

Effects of colloidal particles on the results and reproducibility of batch leaching tests for heavy metal-contaminated soil

Tetsuo Yasutaka^{a,*}, Yukari Imoto^a, Akihiko Kurosawa^a, Masayuki Someya^b,
Kazuo Higashino^b, Ute Kalbe^c, Hirofumi Sakanakura^d

^a National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

^b Tokyo Metropolitan Research Institute for Environmental Protection, Tokyo, Japan

^c Federal Institute for Materials Research and Testing (BAM), Berlin, Germany

^d National Institute for Environmental Studies (NIES), Ibaraki, Japan

Received 31 December 2016; received in revised form 23 May 2017; accepted 1 July 2017

Available online 9 October 2017

Abstract

A simple batch test leaching procedure is used in many countries, as a compliance test, to evaluate the leaching of mainly inorganic substances from soil. However, agitating certain types of soil and then passing the solution through a membrane filter with 0.45- μm pores yields filtrates that have been colored by the colloidal particles. These colloids might affect the results of the inorganic substances obtained in the batch tests. In this study, we evaluated the effects of colloidal particles on the results and the reproducibility of batch tests on contaminated soil using different agitation methods and membrane filters with different pore sizes. The leaching behaviors of As, Pb, Se, F and Cl from three types of soil were studied. The As and Pb concentrations in the leachates of some types of soil were clearly affected by the amount of colloidal particles with a diameter of 0.10–0.45 μm and by the agitation method used. This was probably because As and Pb were present mainly in the particulate form in the leachate that had been passed through a membrane filter with 0.45- μm pores. This is not the case for every type of soil. The results of batch leaching tests showed that not only dissolved but also colloidal forms with a diameter of 0.10–0.45 μm might be included and that the existence of colloidal particles in the leachate decreases the batch leaching test reproducibility.

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1. Introduction

To evaluate the risk of contaminated soil for groundwater contamination and human health, leaching tests are commonly conducted in many countries. Several leaching test methods have been developed including batch tests (International Standardization Organization, 2007a,b; German Standardization Organization, Deutsches Institut für Normung, 2015; European Committee for Standardisation, CEN Comité Européen de

Normalisation, 2002; United States Environmental Protection Agency, 2013b), up-flow column percolation tests (United States Environmental Protection Agency, 2013a; International Standardization Organization, 2007c; Naka et al., 2016) and sequential extraction methods (Arain et al., 2008; Kazi et al., 2005).

Batch tests are used as compliance tests for contaminated soil and waste in many countries, e.g., Japan (Ministry of Environment, 1991), Germany (German Standardization Organization, Deutsches Institut für Normung, 2015) and the United States (United States Environmental Protection Agency, 2013b), and in international standards (International Standardization Organization, 2007a,b) because such tests are simpler than

Peer review under responsibility of The Japanese Geotechnical Society.

* Corresponding author.

E-mail address: t.yasutaka@aist.go.jp (T. Yasutaka).

other leaching tests, such as up-flow column percolation tests, and they can be performed quickly. Therefore, batch test results need to be reproducible and reliable.

The basic procedure for a batch test performed on inorganic substances is quite simple. Firstly, a solid sample is placed in a suitable bottle and a leachant is added at a specified liquid-to-solid ratio. Secondly, the mixture is agitated for a specified period. Next, the solid material is allowed to settle and the mixture is centrifuged. Then, the liquid is decanted and passed through a membrane filter (MF) to obtain the leachate solution. Finally, the contaminants in the leachate are determined. Table 1 shows batch test procedures used by ISO that are widely applied in Europe, Germany, the United States and Japan. The basic test procedures are similar, but there are some differences, e.g., the type of leachant (demineralized water or 1 mmol CaCl₂ solution), the agitation method (rotation, roller table, horizontal or vertical shaking), the agitation intensity (5–200 rpm), the agitation time (6–72 h), the centrifuge rotation speed and centrifuge time (2000–3000g for 20 min for inorganic contaminants and 20,000–30,000g for 30 min for organic contaminants) and the filter pore size and material (membrane filter with 0.45 µm pores for inorganics and glass fiber filter with ≤0.7-µm pores for organics).

There are some important requirements for successful batch test methods. The first requirement is equilibrium; allowing equilibrium or semi-equilibrium conditions to be reached is the most important way of obtaining comparable batch leaching test results (International Standardization Organization, 2007a,b). Every test requires the assumption that equilibrium or semi-equilibrium is reached at the specified contact time. However, the equilibrium status that is reached will depend on the soil type and the species being investigated. In the ISO TS21268-1 procedure, it is stated that contact for 24 h is sufficient for equilibrium to be reached and that 6 h may be sufficient in the following specific cases when “it can be demonstrated that equilibrium or semi-equilibrium is reached or, for quality control purposes, a quick turn-around time is required” (International Standardization Organization, 2007a).

The second requirement is the removal of suspended matter and colloidal particles. It is well known that organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) and PCBs, are strongly adsorbed into colloidal particles, such as organic matter and clay particles (Jacobsen et al., 1998; Prechtel et al., 2002; Massoudieh and Ginn, 2007). To avoid or reduce the effect of organic contaminants adsorbed into colloidal particles, the removal of the colloidal particles is important. In the procedures used in Germany and the ISO TS 21268-2 methods, the supernatant after agitation was centrifuged at 20,000–30,000g for 30 min to remove the colloidal particles without 0.45-µm MF filtration for organic substances. In the German standard, it is specified that the turbidity of the leachate must remain below 20 formazin nephelometric units (International Standardization Organization, 2007a,

German Standardization Organization, Deutsches Institut für Normung, 2015).

Otherwise, little attention is generally paid to the colloidal particles for batch tests for inorganic substances, because the leachate is usually passed through a 0.45-µm MF (see Table 1). However, indirect evidence of the presence of colloids in leachates passed through 0.45-µm MFs and a correlation between colloid concentrations and the concentrations of some inorganic substances has been found in a small number of studies. Bergendahl and Grasso (1998) measured the amounts of particles with diameters less than 1 µm in leachates produced using different agitation times and found that the concentrations of colloids with diameters of 0.72 and 0.83 µm and the total surface area of colloids in the leachate increased as the agitation time increased. Dalgren et al. (2011) found higher Cu, Pb and Zn concentrations in unfiltered column leachate samples than in remediated soil samples that had been passed through a 0.45-µm MF.

