# Functional and Chemical Calibrates of Ceramic Cup Water Samplers in Forest Soils

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## ABSTRACT

A study was conducted to assess the properties of a tension porous-ceramic cup soil-solution sampler and its usefulness in extracting soil solutions in selected forest soils (*haplic Umbrisols*) at "Sierra De Gata" Mountains, CW-Spain. The main characteristics of the sampler evaluated were hydraulic conductivity, the time required to obtain the soil-water sample, and the volume of water uptake for optimum calibration prior to analysis of the chemical composition of the soil water solution. Hydraulic conductivity values were not substantially modified during the sampling (two hydrologic cycles). The time required to obtain the samples was relatively short (mean value 2 h) and the sphere of sampling influence was small (radii ranging from 6 to 15 cm), both depending on the size of the sampler. The chemical analyses obtained after calibrating the ceramic cup sampler pointed to: a) an effect of light adsorption by the ceramic cup, involving $PO_4^{3-}$, DOC, major and minor cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Al^{3+}$, $Mn^{2+}$, and $Zn^{2+}$),

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and $SO_4^{2-}$ and $NO_3^-$ anions; b) a release of $H_4SiO_4$; and c) no clear trend for $Cl^-$. The $Cu^{2+}$ values obtained between a blank soil solution and those obtained after passage through the ceramic cup were not correlated. Relatively low pH values (the pH of these acid forest soils is 5.1–6.2) favor the adsorption of anions and DOC, the latter also increasing the exchange capacity and cation adsorption of the cup. The results point to a generalized tendency of the ceramic cup to adsorb DOC, cations and anions (with the exception of chlorides), $H_4SiO_4$, by contrast, being released.

*Key Words:*   Ceramic cup water samplers; Chemical calibrate; Forest soils; Mediterranean ecosystem; Bioelements.

## INTRODUCTION

Soil water composition is the result of a dynamic equilibrium between environmental factors and specific physical and chemical soil properties, organic and mineral soil components, water fluxes, etc.

A large variety of soil water extraction techniques is available: pressing,[1] centrifugation,[2,3] displacement,[4] tension ceramic-cup samplers,[5,6] and free-tension lysimeters.[7,8] In the present work, tension ceramic-cup samplers were used in order to obtain matricial waters in acid soil forests,[9,10] with a constant water input, during the hydrological cycle.[11]

Ceramic-cup tension samplers permit the extraction of matricial water because an internal negative tension is applied that is higher than the tension at which the matricial water is retained by the soil.

The aim of the present work was to assess the influence of the nature of the ceramic-cup on the characteristics of the soil-solution samples, such as hydraulic conductivity, suction strength applied at both the beginning and the end of the sampling, the time required to obtain samples of matricial water, solution volume, and the viability of the chemical calibrations relating pH, electric conductivity, and dissolved organic carbon (DOC), cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Al^{3+}$, $Mn^{2+}$, and $Zn^{2+}$), anions ($Cl^-$, $NO_3^-$, $PO_4^{3-}$ and $SO_4^{2-}$), and silica ($H_4SiO_4$) concentrations in the matricial water.

## MATERIALS AND METHODS

### Study Site

This study was carried out in selected *Quercus pyrenaica* and *Castanea sativa* deciduous forests, located in the "*Sierra de Gata*" (40°2'40″ N; 3°0'50″

W; C-W Spain). According to Emberger's climogram, the climate is humid Mediterranean (Table 1), with a clear inversion between the rainfall and temperature curves, most of the rainfall being concentrated in the cold part of the year and drought coinciding mostly with the warm season and the vegetative growth period.[12] There is a decreasing NE-SW pluviometric transept (from 1.580 to 870 mm a$^{-1}$).[13] Along that transept, mean annual potential evapotranspiration is between 589 and 725 mm a$^{-1}$.

