



Column percolation test for contaminated soils: Key factors for standardization



Angelica Naka^a, Tetsuo Yasutaka^{b,*}, Hirofumi Sakanakura^a, Ute Kalbe^c, Yasutaka Watanabe^d, Seiji Inoba^d, Miyuki Takeo^e, Toru Inui^e, Takeshi Katsumi^e, Takuro Fujikawa^f, Kenichi Sato^f, Kazuo Higashino^g, Masayuki Someya^g

^a National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan

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

^c Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

^d Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko-shi, Chiba 270-1194, Japan

^e Kyoto University, Yoshida-honmachi, Sakyo, Kyoto 606-8501, Japan

^f Fukuoka University, 8-19-1 Nanakuma, Jonan, Fukuoka 814-0180, Japan

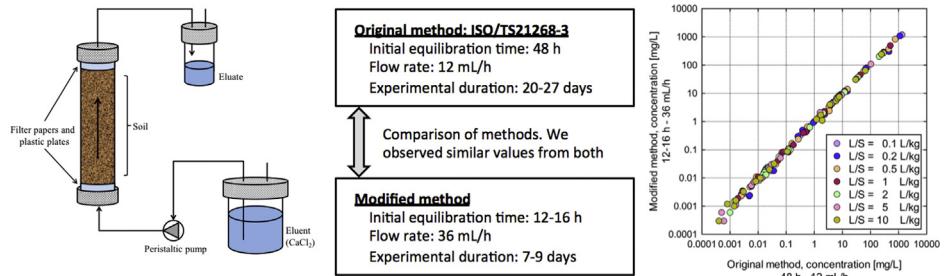
^g Tokyo Metropolitan Research Institute for Environmental Protection, 1-7-5 Shinsuna, Koto, Tokyo 136-0075, Japan

HIGHLIGHTS

- Ways to reduce the duration of column percolation tests specified in ISO/TS 21268-3 were proposed.
- Four equilibrium periods and two flow rates on four different soils were tested.
- The time to perform column percolation tests can be shortened from 20 to 30 days to 7–9 days.
- The recommended initial equilibrium period is 12–16 h, shorten from 48 h.
- The recommended flow rate is 36 mL/h which is three times that specified in ISO/TS 21268-3.

GRAPHICAL ABSTRACT

We evaluate the feasibility of decreasing testing time of up-flow column percolation



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ABSTRACT

Column percolation tests may be suitable for prediction of chemical leaching from soil and soil materials. However, compared with batch leaching tests, they are time-consuming. It is therefore important to investigate ways to shorten the tests without affecting the quality of results. In this study, we evaluate the feasibility of decreasing testing time by increasing flow rate and decreasing equilibration time compared to the conditions specified in ISO/TS 21268-3, with equilibration periods of 48 h and flow rate of 12 mL/h. We tested three equilibration periods (0, 12–16, and 48 h) and two flow rates (12 and 36 mL/h) on four different soils and compared the inorganic constituent releases. For soils A and D, we observed similar values for all conditions except for the 0 h–36 mL/h case. For soil B, we observed no appreciable differences between the tested conditions, while for soil C there were no consistent trends probably due to the difference in ongoing oxidation reactions between soil samples. These results suggest that column percolation tests can be shortened from 20 to 30 days to 7–9 days by decreasing the equilibration time to 12–16 h and increasing the flow rate to 36 mL/h for inorganic substances.

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* Corresponding author.

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

1. Introduction

Soil contamination can result from a number of different activities and events, including industrial, construction, and mining activities; natural disasters, such as tsunamis; and accidents, including nuclear plant accidents that may lead to radioactive contamination of soil. Contaminated soil materials pose major environmental and human health risks. As such, strategies for the remediation or disposal of soils should be carefully planned and managed.

Evaluation of the leaching behavior of contaminated soil is very important for an accurate assessment of the risk of contaminated soils transferring pollutants into seepage water, groundwater, or surface water. Several leaching methods have been developed and implemented into environmental regulations in many countries. These include batch tests [1–6], column tests [7–10], lysimeter tests [11–15], and sequential leaching tests [16–19]. These methods aim to determine the concentrations of chemicals expected in water that has come in contact with contaminated soil or other solid materials for a certain period of time [20].

Batch tests have been extensively used worldwide for compliance testing because their low costs, simple design, and low test duration (usually 24 h) make them convenient for routine testing. However, the disadvantage is that the information produced from the batch test is limited as it only provides a single result at one liquid-to-solid (L/S) ratio, which does not reflect real world conditions. Moreover, with certain type of soils, batch tests require additional effort for centrifugation, minimizing carry over, filtration and separation of suspended solid and water, managing formation of emulsions, etc. This may lead to a higher work load than expected and varying results depending on the experimental conditions before chemical analysis.

Column tests, on the other hand, resemble field conditions more closely and are suitable to assess the long-term release of chemical constituents from soil into water bodies. The column test's advantage over a batch test is that it allows for the observation of high initial concentrations of percolates at low L/S ratios (equilibrium concentrations) and the time-dependent release of chemicals, which is required for the prediction of leaching behavior under field conditions. However, column tests are more costly and time consuming, and more labor intensive compared with batch tests.

Internationally, several standards for column tests are available. In Table 1, we present the scope, apparatus, solid material, particle size, packing method, leachant, equilibration period after saturation, flow rate, and number of collected eluate fractions indicated by the technical specifications or standards of the following agencies: ISO/TS (2007), CEN (2004), NEN (2004), DIN (2009), USEPA (2013), Nordest (1995), ASTM (2001), and OECD (2004) [7–10,21–24]. The ISO-TC190 SC7 WG6, responsible for the development of leaching tests for soil and soil-like materials, has discussed upgrading the ISO/TS 21268-3 to a fully validated standard; Japanese experts are now undertaking that task. As presented in Table 1, column tests specified by ISO/TS 21268-3 require the collection of seven fractions in total, ranging from L/S ratios = 0.1 to 10 L/kg. At higher L/S ratios, the test takes 20–30 days, which is a long period of time, especially if applied to routine evaluations. Thus, there is an interest in shortening the experimental period. To achieve this, at least three possibilities can be considered: (a) increasing the flow rate; (b) decreasing the equilibration period after saturation; and (c) decreasing the height and the diameter of the column.

Focusing on the dimensions of the column, Kalbe et al. [25] and Lopez Meza et al. [26] conducted experiments using columns of different diameters and heights. For flow rates related to fixed contact times ranging from 2.5 to 36 h, they observed no appreciable differences in the leaching behavior of selected inorganic parameters from bottom ash and demolition waste. Contaminated soil was not

considered in that study. ISO/TS 21268-3 [7] states that the equilibration period after soil saturation should be at least 2 days (48 h) to allow equilibration of the system. The addition of this equilibration period to the time required to conduct the experiments further lengthens the total time investment required. There is one robustness validation study available [27] on the effect of flow rate, material grain size, and equilibration period within column tests following prCEN/TS 16637-3 [28] using granular construction products partly derived from waste (the initial draft of this standard, named with the working title TS-3, was very similar to ISO/TS 21268-3). The outcome of the study indicated that the equilibrium adjustment period after saturation can be reduced, and that the flow rate can be increased; both of these adjustments have now been implemented into the procedure [28].

Our objectives are (a) to evaluate the effect of equilibration period and flow rate on the release of hazardous substances, (b) to study the effect of equilibration period after saturation on the leaching of inorganic constituents (decreasing to 0, 12 or 16 h), and (c) to judge whether it is possible to shorten the column percolation experiment time by increasing the flow rate to 36 mL/h from 12 mL/h. If these changes are effective, we will propose that they be included in the upgrade of ISO/TS 21268-3 to a full ISO standard.

2. Materials and methods

2.1. Materials

We used four types of soils with different characteristics to perform the experiments; they are hereafter referred to as soils A, B, C, and D. Table 2 shows the physical and chemical characteristics of the four soils. Soils A and B were anthropogenically-contaminated soils, soil C was excavated from a depth of about 5–10 m and contained natural heavy metals and soil D was a naturally-contaminated soil. We measured the maximum particle size and moisture content by JIS A 1203 (2009) [29], the loss of ignition by JIS A 1226 (2009) [30], the particle density by JIS 1202 (2009) [31] and the particle size distribution by JIS A 1204 (2009) [32]. Detailed methods of these physical and chemical analysis are shown in Table S.1. Total heavy metal contents were determined after melting the soil by microwave digestion, aqua regia or steam distillation (Ministry of Environment, 2012) [33]. We sieved the four soils using a 2-mm opening mesh. We prepared about 10 kg of each soil and used the coning and quartering method to sub-divide the soil into smaller samples.

2.2. Methods

We carried out up-flow column percolation tests following the procedure described in ISO/TS 21268-3 [7]. The procedure of this technical specification and our experimental conditions are shown in Table 3. This technical specification requires at least 2 days (48 h) of equilibration period after saturation and a 12 mL/h flow rate (or a 15 ± 2 cm/day linear velocity) for a column with a diameter of 5 cm. In this study, we tested three additional equilibration times, 0, 12 and 16 h, as well as an extra flow rate of 36 mL/h. Six different laboratories, located in different prefectures in Japan, conducted column experiments according to the conditions specified in Tables S.3–S.6. Chemical analyses of all collected eluates from all column percolation experiments were conducted only in one laboratory.

Table 4 shows the number of experiments for every condition and the sample dry mass packed into each column. We packed the specimen into the columns with moisture content equivalent to field conditions (the specimen was not dried). We used approximately the same amount of soil in each test for every soil type. To prevent soil material loss and to facilitate uniform distribu-

Table 1
Column percolation test standards.

