LEACHING BEHAVIOUR OF HAZARDOUS WASTE UNDER THE IMPACT OF DIFFERENT AMBIENT CONDITIONS.

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ABSTRACT

The overall objective of this study is to provide an improved basis for the assessment of the leaching behaviour of waste marked as hazardous partly stabilised (European waste catalogue code 19 03 04*). Four samples of hazardous partly stabilised waste were subjected to two leaching tests: up-flow column tests and batch equilibrium tests. The research was carried out in two directions: the first aims at comparing the results of the two experimental setups while the second aims at assessing the impact of different

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Abbreviations: DOC, dissolved organic carbon; L/S, liquid to solid ratio; LOD, limit of detection; PCA, principal component analysis; TOC, total organic carbon; TS, total solids; TVS, total volatile solids; WHPS, waste marked as hazardous partly stabilized.

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ambient conditions on the leaching behaviour of waste. Concerning this latter objective the effect of mesophilic temperature, mechanical constraints and acid environment were tested through column percolation tests. Results showed no significant differences between batch and column leaching test outcomes when comparing average concentrations calculated at a liquid to solid ratio of 10 $l \cdot kg^{-1}$TS. Among the tested ambient conditions, the presence of an acid environment (pH 4.5) accelerated the leaching process resulting in a higher cumulative released quantity measured on the majority of the investigated polluting substances. On the contrary, the effect of temperature and mechanical constraints seemed to not affect the process showing final contents even lower than values found for the standard test. This result was furthermore confirmed by the application of the principal component analysis. Column tests represent an effective tool for assessing environmental impact over time finding peak concentrations in the early stages of the elution process that batch tests are not able to detect. Nevertheless, column tests are time-consuming and batch tests can be a valuable alternative when time is a constraint.

Keywords: Hazardous Waste; Leachate; Column Leaching Test; Batch Leaching Test; Landfilling; Partly Stabilised Waste.

1. Introduction

In 2013, more than 1 million tons of hazardous waste were disposed in Italian landfills (ISPRA, 2015). In order to provide environmental protection, the disposal of hazardous waste in landfill is governed by National and European legislations (*European Council Decision 2003/33/EC of 19 December 2002*) that set strict criteria to be fulfilled. Hazardous waste can be disposed in underground storage or in landfills in accordance with the acceptance criteria or due to derogations of the limit values (e.g. inorganic elements, total organic carbon, dissolved organic carbon). In particular, hazardous waste can be disposed in non-hazardous landfills if stable and non-reactive. Considering the definition provided by the European Council (2002), stable and non-reactive means that the leaching behaviour of waste do not change adversely in the long-term under landfill design conditions or foreseeable accidents as the impact of ambient conditions: e.g. temperature, mechanical constraints, etc..

Waste marked as Hazardous Partly Stabilised (WHPS, European waste catalogue code 19 03 04*) are solidified/stabilised waste that after the stabilisation process can release dangerous constituents which have not been changed completely into non-dangerous in the short, middle or long term (EPA, 2002). The composition of WHPS is strongly heterogeneous including hazardous waste from waste processing facilities (e.g. fly and bottom ashes from incinerators) or wastewater treatment plants (e.g. industrial sludge). As a consequence, their chemical characteristics are also heterogeneous and their disposal scenarios concern several possibilities such as underground storage or even non-hazardous landfills in compliance with the acceptance criteria or their derogations. Nevertheless, in accordance with their characteristics, the elution process of this category of waste is not easy to predict and their acceptance in hazardous or non-hazardous landfills may be source of environmental risk due to the uncertainty of the release of polluting substances over time. As such, a deep understanding of the release of contaminants upon contact with water and under different landfill conditions (European Council, 2002) is of prime importance in order to investigate the stability of WHPS .

The release of soluble substances into water phase is the result of several phenomena that can occur simultaneously depending on leaching conditions, properties of the solid matrix and physic-chemical processes (Batchelor, 2006). Leaching tests are common tools for assessing constituent release upon contact with water (Lopez Meza et al., 2008). According to Harwell (1999), leaching tests can be divided into two general categories: static and dynamic extraction tests. In static extraction protocols (batch tests), leaching takes place with a single volume of leachant while in dynamic extraction protocols, the leaching fluid is renewed throughout the test.

Batch equilibrium tests typically consists of contacting a sub-sample of material with a liquid phase in order to establish pseudo-equilibrium conditions. Once equilibrium is established, release is dependent on the geochemistry of the solid phase and on the chemistry of the liquid phase rather than on contact time (Garrabrants and Kosson, 2005).

Dynamic extraction tests provide information about the kinetics of contaminant mobilization and results are presented as a function of time. Among dynamic extraction tests, flow-through tests (e.g. column tests) are used to obtain information on short and long term leaching behaviour (Butcher et al., 1996). Water is percolated through a column of material and collected as a function of liquid to solid ratio (L/S), which is used to represent leaching time. Flow-through leaching test methods can be used to simulate the leaching process of wastes disposed under particular landfill conditions. For example when waste is more permeable than its surrounding materials or when it has degraded under various environmental stresses to a state that ground water can flow-through the waste via the porosity system of the waste matrix (Poon and Chen, 1999). In this case, when the leachant flows through the waste, it carries away the mobile fraction of the contaminants. At the same time the immobile fraction is continuously solubilized to re-establish the equilibrium. The leachant flowing via the porosity system of the solid waste matrix carries away the mobile fraction and causes a contaminant concentration gradient which accelerates the leaching process. Because of its ability to accelerate the leaching process the flow-through leaching test methods can be used to study the long term leaching performance of waste (Poon and Chen, 1999).

In compliance with the standard methods EN 12457, 2002 (L/S=10 $l \cdot kg^{-1}$TS) and CEN TS 14405, 2015 (L/S=0.1 $l \cdot kg^{-1}$TS), batch equilibrium tests and percolation tests are acquired by the *European Council Decision of 19 December 2002* as criteria for acceptance of hazardous waste in landfill.

When comparing batch and column tests, batch experiments offer the advantage of easier design, while column testing provides an optimum approximation to leaching processes that occur under field conditions without compromising reproducibility of experiments (Butera et al., 2015; Delay et al., 2007; Dijkstra et al., 2006). Column tests are more suitable for prediction purposes, but they are often time-consuming, reaching duration of several weeks. Alternatively, batch tests can be carried out in shorter periods of time, varying from several hours to few days. In the light of the practical advantages and disadvantages, it is important to understand the similarities and differences between constituent leaching under batch and column tests with the aim to provide effective tools for environmental decision-making (Lopez Meza et al., 2008).