The above-mentioned studies indicate that the results of batch leaching tests for inorganic substances, particularly inorganic substances that tend to be adsorbed by soil and colloidal particles with high distribution coefficients (such as Pb) by the surface charge of soil and colloidal particles, might be affected by colloidal particles with diameters less than 0.45 µm. Bergendahl and Grasso (1998) did not investigate the influence of agitation on the relationship between the amount of colloids in the leachate and the heavy metal concentrations, but they did find colloids in leachates that had been passed through 0.45-µm MFs under certain conditions.

Batch tests are performed to determine the concentrations of substances of interest that are dissolved from contaminated soil. The results of the above studies indicate that the measured concentrations of inorganic substances by batch tests might include not only dissolved inorganic substances, but also colloid-adsorbed forms of these substances if the filtered leachates include colloidal particles. Furthermore, if the total amount of colloids in a filtered leachate increases as the agitation time is increased, as described by Bergendahl and Grasso (1998), the agitation conditions might affect the reproducibility of the results of batch tests on inorganic substances.

This study was performed with the aim of evaluating the effects of colloidal particles on the results of batch leaching tests on soil contaminated with inorganic substances when different agitation methods and MFs with different pore sizes were applied. Five inorganic substances were evaluated; they were classified into three groups, namely, (1) Pb, which has high adsorption potential because of its positive charge, (2) Se, Cl and Sr, which have low adsorption potential because of their negative charge and (3) As, where the adsorption potential changes according to the soil-water conditions and the form of As used. Five agitation methods and two types of MF (with 0.45- and 0.10-µm pores) were tested using three types of soil. The concentrations of five inorganic substances and the turbidity

Table 1
Batch test procedures used in different countries.

Test name	ISO TS 21268-1 (07-2007)	ISO TS 21268-2 (07-2007)	DIN 19529 (12-2015)	US EPA method 1313	Japanese notification no. 46
Particle size	<4 mm	<4 mm	<32 mm	<5 mm	<2 mm
Scope	Soil, soil-related material	Soil, soil-related material	Soil, soil-related material, waste	Solid material (industrial waste, soil, sludge, combustion residue, sediment, stabilized material, construction material, and mining waste)	Soil
Substances to be determined	Inorganics and non-volatile organics	Inorganics and non-volatile organics	Inorganics and non-volatile organics	Inorganic constituents, semi-volatile organic constituents, and non-volatile organic constituents	Inorganics and organics
Leachant	0.001 mol/L CaCl ₂ or demineralized water	0.001 mol/L CaCl ₂ or demineralized water	Demineralized water	Interference-free water or 2.0 N HNO ₃ or 1.0 N KOH	Demineralized water
Liquid/solid ratio (L/kg)	2 ± 0.04	10 ± 0.2	2 ± 0.05	10 ± 0.05	10
Agitation	24 ± 0.5 h End-over-end rotation at 5–10 rpm or roller table at 10 rpm	24 ± 0.5 h End-over-end rotation at 5–10 rpm or roller table at 10 rpm	24 ± 0.5 h End-over-end rotation at 5–10 rpm	24 ± 2 h (<0.3 mm), 48 ± 2 h (<2.0 mm), 72 ± 2 h (<5 mm) End-over-end rotation at 28 ± 2 rpm	6 h Horizontal or vertical shaking at 200 rpm
Temperature	20 ± 5 °C	20 ± 5 °C	20 ± 2 °C	20 ± 2 °C	
Liquid/solid separation	Settling 15 ± 5 min, centrifugation at 2000–3000g for 20 min using a glass bottle (screw cap, Teflon insert), vacuum or pressure filtration (centrifugation at 10,000–20,000g may be used)	Settling 15 ± 5 min, centrifugation at 2000–3000g for 20 min using a glass bottle (screw cap, Teflon insert), vacuum or pressure filtration (centrifugation at 10,000–20,000g may be used)	Settling 15 min, centrifugation at 20000g for 30 min, until turbidity <20 formazin nephelometric units, using an appropriate bottle (less intense centrifugation with a longer duration is possible e.g., 2000g and 300 min), vacuum or pressure filtration. If only inorganics are measured, only membrane filtration can be used at the stipulated volume/filter area and filtration speed	Standing for 15 ± 5 min, centrifugation at 4000 ± 100 rpm for 10 ± 2 min	Centrifugation at 3000 rpm for 20 min
Filter	Membrane filter with 0.45-µm pores	Membrane filter with 0.45-µm pores	Membrane filter with 0.45-µm pores for inorganics. Glass fiber filter with ≤0.7-µm pores for organics	Membrane filter with 0.45-µm pores	Membrane filter with 0.45-µm pores (only for inorganics)

(used to indicate the amount of colloidal particles) in the leachates were measured.

2. Materials and methods

2.1. Materials

Three types of contaminated soil, each with different characteristics, were used (the three soil types are hereafter called soils A, B and C). A different amount of particulate matter passed through 0.45- μm MFs and into the eluate with each type of soil. Soil samples were air-dried for 2–3 days and sieved to <2 mm prior to use. The physical and chemical characteristics of the soils are shown in Table 2. The contaminants in the soil samples had anthropogenic origins. Loss on ignition was determined using the JIS A 1226 method (Japanese Industrial Standard Association, 2000), particle densities were determined using the JIS 1202 method (Japanese Industrial Standard Association, 2009a) and particle size distributions were determined using the JIS A 1204 method (Japanese Industrial Standard Association, 2009b). The pH and electrical conductivity (EC) of each soil sample were measured by mixing an aliquot of the soil with water at a soil-to-water ratio of 1:10 and then using a portable pH and EC meter (DKK-TOA, Tokyo, Japan). Mineralogical compositions and chemical compositions were measured by X-ray diffraction (Miniflex II, Rigaku Corporation, Tokyo, Japan) and X-ray Fluorescence (EDXL300, Rigaku Corporation, Tokyo, Japan). The methods used to make these physical and chemical measurements are described in detail elsewhere (Naka et al., 2016). About 5 kg of each soil were prepared, and the sample was coned and quartered at least

three times to sub-divide each soil sample into smaller subsamples.

