Study on risk management of heavy metals for reuse of biosolids

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Abstract The behaviour of heavy metals was investigated at 22 wastewater treatment plants (WWTPs). In addition, the survey of heavy metal balance was conducted in detail at one WWTP. For the measurement, 22 types of heavy metals were selected from the chemical materials of pollutant release and transfer register (PRTR). There were some heavy metals, which were detected not in wastewater but in dewatered sludge. By means of the detailed survey at one WWTP, 60 to 80% of some heavy metals, such as B, Mn, Co, Ni and Mo, were discharged with treated water. According to the results of PRTR, Zn, B and Mn accounted for a large part of the discharge into the water course. To estimate the behaviour of heavy metals in the environment, leaching tests were applied to the products made of biosolids. During a series of leaching tests for building materials, it was observed that the concentration of heavy metals was very small, but the ratio of increase keeps a constant value. Therefore, it was considered that the acid extractable contents of heavy metal would be important.

Keywords Heavy metal balance; PRTR (pollutant release and transfer register); risk management

Introduction

Nowadays, approximately 2,000,000 tons (dried solid base) of biosolid is generated at WWTPs every year in Japan. Approximately 60% is beneficially used, 15% for agriculture land and 45% for building material, respectively. The rate of beneficial use increased from 15 to 60% in this decade. As shown in Figure 1, the rate of building material, which includes cement ingredient, increased rapidly in recent years.

On the other hand, the pollutant release and transfer register (PRTR) law was enforced in 2001. The manager of the WWTP had to report the behaviour about chemical materials. This study started from FY2001 to obtain the basic data at WWTP. Generally, heavy metals are known to be concentrated into sewage sludge. We decided to focus on heavy metals from the chemical materials of PRTR. The object of this study is to clarify the behaviour of heavy metals in WWTP and its transportation to the recycle products, and to estimate the behaviour of heavy metals in the environment.

For agriculture land, the amount of heavy metals in products was controlled by a standard. On the other hand, there was no general regulation about reuse of biosolids as building material. However, usually an environmental standard for soil was applied to these products. In 1998, a notification from the Ministry of Health, Labour and Welfare stated that the heavy metal standard of environmental standards for soil was applied to the molten slag, which was generated from municipal solid waste treatment plant.

From the viewpoint of lack of space for land reclamation and cost reduction, it is important to increase the reuse rate. We have to develop technical methods for beneficial use and to maintain quality. It is considered that the recycle products for building material need to meet a standard for not only physical characteristics, but also safety evaluation.

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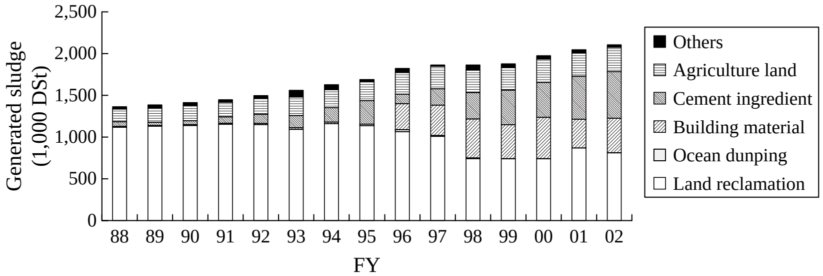

Figure 1 Beneficial use of generated sewage sludge

Materials and methods

Behaviour of heavy metals in WWTP process

Heavy metals in wastewater and de-watered sludge were measured at 22 WWTPs. One WWTP was selected for the survey of balance of heavy metal in detail. Twenty-two types of heavy metals were selected from the chemical materials of PRTR. First specified by PRTR are zinc (Zn), cadmium (Cd), chromium (Cr), hexavalent chromium (Cr + 6), mercury (Hg), selenium (Se), copper (Cu), lead (Pb), arsenic (As), boron (B), manganese (Mn), and 10 types of heavy metals. Second specified by PRTR are antimony (Sb), silver (Ag), vanadium (V), cobalt (Co), nickel (Ni), barium (Ba), beryllium (Be), molybdenum (Mo), indium (In), thallium (Tl), tellurium (Te), tin (Sn), and 12 types of heavy metals.

These heavy metals were analysed by ICP/MS at once. However, mercury was analysed separately. Samples of sewage sludge (0.2 g) could be decomposed with HNO_3/HF (5 mL/1 mL) microwave for the analysis of ICP/MS. In the analysis of standard solid samples, 80–120% recovery rate was obtained. For liquid samples (50 mL), only HNO_3 (5 mL) was sufficient for the decomposition.