Several researches have been performed on various waste categories aim to study the leaching behaviour by means of batch and column tests: stabilised/solidified waste (Barna et al., 1997; De Windt et al., 2007; Liu et al., 2013; Malviya and Chaudhary, 2006; Poon et al., 2001), mining waste (Al-Abed et al., 2008; Turner et al., 2009), construction and demolition waste (Butera et al., 2014; Butera et al., 2015; Delay et al., 2007; Lopez Meza et al., 2008; Nielsen et al., 2006; Roussat et al., 2008), contaminated soils (Cruz Payán et al., 2012; Gardner et al., 2007; Hartley et al., 2004), fly-ash stabilised soils (Bin-Shafique et al., 2006), soils used in construction works (Quaghebeur et al., 2006). To our knowledge, the leaching behaviour of WHPS and its alteration to foreseeable landfill conditions has not yet been studied.

The overall objective of this study is therefore to provide an improved basis for the assessment of constituent release from WHPS. Four WHPS samples obtained from different waste treatment facilities in Tuscany (Italy) were subjected to both batch equilibrium and up-flow column tests and evaluated in relation to: differences between column and leaching test in the release of polluting substances and the impact of different ambient conditions on the leaching behaviour (temperature, mechanical constraints and acid environment).

2. Materials and methods

2.1 Materials

Four WHPS samples (W1, W2, W3 and W4 – European Waste Code 19 03 04*) were obtained from four different treatment facilities in Tuscany (Italy). WHPS samples were selected based on easy procurement of the waste and according to chemical analysis with the intent to study a significant range of cases. According to the description of the production process provided by the facility operators, W1-W4 were obtained after a solidification/stabilization treatment of hazardous and non-hazardous waste. In particular W1-W4 were composed by: fly ashes containing dangerous substances (19 01 13*), bottom ashes and slags containing dangerous substances (19 01 11*), filter cakes from gas treatment (19 01 05*), soil and stones containing dangerous substances (17 05 03*), solid wastes from gas treatment containing dangerous substances (10 02 07*), sludge from treatment of urban waste water (19 08 05), sludge from biological treatment of industrial waste (19 08 12) and sludge containing dangerous substances from biological treatment of industrial waste water (19 08 11*). The hydraulic binders used for the treatment were lime and Portland cement. The sampling was done in compliance with the standard procedure EN 932-1 (1996): sample increments were collected from different positions in the stockpiles by means of a shovel and combined into primary samples (approximately 20 kg) which were transported to the laboratory by means of sealed plastic drums. Sub-samples (test portions) of each of the primary samples were then used for leaching tests. A summary of the physico-chemical characteristics is provided in Table 1.

Here Table 1.

2.2 Batch leaching test and column leaching tests at standard conditions

Two types of leaching were in focus: batch equilibrium tests and up-flow saturated columns.

Batch equilibrium tests were carried out according to EN 12457-2 (2002) standard test for materials with particle size dimensions < 4 mm and by using a L/S of 10 l kg^{-1}TS.

Up-flow column leaching tests with demineralized water as leaching agent (conductivity of 1 $mS \cdot m^{-1}$) were carried out according to CEN TS 14405 (2014) with modification of the column dimensions. Columns made of plastic (PTFE) with a base of 115.2 cm^2 and a volume of 1920 ml were used. The sample packing procedure was carried out firstly fitting the bottom section with a layer of approximately 1 cm of fine-grained inert material. The column was then filled with the test sample in five consecutive layers that were packed by using a weight of 0.5 kg dropping it three times. The weight felt down 20 cm along a rod used as guide. Finally the top section of the column was fit with another layer of approximately 1 cm of fine-grained inert material. The dry mass (m_0) of the sample was determined in accordance with the mass of the sample and total solids (TS) data. Based on the volume of the column, density was also calculated.

The test was started after having saturated the column with the leaching agent using a peristaltic pump (FH10, Thermo Scientific, Italy). In order to equilibrate the system, the saturated material was left in static conditions (without flow rate) for a period of three days. To verify equilibrium conditions at the outlet of the column, pH was measured on a first small portion of eluate (15 ml) and on the first collected fraction. The system was assumed in equilibrium if the pH values measured in the two portions of eluate do not deviate more than 0.5 pH unit. After the equilibrium period, the upwards flow rate was set at 72.1 ml·h^{-1} which corresponds to a linear velocity of 15 cm·d^{-1}. Tests were performed until a L/S of 10 l·kg^{-1}TS was reached. During the experiment seven eluate fractions *i* were collected at predefined intervals (i: 0.1, 0.2, 0.5, 1, 2, 5 and 10 l·kg^{-1}TS). Each fraction was then filtered through a membrane with a pore size dimension of 0.45 µm and stored in sealed bottles before analysis.

For each component the quantities released in all eluate fractions were calculated as in eq. 1:

$$U_i = \frac{(V_i \cdot c_i)}{m_0} \tag{1}$$

where:

i: index of the eluate fraction (L/S=0.1, 0.2, …,10);

U_i: released quantity of a component per quantity of sample in the eluate fraction i (mg·kg^{-1}TS);

V_i: volume of the eluate fraction i (l);

c_i: concentration of the component concerned in the eluate fraction i (mg·l^{-1});

m_0: dry mass of the test portion (kgTS).

When the concentration of a component resulted lower than the limit of detection

(LOD), the upper limit of U_i was calculated by making c_i equal to the LOD (CEN TS 14405, 2014). For each specific component the cumulative released quantity was calculated by accumulating the released quantities measured in the different eluate fractions (U_i).

The parameters analysed in the eluates belong to the list set by European Council (2002) for the acceptance criteria of hazardous and non-hazardous in landfills (leaching limit values). The investigated parameters were selected based on statistical significance. In particular, components were not analysed if after performing the batch equilibrium test they were found under the LOD for at least the half of the investigated samples. As such, the concentration of DOC (dissolved organic carbon) was measured in accordance with APAT (2003) method; the concentrations of Cr, Cu, Ni, Zn by using EPA 6020A (2007); sulphates and chlorides by using EPA 9056A (2007); pH by using APHA (2006).

