Multivariate factorial analysis to design a robust batch leaching test to assess the volcanic ash geochemical hazard

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ABSTRACT

A method to obtain robust information on short term leaching behaviour of volcanic ashes has been developed independently on the sample age. A mixed factorial design (MFD) was employed as a multivariate strategy for the evaluation of the effects of selected control factors and their interactions (amount of sample (A), contact time (B), and liquid to solid ratio or L/S (C)) on the leaching process of selected metals (Na, K, Mg, Ca, Si, Al, V, Mn, Fe, and Co) and anions (Cl^- and SO_4^{2-}). Box plots of the data acquired were used to evaluate the reproducibility achieved at different experimental conditions. Both the amount of sample (A) and leaching time (B) had a significant effect on the element stripping whereas the L/S ratio influenced only few elements. The lowest dispersion values have been observed when 1.0 g was leached with an L/S ratio equal to 10, shaking during 4 h. The entire method is completed within few hours, and it is simple, feasible and reliable in laboratory conditions.

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1. Introduction

Explosive volcanic activity can produce ash deposits with a wide spatial distribution that may affect soils and surface waters [1–3]. One of the most important environmental impacts of ash fall is due to the presence of water soluble materials on volcanic ash particle surfaces, feature already documented at the beginning of the XX century [4]. It is well accepted that volcanic ashfall produces a natural contribution of potentially toxic trace elements (PTTEs) on the earth surface after contact with an aqueous environment [3,5,6]. From an environmental point of view, the elements leached most rapidly are present as soluble salts on the ash surface whereas prolonged exposure of ash to weathering may cause slow release of other elements from the structure of constituent crystalline phases and glass [7]. Although eruptions are often short-lived, thick ashfall deposits can remain in the local environment for years to decades, and may be resuspended by wind storms, causing long-term environmental effects mainly physically since fine ash may reach the deepest parts of the lungs [8]. However, chemically, resuspended ash is much more inert than pristine ash due to leaching of the former in the environment.

The potential impact on the environment of volcanic ashes disposed on land is most frequently assessed and predicted using bench scale laboratory tests although there are many important environmental conditions present in the field which cannot be reproduced in a laboratory. However, most of the soluble constituents of volcanic ash are detected by one stage batch leaching tests [1,2,7–14].

A review of 55 studies reporting ash leachate data for 27 volcanoes concluded that the use of a wide range of methodological variable values (in leachant composition, contact time and liquid to solid or L/S ratio) make the comparison between the different studies difficult [15]. After the exhaustive literature search of leaching protocols of this review, Witham et al. [15] proposed a "standard protocol" simply based on the most common used methodologies rather than the optimal conditions. The present study attempts to determine this optimum through logical experiment design, careful measurement, and statistical analysis. A better understanding of experimental conditions allows the identification of the parameters affecting the mobility of PTTEs from ash. Consequently, designing more realistic and appropriate leaching tests will help to model more accurately the environmental impact of volcanic ash.

The aim of this work was to develop a method to obtain robust information on short term leaching behaviour of volcanic ashes. A mixed factorial design (MFD) was built in order to investigate the influence of control factors (and their interactions) over the

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leaching process of selected metals (Na, K, Mg, Ca, Si, Al, V, Mn, Fe, and Co) and anions (Cl$^-$ and SO$_4^{2-}$) using ANOVA tests. Regression analysis was also used to evaluate the predictability of the single batch leaching process. Finally, box plots of the data acquired were used to evaluate the reproducibility achieved at different experimental conditions.

2. Experimental

The rate and amount of element released in a leaching test depend on several factors including chemical and mineral composition of ash, leachant type, and pH (chemical factors); and, particle size, porosity, contact time, L/S ratio and temperature (physical factors). Among these factors, there is a group intrinsically linked to the properties and composition of ash (primary factors), whereas some others depend on leaching conditions that can be varied to design more suitable procedures (control factors).

For practical purposes, the primary factors and many control factors may be considered fixed in a leaching test. Thus, the number of factors to study experimentally may be considerably reduced and the attention can be focused in the most relevant. The fixed factors of the present work were based on the most common protocols used and the recommendations of Witham et al. [15] (e.g., ungrounded and unsieved ash sample, ultrapure water as leachant, room temperature, and 0.45 μm membrane filters). On the other hand, the control factors selected to study experimentally were amount of sample, contact time, and L/S, which were varied taking as reference the proposed conditions by Witham et al. [15] (i.e., shake an ash-leach mixture for 90 min in a sealed container; using an ash (g) to water (ml) ratio of 1:25).

2.1. Sampling and storage

Two rhyolitic volcanic ash samples described elsewhere [8,13], have been selected to cover a wide range of ash age. Sample 719 corresponds to an ancient volcanic ash deposit from the southern Puna, NW Argentina, and CHA sample to a pristine volcanic ash erupted in the recent eruption of Chaiten volcano in 2008, Chile. The former sample was collected by a plastic shovel excluding the most superficial (2 cm depth) ash to avoid any possible surface contamination [8]. Pristine volcanic ash was collected directly by using plastic trays during the ash fall out. About 1 kg of samples were placed in polyethylene bags and carried to the laboratory. Samples were dried at 40 °C in an oven and stored in polyethylene (HDPE) vessels until preparation in the laboratory. Ash drying homogenises the humidity of samples before the leaching experiments and, in the case of pristine ash, preserves the original features of the ash as much as possible.

2.2. Instrumental

Concentrations of major elements in volcanic ash leachates were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 3100, Perkin Elmer), and trace elements were determined by using two spectrometers (ICP-MS, Elan 6000, PerkinElmer and HR-ICP-MS, Element XR, Thermo Scientific). Ultrapure water was obtained from a Milli-Q system from Millipore (Barnstead, US).

2.3. Leaching experiments

The leaching tests were carried out in batch conditions at room temperature, using unground and unsieved volcanic ash, and a non-aggressive leachant as ultrapure water. For each batch leaching test four replicates were run to ensure the trueness of the experimental data, resulting 18 tests by ash sample and a total

of 72 leachate samples. The mixture of leachant and ash sample was shaken at 20 rpm at room temperature in polypropylene test tubes (14 mm × 100 mm) or polyethylene (HDPE) reactors (50 and 100 ml), depending on the leachate volume. Three different contact times were used in the experiments (1.5, 4 and 16 h). Leachate solutions, previous centrifugation (3000 rpm) during 15 min, were filtered through PVDF syringe filters with tube tip (Whatmann, 25 mm diameter and 0.45 μm pore size) and made up to 100 ml volume in 1% (v/v) HNO$_3$. These solutions were analysed by ICP-OES, ICP-MS, and HR-ICP-MS. The analytical reproducibility was lower than 3%. Given the physico-chemical characteristics of the samples studied, Cl and S concentrations were expressed as Cl$^-$ and SO$_4^{2-}$, respectively. The methods to determine major and trace elements using ICP-MS were described previously [16,17]. Leaching concentrations have been expressed as mg kg^{-1} (major elements) or μg kg^{-1} (trace elements) of dry ash to compare directly the different experimental conditions tested.