	ISO (2007)	CEN (2004)	NEN (2004)	DIN (2009)	USEPA (2013)	Nordest (1995)	ASTM (2001)	OECD (2004)
Scope	Inorganic and organic	Inorganic	Inorganic	Inorganic and organic	Inorganic and organic	Inorganic	Inorganic and organic	Unlabeled or radio labelled
Apparatus ^a	30±5 cm×5 or 10 cm	30±5 cm×5 or 10 cm	≥20 cm×5 cm	≥4 times diameter × 5 cm or 10 cm	30 cm×5 cm	At least 20 cm×5 cm	30 cm×10 cm	At least 35 cm×4 cm
Solid material	Soil and soil-like materials	Waste	solid earthy and stony materials and wastes	Granular materials	Wide range of granular solids	Granular waste materials: ashes, slags	Waste	Soil
Particle size	Maximum 4 mm (>95%)	5 cm ^b : <4 mm ($\geq 95\%$) 10 cm ^b : <4 mm ($\leq 80\%$) and ≥10 mm ($\leq 5\%$)	Maximum 4 mm (>95%)	Maximum 32 mm	Maximum 2.5 mm	Maximum 4 mm	Maximum 10 mm	Maximum 2 mm
Packing	5 layers, 3 sublayer/layer. Packing: 3 times using a 125 g or 500 g rammer from 20 cm	5 layers, 3 sublayer/layer. Packing: 4 times using a 200 g rammer from 20 cm	5 cm/layer. Packing: 4 times using a 200 g rammer from 20 cm	Using rammer (1.2–2 g/cm ² from 20 cm), rubber hammer (5 times, gently), or using vibration of a sieving machine	From top to bottom. 5 layers, no rammer	Without compaction	In 5 equal layers. Same density as in the field	Added in small portions and pressed with a plunger with simultaneous gentle vibration
Method Eluate	Up-flow CaCl ₂ 0.001 M	Up-flow Water	Up-flow Water	Up-flow Water	Up-flow Water or CaCl ₂ 0.001 M	Up-flow Water pH 4 acidified with HNO ₃	Up-flow Water	Down-flow CaCl ₂ 0.01 M
Equilibration	2 days	3 days	18 to 72 h	2 h	21 h ± 3 h	Not specified	Using Test Method D 2434	Bottom to top
Flow rate	15 cm/day	15 cm/day	0.021 × m ₀	q=(l × π × r ² × n)/(t × 60)	0.5 to 1.0 L/S per day	0.03 to 0.1 L/S per day	1 void volume exchange in 24 ± 3 h	200 mm/48 h
Number of samples	7	7	7	4 Compliance test: 1	9	4 to 5	As discrete void volume increments	Not specified. Eluate and extracted

^a Height × diameter.

^b Diameter of the column.

Table 2

Properties of the soils used in up-flow percolation tests.

Parameter	Dimension	Soil A	Soil B	Soil C	Soil D
Maximum particle size	mm	2	2	2	2
Moisture content	% by mass	37.1	10.9	20.8	26.6
Loss of ignition	% by mass	8.9	NA	1.3	NA
Particle density	g/cm ³	2.746	2.742	2.641	2.740
Particle size distribution	% by mass				
0.075–2 mm		46.5	77.8	88.3	NA
0.005–0.075 mm		22.9	10.1	4.8	NA
<0.005 mm		30.6	12.1	6.9	NA
Total elemental content	mg/kg dry mass				
F		125	4108.7	140	NA
Pb		412	1262.2	6.3	NA
As		9.4	745.9	3.3	NA
Cu		235	NA	6.7	NA
Cd		NA	4.3	NA	NA
Cr		NA	43.4	NA	NA
Se		NA	32.8	NA	NA

NA: not available.

The fill volume of the column was $596 \pm 9 \text{ cm}^3$ (soil A), $571 \pm 16 \text{ cm}^3$ (soil B), $589 \pm 34 \text{ cm}^3$ (soil C), and 589 cm^3 (soil D); the internal diameter was $4.99 \pm 0.01 \text{ cm}$ (soil A), 5 cm (soil B), $4.99 \pm 0.01 \text{ cm}$ (soil C), and 5 cm (soil D); the fill height was $30.4 \pm 0.4 \text{ cm}$ (soil A), $29.1 \pm 0.8 \text{ cm}$ (soil B), $30.2 \pm 1.4 \text{ cm}$ (soil C), and 30 cm (soil D); the sample dry mass was $498 \pm 12 \text{ g}$ (soil A), $689 \pm 0.6 \text{ g}$ (soil B), $784 \pm 28 \text{ g}$ (soil C), and $500 \pm 0.8 \text{ g}$ (soil D); the bulk density was $0.84 \pm 0.03 \text{ g/cm}^3$ (soil A), $1.19 \pm 0.03 \text{ g/cm}^3$ (soil B), $1.33 \pm 0.04 \text{ g/cm}^3$ (soil C), and $1.19 \pm 0.03 \text{ g/cm}^3$ (soil D).

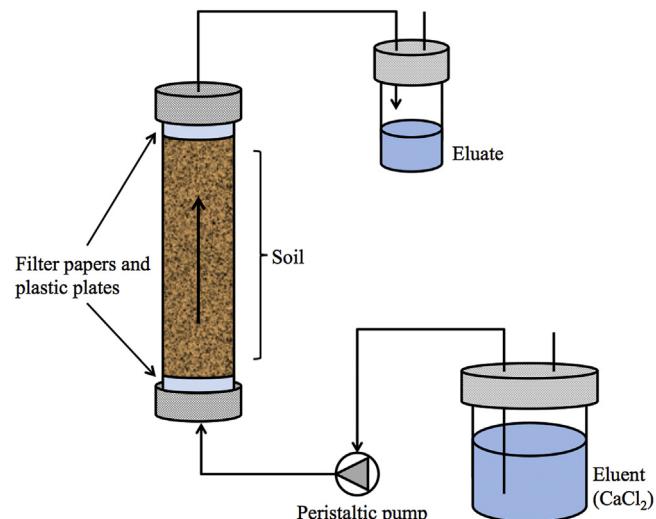
Table 3

Basic experimental conditions.

Parameter	Dimension	Experimental conditions
Sampling cumulative L/S	L/kg	0.1, 0.2, 0.5, 1, 2, 5 and 10
Column diameter	cm	4.99 ± 0.01
Sample height	cm	30.4 ± 0.4
Sample state	–	Wet
Flow rate	mL/h	12 and 36^a
Initial equilibration (time after saturation)	h	$0^a, 12^a, 16^a$ and ≥ 48
Packing method	–	The sample was packed in 15 layers using a 125 g rammer. The weight was dropped three times onto each layer, letting it fall down 20 cm along a rod used as a guide.
Eluent	–	Deionized water with 0.001 M CaCl_2
Filter paper	μm	5.0 or 8.0

^a This condition is modified compared to ISO/TS 21268-3.

tion of the eluent, we placed a filter paper (Whatman filter paper Grade 2, GE Healthcare, Maidstone, United Kingdom; and Advantec No.2, Advantec, Tokyo, Japan) and a plastic plate with several holes, approximately 3 mm in width, at the bottom of the column before packing the column with soil. We filled the column with the soil specimen up to a height of $30 \pm 5 \text{ cm}$ in five layers, as per the method described in Table 3. After the final sub-layer was packed,

**Fig. 1.** Diagram of the up-flow column percolation test system (modified from [10]).

we placed a plastic plate and a filter paper on the top section of the column.

We connected Tygon tubes (inner diameter of 0.8–6 mm, depending on the design of the column) to the bottom and top of the columns. We connected the bottom (inlet) to a tank containing 0.001-M CaCl_2 (eluent) and the top (outlet) to an eluate collection

Table 4

Information of each soil column and associated experimental conditions.

			Soil A	Soil B	Soil C	Soil D
Sample dry mass in column		g	498 ± 12	680 ± 0.6	784 ± 28	500 ± 0.8
Height of soil in the column		cm	30.4 ± 0.4	29.1 ± 0.8	30.2 ± 1.4	30
The number of tests		8	1	10	4	4
1	Flow rate	12 mL/h	1	1	1	1
	Initial saturation	48 h				
2	Flow rate	12 mL/h	1	–	1	–
	Initial saturation	12 or 16 h				
3	Flow rate	36 mL/h	3	1	4	1
	Initial saturation	48 h				
4	Flow rate	36 mL/h	1	1	1	1
	Initial saturation	12 or 16 h				
5	Flow rate	36 mL/h	2	1	3	1
	Initial saturation	0 h				