2.3 Column leaching tests assessing ambient conditions

In order to evaluate the impact of ambient conditions on the leaching behaviour of WHPS, column leaching tests were performed on W1 and W2 by assessing mechanical constraints, temperature and acid environment. The results of these tests were compared with the results obtained through the application of the standard protocol (used as blank assay). W1 and W2 were selected among the tested samples as cases of high contamination (W1) and low contamination (W2). Column leaching tests were preferred to batch equilibrium tests for their capability of investigating the leaching behaviour and thus the stability of waste over time. Temperature and mechanical constraints were studied following the indications of the European Council (2002). Even if the landfill body is mostly characterized by alkaline environment, acid conditions were studied ad absurdum as a critical aspect that can accelerate the elution process (Du et al., 2012; Liu et al., 2013).

The mechanical constraint effect was obtained replying five times the packing procedure used for the standard test. In this case a weight of 1 kg was used. This operation provided an increase of density inside the column of approximately 15% for both waste. In order to contextualise this phenomenon with field conditions, the increase of density occurs inside the landfill body in relation to an increase of depth and effective stress (Beaven, 2000).

The temperature effect was assessed warming the leachant up to 40°C. This temperature can be reached inside the landfill body under mesophilic conditions (Raga and Cossu, 2013; Tong et al., 2015; Wang et al., 2012). The column was furthermore enveloped with an heating coil where water at 40°C was continuously passed through. In order to avoid heat dispersion the system was rolled with an insulation material. Leachant temperature was continuously heated by means of an immersion thermostat heater (Fa 90, Falc Instruments, Italy).

Several studies evaluated the leaching behaviour of waste under acid leachant (Baba et al., 2008; Cruz Payán et al., 2012; Hartley et al., 2004; Liu et al., 2013). In the present research acid conditions were assessed performing the column leaching test by using acidified demineralised water as leaching agent. In particular, demineralised water was acidified to pH 4.5 with concentrated nitric acid, HNO_3 (Du et al., 2012).

3. Results and discussion

3.1 Comparison between leaching tests

Considering column test results, Fig. 1 represents the cumulative trends of W1-W4 (expressed in terms of $mg \cdot kg^{-1}TS$) as function of L/S. The analysed constituents showed similar behaviours over time. In particular two different phases were determined. The first phase was characterized by a deep mobilisation of the constituents. This step is represented by a high slope of the cumulative curves and it is generally associated with the first five fractions, until the L/S=2 l·kg-1TS. As demonstrated by Delay et al., 2007, in this phase, dissolution and surface wash-off processes play a dominant role. The second phase was characterized by a lower slope of the curve. The trends tended towards a horizontal asymptote with the increase of L/S. As reported by other studies (Kalbe et al., 2008; Simon et al., 2008), the depletion of soluble components leads to lower concentrations in the eluates over time until steady state conditions are reached.

Different trends were found for Zn for W2, Cu and Ni for W4 and for sulphates in general. In these cases high concentrations of the contaminant were still persistent in the last collected fractions determining a slow release of the component over time. Anyway, a slight decreasing trend was also observed after the fourth/fifth fraction.

Here Figure 1.

With the aim of comparing batch and column tests, if batch test concentrations ($c_{i,b}$) are compared with column eluates at the same $L/S=i$ the main outcome is an overestimation of the static method (Delay et al., 2007). This is explained by the fact that while in batch tests the eluent is in continuous contact with the material, in column tests the elution agent is constantly renewed. As such $c_{i,b}$ were compared with an average concentration ρ_i calculated for column leaching tests as proposed by Delay et al. (2007). In particular, ρ_i ($mg \cdot l^{-1}$) is determined by the ratio between the total released amount of a constituent (expressed in mg) and the total elution volume (expressed in l) at a given $L/S=i$ (eq. 2).

$$\rho_i = \frac{m_0 \cdot \sum_{i=0.1}^{i} U_i}{\sum_{i=0.1}^{i} V_i} \tag{2}$$

Considering DOC results, the calculated average concentrations at a L/S of 10 $l \cdot kg^{-1}$ ρ_{10} (738 mg/l, 45 mg/l, 429 mg/l and 210 mg/l for W1, W2, W3 and W4 respectively), were found comparable to $c_{10,b}$ (measured to be 656 mg/l, 50 mg/l, 316 mg/l and 152 mg/l). This result was found valid for each of the tested constituents. In order to verify the agreement between batch test results and ρ_{10} a Welch's t-test was applied for each of the tested components to identify significant differences between the two statistical populations. Under this perspective, Tab.2 and Fig.2 provide a comparison between c_{10} and $\rho_{av,10}$. In particular the ratio $c_{10,b}/\rho_{10}$ and its inverse were also analysed (values > 1 indicate overestimation of the batch test, values < 1 indicate underestimation).

Here Table 2.

Here Figure 2.

The two values were generally in agreement, with differences of less than a factor of two for the 90% of the measured elements. This outcome is comparable to the findings achieved by Butera et al., 2015 for the comparison of column and lysimeter experiments. The result was furthermore confirmed by the application of the Welch t-test which underlined that statistically differences were not found between the two data sets ($p > 0.05$). Differences between the two methods were found only for W2 which is characterized by low concentrations, measured even below the LOD for Cu and Ni.

In general column tests represent an effective tool for assessing environmental impact over time. In particular, WHPS present a high release of constituents in the first stage of the elution process while with the increase of L/S and the depletion of soluble substances the leaching behaviour seems to tend towards an horizontal asymptote.

These results are concurring with the findings of Lopez Meza et al. (2008) for other granular waste (bottom ashes, fly ashes, construction debris and laboratory formulated concrete), Delay et al. (2007) and Nielsen et al. (2006) for demolition waste, Quaghebeur et al. (2006) for soils and Bin-Shafique et al. (2006) for fly-ash stabilised soils. Anyway, batch equilibrium tests are valuable tools in order to give a first indication on the leaching behaviour of WHPS resulting in a good approximation with the average concentration leached over time.

3.2 Comparison between different ambient conditions

In order to investigate the impact of ambient conditions, column tests were preferred to batch tests due to their peculiarity to analyse the leaching behaviour over time. As such, mechanical constraints (C), temperature (T) and acid environment (A) were evaluated. Fig. 3 and Fig. 4 represent the different cumulative trends in function of L/S for W1 and W2 respectively.

Here Figure 3.

Here Figure 4.

Analysing the trends over time, the effect of ambient conditions seems to not alter the overall shape of the curves. Also in these cases the leaching behaviour was characterized by a first phase of deep release of constituents and by a second phase characterized by low concentrations.