2.4. Element selection

Element selection covers the geochemical behaviour range of the main groups of elements implied and takes into account:

(1) the less mobile major elements during the leaching processes (i.e., Si, Al, Mn, Fe, and Ca);
(2) highly soluble components (SO$_4^{2-}$ and Cl$^-$) with preferential enrichment on tephra surfaces [18]; and
(3) elements dominantly combined with halogens and sulphate forming salts (e.g., Na, Mg and K) and acid droplets on particle surfaces in pristine ashes or associated with the volcanic glass dissolution during weathering for ancient ashes (e.g., V and Co) [19].

2.5. Data processing and statistical analysis

A MFD was employed as a multivariate strategy for the evaluation of the effects of selected control factors on the element stripping (Table 1). In our knowledge, it is the first time that this methodology is applied to the design of a leaching protocol for volcanic ashes. Thus, in addition to this section, details of statistical methods are provided in Supplementary material. Three variables (i.e., amount of sample (A), contact time (B), and L/S (C)) were regarded as factors, while the arithmetic mean of the element concentration (*n* = 4) for each batch leaching test was the dependent variable. The factor levels were selected according to previous works on ash leaching tests [15].

3. Results and discussions

A multivariate strategy was used to evaluate the experimental conditions affecting the leaching process, enabling graphical and numeric interpretations of the experimental, but avoiding complex and time-consuming one-at-a-time factor studies.

A MFD was built for the estimation of the effects of amount of sample (A), contact time (B), and L/S (C) and its interactions

Table 1
Variables and levels used for mixed factorial design (MFD).

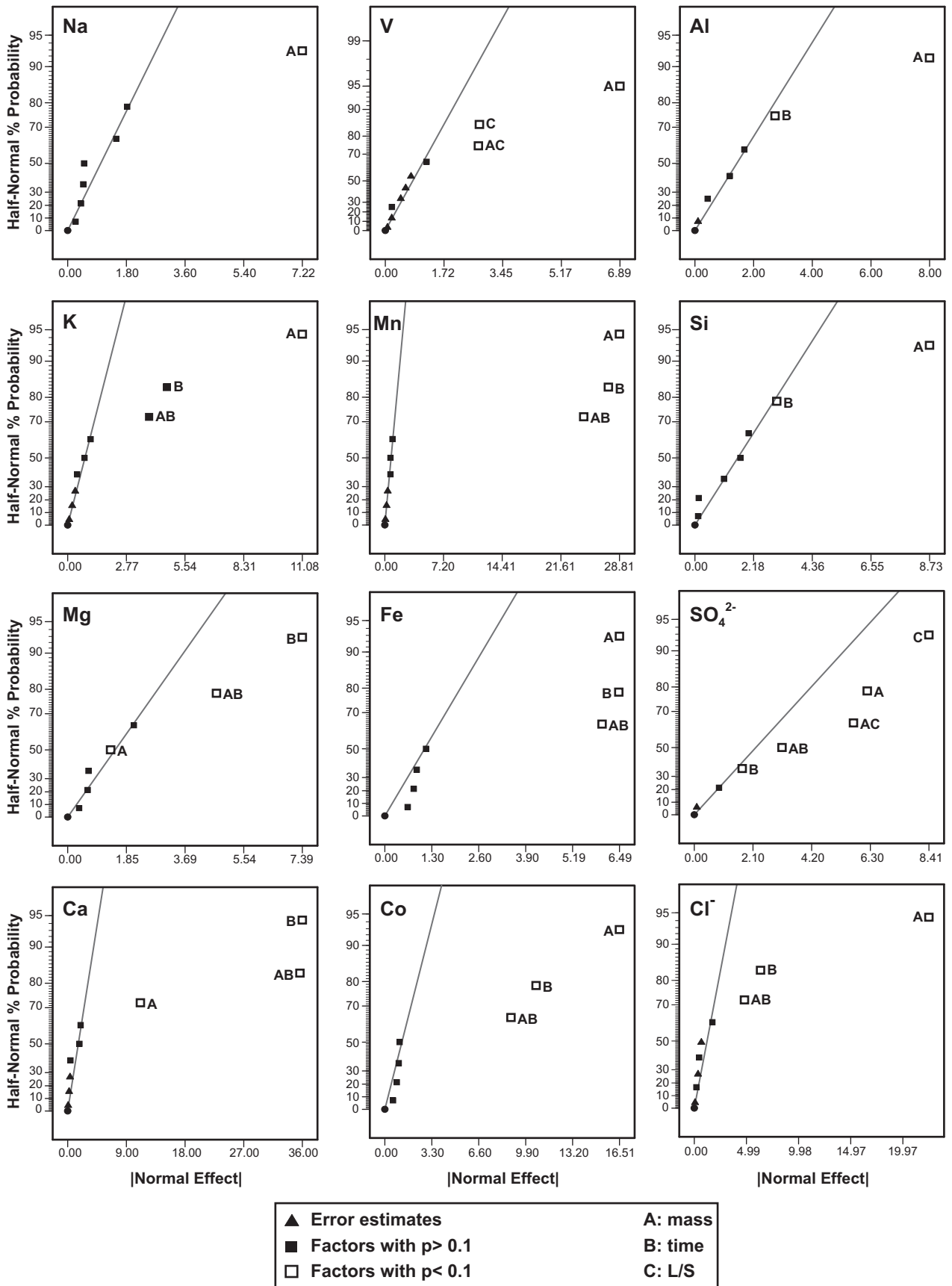| Factor	Variable	Unit	Level 1	Level 2	Level 3
			Actual	Actual	Actual
A	Amount of ash	g	0.1	1	–
B	Contact time	h	1.5	4	16
C	L/S	ml g^{-1}	10	25	50

