4 (370 mg kg\(^{-1}\)) and C14 (610 mg kg\(^{-1}\)). These results indicate that distributions and contents of heavy metals in the combined sewer sediments are specific to the sampling points probably due to different conditions of drainage area or piping structures of each site.

Heavy metal contents in different size fractions of the combined sewer sediments are shown in Figure 4. On average, the heavy metal contents of size-fractions C (63-106 µm) and D (less than 63 µm) were higher than those of larger size-fractions A (250-2000µm) and B (106-250 µm). Though fractionation regime was not identical to our study, Houhou et al. (2009) reported similar trend. Figure 4 also shows the averaged content distribution of different particle size for each metal. Since the mass distribution of size-fractions C and D is small as shown in Figure 1, the fine particles fractions were not dominant in the heavy metal content of the whole sediments. According to the literature (CIRIA Report 141, 2002), particles in sewer sediments of less than 150 µm in size can be transported in suspension. Although the fine particles mass fractions were very small and the heavy metal content contribution is around 10% in whole sediments, it should be noted that the fine particles could be easily discharged and have nonnegligible influence in heavy metal loading from CSO events.

![Figure 3: Total contents of Cr, Ni, Cu, Zn and Pb in the combined sewer sediments.](https://iwaponline.com/wpt/article-pdf/5/3/wpt2010057/382572/57.pdf)
Heavy metal speciation

Figure 5 shows the relative compositions of four chemical speciations for Cr, Ni, Zn, Cu and Pb at the sampling points. When the averaged distributions were examined, dominant fractions for Cr were Fraction 2 [46% (8-83%)] and Fraction 4 [45% (3-90%)] ([mean (min-max)]). It indicates that Cr was likely to be associated with iron or exist as inert forms. Ni mostly existed in Fraction 1 [35% (15-63%)] and Fraction 4 [34% (6-70%)]. Mobility of Ni seems relatively high since Fraction 1 includes easily exchangeable species. Dominant speciations of Cu were Fraction 4 [55% (18-92%)] and Fraction 3 [35% (3-69%)], indicating that Cu in the sediments could be inert or associated with sulfide or organic matter. However, the percentages of Cu in Fraction 3 and ignition losses at each sampling point did not correspond with each other. Fraction 1 [41% (21-66%)] was dominant for Zn,

Figure 4: Total contents of Cr, Ni, Cu, Zn and Pb in different size fractions and averaged content distribution of different particle size for each metal.
suggested that Zn in the sediments exhibits high mobility. Both Fraction 4 [49% (13-96%)] and Fraction 1 [37% (3-78%)] were dominant for Pb as well as Ni. Although some dominant fractions of each metal were different in the averaged distributions as we discussed above, it should be noted that the relative abundances of the fractions for each metal varied widely among sampling points. For example, Cr speciations at sampling points C3 and C10, where total content of Cr ranked in the top two, were significantly different. Approximately 70% of Cr was in the Fraction 2 at C3 while Fraction 4 dominated nearly 80% at C10. Thus, heavy metal speciations in the sediments could be rather site-specific probably due to different environmental conditions at sampling points.

Houhou et al. (2009) reported that Cu, Zn and Pb in sewer sediments were mainly present as CuS, ZnS, and PbO or PbS, respectively. In the sequential extraction method, sulfurized metal such as CuS, ZnS and PbS was extracted in Fraction 3, and oxidized metal such as PbO was fractionated in Fraction 1. Our results were consistent with this previous study in case of Cu and Pb, which were mainly in Fraction 3 and Fraction 1, respectively, but not for Zn, which was mainly in Fraction 1. Moreover, Fraction 3 was not the major fraction for Pb for any samples in our study. Houhou et al. (2009) also reported that most oxidized metals and alloys were partially sulfurized. In addition, Samrani et al. (2004) reported that metals speciation could change in the sewer systems. Therefore, it might be implied that the corrected sediments in our study had limited retention time in sewer system so that they were still present in exchangeable and oxidized form. In other words, the amount of exchangeable form may decrease when the retention time is extended in the sewer systems.

![Graph showing the distribution of Cr, Ni, Cu, Zn and Pb speciation in the combined sewer sediments.](https://iwaponline.com/wpt/article-pdf/5/3/wpt2010057/382572/57.pdf)

Figure 5: The distribution of Cr, Ni, Cu, Zn and Pb speciation in the combined sewer sediments.
Heavy metal speciations of the size-fractionated sediments (average) are shown in Figure 6. The total of Fraction 1 to Fraction 3 can be recognized as a potentially mobile fraction. On average, the ratios of the potentially mobile fraction were the highest in the size-fraction D (less than 63 µm) for Cr, Ni, Cu and Zn. This result suggests that these metals associated with finer particles could be more unstable and easily eluted from the sediments if environmental condition changes. In case of Pb, the largest content of the potentially mobile fraction was observed in the size-fraction B (106-250 µm). Considering that heavy metal contents in finer particles were higher than larger particles, priority should be given to particle size less than 250 µm to control heavy metal pollution from CSO.

Since Fraction 1 includes easily exchangeable metals, content of Fraction 1 is probably essential for assessing the risk of heavy metals. The relationship between Fraction 1 and total content for each metal is demonstrated in Figure 7. The result revealed that contents of Fraction 1 were strongly correlated with total contents for Cr, Ni, Zn and Pb. For these metals, amounts of Fraction 1 could be well estimated from the total contents. Judging from the slopes of the regression lines obtained, the ratio of Fraction 1 to total content followed the order of Ni (45%) > Zn (41%) > Pb (24%) > Cr (17%). On the other hand, correlation between Fraction 1 and total content was weak for Cu since Fraction 1 was minor speciation for Cu.

Figure 6: The distribution of Cr, Ni, Cu, Zn and Pb speciation in the different size fractions (averaged data at C1-C16).
**Figure 7:** The relationships between Fraction 1 and total contents for Cr, Ni, Cu, Zn and Pb.

**CONCLUSIONS**

The heavy metal contents (Cr, Ni, Cu, Zn and Pb) and their speciations were determined for the combined sewer sediments collected from 16 points in Tokyo. The total contents of these metals were dependent on the sampling points. Although the speciations of all metals differed among sampling points probably due to different environmental conditions, easily exchangeable fraction was relatively dominant for Ni, Zn and Pb. Moreover, the content of easily exchangeable fraction was strongly correlated with total content for all the metals except for Cu. Size-fractionation indicated that finer size-fractions, which could be easily discharged in case of CSO event, had larger contents of heavy metals. In addition, potentially mobile fraction including easily exchangeable fraction were more abundant in the finer size-fractions. Thus, control of finer particles in the combined sewer sediments is important to control heavy metal pollution caused by CSO.

**REFERENCES**