In order to compare the impact of ambient conditions on the leaching behaviour, results were compared with the outcomes of the standard protocol (used as blank assay). In particular the average concentration at L/S=10 $l \cdot kg^{-1}$TS was calculated for each of the tested conditions and used as following, eq. 3:

$$\Delta\rho_{10,X} = \frac{\rho_{10,X} - \rho_{10}}{\rho_{10}} \quad (3)$$

where:

$\Delta\rho_{10,X}$: variation of the average concentration of a component compared to blank assay results. X represents C, T and A alternatively (%);

$\rho_{10,X}$: average concentration of a component calculated for the different ambient conditions ($mg \cdot l^{-1}$);

ρ_{10}: average concentration of a component calculated for the blank assay ($mg \cdot l^{-1}$).

Tab. 3 shows the percentage variation $\Delta\rho_{10}$ calculated for C, T and A experiments in comparison with the standard test.

Here table 3.

Evaluating $\Delta\rho_{10}$ results, acid environment showed a higher impact on Cr, Cu and chlorides for both W1 and W2. In the same way, the effect of mechanical constraint was mainly relevant for DOC and chlorides. For Ni the application of ambient conditions reported different results for W1 and W2. Indeed while for W1 all the ambient conditions reported an increase of average concentration, for W2 only the impact of temperature reported a significant increase. Considering Zn and sulphates, the effect of conservative conditions seemed to not alter their cumulative release at standard conditions. Only for sulphates the effect of the acid environment produced an increase of cumulative release for W2.

Principal Component Analysis (PCA) is increasingly used for experimental data analysis on environmental topics to extract a small number of latent factors with the intent of analysing the relationship among the observed variables (Singh et al., 2016). While it is commonly used to identify the sources of pollution, in the present research PCA was performed with the aim to deeply investigate the leaching behaviour of W1 and W2 in relation to the application of batch and column tests and regarding the application of different ambient conditions. As such, the analysis was performed considering 5 parameters: ρ_{10}, $\rho_{10,A}$, $\rho_{10,T}$, $\rho_{10,C}$ and $c_{10,b.}$ In accordance with Kaiser normalization, only the components with eigenvalue higher than 1 were considered as relevant. In particular, the two principal components extracted accounted for 84.5% of the total variance. The first component was dominated by high positive loading in DOC, Ni and sulphates (0.967, 0.855 and 0.950 respectively) and a high negative loading in chlorides and Zn (-0.829 and -0.767 respectively). The second component had a strong positive loading only on Cr (0.840) and moderate positive loadings on Cu, Zn and chlorides. By comparing the different loadings and the score plot (Fig. 5) it was possible to confirm the relationship between the different concentrations previously highlighted. In particular, the tests performed on W1 were clustered together with the exception of the outcome obtained for acid environment (W1- $\rho_{10,A}$). In this case its position on the score plot was found far from the other dots representing the batch test and the other ambient conditions. This result confirmed that the impact of mechanical constraint and temperature do not affect the leaching behaviour while acid environment produces an overall higher release of polluting substances. Here again, in the light of the score plot, it can be noticed that there is no significant difference between standard column test and batch test results (W1- $\rho_{10,}$ W1- $c_{10,b}$). This results was not evident for W2 since W2- ρ_{10} and W2- $c_{10,b}$ dots were distant from each other reflecting what previously reported in chapter 3.2 for W2. Even if with a lighter effect, also in this case the acid conditions seemed to worsen the overall release of polluting substances. The score plot furthermore confirmed that mechanical constraints and temperature do not impact the leaching behaviour of W2 since their dots are placed in a free-component space.

Here Figure 5.

In order to assess the stability of waste, column leaching tests are viable tools to investigate the changes of leaching behaviour over time under the effect of ambient conditions. With respect to WHPS, acid environment seems to accelerate the leaching process resulting in a higher cumulative released quantity measured on a consistent number of tested components. The harmful impact of an acid leachant is concurring with main findings of Liu et al. (2013) who found an increase of phenol leaching for solidified/stabilised hazardous waste under pH = 4.9. On the contrary, the effect of temperature and mechanical constraint did not affect the process showing final contents even lower than values found for blank assay.

4. Conclusions

The leaching behaviour of four WHPS samples was tested using two different leaching tests: batch and column tests. The impact of ambient conditions such as temperature, mechanical constraints and acid environment was also assessed performing column tests. While temperature and mechanical constraint are impacts that commonly occur inside the landfill body, it is interesting to study the effect of acid conditions since it is a critical aspect that can accelerate the elution process.

Batch tests results showed good agreement with column test results in terms of average concentration calculated at a liquid to solid ratio of 10 $l \cdot kg^{-1}$TS. As such, when time is constraint in the decision-making process or when column tests are not accessible, batch tests can be an optimum alternative for an overall indication. Despite this, column tests deeply assess the leaching behaviour of WHPS finding peak concentrations in the early stages of the elution process that batch tests are not able to show. Under this perspective column tests are viable tools to analyse the release of constituents over time, in the short, medium and long term.

In the matter of evaluating the impact of ambient conditions, only the application of acid environment seems to accelerate the leaching process of WHPS. In this case a deeper mobilisation of the polluting substances was observed. This condition was studied ad absurdum since alkaline condition are mostly present inside the landfill body. On the contrary, the effect of temperature and mechanical constraint did not affect the process showing final contents even lower than values found for the test performed at standard conditions.

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Highlights

- The leaching behaviour of waste marked as hazardous partly stabilised is studied.
- Column and batch tests are performed and their results are compared.
- The impact of temperature, compaction and acid conditions are tested with column tests.
- Column results are comparable with batch results in terms of average concentration.
- Acid environment accelerates the leaching process.

Figure Captions

Fig. 1. Cumulative release of DOC, Cr, Cu, Ni, Zn, chlorides and sulphates in terms of mg·kg^{-1}TS in function of L/S ratio for W1 (indicated by rhombus), W2 (squares), W3 (triangles) and W4 (circles).

Fig. 2. Comparison between average concentration ρ_{10} from column tests and measured concentrations in batch tests $c_{10,b}$ at L/S=10 l·kg^{-1}TS. Four dots for each element are present in the graph representing each of the four samples tested.

Fig. 3. Cumulative release of DOC, Cr, Cu, Ni, Zn, chlorides and sulphates in terms of mg·kg^{-1}TS in function of L/S ratio for W1. Standard conditions (W1) are represented by continuous line, mechanical constraint (W1-C) by dotted line, temperature (W1-T) by dash-dotted line, acid environment (W1-A) by dashed line.