Fig. 1. Half-normal probability plot of the normalised effects of the selected factors: (A) amount of ash; (B) contact time; (C) L/S ratio for sample 719 (*p*-values obtained by ANOVA not included). Only model terms are labeled.
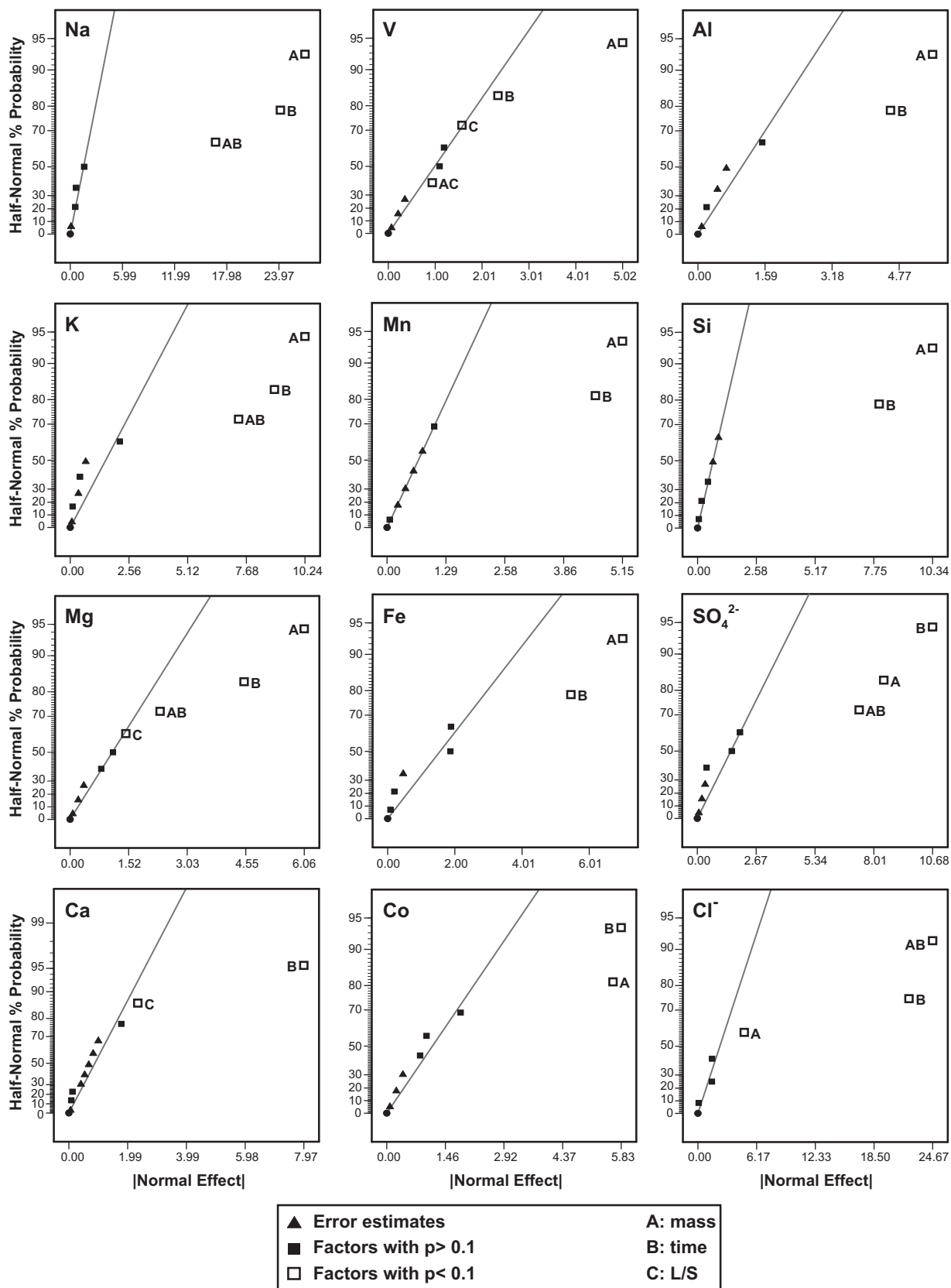
Fig. 2. Half-normal probability plot of the normalised effects of the selected factors: (A) amount of ash; (B) contact time; (C) L/S ratio for sample CHA (*p*-values obtained by ANOVA not included). Only model terms are labeled.

(e.g. AB, AC, BC and ABC). The first factor was evaluated at two levels, while the others at three levels (Table 1). Once outliers were removed from the data sets (one for 719 and one for CHA leaching tests, Table 2a and Table 2b), those factors that were not significant ($p > 0.100$) were removed to improve the models. The significance of each factor was then analysed by means of analysis of variance tests (ANOVA) and represented as Half-probability plots (Figs. 1 and 2) at 95% confidence level.

Fig. 1 shows the results obtained for sample 719 which correspond to an ancient volcanic ash deposited some hundreds of thousands of years ago on land and subjected to hydrological and soil processes, which effectively removed any soluble salts attached to the surface of the ash particles. Thus, the chemical composition must have sourced from transformation processes during the weathering (i.e., hydrological and soil processes as oxidation and washing by meteoric water). Fig. 2 shows the results obtained for
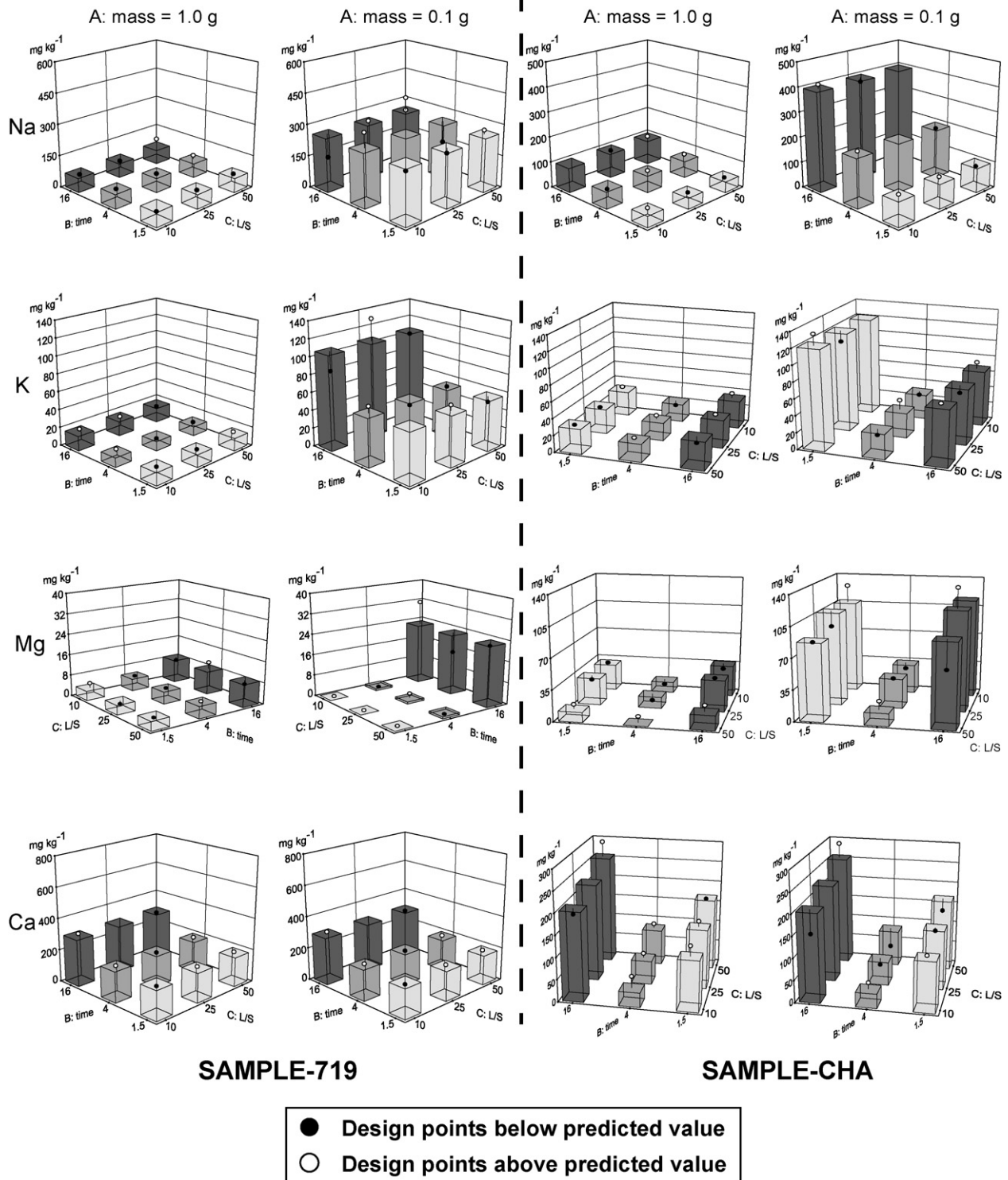