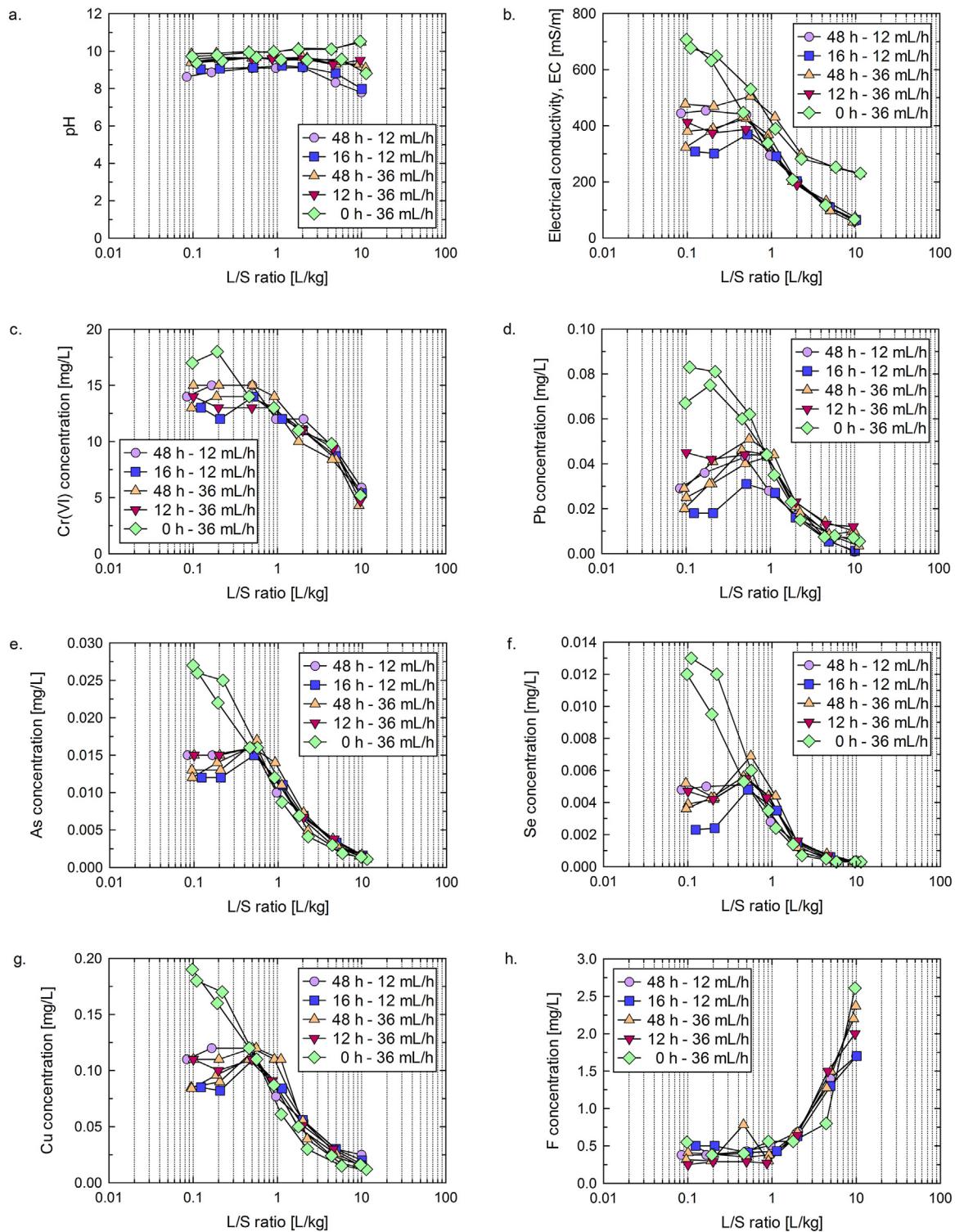


Fig. 2. The parameters (a) pH, (b) EC, (c) Cr, (d) Pb, (e) As, (f) Se, (g) Cu, and (h) F as a function of the liquid-to-solid ratio for soil A.

bottle of an appropriate size plastic bottles with volumes ranging from 100 mL to 4 L (AS ONE I-boy PE bottles, AS ONE Corporation, Osaka, Japan; and Thermo Scientific Nalgene FLPE bottles, Thermo Scientific, Waltham, Massachusetts, USA). We prepared the eluent solution, 0.001-M CaCl_2 , using high purity CaCl_2 and Milli-Q (EMD Millipore, Merck KGaA Darmstadt, Germany) water. The system was equipped with a peristaltic pump (ATTO SJ-1211II-H and ATTO SJ-1211L, ATTO Corporation, Tokyo, Japan; and EYELA MP-2000/2001, Tokyo Rikakikai, Tokyo, Japan) to let the eluent pass

through the column (from the bottom to the top) at a constant flow rate (12 or 36 mL/h). A diagram of the column system is presented in Fig. 1.

We saturated the samples using a peristaltic pump until the eluent reached the top of the column. We set four equilibration times after the saturation: 0 (sample collection started immediately), 12, 16, and 48 h (eluent flow was interrupted for this time) to evaluate the effect of the length of this period on the leaching of constituents. The fractions collected were 0.1 ± 0.02 , 0.2 ± 0.04 ,

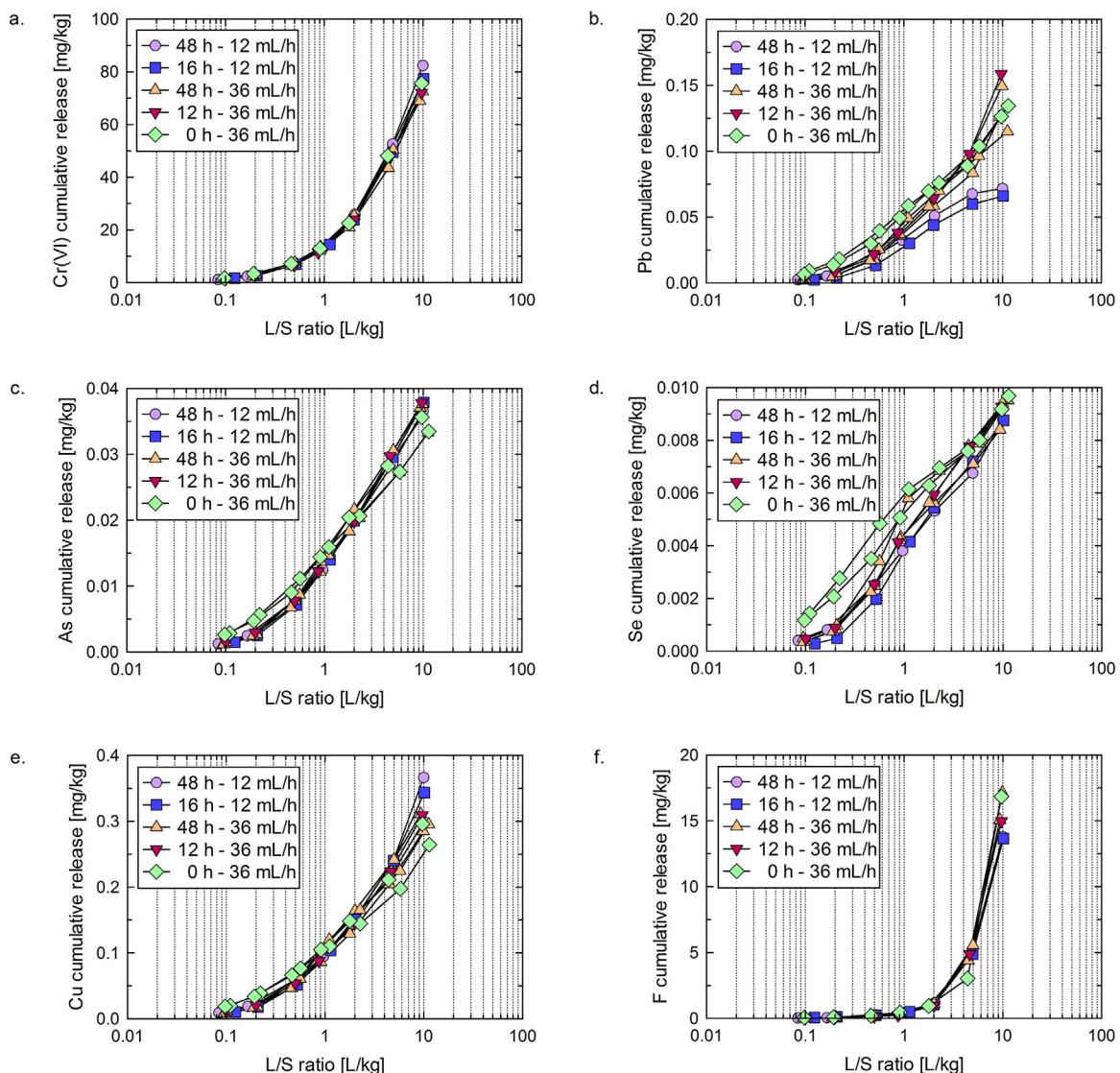


Fig. 3. Cumulative releases of (a) Cr, (b) Pb, (c) As, (d) Se, (e) Cu, and (f) F as a function of liquid-to-solid ratio for soil A.

0.5 ± 0.08 , 1 ± 0.15 , 2 ± 0.3 , 5 ± 0.4 , and 10 ± 1 L/kg of dry mass. As soon as the samples were collected, we recorded the weight then removed a small portion of the sample for pH (Horiba F-51, Horiba F-54, and Horiba F-22, Horiba, Kyoto, Japan; and DKK-TOA HM-25, DKK-TOA HM-20P, and DKK-TOA WM-32EP, DKK-TOA, DKK-TOA Corporation, Tokyo, Japan) and electrical conductivity (EC) analysis (Eutech EC Testr11+, Thermo Scientific Eutech Instruments Water Analysis Solutions, Singapore; Horiba F-54, Horiba DS-12, and Horiba B-173, Horiba, Kyoto, Japan; and DKK-TOA CM-30R, DKK-TOA Corporation, Tokyo, Japan). We filtered the eluate afterwards using a $0.45\text{-}\mu\text{m}$ pore size membrane filter (Sartorius Minisart, Goettingen, Germany; MF-Millipore, EMD Millipore, Merck KGaA Darmstadt, Germany; and Advantec No. 2, Advantec, Tokyo, Japan), then separated it into two aliquots: one preserved with 0.5% concentrated nitric acid for cation analysis, and the other remained unpreserved for anion concentration analysis. We measured Pb, As, Se, Cu, Mg and B concentrations with inductively coupled plasma-optical emission spectrometry (ICP-OES) (Vista-PRO Simultaneous ICP-OES, SII and Varian, Agilent Technologies, Santa Clara, California, USA) and inductively coupled plasma-mass spectrometry (ICP-MS) (ICP-MS 8800 Series, Agilent Technologies, Santa Clara, California, USA), and measured Cr(VI) and F by IC (Dionex ICS-2000

ion chromatograph, Thermo Scientific, Sunnyvale, California, USA). We measured dissolved organic carbon (DOC) with a total organic carbon (TOC) analyzer (Shimadzu TOC-VCPh, Shimadzu Corporation, Kyoto, Japan).