2.2. Method

An aliquot (10 g) of an air-dried soil sample with particles <2 mm in diameter was placed in a 250-mL plastic polyethylene bottle (As One, Japan), and demineralized water at pH 5.8–6.3 was added to give a liquid-to-solid ratio of 10 L/kg. The bottle was then shaken using one of the five agitation methods, as specified in Table 3. The agitation methods were horizontal shaking at 200 rpm (from Japanese test no. 46 (Ministry of Environment, 1991)), vertical shaking at 200 rpm (also from Japanese test no. 46), horizontal shaking at 100 rpm, horizontal shaking at 50 rpm and rotation at 5 rpm (from ISO-TS21268-2). Agitation was achieved using a TS-20 horizontal shaker (Taitec, Japan), a Strong Shaker SR-2DW vertical shaker (Taitec, Japan) and a YGG rotating shaker (Yayoi, Japan). Each test was performed in duplicate.

After a sample had been shaken, the mixture was allowed to settle for 15 min and then centrifuged at 1700g (3000 rpm) for 20 min. Next, the supernatant was passed through a 0.45- μm MF (A045A047A; Advantec Toyo, Japan) or a 0.10- μm MF (A010A047A; Advantec Toyo, Japan) and the filtered leachate was analyzed. The turbidity of each filtered leachate was then determined by performing light scattering measurements using a Turb 550 instrument (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany).

The As, Pb and Se concentrations in the filtered leachate samples were measured using an ICP-MS 8800 Series inductively coupled plasma mass spectrometer

Table 2
Properties of the soils used in the study.

Parameter	Units	Soil A	Soil B	Soil C
Maximum particle size	mm	2	2	2
pH	–	7.74	8.96	8.95
Water content	% by mass	1.4	4.2	3.6
Loss on ignition	% by mass	6.8	6.0	9.6
Electrical conductivity	$\mu\text{S}/\text{m}$	9.6	101	129
Particle size distribution	% by mass			
2–0.075 mm		75.6	41.8	47.2
0.075–0.005 mm		10.4	39.0	30.6
0.005–0.001 mm		2.6	7.8	10.9
<0.001 mm		11.4	11.4	11.3
Mineralogical compositions	–	Feldspar >>Quartz	Feldspar > Quartz	Quartz \approx Kaolinite
Chemical compositions	mol% by mass			
Mg		0.5	0.7	0.7
Al		5.6	6.1	6.1
Si		18.7	18.0	14.3
S		0.6	0.2	N.D.
K		0.5	0.6	0.5
Ca		1.0	1.5	2.6
Ti		0.2	N.D.	0.2
Fe		3.8	1.5	1.6
Pb		N.D.	N.D.	0.1
Na		1.5	1.9	1.1

Table 3
Experimental conditions used for the five experimental cases.

	Case 1		Case 2		Case 3		Case 4		Case 5	
Agitation method	Shaking		Shaking		Shaking		Shaking		Rotation	
Agitation direction	Horizontal		Vertical		Horizontal		Horizontal		Rotation	
Bottle direction	Horizontal		Vertical		Horizontal		Horizontal		Horizontal	
Revolutions per minute	200		200		100		50		5	
Agitation time	6 h		6 h		6 h		6 h		24 h	
Filter pore diameter (μm)	0.45	0.10	0.45	0.10	0.45	0.10	0.45	0.10	0.45	0.10
Standard	No. 46 ^a		No. 46 ^a		–		–		ISO ^b	

^a No. 46: Notification no. 46 published by the Japanese Environment Ministry.

^b ISO: ISO-TS 21286-2 procedure.

(Agilent Technologies, USA), and the Cl^- and F^- concentrations were measured using a Dionex ICS-2000 ion chromatograph (Thermo Scientific, USA).

To derive a calibration curve between the concentration of colloidal particles and the turbidity, additional experiments were conducted. The soil samples were agitated under the following conditions: 2, 3, 4.5 and 6 h by horizontal shaking at 200 rpm and 6 h by vertical shaking. After agitation, the samples were centrifuged as described above. The supernatant was then passed through a 0.45- μm MF and the turbidity of the filtrate was measured. The obtained filtrate was then passed through a 0.10- μm MF and the weight of the colloidal particles on the 0.10- μm MF was measured.

3. Results

3.1. Turbidity

The turbidities of the soil extracts with different agitation methods and MF pore sizes are shown in Fig. 1. The highest turbidities of the 40–80 nephelometric turbidity units (NTU) were found for the 0.45- μm filtrates of the soil A and B extracts that had been shaken horizontally at 200 rpm. The turbidities of the 0.45- μm filtrates of the extracts produced using the other agitation conditions decreased in the order of 100 rpm horizontal

shaking > 5 rpm rotation > 50 rpm horizontal shaking. The lowest turbidity, approximately 1 NTU, was found for the samples that had been shaken horizontally at 50 rpm. The 0.10- μm filtrates of the soil A and B extracts had turbidities of approximately 0.1 NTU and were colorless and transparent. Images of the 0.45- and 0.10- μm filtrates of the soil A extracts, produced by shaking horizontally at 200 rpm, are shown in Photograph 1. The 0.45- and 0.10- μm filtrates of the soil C extracts, produced using all of the agitation conditions, had turbidities around or below 0.1 NTU.

These results indicate that the amount of particulate matter in a 0.45- μm filtrate depended on the agitation method (shaking or rotation), the agitation speed and the shaking direction (horizontal or vertical), and that most of the colloidal particles in the 0.45- μm filtrates had diameters of 0.10–0.45 μm . The 0.45- μm filtrates of the soil A and B extracts after horizontal shaking at 50 rpm had turbidities below 1 NTU. This might indicate that the original soil A and B samples contained only small amounts of suspended particles with diameters less than 0.45 μm and that the relatively large amounts of suspended particles in the filtrates after the other agitation methods had been used were caused by the agitation procedures themselves.