Fig. 3. Model predictions as a function of contact time and L/S. (a) Alkali and alkaline earth elements; (b) transition metals and (c) Al, Si, Cl and SO_4^{2-}.
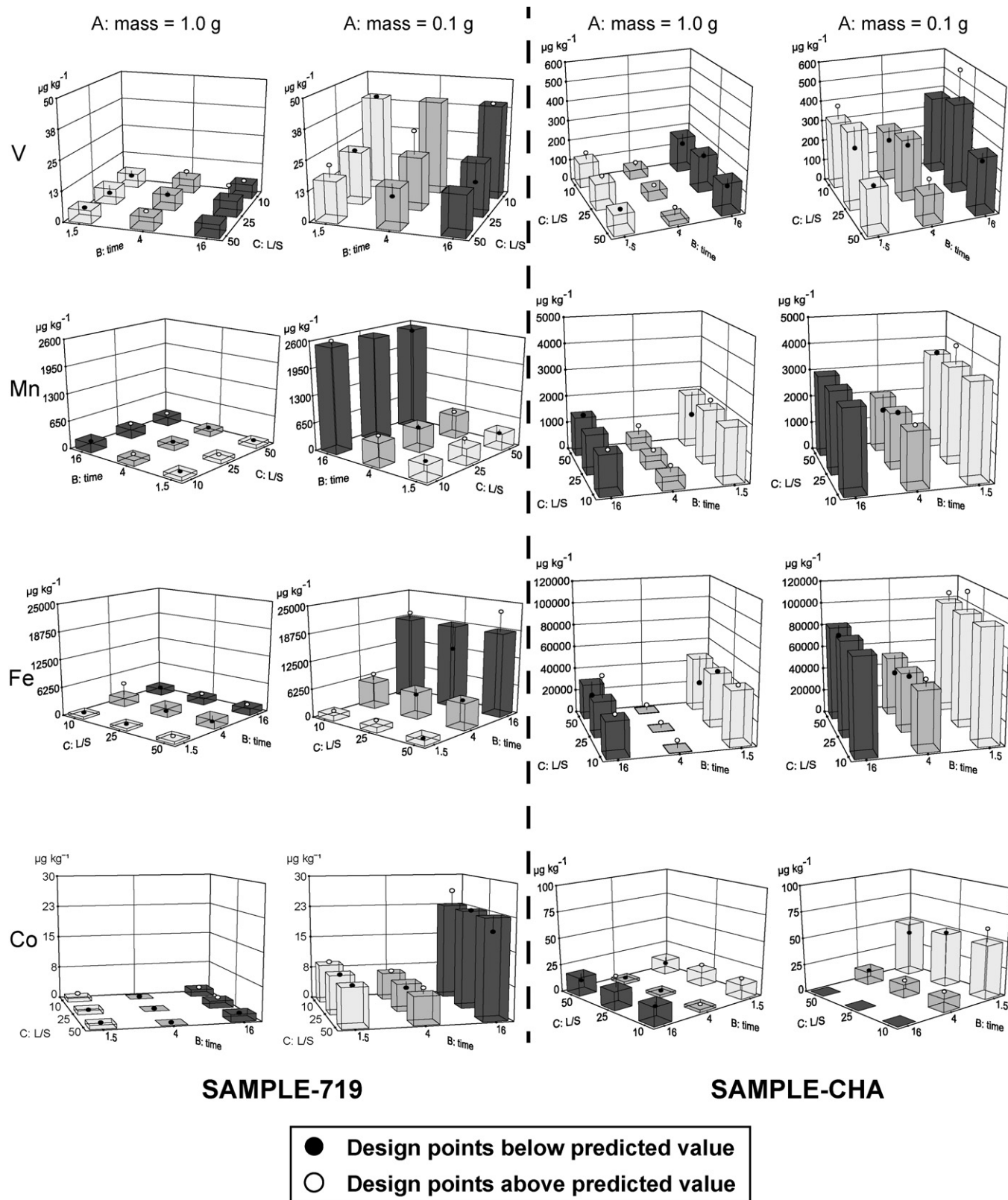
Fig. 3. (Continued)

sample CHA, a pristine ash with deposited salts on its surface that were formed in the plume of the volcanic eruption. This process occur through gas–particle interaction or the partial dissolution of the ash with acidic gases (i.e., mainly SO_2, HCl, and HF) and aerosols (i.e., H_2SO_4), followed by precipitation at the ash–liquid interface, especially for elements with a low volatility in magma (lithophilic elements as V and Co) [18].