Fig. 4. Cumulative release of DOC, Cr, Cu, Ni, Zn, chlorides and sulphates in terms of mg·kg^{-1}TS in function of L/S ratio for W2. Standard conditions (W1) are represented by continuous line, mechanical constraint (W1-C) by dotted line, temperature (W1-T) by dash-dotted line, acid environment (W1-A) by dashed line.

Fig. 5. PCA score plot. W1 parameters (W1-ρ_{10}, W1-$\rho_{10,A}$, W1-$\rho_{10,C}$, W1-$\rho_{10,T}$, W1-c,b_{10}) are represented by rhombus while W2 parameters (W2-ρ_{10}, W2-$\rho_{10,A}$, W2-$\rho_{10,C}$, W2-$\rho_{10,T}$, W2-c,b_{10}) are represented by squares.

Figure 1

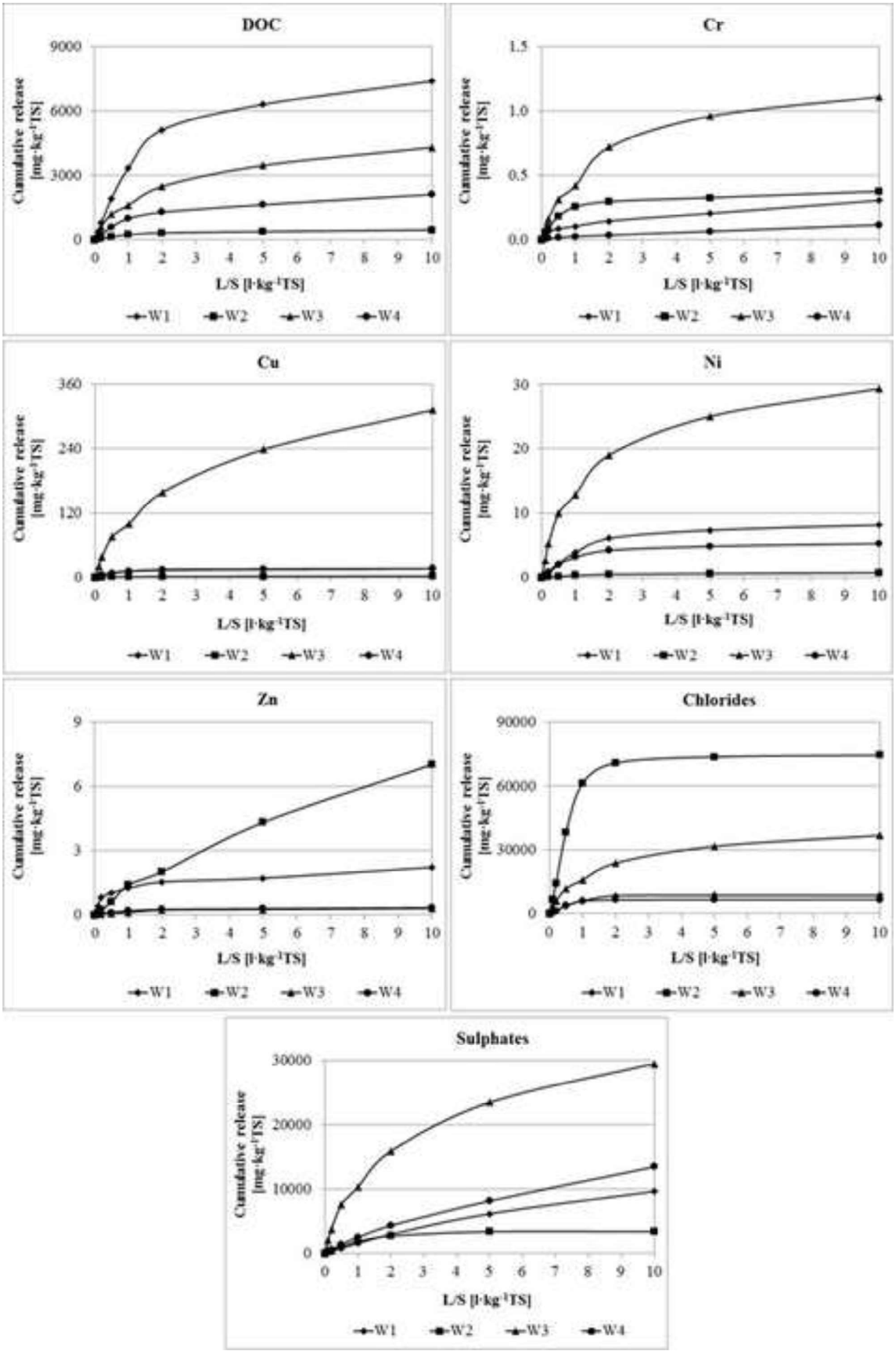
DOC
Cumulative release [mg·kg⁻¹TS]
9000
6000
3000
0
L/S [l·kg⁻¹TS]
0 1 2 3 4 5 6 7 8 9 10
W1
W2
W3
W4
Cr
1.5
1.0
0.5
0.0
Cu
360
240
120
0
Ni
30
20
10
0
Zn
9
6
3
0
Chlorides
90000
60000
30000
0
Sulphates
30000
20000
10000
0