The calibration curve between the concentration of colloidal particles and the turbidity for soils A and B is shown in Fig. 2. As can be seen, the concentration of

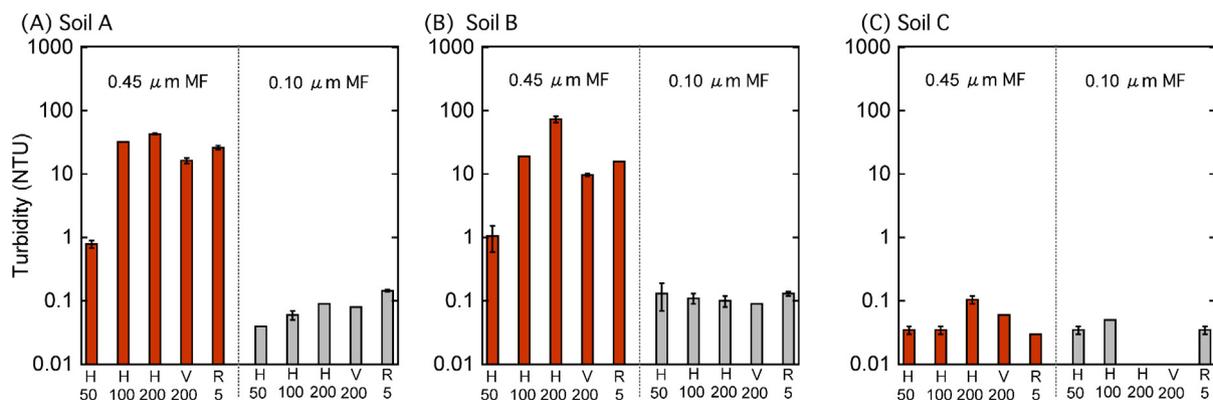
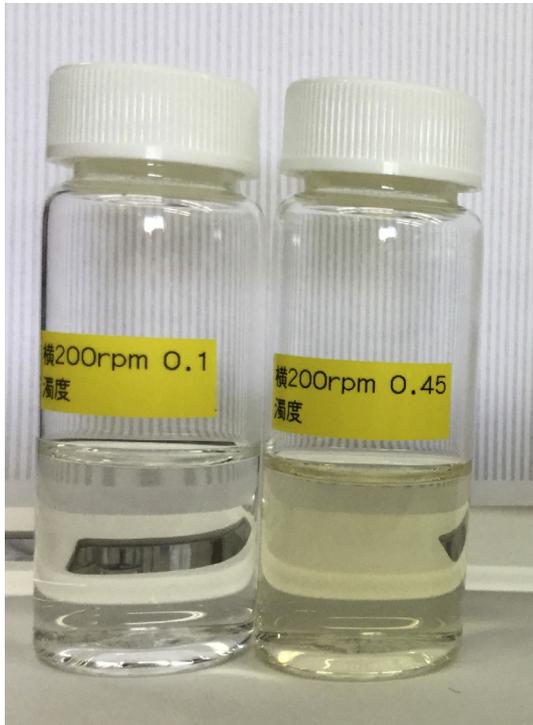


Fig. 1. Turbidities of the extracts of soils A, B and C when different agitation methods and membrane filter (MF) pore diameters were used. *x*-axis labels H, V and R mean horizontal shaking, vertical shaking and rotation, respectively, and the numbers below them indicate the speed of the shaking/rotation in rpm.



Photograph 1. Images of soil A extracts produced by shaking horizontally at 200 rpm and passing the extracts through (left) a 0.10- μm membrane filter and (right) a 0.45- μm membrane filter.

colloidal particles correlated with the turbidity and each soil had a different relationship between the concentration of colloidal particles and the turbidity in the 0.45- μm MF filtrate. For an accurate discussion, the concentration of colloidal particles in the filtrate is a much better indicator than turbidity. However, the obtained detection limit for the concentration of colloidal particles (7 mg/L, which is 10–30 NTU conversion into turbidity) is much higher than

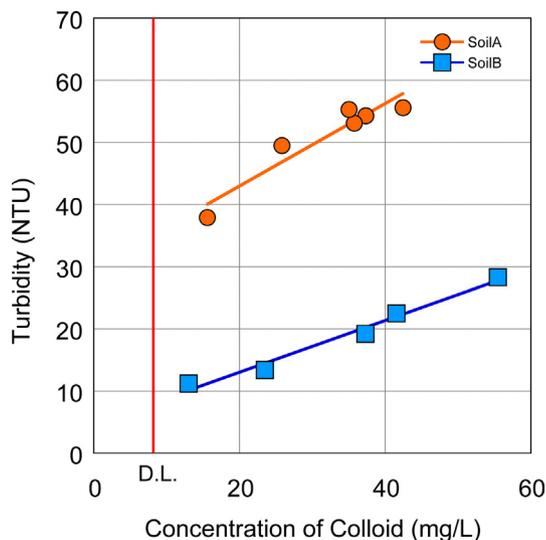


Fig. 2. Relationships between turbidities and concentrations of colloid particles with diameter 0.10–0.45 μm in the leachates filtrated 0.45- μm membrane filter for soils A and B.

that of turbidity (0.01 NTU). For this reason, the turbidity was used as the index of the amount of colloidal particles.

3.2. Lead

The Pb concentrations found when different agitation methods and MF pore sizes were used are shown in Fig. 3A–C. The highest Pb concentrations in the 0.45- μm filtrates of soils A and B were 0.02–0.03 mg/L, observed in extracts that had been shaken horizontally at 200 rpm. The concentrations decreased in the order 200 rpm horizontal shaking > 100 rpm horizontal shaking > 5 rpm rotation > vertical shaking 200 rpm. The Pb concentrations in the 0.10- μm filtrates for all of the soil A and B extracts and in the 0.45- μm filtrates after horizontal agitation at 50 rpm were the lowest, with values of 0.001–0.003 mg/L.

The Pb concentrations and turbidities of the soil A and B extracts were clearly correlated when the turbidity exceeded 1 NTU (Fig. 4A–C). The highest Pb concentration (0.03 mg/L) was found in the 0.45- μm filtrates of the extracts that had been shaken horizontally at 200 rpm, which also had high turbidities. The Pb concentration clearly decreased as the turbidity decreased, but the Pb concentration remained almost constant at around 0.001 mg/L when the turbidity was less than 1 NTU. This suggests that the Pb in the soil A and B extracts was mainly associated with the colloidal particles. These results show that the agitation method and the MF pore size will strongly affect the amounts of particles with diameters of 0.10–0.45 μm and the Pb concentrations in extracts of some types of soil.