The outcome of these studies showed that in the case of the ancient sample, the amount of sample (factor A) had a significant effect over the releasing of alkali elements (Na and K). A
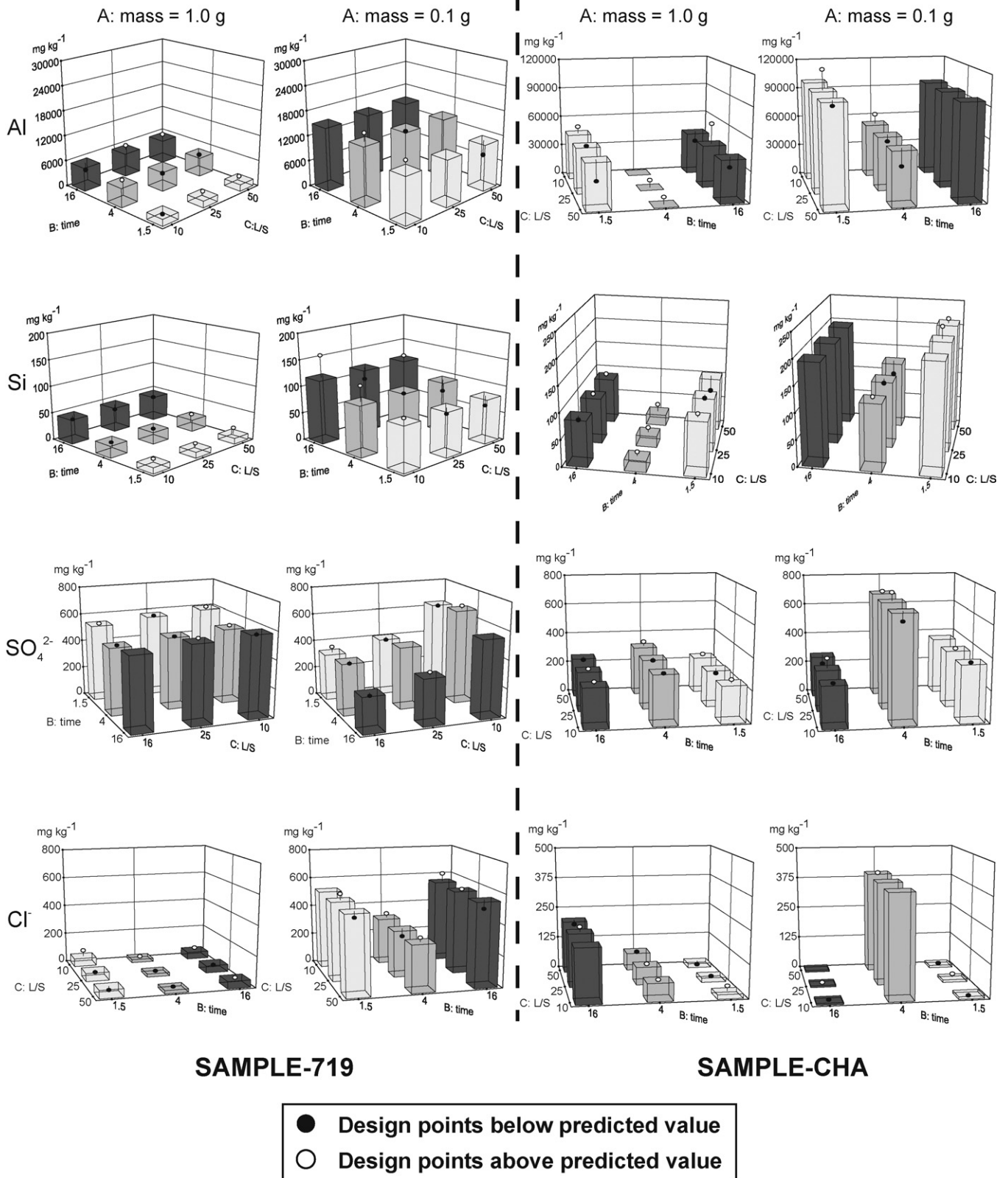
SAMPLE-719   SAMPLE-CHA

● Design points below predicted value
○ Design points above predicted value

Fig. 3. (*Continued*)

reasonable explanation involves the solubilisation of their halide salts and by ionic exchange with H⁺ as mechanism influencing the concentration of these elements in the leachates. Consequently, concentration in the liquid phase is limited only by the solubility and the pH solution. Beyond Na and K also Al and Si showed an influence of the amount of ash as well. In this case, they are solubilised by the destabilization of the silicate framework [13]. Both amount of ash (A) and leaching time (B) influenced the amount of Mg, Ca, V, Mn, Fe, and Co implying exchange process with H⁺ (once alkali elements were solubilised); but as their solubilised

amount (and pH) increases, they have the chance to precipitate or be adsorbed on the solid surface, generating changes in their concentration. With the exception of SO_4^{2-} ion, none of the elements are influenced by the L/S ratio (C).

The scheme depicted with the pristine sample (Fig. 2) was quite different in some cases. This fact is due to two main reasons: (1)

the presence of salts and oxides in the ash surface are additional sources of metal; and (2) since neither natural weathering nor leaching have been occurred, there is still a number of non accessible sites in the solid structure, resulting in slower exchange kinetics. Phenomena of salt dissolution, ionic exchange (at first with H^+, but later with alkali elements), precipitation and adsorption run
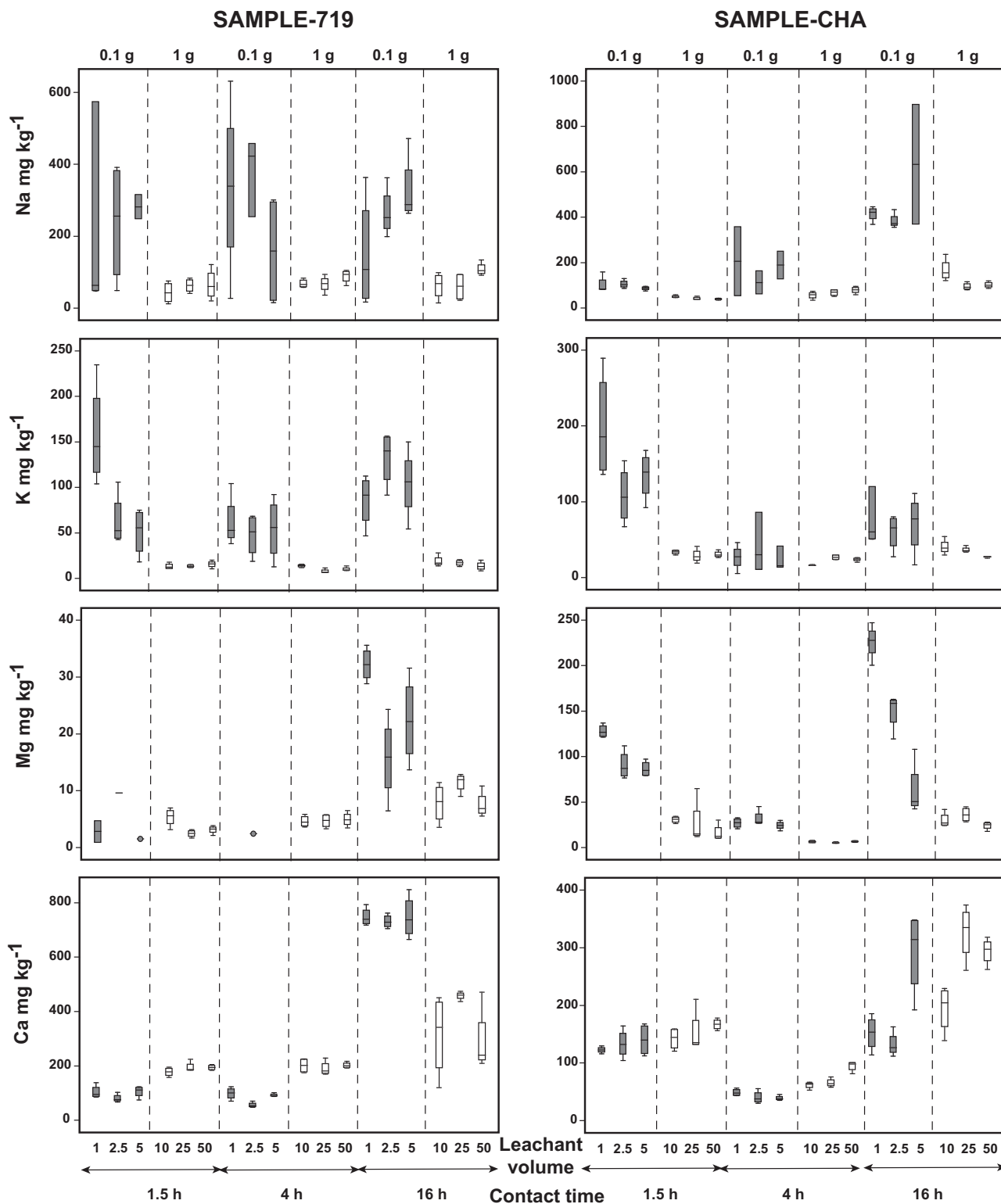