3. Results

The results of the concentrations and cumulative releases of column percolation tests conducted on soils A, B, C, and D are shown in Figs. 2–9. The pH, EC, and release concentration of cations, anions, and DOC were plotted for all soils (Table S.2). Each set of data contains information on equilibration time (0, 12, 16, or 48 h) and flow rate (12 mL/h or 36 mL/h); one of the aims of our study was to understand the impact of these parameters on the release of constituents over time and to determine whether the flow rate can be increased and/or the equilibration time decreased.

3.1. Soil A

For soil A, EC, pH and concentration of inorganic constituents were similar for the duration of the test at all tested conditions except for an equilibration time of 0 h and a flow rate of 36 mL/h. At a

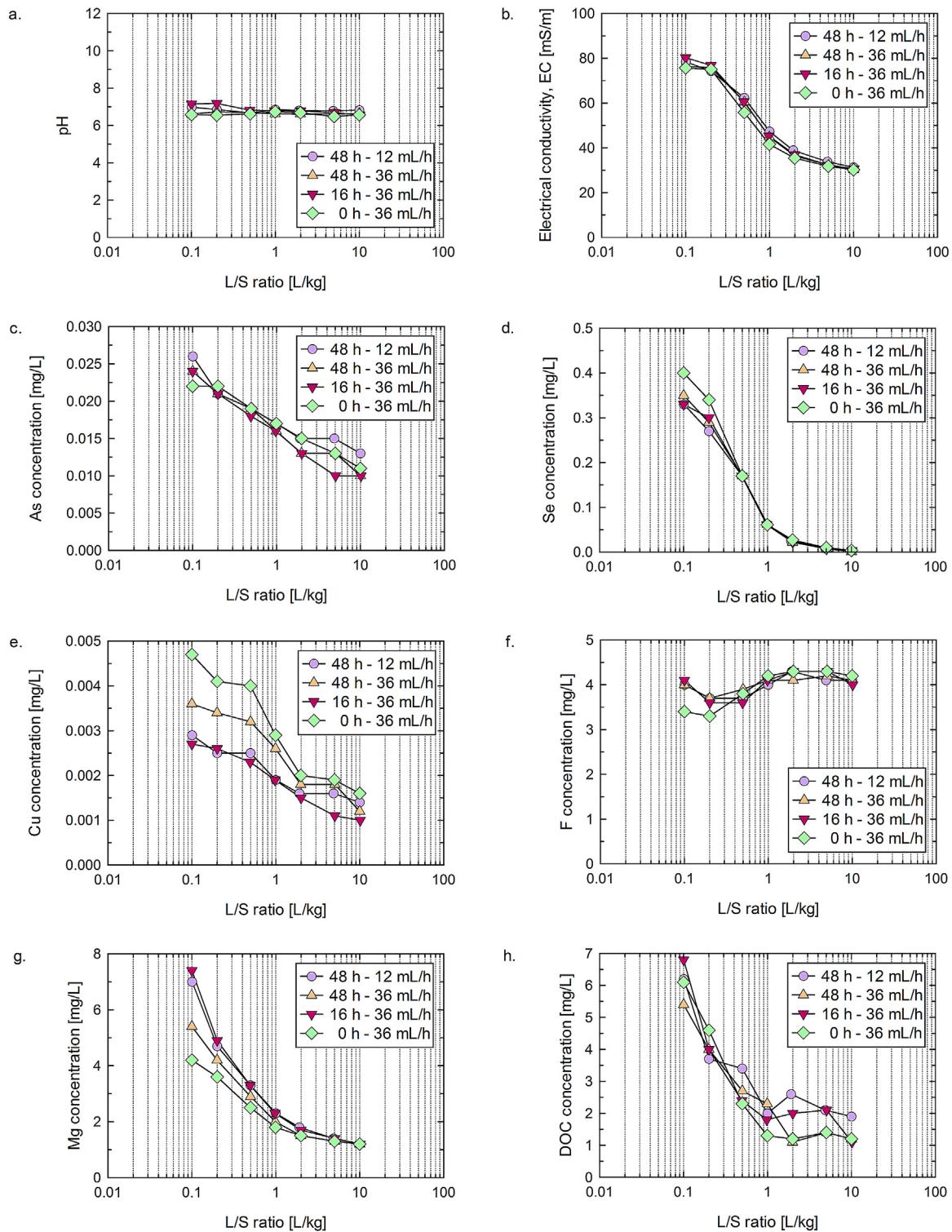


Fig. 4. The parameters (a) pH, (b) EC, (c) As, (d) Se, (e) Cu, (f) F, (g) Mg, and (h) DOC as a function of liquid-to-solid ratio for soil B.

0 h equilibration and with flow rate of 36 mL/h, we observed higher values of EC (Fig. 2b) corresponding to higher concentrations of Cr, Pb, As, Se, and Cu (Fig. 2c-g) at L/S ratios <1 L/kg when compared to other results; however, for L/S ratios >1 L/kg, the results are similar for all cases after.

Though there was a clear difference between Cr, Pb, As, Se, and Cu concentrations at an equilibration time of 0 h and a flow rate of 36 mL/h for at L/S ratios <1 L/kg. Results for

cumulative releases were similar under all tested conditions (48 h-12 mL/h, 16 h-12 mL/h, 48 h-36 mL/h, 12 h-36 mL/h, and 0 h-36 mL/h) (Fig. 3).

We observed two types of breakthrough curves (BTCs) for the measured substances. Electrical conductivity and concentrations of Cr, Pb, As, Se, and Cu (Fig. 2b-g) appear to have the same pattern and values for both flow rates at L/S ratios >1 L/kg. However, the concentration of F followed the opposite trend; the concentration

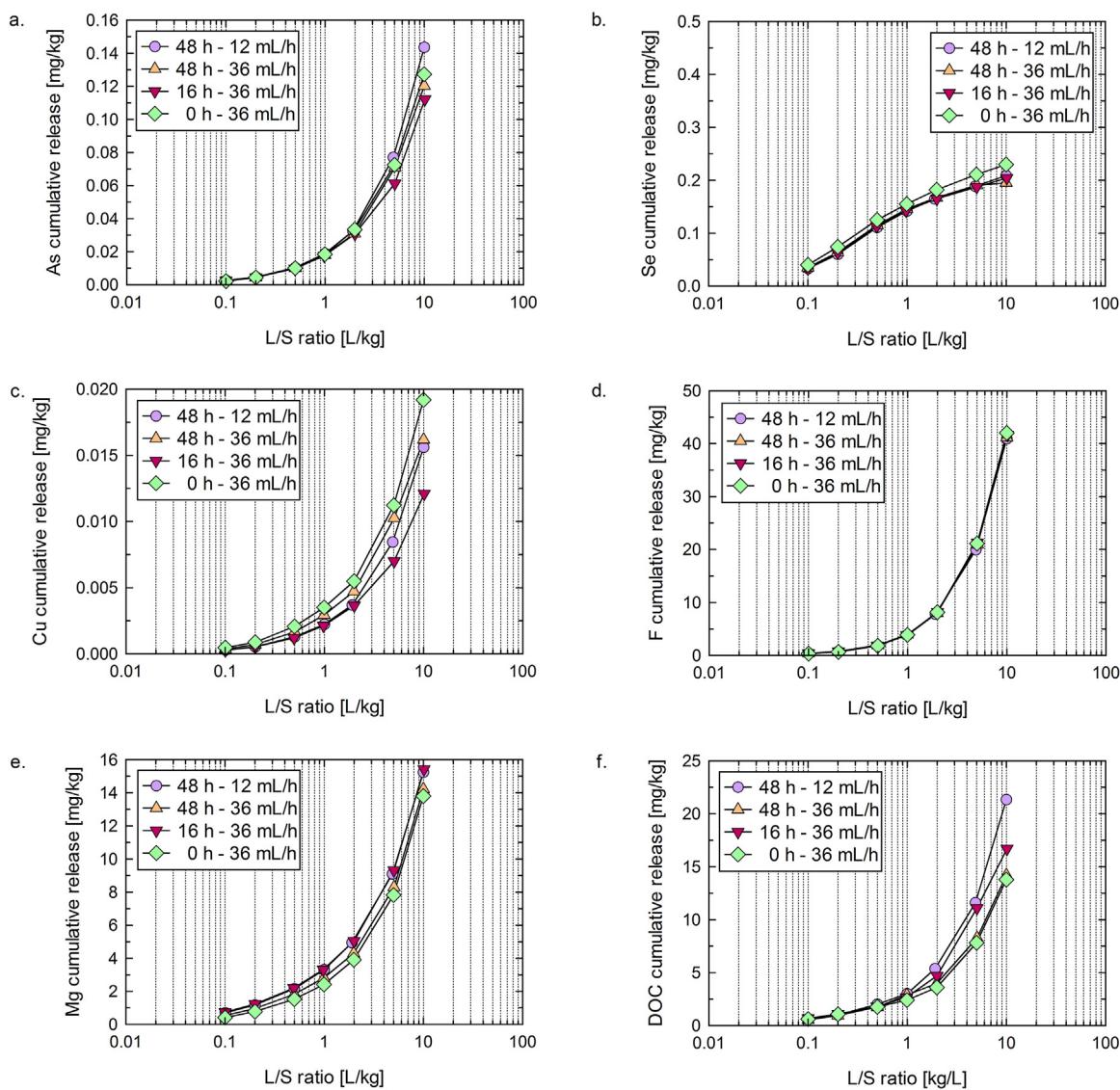


Fig. 5. Cumulative releases of (a) As, (b) Se, (c) Cu, (d) F, (e) Mg, and (f) DOC as a function of liquid-to-solid ratio for soil B.

was in equilibrium at L/S ratios <1 L/kg and subsequently increased exponentially with time (Fig. 2h). There was no difference in pH at different flow rates for the duration of the test (Fig. 2a).