The lithology of the area studied consists of greywackes and shales, forming the Palaeozoic basement—affected by regional and contact metamorphism—and two-mica granite intrusions.[14] This basement has been subject to a weathering process, producing kaolinite enrichment and losses of silica and bases; a second weathering process involved profile silicification and the transformation of kaolinites in aluminum-rich smectites.[15,16]

The soils studied here are acid because they are derived from an acid substrate.[17] The soil is poor-to-moderately developed (from 0.1 to 0.6 m) in the unweathered rock substrate and fairly well developed (from 0.6 to 1.2 m) in the previously weathered rock substrate. Moderate temperatures and a relatively high pluviometry favor soil organic-matter accumulation. Iron (Fe) oxides, as a valuable index of the intensity of the pedological process, are released to an appreciable extent from the mineral structure and hence sesquioxides are present in soils; *brunification* is the predominant pedological process in these profiles.[18] The soils studied soils were *haplic Umbrisols*[19] on granite and greywake substrates. The particular profile studied is of the *AhBwC* type, with a thickness of 0.5 to 0.9 m; the *A* horizon is *umbric*, with a good structure and dark color; the *B* horizon is cambic (*Bw*) with light green-brown color owing to a noteworthy degree of weathering. *Gleyic Umbrisols* are developed on granite sites, with poor internal drainage.

## Characteristics of the Ceramic-Cup Sampler

Commercially available ceramic-cup tension samplers (*Soilmoisture* Equipment, Santa Barbara, CA, USA; 1900 model) were used, following an original design by Wagner.[5] Different tube lengths were employed (0.15, 0.3, 0.6, 0.9, and 1.1 m, approximately). The negative pressure value of the ceramic cup was −0.2 MPa (pore size equivalent = 1.44 μm). The negative pressure programmed was −80 kPa, although in the field a range between −75 ± 5 kPa was obtained (Table 2).

*Table 1.* General characteristics of the soil profiles studied.

| Forest plots | San Martín de Trevejo (SM) | Navasfrías (NF) | Villasrubias (VR) | Fuenteguinaldo (FG) |
|---|---|---|---|---|
| Altitude (m.a.s.l.) | 940 | 960 | 900 | 870 |
| Soil type (F.A.O., 1998) | *haplic Umbrisol* | *haplic Umbrisol* | *haplic Umbrisol* | *gleyic Umbrisol* |
| Lithology | granite *s.l.* | schist & mottled greywakes | schist & greywakes | granite *s.l.* |
| Mean annual temperature (°C) | N.d.[a] | 10 | N.d.[a] | 13 |
| Mean annual rainfall (mm $a^{-1}$) | 1150 | 1580 | 872 | 720 |
| Number of years registered | 19 | 13 | 17 | 20 |
| Texture: sand-silt-clay (%) | 67-21-12 | 35-47-18 | 13-71-16 | 51-33-16 |
| Horizons | $Ah_1/Ah_2/ABw/C$ | $Ah_1/Ah_2/Bw/CR$ | Ah/Bw/C | $Ah_1/ABw/Bw/BC/Cg$ |
| Thickness (cm) | 30/20/35/ + 50 | 20/20/25/ + 50 | 20/20/ + 50 | 20/10/15/25/ + 50 |
| Soil organic matter content in $Ah_1/Ah_2/Bw/C$ (%) | 7.8/5.9/3.1/ 1.2 | 9.8/3.8/0.8/N.d. | 7.4/1.3/0.8 | 3.2/1.3/0.5/0.3/ N.d.[a] |

[a]N.d.: Not determined.

*Table 2.* Mean suction range obtained during the uptake of soil water by suction cups, sample volume, hydraulic conductivity values of ceramic cups, filling time, and flow value of the samplers.