The soil C extracts generally had low turbidities that were much lower than those in soils A and B, but had rather high Pb concentrations (up to 0.04 mg/L; Fig. 3C) when compared with soils A and B. However, there was no clear relationship between the turbidity and the Pb concentration for soil C (Fig. 4C). The Pb concentrations varied little when the different agitation methods and MF pore sizes were used. These findings suggest that Pb was present in dissolved forms in the soil C filtrates.

3.3. Selenium, chlorine and fluorine

The Se concentrations found when different agitation methods and MF pore sizes were used are shown in Fig. 3D–F. The Se concentrations were almost the same in the 0.45- and 0.10- μm filtrates of extracts produced using the same agitation method. The Se concentrations in the 0.45- and 0.10- μm filtrates of the soil A and B extracts increased as the agitation speed increased. In particular, the Se concentrations in the 0.45- and 0.10- μm filtrates were 1.5 times higher after horizontal shaking at 200 rpm than after horizontal shaking at 50 rpm.

The correlations between the Se concentrations and the turbidities are shown in Fig. 4D–F. No clear correlation was found between the turbidity and the Se concentration for any of the soil samples.

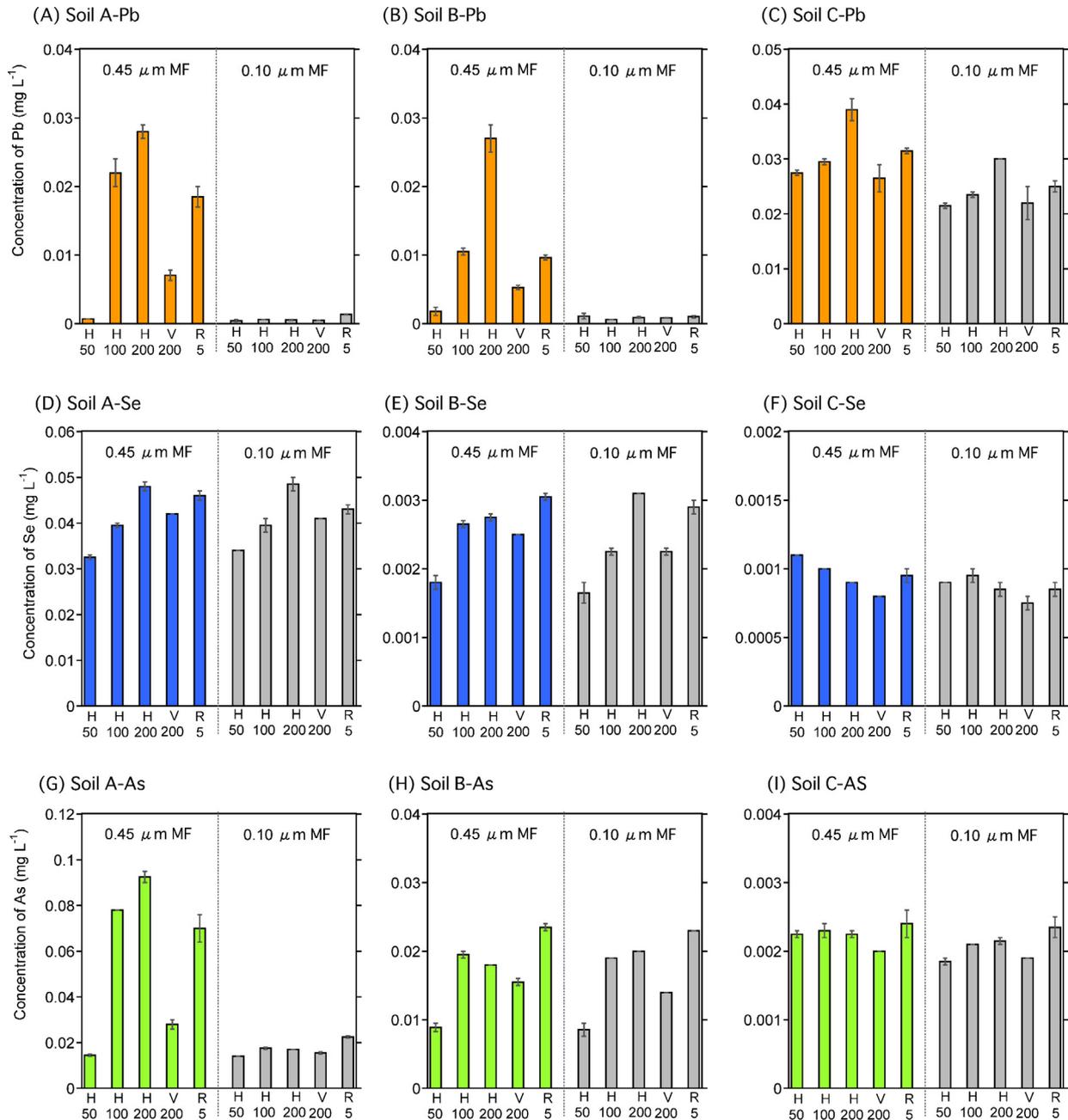


Fig. 3. Pb, Se and As concentrations in the extracts of soils A, B, and C when different agitation methods and membrane filter (MF) pore diameters were used. x-axis labels H, V and R mean horizontal shaking, vertical shaking and rotation, respectively, and the numbers below them indicate the speed of the shaking/rotation in rpm.

These results indicate that (1) Se was present in the extracts in dissolved forms and minimal amounts of Se were adsorbed into the suspended particulate matter and that (2) the dissolved Se concentration increased as the agitation intensity increased. Increasing the agitation intensity will increase the soil particle surface area because of the particles becoming abraded, and this could cause more Se to be leached from the soil.

The Cl and F results (shown in Fig. 5) were similar to the Se results. This suggests that Cl and F were present mainly in dissolved forms in all of the filtrates, and

therefore, that the turbidity did not affect the Cl and F concentrations.