3.2. Soil B

For soil B, the EC and the concentrations of As and DOC (Fig. 4b,c and h, respectively) showed the same trend and had similar values for the duration of all the tests. However, we observed slightly higher concentrations of Se and Cu (Fig. 4d and e, respectively) for an equilibration time of 0 h and a flow rate of 36 mL/h at L/S ratios <1 L/kg, but we observed no difference for L/S ratios >1 L/kg; this finding was similar to that observed for soil A. For F and Mg (Fig. 4f and g, respectively), the opposite trend was observed: the concentration was lower at an equilibration time of 0 h and a flow rate of 36 mL/h for L/S ratios <1 L/kg, but no difference was observed for L/S ratios >1 L/kg. We observed no difference in the cumulative releases of As, Se, Cu, F, Mg, and DOC between the four tested conditions: 48 h-12 mL/h, 48 h-36 mL/h, 16 h-36 mL/h, and 0 h-36 mL/h (Fig. 5). The pH values were the same under all tested conditions (Fig. 4a).

3.3. Soil C

Contrary to observations made for soils A and B, the pH of soil C increased approximately from 2.5 to 4.5 during the test period (Fig. 6a). We observed the same trend for the EC and the concentrations of Pb, As, Cu, and F (Fig. 6b-f, respectively). Additionally, the EC and the concentrations of Pb, As, Cu, and F were quite different from one another at L/S ratios <1 L/kg even under the same equilibration time and flow rate. However, results were similar for all tested cases with L/S ratios >1 L/kg. Results of the cumulative releases of Pb, As, Cu, and F followed the same trend, but the values were different for all tested cases (Fig. 7).

3.4. Soil D

For soil D, we observed the same trend for the pH, the EC and the concentrations of As, Se and Cu (Fig. 8a-e): higher concentrations at L/S ratios <1 L/kg. The highest concentration among all four experimental conditions at L/S <1 L/kg was observed for 0 h-36 mL/h case, followed by 48 h-12 mL/h and 16 h-36 mL/h cases, which showed similar values. The lowest concentration at L/S <1 L/kg was for 48 h-36 mL/h case. Boron concentration results for 0 h-36 mL/h

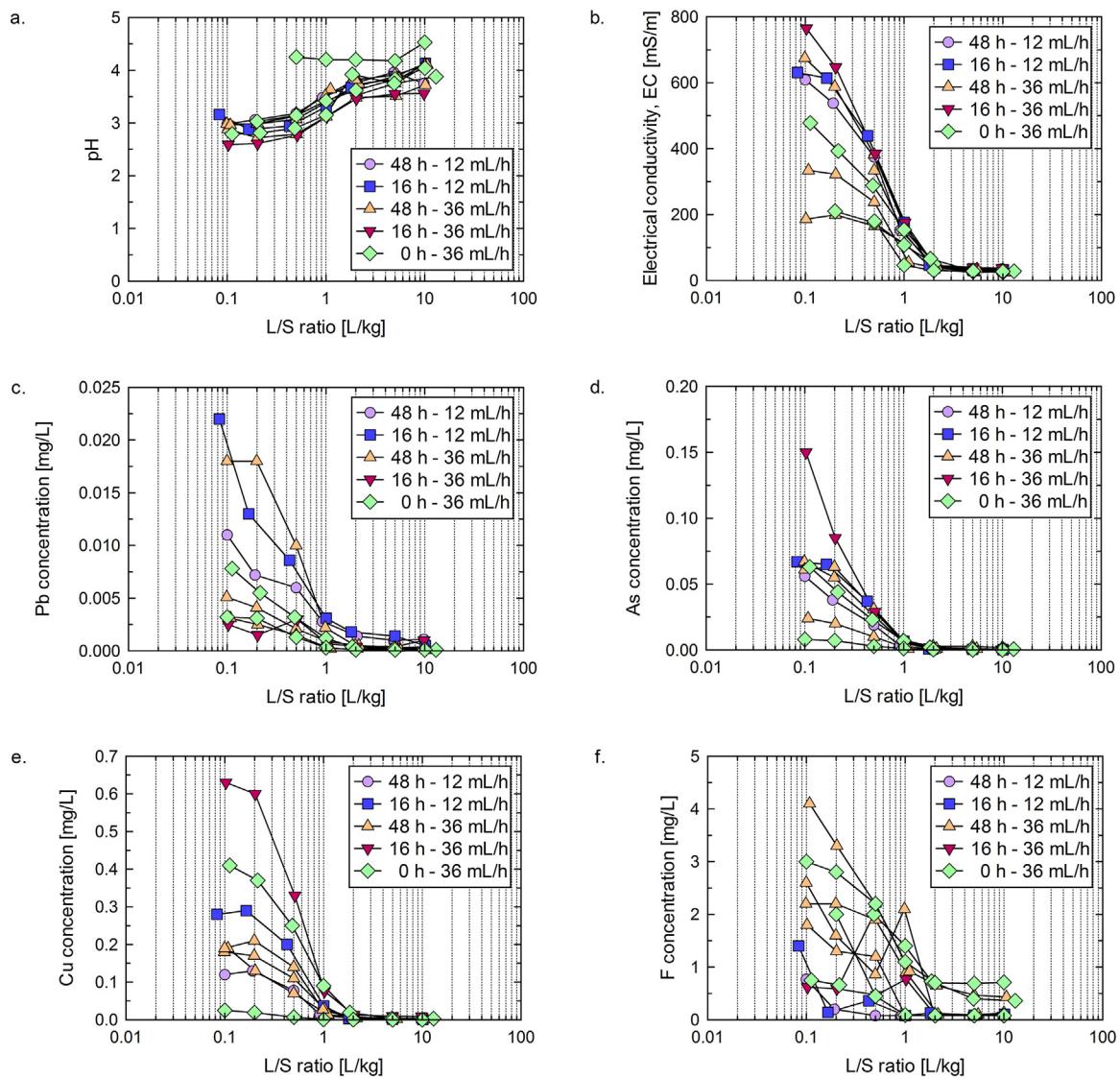


Fig. 6. The parameters (a) pH, (b) EC, (c) Pb, (d) As, (e) Cu and (f) F as a function of liquid-to-solid ratio for soil C.

case showed slightly lower concentrations than other experimental conditions at $L/S < 1 \text{ L/kg}$, but similar concentration results for all cases at $L/S > 1 \text{ L/kg}$. We found no great difference in the cumulative release of all measured substances for the four tested cases (Fig. 9).

4. Discussion

In this section, we discuss the effect of equilibration time, the effect of flow rate, reproducibility, the variation in experimental conditions on the results and the difference between the original column test method and a modified column test method (12–16 h–36 mL/h case) for soils A, B and D. We also discuss potential reasons for the observed variation in results between laboratories for soil C at L/S ratios $< 1 \text{ L/kg}$ and the limitations of this research.

4.1. Effect of equilibration time

We tested four equilibration times, 0, 12, 16, and 48 h, at flow rates of both 12 and 36 mL/h. The results demonstrate that equilibration times greater than or equal to 12–16 h have no impact on the leaching of ions (Figs. 2–9) even when the flow rate is three

times higher than that stipulated by ISO/TS 21268-3. The absence of an equilibration period after saturation in the case with the higher flow rate (the 0 h–36 mL/h case) may lead to the saturated specimen initially releasing higher concentrations of inorganic anions and cations.

This behavior may be related to the following processes. First, at the equilibration phase, the highest concentration likely appears in the upper end of the column because of elution from the soil and advective transport in the column. This phenomenon was observed in this study for soils A, B and D at L/S ratios $< 0.5 \text{ L/kg}$ and Grathwohl and Susset [20] considered it in their leaching model. Secondly, taking a sufficient initial equilibration time, the concentration of target substances in the column are homogenized by diffusion, driven by the initial steep concentration gradient. This initial equilibration period for waste material was suggested to be between 12 and 16 h [26]. Our results indicate that the equilibration time should be greater than or equal to 12–16 h for soils A, B and D because no difference was observed between equilibration periods of 12, 16, and 48 h.