Figure 2

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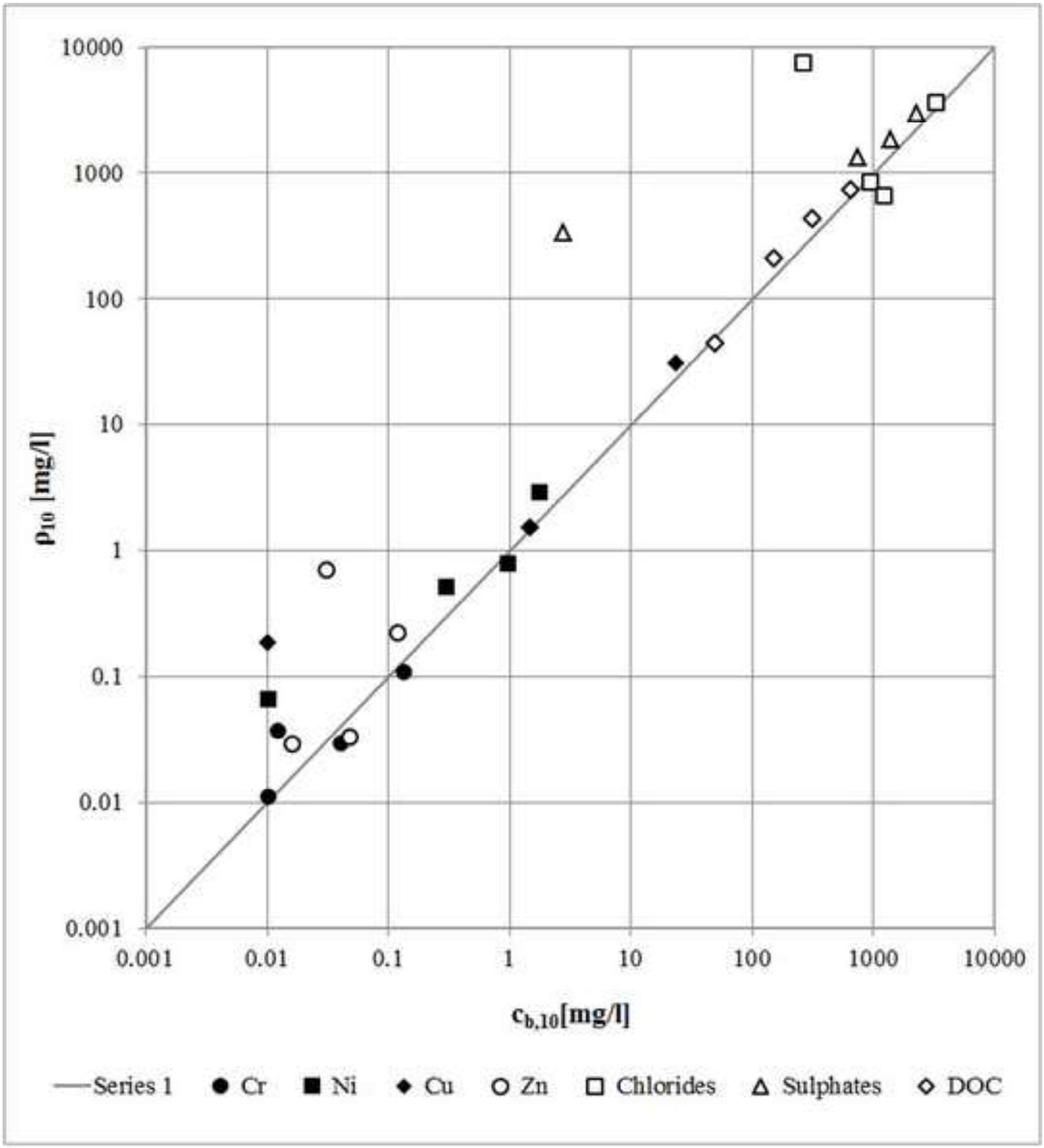


Figure 3

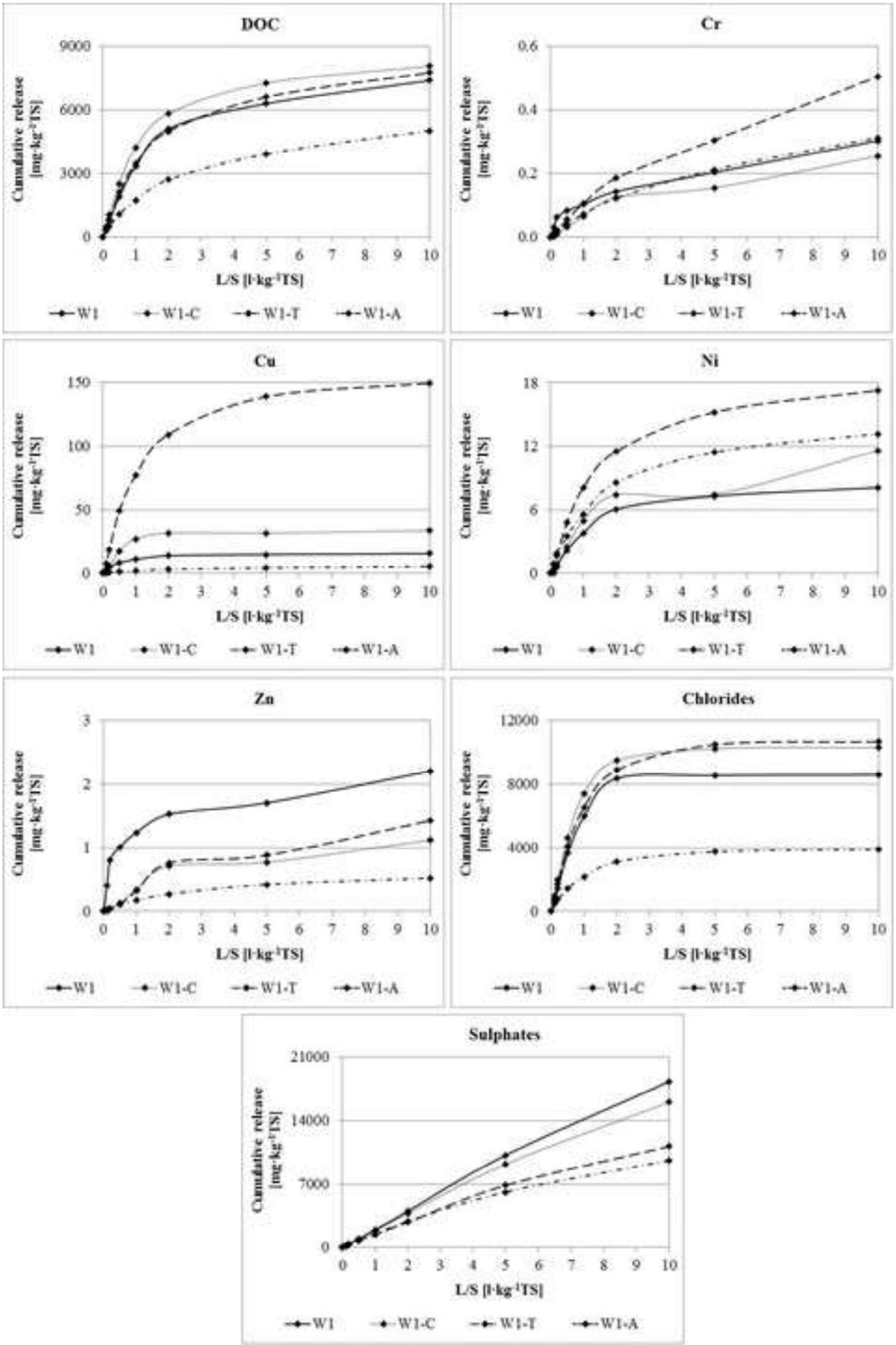

DOC
Cr
Cu
Ni
Zn
Chlorides
Sulphates
Cumulative release [mg·kg⁻¹TS]
L/S [l·kg⁻¹TS]
0
1
2
3
4
5
6
7
8
9
10
9000
6000
3000
0.6
0.4
0.2
0.0
150
100
50
18
12
6
3
2
1
12000
8000
4000
21000
14000
7000
W1
W1-C
W1-T
W1-A