Behaviour of heavy metals in the environment

Table 1 shows two types of leaching test method. The Japanese environment method is a legal method to maintain the environmental standards for soil. Evaluation of re-products is a method developed by PWRI for the recycling products made of biosolids. The difference of these two methods is mainly sample size and elution agent. Considering the effect of acid rain, the latter method uses de-ionised water saturated with carbonic acid gas (carbon dioxide).

To estimate the behaviour of heavy metals in the environment, the evaluation of re-products method was applied to slag and burnt bricks, which were made of 100% biosolids. The leaching test was applied six times to the same sample.

Risk assessment was also attempted by using the results of the evaluation of re-products method. In addition, the rate of hazard was calculated. In this case, a man whose

Table 1 Leaching test methods

Method	Japanese Environmental Standard	Evaluation of re-products
Size	<2 mm	20–50 mm
Elution agent	de-ionised water, pH 5.8–6.3	de-ionised water saturated with CO_2, pH = 4.0
pH-value	no control	no control
Elution time	6 h	24 h
Filter	0.45 μm MF	0.45 μm MF
Liquid: solid	10:1	10:1
Movement	turntable (200 rpm)	stirrer (200 rpm)

weight is 50 kg, drinks 2 L of water every day and the water has same concentration as that of leachate. The data of tolerable daily intake (TDI), which was used for establishing Environmental Law in Japan, was referenced for the calculation.

Results and discussion

Behaviour of heavy metals in WWTP process

Figure 2 indicates the relationship between ratio of heavy metal concentration in suspended solid (SS) and the removal ratio of each element. These two types of data were examined in the secondary pond at the WWTP, where the detailed survey was conducted. Because the heavy metals in SS were easily removed by biological treatment, the larger the heavy metals concentration in SS, the larger the removal ratio became.

There were some heavy metals which were detected not in wastewater but in de-watered sludge. Figure 3 shows the concentration of each element in wastewater. Their average and distribution were indicated. The square mark was the data of WWTP, which was investigated in detail, and it was distributed in the range. Figure 4 shows the concentration of heavy metals in de-watered sludge. As a result, heavy metals were concentrated into de-watered sludge, such as Be, Co, Se, In, Sb, Te, Tl and Hg, because the value was larger than the detection level.

Figure 5 indicates a picture of the balance of heavy metal at the WWTP. Water samples were examined at influent and effluent from a primary pond and a secondary pond, and the recycle flow from sludge treatment. De-watered sludge and ashes were examined as sludge samples. Exhaust gas from incinerator was also examined. For other samples, the concentration of heavy metal was calculated.

By means of the detailed survey at the WWTP, three types of heavy metal balance were found. The first type was that the element was hard to treat in WWTP. So the element was discharged into the environment with treated water. Figure 6 shows the balance of B, Mn, Co, Ni and Mo had this tendency and 60–80% of its element was discharged with treated water. The second type was that the element was concentrated into sewage sludge. So the element was discharged from the WWTP with biosolid. Figure 7 shows the balance of Pb, V, Cu, Ag, Cd, Sb and Ba had this tendency and 60–80% of its element were discharged with ashes. The third type was that the element remained in both treated water and sewage sludge. As and Zn had this tendency.