| Study plot | Depth (m) | Suction range (kPa) | S.d[a](%) | Sample volume (L) | S.d[a](%) | Hydraulic conductivity (m s$^{-1}$) | S.d[a](%) | Filling time (seconds) | Flow (mL h$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| SM | 0.3 | 55 | 4 | 0.38 | 21 | $3.6*10^{-9}$ | 30 | 192 | 239 |
| SM | 0.6 | 56 | 4 | 0.73 | 35 | $2.9*10^{-9}$ | 56 | 456 | 191 |
| SM | 0.9 | 53 | 3 | 1.04 | 50 | $3.1*10^{-9}$ | 30 | 612 | 205 |
| SM | 1.1 | 43 | 3 | 1.26 | 66 | $4.7*10^{-9}$ | 45 | 480 | 315 |
| NF | 0.2 | 37 | 4 | 0.15 | 14 | $1.4*10^{-9}$ | 40 | 192 | 94 |
| NF | 0.3 | 19 | 5 | 0.09 | 19 | $3.1*10^{-9}$ | 56 | 120 | 188 |
| NF | 0.6 | 49 | 3 | 0.68 | 30 | $5.0*10^{-9}$ | 43 | 252 | 326 |
| NF | 0.9 | 19 | 3 | 0.37 | 43 | $4.2*10^{-9}$ | 26 | 156 | 282 |
| VR | 0.2 | 27 | 4 | 0.12 | 12 | $1.3*10^{-9}$ | 24 | 36 | 393 |
| VR | 0.3 | 27 | 4 | 0.23 | 26 | $1.5*10^{-9}$ | 35 | 276 | 100 |
| VR | 0.6 | 12 | 3 | 0.16 | 21 | $1.1*10^{-9}$ | 59 | 264 | 74 |
| FG | 0.2 | 58 | 4 | 0.21 | 14 | $2.0*10^{-9}$ | 43 | 192 | 128 |
| FG | 0.3 | 51 | 4 | 0.36 | 23 | $2.6*10^{-9}$ | 41 | 252 | 172 |
| FG | 0.6 | 34 | 4 | 0.51 | 44 | $6.0*10^{-9}$ | 49 | 156 | 389 |
| FG | 0.9 | 25 | 4 | 0.56 | 58 | $5.0*10^{-9}$ | 27 | 204 | 327 |
| FG | 1.1 | 30 | 4 | 0.77 | 77 | $7.0*10^{-9}$ | 44 | 204 | 454 |
| Mean | 0.6 | 37 | 4 | 0.48 | 35 | $3.6*10^{-9}$ | 41 | 256 | 228 |

[a] S.d. = standard deviation of the value.

The hydraulic conductivity of the ceramic cups was defined by[20].

$$K = (Q*D)/(A*\Delta h*\Delta t) \qquad \text{(Eq I)}$$

where: $K$ is hydraulic conductivity $(cm\,s^{-1})$; $Q$ is water volume $(cm^3)$; $D$ is cup thickness $(0.24\,cm)$; $A$ is the internal surface area of the cup $(68\,cm^2)$; $\Delta h$ is the hydraulic gradient of the sampling tube, subjected to progressive suction, which decreases over time from $-75$ to $-10\,kPa$,; and $\Delta t$ is incremental flux time (in seconds).

The ceramic-cup samplers were installed on the different horizons in selected study plots (Table 1), as a function of the thickness of their soil horizon, type, and the lithology of the soil profiles: 5 lysimeters were installed at the Fuenteguinaldo plot (FG, with 0.15, 0.3, 0.6, 0.9, and 1.1 m depth), 4 at the San Martín de Trevejo (SM, with 0.2, 0.6, 0.9, and 1.1 m depth) and at the Navasfrías plots (NF, with 0.15, 0.3, 0.6, and 0.9 m depth), respectively, and 3 at the Villasrubias plot (VR, with 0.15, 0.3, and 0.6 m depth).

Prior to their installation, the ceramic-cup was rinsed with deionized water, applying suction three times. Several authors[10,21–24] have suggested that it is more appropriate to rinse ceramic cups with diluted HCl or $HNO_3$.[25] Like other authors,[26–28] however, here we decided to rinse the ceramic cups only with deionized water, because acid rinsing could increase phosphate sorption.

The ceramic-cup samplers were saturated in water before installation. In order to ensure intimate contact between the ceramic cup and the soil, a narrow hole was made in the soil with a manual auger. The displaced soil was mixed with deionized water and used to fill the hole between soil and the sampler. A cut funnel was placed over each lysimeter to protect the sampler from percolation.

The period sampled was longer than two hydrologic periods (28 months: from March 1992 to July 1994; the first 5 months were considered a stabilization period) and water samples were collected every 1–2 weeks.

## Chemical Analyses

Sampling conditions (before chemical analysis) involved[29] the use of PVC recipients, refrigerated conservation (4°C), and acidification of the samples at pH < 2 (with nitric acid) for cation analysis.