3.4. Arsenic

The As concentrations are shown in Fig. 3G–I, and the correlations between the As concentrations and the turbidities of the filtrates are shown in Fig. 4G–I.

For soil A, the As concentration was higher in the 0.45- μm filtrate than in the 0.10- μm filtrate when the agitation conditions were the same except for when the sample

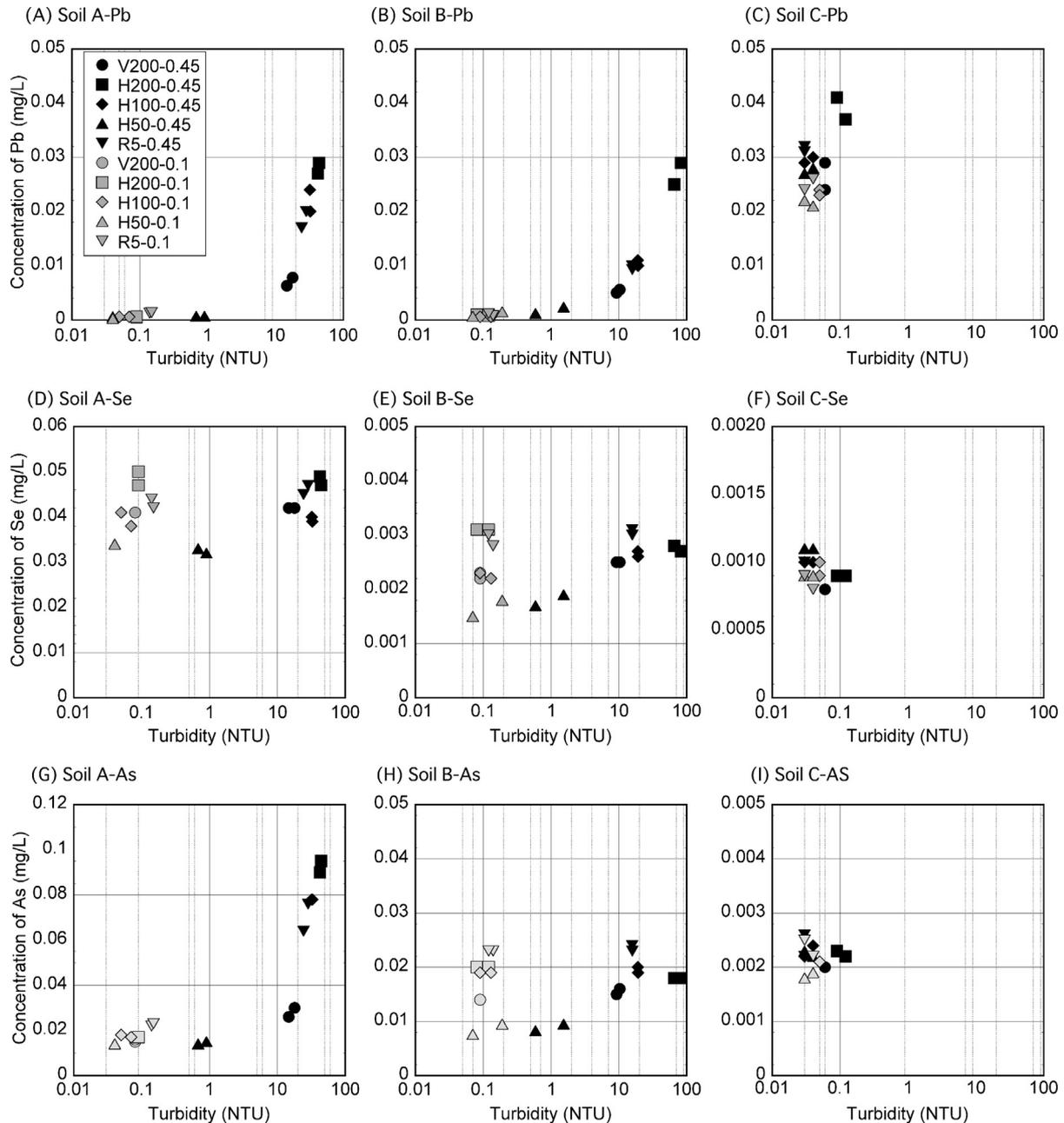


Fig. 4. Correlations between the Pb, Se and As concentrations in and turbidities of the extracts of soils A, B and C when different agitation methods and membrane filter pore diameters were used. In the legend, H, V and R mean horizontal shaking, vertical shaking and rotation, respectively, the number following each letter indicates the speed of the shaking/rotation in rpm and the number after the hyphen indicates the membrane filter pore size (in μm).

had been shaken horizontally at 50 rpm (Fig. 3G). It is clear that the turbidity and As concentration were positively correlated when the turbidity was higher than 1 NTU (Fig. 4G), similar to the results for the Pb in soils A and B. The highest As concentration (0.10 mg/L) was found in the 0.45- μm filtrate after horizontal shaking at 200 rpm, which also had high turbidity. The 0.45- μm filtrate after horizontal shaking at 50 rpm and the 0.10- μm filtrates after all of the agitation methods had As concentrations of 0.015–0.020 mg/L regardless of the turbidity. These results suggest that (1) predominantly dissolved As was present in the extracts at concentrations of

0.015–0.020 mg/L and that (2) As in both dissolved and particulate forms was present in the 0.45- μm filtrates after horizontal shaking at 200 and 100 rpm, vertical shaking at 200 rpm and rotation at 5 rpm.