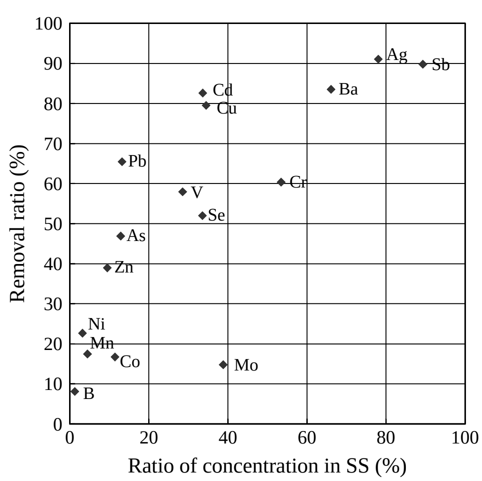

Figure 2 Effect of SS to removal ratio

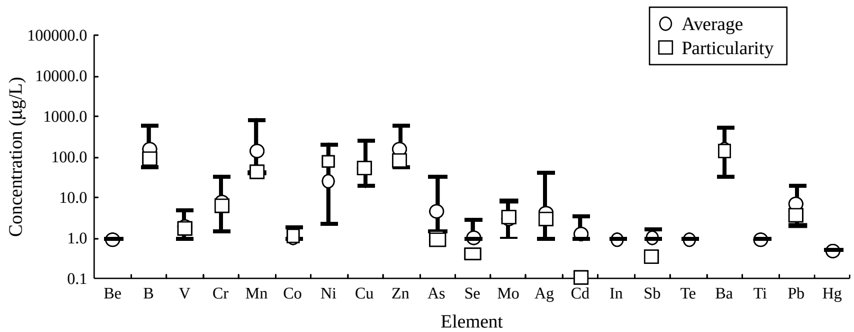

Figure 3 Heavy metal concentration of each element in wastewater

On the other hand, there was another type of element. It was circulated between wastewater treatment and sewage sludge treatment in the WWTP. Figure 8 shows the balance of Se. Approximately 40% of its element was returned to wastewater treatment from the recycle flow of incinerator. The main part of inflow was discharged with treated water. In the case of Cr, approximately 20% of its element was returned from the dewatering machine. The main part of inflow was discharged with sewage sludge. It was known that Se evaporates in an incinerator and transfers to a recycle flow during a gas clarification. When ashes are gathered by bag-filter at a relatively low temperature, Se is condensed into ashes again.

Recently, the Ministry of the Environment announced the results of PRTR. Figure 9 indicates the volume of discharge into the air or water course. Almost all of the volume was discharged into the water course. B, Mn and Zn accounted for a large part of the results. As stated above, B and Mn were classified into the first type in this study. Therefore, it was considered that the discharge of those heavy metals at the WWTP was typical behaviour. Figure 10 shows the volume of transfer to the sewerage system or the waste. Almost all of the volume was discharged to the waste. Zn, Mn and Cu accounted for a large part of the results. By means of the detailed survey at one WWTP, Zn, Mn and Cu were discharged with ashes of 48, 23 and 65% of their volume respectively.

Behaviour of heavy metals in the environment

Figure 11 shows the result of Mn. At the vertical line, the value of which the elution divided by the content is indicated. The value of slag was always lower than that of burning bricks. Figure 12 shows the result of As. In the first half of time, the value of slag was higher than that of burnt bricks. However, in the latter half of time, the value became small. In this study, the hazard rate of building material was much lower than 1.0 for