It should be noted that the time for equilibrium adjustment in these columns varies according to the soil's physical and chemical properties or the characteristics of target substances. However,

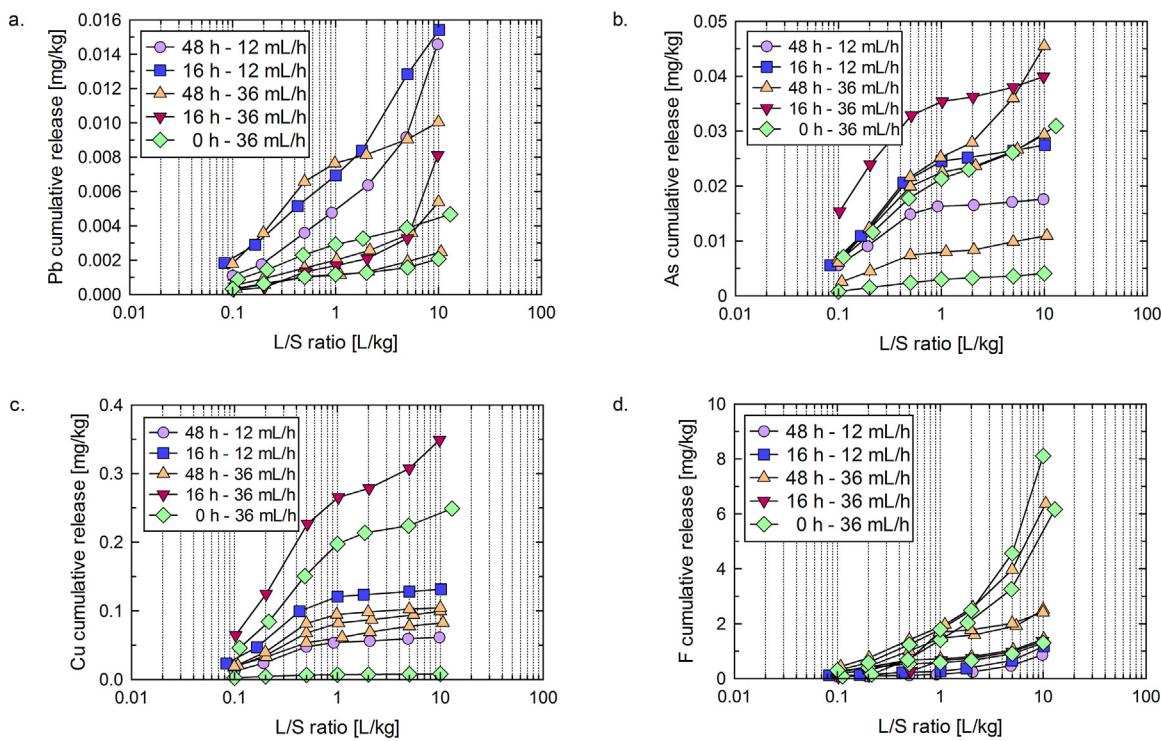


Fig. 7. Cumulative releases of (a) Pb, (b) As, (c) Cu, and (d) F as a function of liquid-to-solid ratio for soil C.

according to our results, it appears that the homogenization of concentrations in column tests takes place during the initial equilibration time of 12–16 h. At this point, users can select the initial equilibration time depending on their purpose. If homogenized concentration in the columns is required, the initial equilibration time should be greater than or equal to 12–16 h.

On the other hand, cumulative release values were similar for soils A, B and D at all L/S values because, although high concentrations were observed at L/S 0.1 or 0.2 L/kg, the eluate volume is so small that it does not greatly contribute to the cumulative release. This finding may indicate that equilibration period has no great impact on the cumulative release amount, especially at L/S = 2 or 10 L/kg, both target L/S values chosen for practical purposes.

4.2. Effect of flow rate

For soils A and B, the results of differences in flow rates demonstrate that the two flow rates tested in this research project (12 and 36 mL/h) had little or no effect on the release of cations and anions (Figs. 2–5), except for the case in which there was no equilibration period (the 0 h–36 mL/h case).

Lopez Meza et al. [26] studied the effect of contact time on the release of inorganic components from bottom ash and demolition waste. They stated that tests using different column dimensions lead to comparable results by the application of similar contact times. They also found that a difference in contact times (2.5, 5, and 16 h) had little effect on the leaching of constituents, which included copper, chromium, sulfate, and chloride, and on pH and EC.

In this study, contact times between 11.5 and 37.5 h for soil A (Table S.3), between 8.6 and 26.1 h for soil B (Table S.4) and 11.3 to 32.7 for soil D (Table S.6) lead to similar results, except when the equilibration time was 0 h (0 h–36 mL/h case). Our results for contact time were similar to those of Lopez Meza et al. [26]; we observed no appreciable impact on pH, EC, or release of anions, cations or DOC at flow rates of 12 mL/h or 36 mL/h.

Two studies conducted on alternative construction materials [27,34] also point in the direction that for some materials variation of the flow rate is less important than for others. Soil materials were not under consideration.

4.3. Evaluation of reproducibility and variance at different test conditions

In general, column tests have been proven as well repeatable and reproducible for waste and soil materials by inter-laboratory comparisons [25,26,35,36]. A reproducibility (between-lab-variation) between 6 and 42% was found for a contaminated soil and the 8 elements considered, whereas by far the highest value was obtained for a lower concentrated element (Hg) [35]. The repeatabilities (within-lab variation) were approximately a third of the reproducibilities.

The influence of the test conditions on the performance characteristics was less considered. On the contrary, variations of test conditions of a robustness study were only considered as acceptable if the obtained results were within the range of ± 2.8 standard deviations (SD) [26].

In order to evaluate reproducibility and variance of the results of this study at different equilibration times and flow rates, we calculated the coefficient of variation (C_V) of the results for soils A (Fig. 10) and B (Fig. 11). We calculated C_V for all data by dividing the standard deviation by the mean and multiplying it by 100 to report C_V values as percentages.

Fig. 10a and b show C_V values for both the concentrations and the cumulative release of Pb, As, Se, Cu, and F for soil A for all tested cases. Coefficients of variation for all elements ranged between 4 and 71%. The C_V values were above 30% for L/S ratios < 1 L/kg. This result can be explained by the high variance introduced when the data of the 0 h–36 mL/h case are taken into account.

Coefficients of variation were re-calculated for the same set of data, but results obtained at a flow rate of 36 mL/h and an equilibration time of 0 h were excluded (Fig. 10c and d). The overall

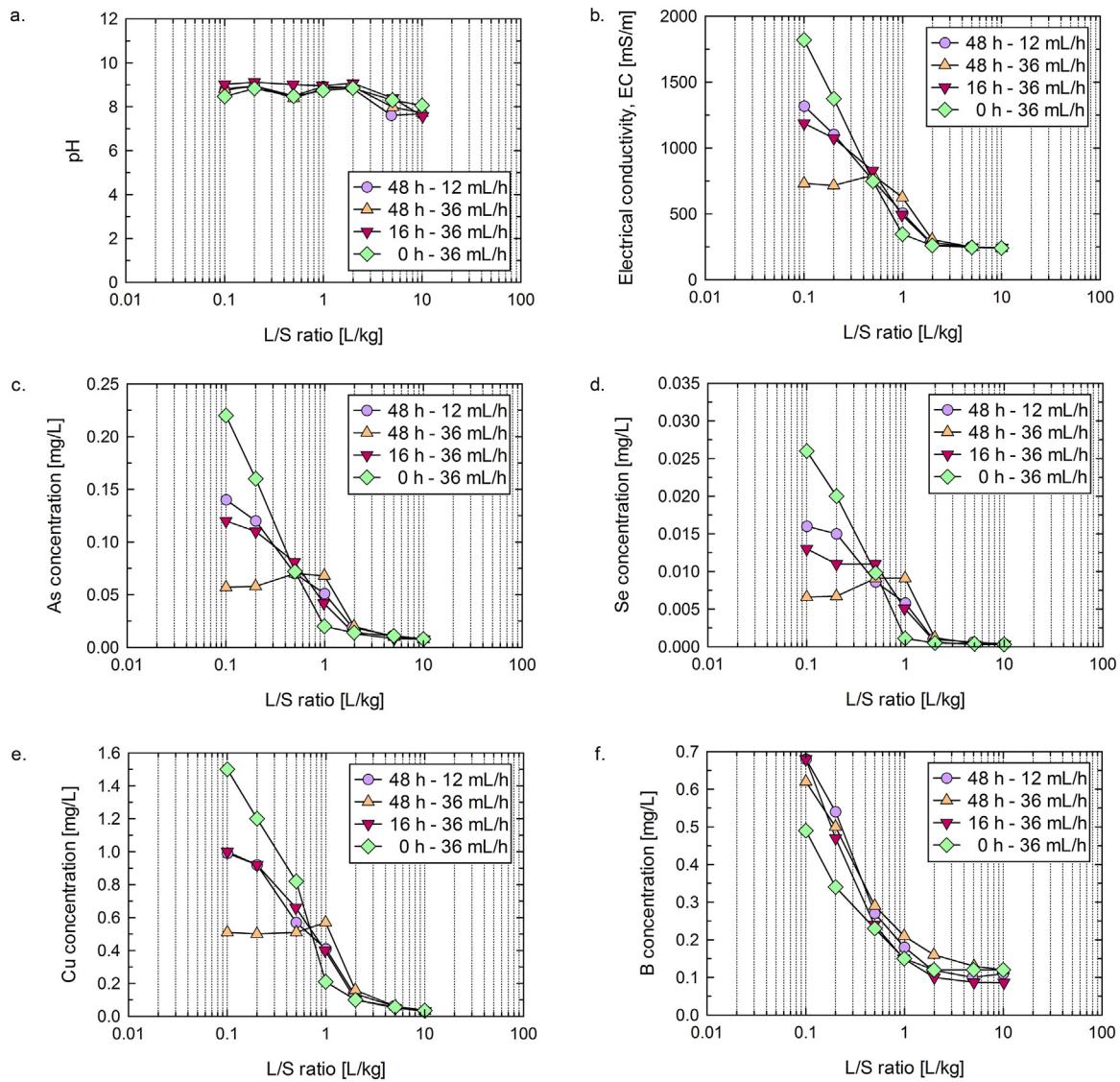


Fig. 8. The parameters (a) pH, (b) EC, (c) As, (d) Se, (e) Cu and (f) B as a function of liquid-to-solid ratio for soil D.

data show that C_V values ranged from 4 to 80%. However, of these data, 90% of the C_V values, even at L/S ratios <1 L/kg, were below 30%. Pb showed high C_V values for the concentration ($C_V = 35\%$ at L/S 0.1 L/kg, 40% at L/S 5 L/kg and 80% at L/S 10 L/kg). These high C_V values can be attributed to their low concentrations (1–10 ppb) at high L/S ratios (5–10 L/kg) and their corresponding high measurement uncertainty. A high C_V value for the concentration of F (43%) at an L/S ratio of 0.5 L/kg can probably be explained by differences in systems between laboratories.