Fig. 4. Box plots ($n = 4$) of the experimental results obtained for each element. (a) Alkali and alkaline earth elements; (b) transition metals and (c) Al, Si, Cl and SO_4^{2-}. Leachant volume is expressed in ml.
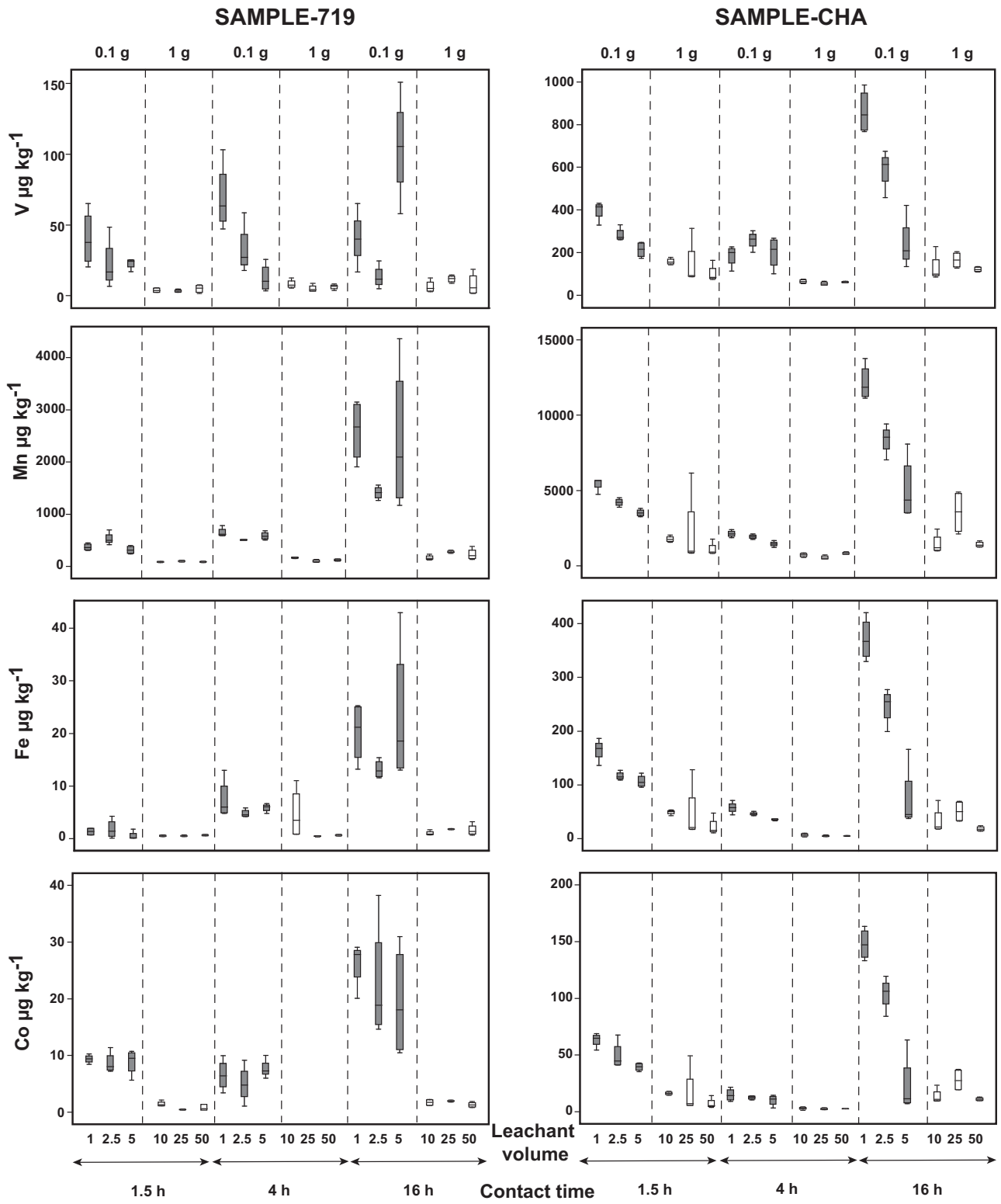
Fig. 4. (*Continued*)

consecutively. At this point, the mass (A) and leaching time (B) seems to be significant for all the elements studied. Exceptions to this are V (only the ash mass is significant) and Ca (only the contact time is significant).