Figure 4

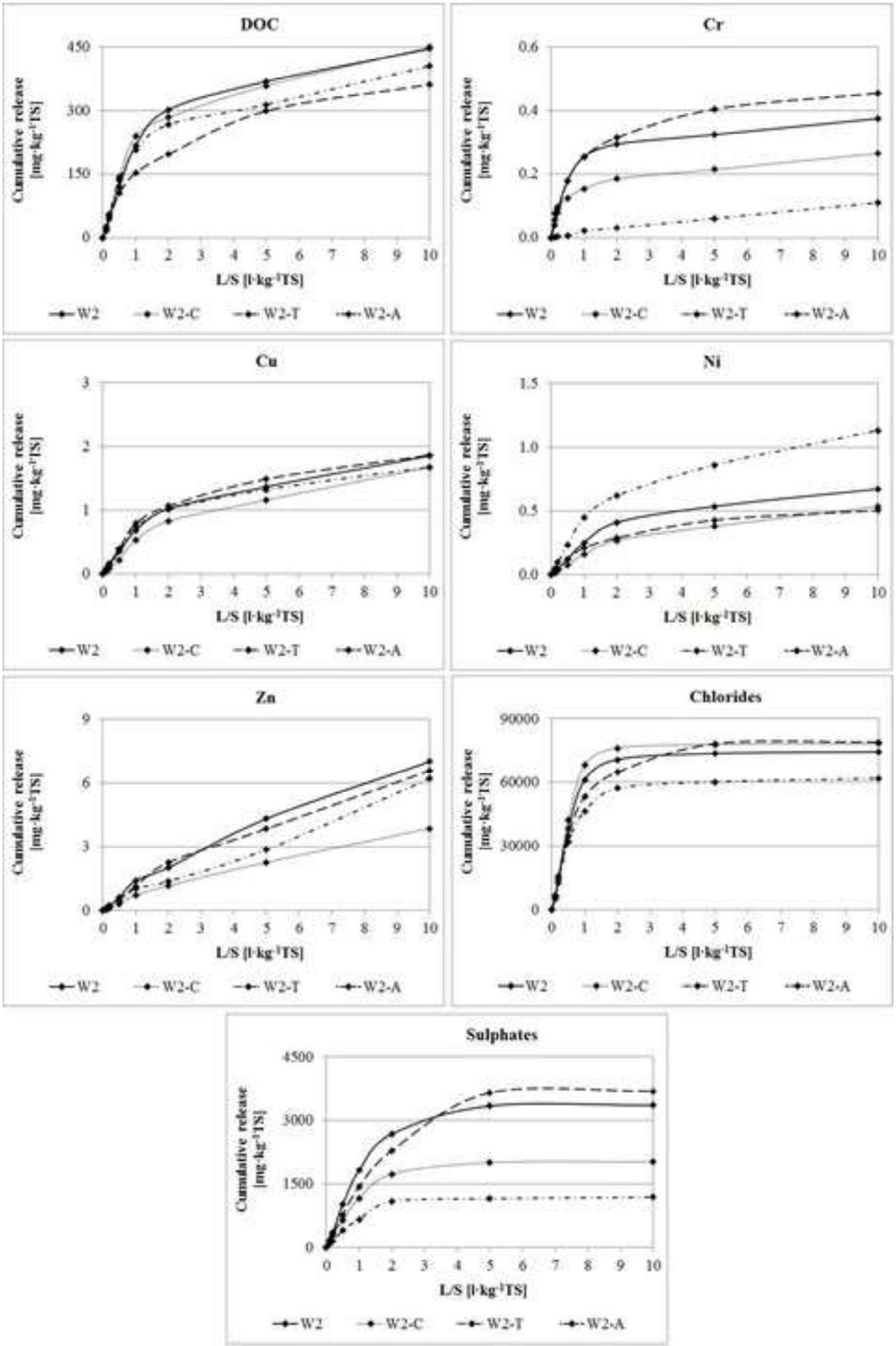
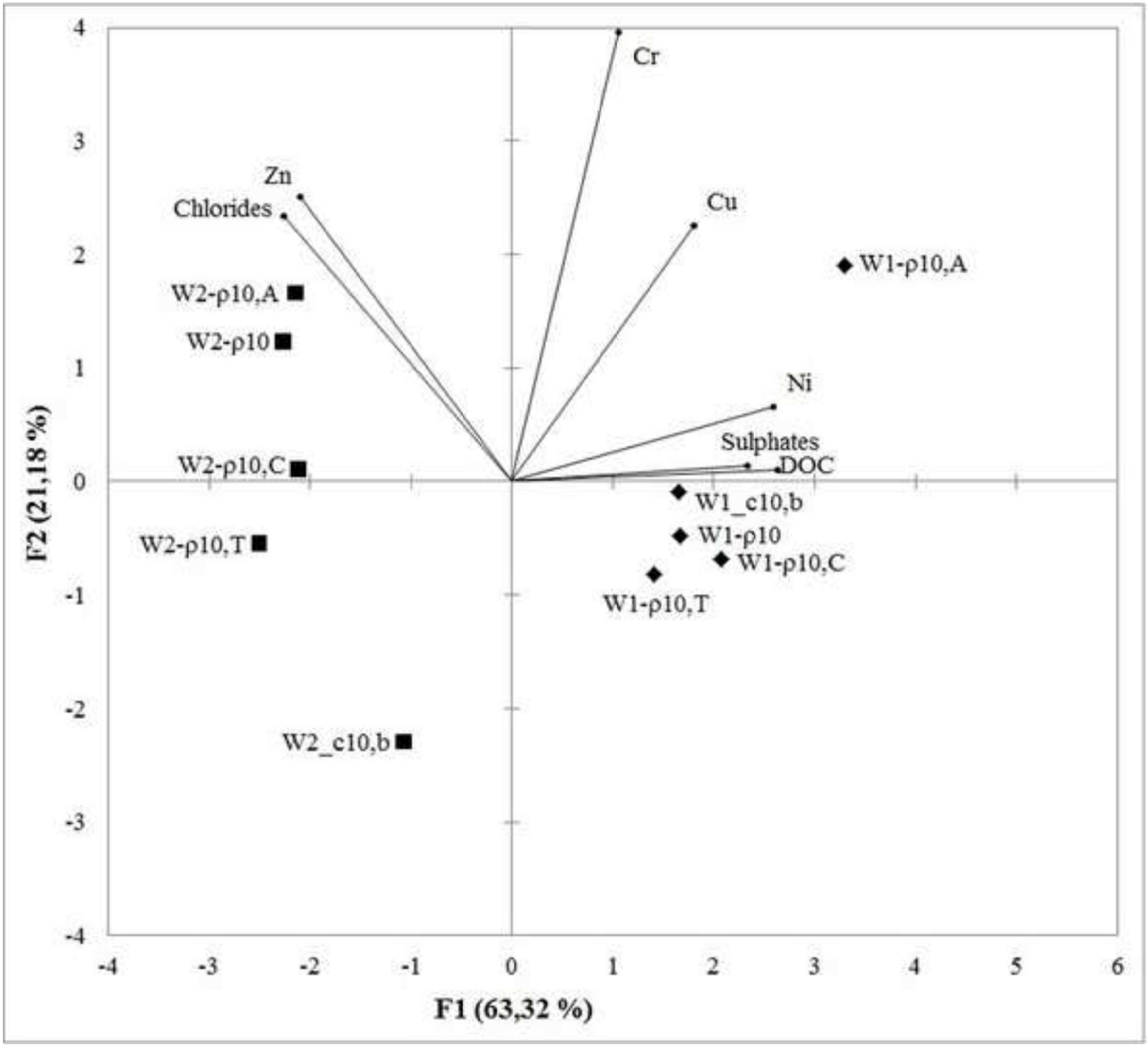