Another calculation was performed on three sets of data corresponding to a flow rate of 36 mL/h and an equilibration time of 48 h by three different laboratories (Fig. 10e and f). In this case, C_V ranged from 0 to 49%, but more than 85% of the C_V values for the concentration and 100% of the C_V values for the cumulative release were below 30%, which indicates high reproducibility under the same conditions of equilibration time and flow rate.

Fig. 11a and b show that C_V values ranged between 0 and 47%. In addition, more than 95% of the C_V values for both the concentration and the cumulative release of As, Se, Cu, F, Mg, and DOC for soil B were below 30%, even when the equilibration time was 0 h (the 36 mL/h-0 h case). We re-calculated C_V values for the same set of data (overall C_V ranged from 0 to 59%), but results obtained at a

flow rate of 36 mL/h and an equilibration time of 0 h were excluded (Fig. 11c and d). We observed that more than 95% of the C_V values were below 30%. High C_V values for Se (59%) at L/S = 10 L/kg can be attributed to their low concentrations (1–4 ppb). It appears that equilibration time after saturation does not have a significant impact on the leaching of ions from soil B.

Differences in the chemical behavior of soils A and B at L/S ratios <1 L/kg can be attributed to several factors, including the type of ion, ion competition, initial concentration of elements in the soils (soil composition), hydraulic conductivity, porosity, sorption-desorption mechanisms, and contact area. It is not possible to explain the differences between the result for soils A and B accurately because of the number of variables involved, and the fact that some measured parameters were below detection limits in soil A, or not measured in soil B (e.g. Cr and Pb). Also, some parameters reported for soil B were not reported for soil A (e.g. Mg, DOC).

The overall results suggest that the reproducibility was acceptable and results were similar for soils A and B at all tested conditions, except for the 0 h-36 mL/h case for soil A, for which higher values were observed at L/S ratios <1 L/kg. This suggests that results might be similar when tests are performed either at equi-

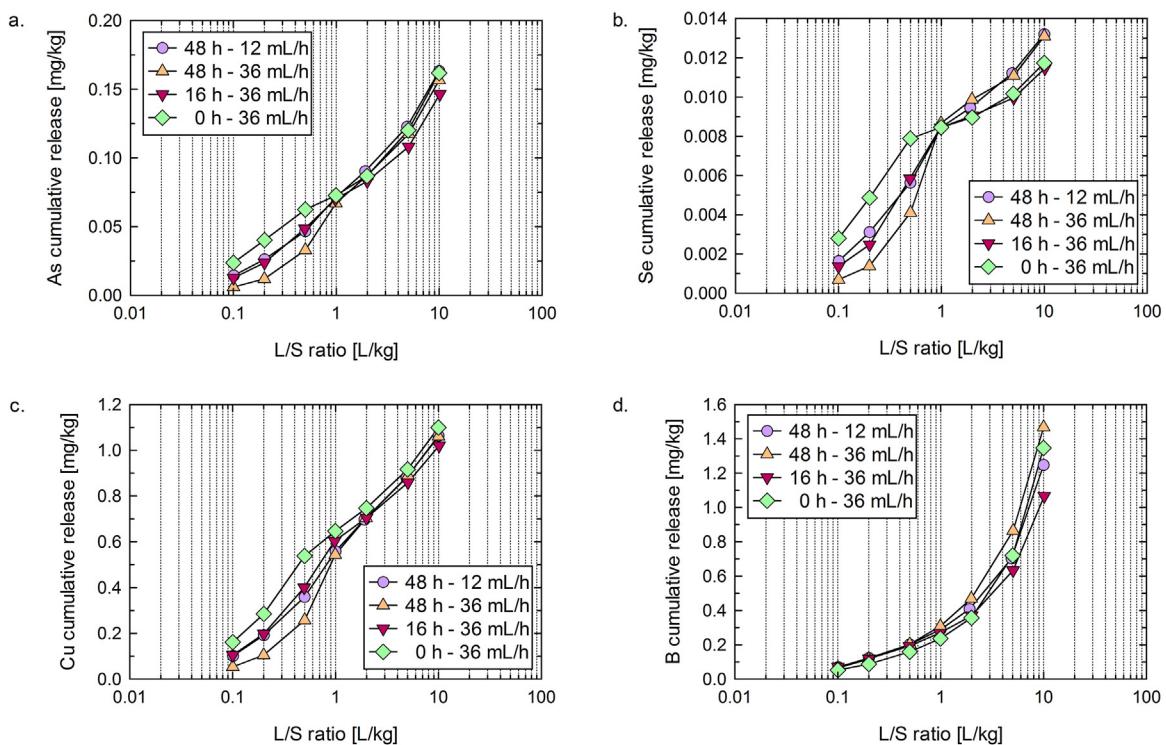


Fig. 9. Cumulative releases of (a) As, (b) Se, (c) Cu, and (d) B as a function of liquid-to-solid ratio for soil D.

libration times greater than or equal to 12–16 h or flow rates of 12–36 mL/h.

4.4. Comparison between original method (48 h–12 mL/h) and modified method (12–16 h–36 mL/h)

According to the discussion presented in Sections 4.1 and 4.2, it appears that the best method to reduce the experimental time of column tests without affecting its validity compared with ISO/TS 21268-3 (48 h–36 mL/h) is by reducing the initial equilibrium time from 48 h to 12–16 h and increasing the flow rate from 12 mL/h to 36 mL/h. In order to demonstrate whether this assumption is accurate, we calculated the ratio of the modified method (12–16 h–36 mL/h) and the original method (48 h–12 mL/h) for soils A, B, C and D. We found that the ratio in the majority of cases is close to 1, except for soil C in which ongoing oxidation reactions are introducing variability in the results (Tables S7 and S8). The ratios for soils A, B, and D indicating good agreement between the modified and original method are presented in Fig. 12 and Fig. S.1 for comparisons of concentration and cumulative release, respectively. This suggests that the column experimental time can be probably reduced from 20 to 30 days to 7–9 days by the modified method.

4.5. Reason of variation for soil C

We observed differences in the concentrations at L/S ratios <1 L/kg for soil C in all cases. This is probably because of the chemical characteristics of this soil and the fact that the pH of the eluates was the lowest of the three soils tested (Fig. 6a).

The first hypothesis that may explain this phenomenon is the difference in the degree of oxidation of samples before and during the tests. It is well known that certain natural soils undergo oxidation reactions after sampling because of the change in the environment (from reducing to oxidizing environment) and this series of oxidation reactions may lead to the decrease in pH

and change in leachability of heavy metals [37]. Evidence of ongoing oxidation reactions in soil C is the acidic pH (2.5–3.1 at L/S = 0.1 L/kg) compared with other soils, and the continuous increase of this value from 2.5–3.1, then from 3.5–4.5 (Fig. 4a). Soil C was excavated from a 5–10 m-deep aquifer zone and, thus, it was under reducing conditions prior to sampling. After sample delivery, the four laboratories that participated in this test stored the soil at approximately 4° and started the test on different dates. We did not use de-aired water for the experiments, using instead deionized water with 0.001-M CaCl₂. Considering that soil C has the potential to undergo oxidation, sample handling and experimental conditions may significantly impact the results and, therefore, efforts to prevent oxidation should have been made.

The second hypothesis that may explain this behavior is that the low pH of the eluates of soil C for the duration of the test, compared with the other three soils, may favor the release of chemicals. Additionally, results presented in Fig. 6a show that pH values were different at the same L/S ratios. For instance, the pH at an L/S ratio of 1.0 ranged from 3.0 to 3.6, suggesting that each sample was under different oxidation conditions at the starting point of the experiments. As a result, for soil C, it was not possible to identify the impact of flow rate and equilibrium time on the mobilization of cations and anions because of the variations in the pH of the sample itself prior to the start of the tests.

Sample handling procedures, storage methods, starting time of the tests, and the type of water used for the column percolation tests become, therefore, critical when there is a reactive soil or a series of reactions occurring in the sample. We have to pay particular attention to chemical characteristics of soils and, if necessary, set the required conditions for column experiments before starting the tests. For example, degassed water or nitrogen purged water may be used as a measure to minimize oxidation of samples or biodegradation.