For soil B, the relationship between the As concentration and the turbidity was quite similar to the relationships between the Se concentration and the turbidity for soils A and B. The As concentrations in the 0.45- and 0.10- μm filtrates were almost the same when the same agitation method was used (Fig. 3H), and no clear correlation was found between the turbidity and the As concentration (Fig. 4H). However, the As concentration in the 0.45- μm

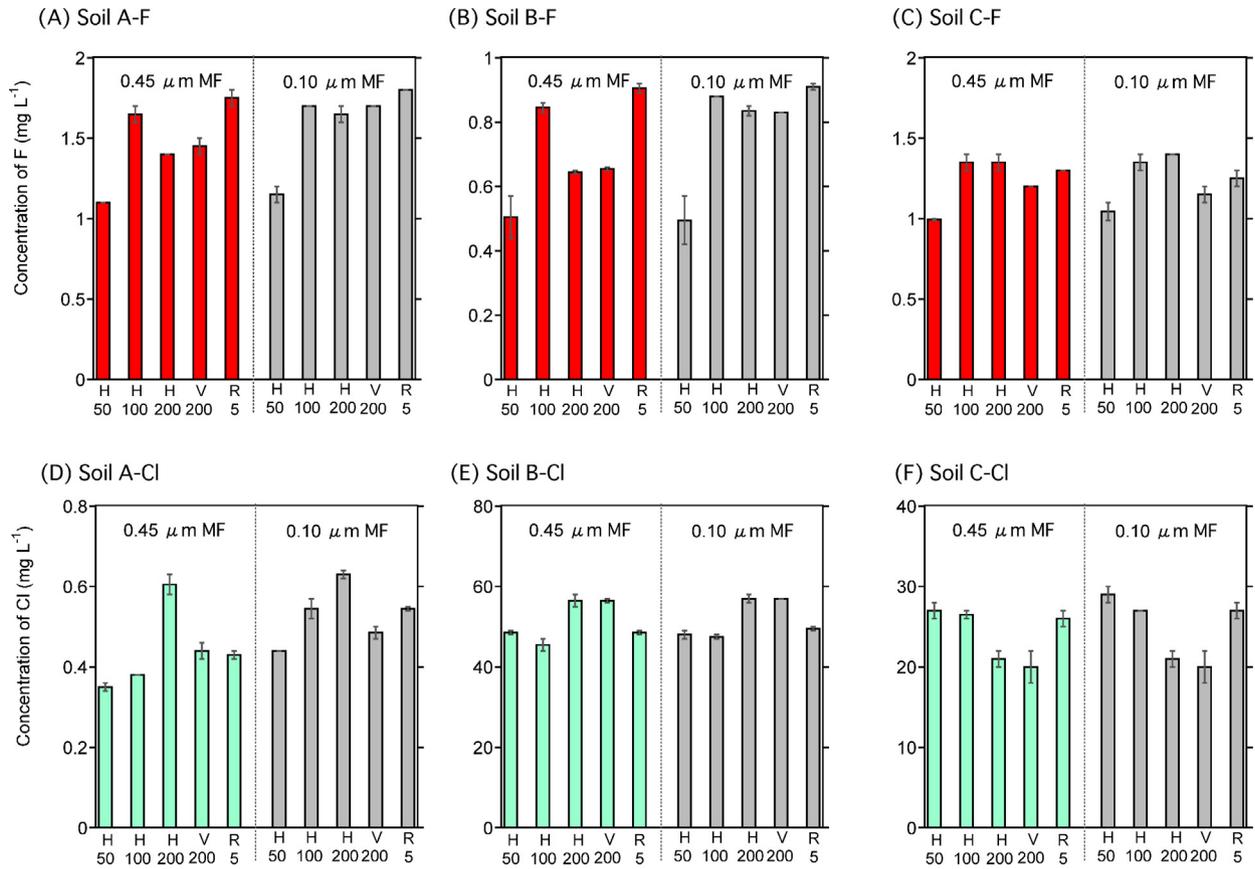


Fig. 5. F and Cl concentrations in the extracts of soils A, B and C when different agitation methods and membrane filter (MF) pore diameters were used. x-axis labels H, V and R mean horizontal shaking, vertical shaking and rotation, respectively, and the numbers below them indicate the speed of the shaking/rotation in rpm.

filtrates increased as the agitation intensity increased. The same trend was found for the 0.10- μm filtrates as was found for the Se in soils A and B. These results suggest that As was present in dissolved forms in soil B. No clear relationship between turbidity and the As concentration was found for soil C, as was the case for the other analytes.

4. Discussion

4.1. Mechanism of increase in amounts of Pb and As bonded colloidal particles

The effects of colloidal particles on the results of batch leaching tests on contaminated soil, using different agitation methods and MF pore sizes, were evaluated. The results suggest that, for some types of soil, the colloidal particles, including particulate-bound As (soil A) and Pb (soil B), strongly affected the batch test results. It was found that this was mainly caused by the colloidal particles with diameters 0.10–0.45 μm being generated during the agitation process and the colloidal particles adsorbing inorganic substances (such as As and Pb).

In an attempt to gain an understanding of the mechanism through which the Pb concentrations in the soil A and B extracts increased, the forms of Pb that were present

in the extracts are firstly discussed. There were some indications that Pb was associated with colloidal particles in the 0.45- μm filtrates. For soils A and B, the Pb concentrations and the turbidities were low for the 0.10- μm filtrates, but higher for the 0.45- μm filtrates (Fig. 4A and B). It is well known that Pb is strongly adsorbed into the negative surface of soil particles (Adhikari and Singh, 2003). The negative charge on the surface of soil particles increases with an increase in the specific surface area, and the adsorption capacity of colloidal particles is relatively high compared to that of larger soil particles such as sand. Furthermore, the results suggest that the Pb in the 0.45- μm filtrates of the soil A and B extracts was associated with the colloidal particles having diameters of 0.10–0.45 μm . The amounts of these particles increased as the agitation intensity and turbidity increased.

The second aspect to be discussed is the mechanism through which the amounts of colloidal particles in the soil extracts increased during the batch leaching tests. Colloidal particles are present in soil in several forms. Some colloidal particles are in pore water and are mobile, some are initially attached or adsorbed into soil grains, some are captured within the soil structure and some are present at the air–water interface (Massoudieh and Ginn, 2007). Those at the air–water interface can be ignored in relation

to the batch tests. Colloidal particles can become detached from soil grains and released from the soil structure during batch tests because of the soil structure collapsing with the agitation force. The degree to which colloids become detached from soil grains will depend on the chemical and physical characteristics of the colloids, the surfaces of the soil grains and the chemical characteristics of the solution (Ryan and Elimelech, 1996).