In the light of the findings of the MFD, it is obvious that both mass and contact time are the control factors with the strongest influence on the leaching for the most elements; and the L/S ratio

is influencing for fewer elements. Fig. 3a–c depicts 3D bar plots featuring the experimental domain, where the analyte responses (predicted) varies as a function of time and L/S when 0.1 or 1.0 g of ash was used. In those figures, the real values (white or black points) are compared with those adjusted (columns). It is evident that when the leaching tests were carried out with 1.0 g of ash, the analyte concentrations varied less with L/S or time as a general
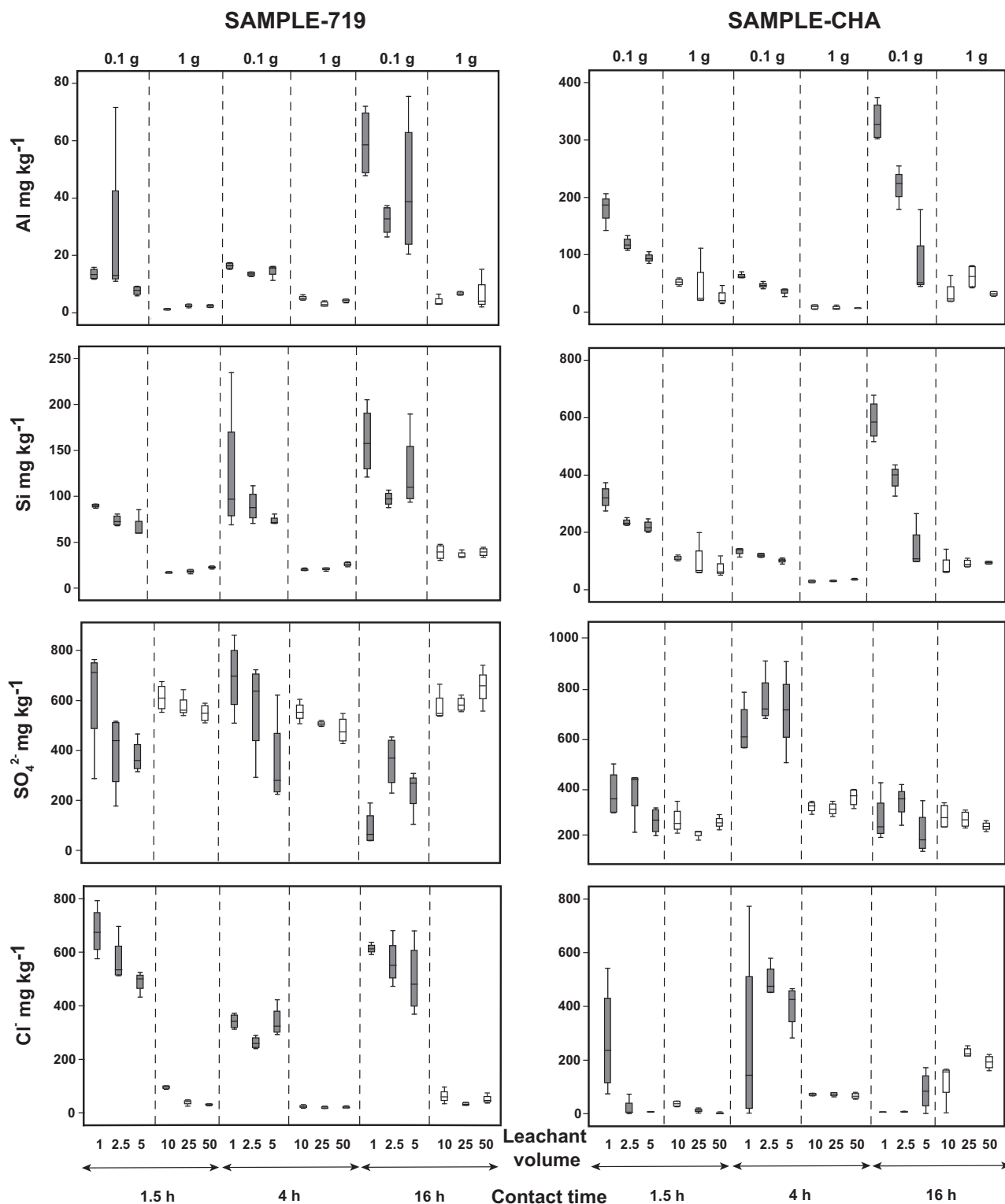
Fig. 4. (*Continued*)

trend. This is to say that, within the levels selected, the higher the mass leached, the lower the effect of the other two control variables. The studentised residuals of the model also evidence this feature (see Supplementary material). On the other hand, even at 1.0 g of ash, the effect of leaching time is more severe for V, Mn, Fe and Co than for alkaline earth elements, Si, Al, Cl, and SO_4^{2-}. The role of mass as control factor is difficult to interpret from a chemical point of view. A possible explanation could be that differences in

grain size distribution produced heterogeneities in samples of 0.1 g. Larger sample mass should be investigated to shed further light to the results shown (e.g., 10, 50 and 100 g of ash).

The precision of the procedure is a combination of the errors of each individual step: sampling, weighing, sample preparation, dilution, sample application, development, detection, evaluation and calculation. As a consequence, precision must considered the degree of agreement among individual test results when the

Table 2a
Mixed factorial design ($2^1 \ast 3^2$, 18 experiments) and arithmetic mean values ($n = 4$) of element and compound concentrations for 719 sample.

Experiment	Ash Amount (g)	Contact Time (h)	L/S (ml g⁻¹)	Ca	Mg	Na	K	Si	Cl	SO₄²⁻	Al	V	Fe	Mn	Co
1	0.1	1.5	10	103.4	nd	228.5	*	89.6	*	619.2	13577	40.3	1357	370.0	9.38
2	1	1.5	10	177.2	5.34	43.4	13.4	16.9	95.2	612.1	1222	3.85	548	86.6	1.48
3	0.1	4	10	98.5	nd	334.2	62.0	124.5	341.6	691.6	16331	*	7463	652.3	6.55
4	1	4	10	201.2	4.60	68.2	13.8	20.1	23.9	554.2	5246	8.18	4721	168.4	nd
5	0.1	16	10	747.5	32.2	149.0	85.6	160.4	613.7	*	*	40.5	20208	2598	26.2
6	1	16	10	313.6	7.81	62.8	19.0	39.3	62.7	574.1	3957	6.41	1042	168.5	1.72
7	0.1	1.5	25	80.3	nd	238.1	63.3	73.5	568.9	393.3	*	22.1	1817	529.4	8.69
8	1	1.5	25	195.6	2.48	62.9	13.5	18.3	39.6	576.2	2527	3.33	533.1	101.9	0.46
9	0.1	4	25	56.0	2.47	378.2	47.5	89.5	262.2	*	13504	32.6	4812	509.1	4.96
10	1	4	25	190.0	4.68	66.9	7.81	20.9	19.6	507.2	3077	5.13	468	102.1	nd
11	0.1	16	25	731.1	15.6	266.1	132.0	97.3	564.1	355.6	*	13.3	13186	*	22.7
12	1	16	25	*	11.4	59.5	17.1	36.1	32.9	585.0	6693	11.8	1811	277.6	1.97
13	0.1	1.5	50	105.2	nd	281.8	51.2	66.5	489.3	375.5	7726	22.7	542	316.7	8.85
14	1	1.5	50	194.1	3.15	65.7	15.7	22.6	30.7	549.5	2360	4.9	670	88.5	0.78
15	0.1	4	50	92.2	nd	158.6	54.2	73.6	340.5	351.3	*	12.4	5888	586.9	7.66
16	1	4	50	202.2	4.94	88.8	10.2	26.0	20.9	480.7	4254	6.24	661	122.8	nd
17	0.1	16	50	746.9	22.4	327.8	104.1	125.8	502.3	238.0	*	*	23277	2431	19.4
18	1	16	50	290.1	7.53	108.4	13.7	39.3	50.9	*	6348	*	1662	232.1	1.32