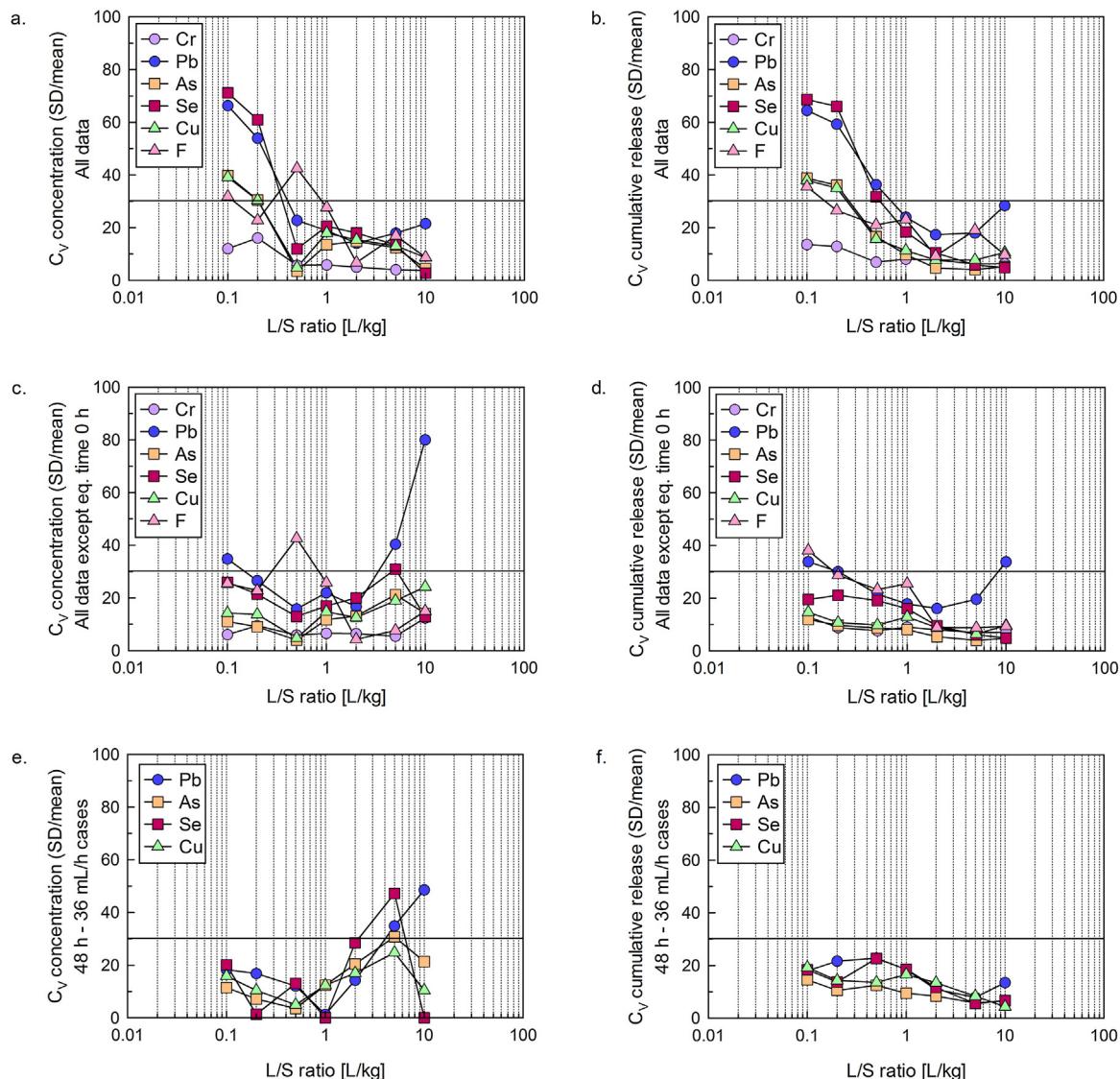


Fig. 10. Coefficient of variations for soil A: (a) concentrations of all data, (b) cumulative releases of all data, (c) concentrations of all data, except equilibration time = 0 h, (d) cumulative releases of all data, except equilibration time = 0 h, (e) concentrations of the 48 h–36 mL/h cases, and (f) cumulative releases of the 48 h–36 mL/h cases.

4.6. Limitations of this study

In this study, we evaluate the feasibility of decreasing column testing time by increasing the flow rate and decreasing the equilibration time compared to the conditions specified in ISO/TS 21268-3 using four different soils (A–D). As mentioned in the previous sections, it appears that the best method to reduce the experimental time of column tests is by reducing the initial equilibration time to 12–16 h and increasing the flow rate to 36 mL/h.

However, our results have some limitation for usage in standardization. One of the limitations is that, in this research our focus was on inorganic substances, but the ISO/TS 21268-3 addresses not only inorganic but also organic substances. It is well known that adsorption mechanisms and solubility of organic substances are different from inorganic substances and their behavior can be related to the octanol-water partition coefficient.

The second limitation is regarding reproducibility and repeatability. We did not perform two or more column tests to assure reproducibility and repeatability of the modified method (12–16 h–36 mL/h case) that we are proposing in this study.

Overall, additional investigations are needed for standardization purposes. There are currently some investigations on these issues being conducted in Japan and Germany that are expected to provide more results and conclusions.

5. Conclusions

We tested the effect of five combinations of initial equilibration times and flow rates (48 h–12 mL/h, 16 h–12 mL/h, 48 h–36 mL/h, 12–16 h–36 mL/h, and 0 h–36 mL/h) on pH, EC, the release of inorganic ions and DOC in four soils (A–D). Our results indicate that equilibration times of 12, 16, or 48 h and flow rates of 12 mL/h or 36 mL/h have no appreciable impact on the pH, EC, release of anions and cations, or DOC. However, an equilibration time of 0 h (the 0 h–36 mL/h) resulted in higher EC values and release concentrations at L/S ratios <1 L/kg, particularly for soil A, B and D. However, for the same soils, we observed no difference in cumulative releases when the overall mobilization of substances was compared. For soil C, high variability of results was observed at L/S ratios <1 L/kg, as a result of the soil's intrinsic characteristics (high reactivity).

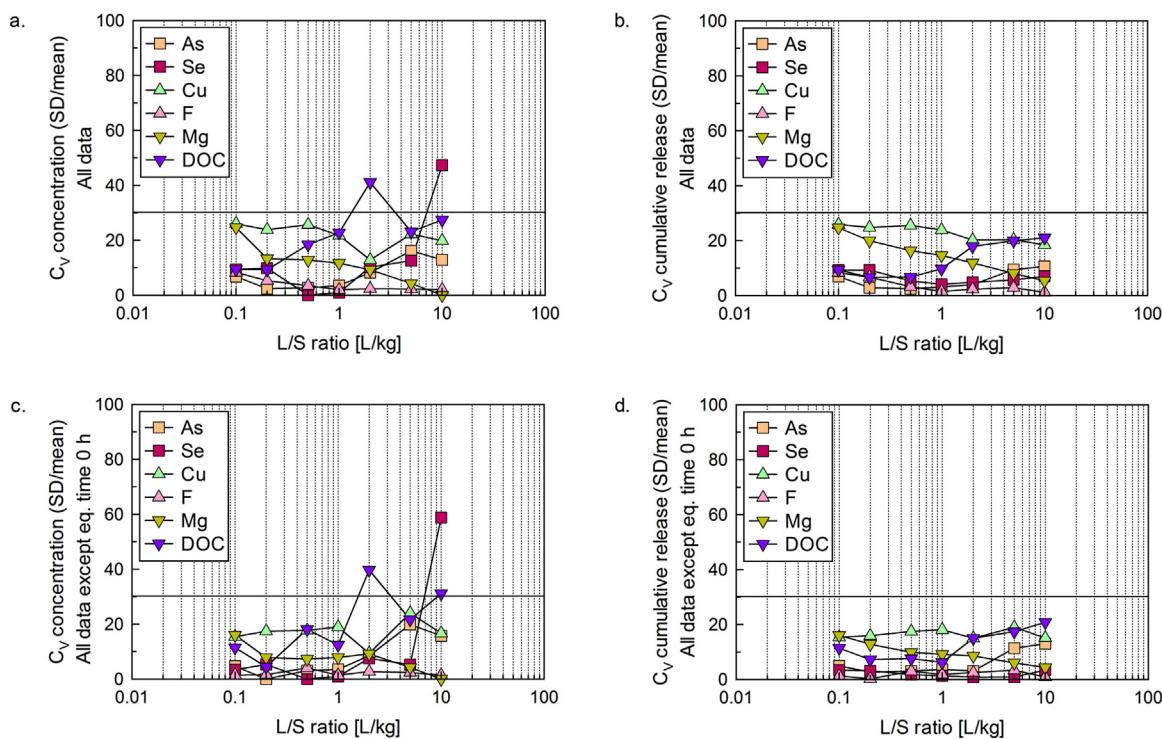


Fig. 11. Coefficient of variations for soil B: (a) concentrations of all data, (b) cumulative releases of all data, (c) concentrations of all data, except equilibration time = 0 h, and (d) cumulative releases of all data, except equilibration time = 0 h.

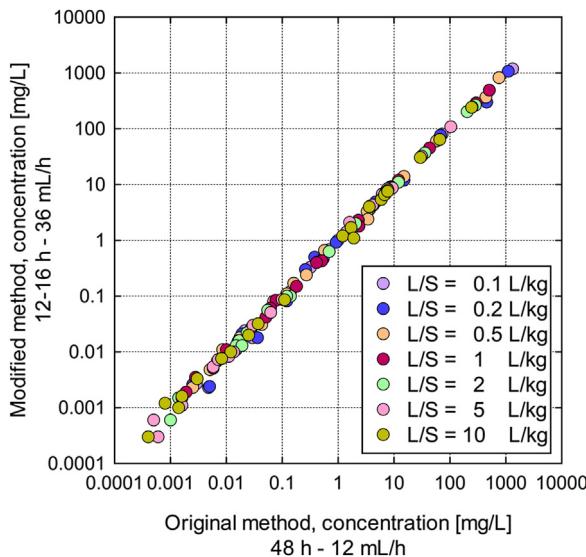


Fig. 12. Relationship between the concentration of modified method (12–16 h–36 mL/h) and original method (48 h–12 mL/h) for soils A, B, and D.

We calculated the reproducibility of column performance tests for soil A and B through the C_V ; more than 90% of the values were within 30%, except for initial equilibration time of 0 h, which represents an acceptable reproducibility. We also compared all data of modified (16 h–36 mL/h) and original results (48 h–12 mL/h) for both analyte concentrations and cumulative releases for Soil A, B, and D, and found good agreement with ratios consistently very close to 1. Overall, these results suggest that, in terms of practicability, column percolation tests can be shortened from 20 to 30 days to 7–9 days by decreasing the equilibration time to 12–16 h and increasing the flow rate up to three times that specified in ISO/TS 21268-3 for inorganic substances. However, in order to validate

this method for a wider range of soil types, further research on the influence of the suggested modifications should be done.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.08.046>.

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