For soils A and B, the 0.45- μm filtrates after horizontal shaking at 50 rpm had low turbidities (less than 1 NTU), while the 0.45- μm filtrates after the other agitation methods had higher turbidities (Fig. 1). These results seem to indicate that the original soil A and B samples contained only small amounts of colloidal substances with diameters less than 0.45 μm and that most of the particles in the 0.45- μm filtrates were generated during agitation. Bergendahl and Grasso (1998) also found that the amount of colloidal particles increased as the agitation intensity increased. It is concluded here that agitation causes the soil structure to collapse or the colloids to become detached from soil grains because of the mechanical energy applied during agitation, particularly at high agitation intensities.

The reason for the small amounts of colloidal particles in the 0.45- μm filtrates of the soil C extracts was investigated. The soil particle size distributions (Table 2) showed that the amount of particles that had diameters of <1 μm were similar in soils A, B and C. However, large amounts of colloidal particles were found in the 0.45- μm filtrates of soils A and B, but only small amounts of colloidal particles were found in that of soil C.

The ionic strength of the soil, represented by the EC, is also an important parameter for colloid formation. It is well known that high ionic strength causes the agglomeration of colloidal particles. From this viewpoint, reasonable results were obtained from soil A (low EC value and high turbidity) and Soil C (high EC value and low turbidity). However, the eluate of soil B had a high EC value, but high turbidity. Another potential reason for the difference in the results is the organic matter. Soil C contained somewhat more organic matter (loss on ignition) than soils A and B, and the organic matter might have been a source of colloids. From our results, it is not clear why only small amounts of colloidal particles were released by soil C, and thus, further research is needed.

The present results indicate that if a batch test is performed to evaluate the release of dissolved inorganic substances, the analyst should pay a great deal of attention to the effects of the colloidal particles having diameters between 0.10–0.45 μm in the filtrate of leachate filtered through a 0.45- μm MF and take measures to decrease the influence of the turbidity. Examples of measures that can be taken include (1) using a high centrifugation speed or a long centrifugation time, such as specified in the German standard mentioned earlier (German Standardization Organization, Deutsches Institut für Normung, 2015), and (2) using a 0.10- μm MF to remove the colloidal particles having diameters between 0.10 and 0.45 μm .

4.2. Mechanism of increased amounts of dissolved inorganic substances during batch tests

The Cl, F and Se in all of the soils (Fig. 3D–F and 5), the As in soils B and C (Fig. 3H–I) and the Pb in soil C (Fig. 3C) were mainly in the dissolved form, as shown by the concentrations in the 0.10- μm filtrates being in the same order of magnitude as the concentrations in the 0.45- μm filtrates when the same agitation conditions were used. Their concentrations were not affected by the turbidity (Fig. 4C–F and H–I).

The amounts of the analytes in dissolved forms in the extracts varied depending on the agitation conditions used (i.e., the method, the direction and the intensity). For example, the Se concentrations in the soil A and B filtrates (0.10 and 0.45 μm ; Fig. 3D–F) after horizontal shaking at 200 rpm were 1.5 times higher than the Se concentrations after horizontal shaking at 50 rpm. These results indicate that the dissolved Se concentrations increased as the agitation intensity increased. The concentrations of the dissolved inorganic substances could have been different after different agitation conditions were used because (1) equilibrium or semi-equilibrium was not reached when low agitation intensities were used, because the water and soil were insufficiently mixed, or (2) the soil particle surface area increased because of abrasion at high agitation intensities. Bergendahl and Grasso (1998) found that the surface areas of the colloidal particles in filtrates increased as the agitation intensity increased, and this supports the second reason given above. The authors concluded that different agitation intensities and methods might lead to variable concentrations of dissolved inorganic substances for some types of soil.

4.3. Effects of colloidal particles on reproducibility of batch leaching test results

Batch tests are used as compliance tests in several countries, and the results are compared with threshold values to assess the environmental impacts. The results of batch tests used in this way need to be very reproducible and reliable for all types of soil. The results of this study and other studies indicate that the reproducibility of a batch test will be affected by the amount of colloidal particles in the filtrate and that the amount of colloidal particles present will be controlled not only by the soil type, but also by the agitation method (i.e., agitation time, frequency, method and direction). Good reproducibility requires the same amount of colloid-facilitated inorganic substances in the eluate obtained from batch tests using the same soil.

This could be achieved in several ways. As stated in Section 4.1, one option is to use a high centrifugation speed or a long centrifugation time, as stipulated in the German batch test standard (German Standardization Organization, Deutsches Institut für Normung, 2015). Passing each extract through a 0.10- μm MF is a good option because colloidal particles with diameters of 0.10–0.45 μm

will be removed. However, if the analyst wishes to include inorganic substances associated with particulate matter with diameters of less than 0.45 μm , to comply with the usual practice, the agitation method, frequency, time and direction need to be stipulated in detail in order to yield reproducible batch test results.

The same applies to dissolved inorganic substances, such as Cl, F and Se. The present results indicate that certain agitation conditions increased the concentrations of dissolved analytes, but that the agitation conditions influenced the Cl, F and Se concentrations less than the mobilization of the particulate-bound As and Pb.

5. Conclusions

In the present study, the effects of colloidal particles on the results of batch leaching tests have been evaluated using soil contaminated with inorganic substances. It was found that the Cl, F and Se concentrations were affected to some degree by the agitation conditions, but not by the amounts of colloidal particles that were mobilized (determined from the turbidity) because Cl, F and Se were mainly in dissolved forms. The As and Pb concentrations in the 0.45- μm filtrates of the extracts of some types of soil were affected by the presence of colloidal particles with diameters of 0.10–0.45 μm generated during agitation because some types of As and Pb have strong affinities for soil particulate matter. The amounts of colloidal particles in the 0.45- μm filtrates, and therefore, the As and Pb concentrations, increased as the agitation intensity increased. This was not the case for every type of soil, but the results of batch leaching tests might have included not only dissolved forms, but also colloidal forms, of As and Pb concentrations, and a decrease in the batch leaching test reproducibility. Therefore, the analyst must pay close attention to the amounts of colloidal particles in the 0.45- μm filtrates of batch test extracts by measuring the turbidities of such extracts.

Acknowledgments

This work was supported by JSPS KAKENHI, Grant number 15H02264, and AIST Intellectual Property and Standardization Promotion Division. We would like to thank the TIA Central Office, Open Research Facilities Station of AIST, for their technical assistance with the X-ray diffraction analysis.

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