Ca, Mg, Na, K, Si, Cl, SO₄ in mg kg⁻¹, Al, V, Mn, Fe, Ni, As, Sr, Mo, Ba in µg kg⁻¹, *outliers, nd, not detected (taken as zero for the factorial analysis).

Table 2b
Mixed Factorial design ($2^1 \ast 3^2$, 18 experiments run) and arithmetic mean values ($n = 4$) of element and compound concentrations for CHA sample.

Experiment	Ash amount (g)	Contact time (h)	L/S (ml g⁻¹)	Ca	Mg	Na	K	Si	Cl	SO₄²⁻	Al	V	Fe	Mn	Co
1	0.1	1.5	10	122.7	128.0	102.3	*	*	nd	364.9	*	397.5	*	*	63.3
2	1	1.5	10	142.2	30.8	50.2	33.7	110.7	37.1	258.4	52322	158.1	49209	*	16.2
3	0.1	4	10	49.0	27.0	206.4	26.8	133.9	*	625.1	63086	185.6	57877	2126	14.9
4	1	4	10	61.5	6.56	56.3	16.4	29.4	71.4	312.1	*	65.0	6830	720.7	3.06
5	0.1	16	10	151.8	*	414.6	77.0	*	6.57	266.0	*	*	*	*	*
6	1	16	10	194.3	30.1	*	40.6	82.7	*	274.9	32062	128.7	33347	1465	13.7
7	0.1	1.5	25	133.2	90.6	105.5	108.3	234.9	21.6	371.0	118820	284.0	116420	4212	49.5
8	1	1.5	25	153.3	26.7	42.8	28.8	98.1	12.3	205.1	45025	146.8	46873	2241	17.3
9	0.1	4	25	40.4	32.0	*	42.5	120.5		741.1	46794	258.5	46260	1947	12.6
10	1	4	25	65.7	5.39	68.4	26.8	30.8	72.3	304.0	7420	55.0	5043	558.5	2.51
11	0.1	16	25	*	149.8	383.5	59.8	*	7.35	332.2	*	589.6	*	*	*
12	1	16	25	*	36.3	95.3	36.8	91.9	228.7	262.3	61992	165.4	50583	*	28.0
13	0.1	1.5	50	140.0	86.6	86.7	134.7	220.2	7.11	*	94256	213.3	106777	3529	39.5
14	1	1.5	50	167.1	16.4	39.6	30.6	73.8	2.09	249.7	25438	101.6	22446	1111	7.30
15	0.1	4	50	39.0	24.3	190.0	23.8	101.7	399.9	694.6	36214	200.2	35647	1447	10.1
16	1	4	50	94.5	6.85	78.9	23.9	36.5	66.3	349.6	6942	62.3	5085	834.8	2.64
17	0.1	16	50	292.1	63.1	*	70.6	*	*	208.2	*	243.6	73377	*	*
18	1	16	50	293.8	24.1	102.4	27.3	95.0	191.7	234.9	32076	121.6	18435	1415	11.2

Ca, Mg, Na, K, Si, Cl, SO₄ in mg kg⁻¹, Al, V, Mn, Fe, Ni, As, Sr, Mo, Ba in µg kg⁻¹, *outliers, nd, not detected (taken as zero for the factorial analysis.

procedure is applied repeatedly to multiple samplings of a homogeneous sample. Box plots were performed (Fig. 4a–c) to enable both graphical evaluation and comparison of the precisions at different experimental conditions for the two data sets. As it was expected from the all stated, the best conditions in terms of precision were achieved when 1.0 g of ash were leached in any set of conditions. Low amount of sample (0.1 g) is not always representative of the ash under study, because it is more difficult to reach the chemical equilibrium in these experimental conditions. In general, the leachant volume has a low influence on the element release when 1 g of sample is employed in the leaching tests. Lower reproducibility was obtained at high L/S ratio, mainly at high contact time. The working hypothesis to explain these findings is the incongruent dissolution of glasses and other compounds occurring in volcanic ashes, as in the early stages of weathering [8]. Furthermore, it is an interesting variable designing a leaching test due to analytical reasons. The choice of a high L/S ratio means a larger dilution, which could lead to the inconvenience of concentrations close or lower to the detection limits. In general, the lowest dispersion was observed when 1.0 g of ash was leached with L/S ratio equal to 10 and shaking during 4 h.

4. Conclusions

The batch leaching principles of volcanic ashes have been examined in this work. Most of the soluble constituents of volcanic ash have been evaluated by one stage leaching tests. In this study we have shown that certain control factors significantly affect the results obtained in terms of concentration of elements relative to ash mass. Of the three factors studied, it was evident that the mass of ash affected not only the variability of the data, but also the influences of the other two factors (e.g., time of contact and liquid-to-solid ratio). The sample mass is difficult to explain as control factor from a chemical point of view and probably is consequence of sample heterogeneity associated with differences in grain size distribution among samples of 0.1 g. Thus, the results are not conclusive on this feature and larger sample mass should be investigated to shed further light to the results shown.

With the available data, the recommended methodology for batch leaching tests of volcanic ashes is based on the use of a L/S ratio of 10, using 1.0 g of unsieved and unground ash and 10 ml of ultrapure water, shaking the mixture for 4 h. The entire method is completed within few hours, and its design is simple, feasible and reliable in laboratory conditions.

The recommended protocol discussed in this work differs from protocols used in earlier studies and the protocol proposed by Witham et al. [15] (i.e., shake an ash-leach mixture for 90 min in a sealed container; using an ash (g) to water (ml) ratio of 1:25), which no longer seem appropriate to harmonize the obtained results. The main differences are related to the contact time (too short or too long than 4 h). These findings demonstrate the need of define the optimum leaching conditions and adopt a standard protocol to leachate volcanic ash.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.091.

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