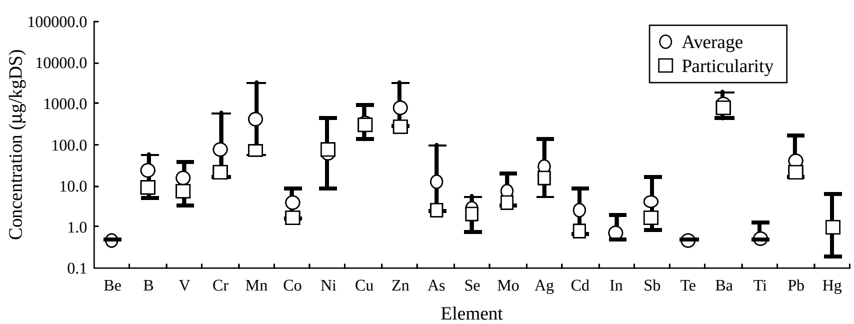

Figure 4 Heavy metal concentration of each element in de-watered sludge

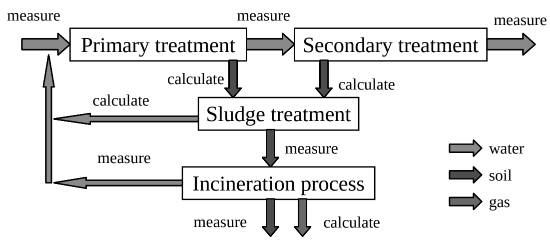

Figure 5 Balance of heavy metal

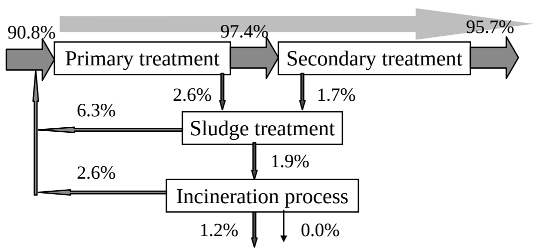

Figure 6 Balance of heavy metal B

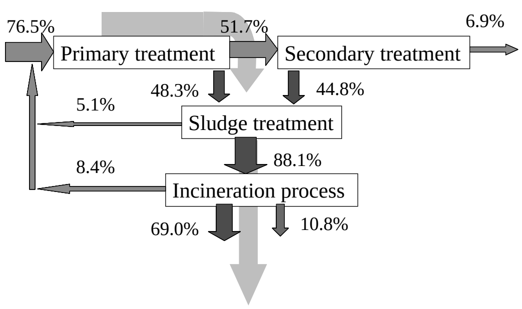

Figure 7 Balance of heavy metal Pb

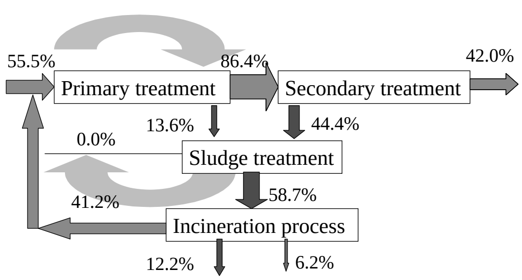

Figure 8 Balance of heavy metal Se

both burnt products and non-burnt products. In a real case, heavy metal is diluted or concentrated before a man takes it with drink or food. In addition, it is possible that a man will take other risks. So these conditions will be considered carefully for risk assessment. During the series of leaching tests, it was observed that the concentration was very small, but the ratio of increase remains at a constant value. Therefore, the content of heavy metal will also be important.

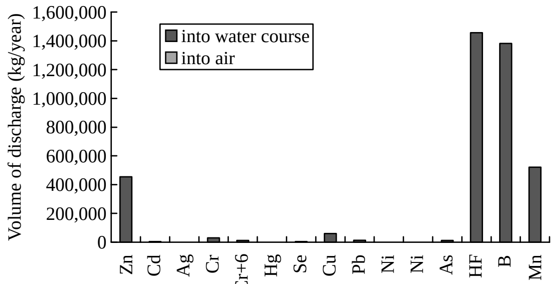

Figure 9 Discharge from WWTP in PRTR

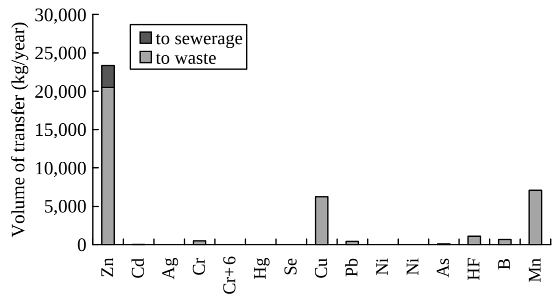

Figure 10 Transfer from WWTP in PRTR

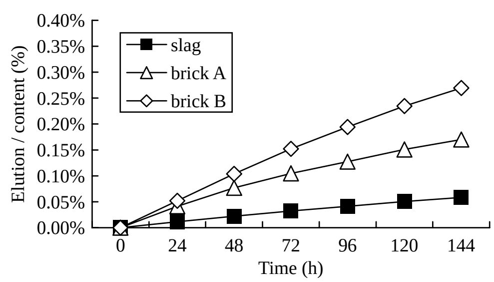

Figure 11 Behaviour of Mn in leachate

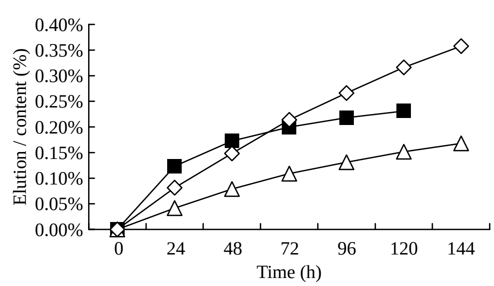

Figure 12 Behaviour of As in leachate

Recently, new standards for building material were established by the Ministry of Economy and Industry. The slags as aggregate for road construction and aggregate of concrete were on the list. The committee thought that the safety evaluation was one of the most important issues for establishing the new standards from the viewpoint of quality control. Regarding the size of samples for leaching test, it was considered that an original size would be available instead of a crushed sample. In addition, an extracting test by acid was accepted instead of a content test.

For promoting the utilisation of re-products, the products should be recycled in real condition. After that, the physical characteristics and the safety will be evaluated from the viewpoint of long-term durability. At the same time, both producers and users should discuss new standards for re-products and the assessment methods. After that, suitable leaching test methods will be established considering the actual condition.

Conclusions

There were some heavy metals which were detected not in wastewater but in de-watered sludge. As a result, those heavy metals were concentrated into de-watered sludge. There was a tendency that the heavy metals in SS were easily removed by biological treatment. The larger the heavy metals concentration in SS, the larger the removal ratio became.

By means of the detailed survey at one WWTP, 60–80% of some heavy metals, such as B, Mn, Co, Ni and Mo, were discharged with treated water. According to the results of PRTR, Zn, B and Mn accounted for a large part of the discharge into the water course.

During the series of leaching tests for building materials, it was observed that the concentration of heavy metals was very small, but the ratio of increase remains at a constant value. Therefore, it was considered that the acid extractable contents of heavy metal would be important.

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