DOC
Cr
Cu
Ni
Zn
Chlorides
Sulphates
Cumulative release [mg·kg^{-1}TS]
L/S [l·kg^{-1}TS]
W2
W2-C
W2-T
W2-A
0
150
300
450
0.0
0.2
0.4
0.6
1
2
3
0.5
1.0
1.5
6
9
30000
60000
90000
1500
3000
4500
0 1 2 3 4 5 6 7 8 9 10

Figure 5

Click here to download high resolution image



Tables

Table 1

Summary of the physico-chemical characteristics of the four samples studied (W1-W4).

Parameter	Unit	W1	W2	W3	W4
Description		Granular	Granular	Granular	Granular
Total Solids (TS)	%	69.4	83.4	50.6	81.6
Total Volatile Solids (TVS)	%	25.2	1.8	14.5	21.7
Total Organic Carbon (TOC)	%	16.2	4.1	5.1	12.4
pH	pH unit	9.1	13.1	11.2	9.5
Cr	$mg \cdot kg^{-1}TS$	390	78	3052	267
Cu	$mg \cdot kg^{-1}TS$	2457	7916	3437	2238
Ni	$mg \cdot kg^{-1}TS$	1767	36	2939	816
Zn	$mg \cdot kg^{-1}TS$	8235	10355	4115	19909
Density	$kg \cdot m^{-3}$	912	1024	954	980
Fraction ≥ 10 mm	%	< 5	< 5	< 5	< 5
Fraction < 4 mm	%	< 80	< 80	< 80	< 80

Table 2

Comparison between the concentrations measured in the batch test $c_{10,b}$ and the average concentrations ρ_{10} calculated for column testing. The two concentrations are compared in terms of ratio and Welch t-test (values are not statistically different when $p > 0.05$). The inverse ratio is indicated in brackets. Data are emphasized in italics to underline that results from one of the two concentrations is below LOD (0.01 mg·l^{-1} for metals) and that the comparison should be regarded in a qualitative way.

	W1			W2			W3			W4			
	$c_{10,b}$	ρ_{10}	$c_{10,b}/\rho_{10}$	$c_{10,b}$	ρ_{10}	$c_{10,b}/\rho_{10}$	$c_{10,b}$	ρ_{10}	$c_{10,b}/\rho_{10}$	$c_{10,b}$	ρ_{10}	$c_{10,b}/\rho_{10}$	
Unit	mg·l^{-1}	mg·l^{-1}	n	mg·l^{-1}	mg·l^{-1}	n	mg·l^{-1}	mg·l^{-1}	n	mg·l^{-1}	mg·l^{-1}	n	Welch t-test
DOC	656	738	0.9 (1.1)	50	45	1.1 (0.9)	316	429	0.7 (1.4)	152	210	0.7 (1.4)	0.38
Cr	0.04	0.03	1.3 (0.8)	0.01	0.04	0.3 (3.1)	0.13	0.11	1.2 (0.8)	0.01	0.01	0.9 (1.1)	0.50
Cu	1.47	1.54	1.0 (1.0)	< 0.01	0.18	*0.1* *(18.5)*	23.72	31.16	0.8 (1.3)	1.49	1.53	1.0 (1.0)	0.42
Ni	0.96	0.81	1.2 (0.8)	< 0.01	0.07	*0.1* *(6.7)*	1.75	2.93	0.6 (1.7)	0.30	0.52	0.6 (1.7)	0.34
Zn	0.12	0.22	0.5 (1.8)	0.03	0.70	0.0 (22.6)	0.02	0.03	0.5 (1.8)	0.05	0.03	1.5 (0.7)	0.16
Chlorides	939	859	1.1 (0.9)	265	7441	0.0 (28.1)	3329	3668	0.9 (1.1)	1228	666	1.8 (0.5)	0.19
Sulphates	1388	1832	0.8 (1.3)	3	335	0.0 (119.7)	2277	2948	0.8 (1.3)	746	1345	0.6 (1.8)	0.25

Table 3

Variation of the average concentration $\Delta\rho_{10}$ between ambient conditions and the application of the standard test. C, A and T represent the impact of mechanical constraint, acid environment and temperature respectively. (-) means negative data.

	W1			W2		
	$\Delta\rho_{10,C}$ [%]	$\Delta\rho_{10,A}$ [%]	$\rho_{10,T}$ [%]	$\Delta\rho_{10,C}$ [%]	$\Delta\rho_{10,A}$ [%]	$\Delta\rho_{10,T}$ [%]
DOC	9%	5%	-	1%	-	-
Cr	-	67%	3%	-	21%	-
Cu	118%	876%	-	-	1%	-
Ni	43%	113%	63%	-	-	69%
Zn	-	-	-	-	-	-
Chlorides	20%	24%	-	5%	6%	-
Sulphates	-	-	-	-	10%	-