The parameters analyzed[30] were pH (Crison micropH 2002, using an Ingold-104053931 electrode) and electrical conductivity (WTW-LF91 electrode), and DOC (TOCA 315A from Beckman); the ions analyzed were $Na^+$ and $K^+$ (flame emission, Varian AA-1475), $Ca^{2+}$ and $Mg^{2+}$ (atomic

absorption spectrometry, AAS, Varian AA-1475), $Al^{3+}$, $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$, $Zn^{2+}$, and $H_4SiO_4$ (ICP 2, Perkin-Elmer), and $Cl^-$, $NO_3^-$, $PO_4^{3-}$, and $SO_4^{2-}$ (ion-chromatography Dionex-350).

## Chemical Calibrates of Matricial Solution in Ceramic Cup

At the end of the sampling period, ceramic-cup samplers were calibrated chemically at the laboratory. Each lysimeter was calibrated four times with water obtained from zero-tension lysimeters[31] at the same depth as the tube samplers; this solution was considered as the blank test solution (BTS). The solution obtained from the sampler was made to pass through the cup (TCS). The parameters calibrated were pH, electrical conductivity, DOC, and the major cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Al^{3+}$, $Mn^{2+}$, and $Zn^{2+}$), major anions ($Cl^-$, $NO_3^-$, $PO_4^{3-}$ and $SO_4^{2-}$), and silica ($H_4SiO_4$) of the soil solution.

Regression equations were obtained to perform an accurate test of the relationship between the zero-tension lysimeter and ceramic cup soil-solution values, and coefficients were deduced by geometric means and standard errors of the values.

## RESULTS AND DISCUSSION

### Tension of Sampling Cups During Water Collection

An initial pressure was applied, with values of $-75 \pm 5$ kPa, but the water volume obtained differed from sample to sample as a function of sampler length (Table 2), in agreement with previous research.[32,33] Additionally, the concentrations of the soil water sampled were not significantly influenced by the suction applied.[33] Taking into account that the same tension was applied to all the tubes, the water volume collected was directly related to the internal volume of the sampler tube because in the longer tubes more air is displaced owing to the higher volume of the samplers.

The final tension registered at the moment of sample collection (1–2 weeks) was not zero in the periods when the soil was wet (winter), and in this case samples were available. Even at the beginning of dry periods (spring), when no matricial water could be obtained, some residual tension was present ($-2$ a $-4$ kPa). These results confirm the good closure and effectiveness of the soil-solution samplers.

## Hydraulic Conductivity of Ceramic-Cup Samplers

Hydraulic conductivity values ranged from 1 to $7 \times 10^{-7}$ cm s$^{-1}$ (Table 2). These values lie within the range of calibrations provided by the *Soilmoisture* Company. The highest values of hydraulic conductivity corresponded to the longest tube-samplers. Morrison and Lowery[34] concluded that, when the same initial suction pressure is applied, hydraulic conductivity is directly related to the internal volume of sampler. This trend was also observed here, with the exception of the VR plot (with low and constant values), probably due to the obstruction of ceramic pores by silt, iron oxides (particularly more abundant in this plot), and soil organic matter (Table 1).

## Sphere of Water Uptake

The volume of soil affected by water uptake through the ceramic-cup sampler was restricted to a narrow surrounding zone (Table 3). Evidently,

*Table 3.* Calculations of water catchment radius from ceramic cups at the profiles studied.

| Study plot | Depth (m) | W$^a$ (%) | V$^b$ (dm$^3$) | Z$^c$ (dm$^3$) | r$^d$ (cm) |
|---|---|---|---|---|---|
| SM | 0.3 | 9.2 | 0.38 | 4.16 | 11 |
| SM | 0.6 | 9.4 | 0.73 | 7.73 | 14 |
| SM | 0.9 | 8.8 | 1.04 | 11.85 | 16 |
| SM | 1.1 | 8.4 | 1.26 | 14.99 | 17 |
| NF | 0.2 | 9.9 | 0.15 | 1.53 | 8 |
| NF | 0.3 | 11.0 | 0.09 | 0.86 | 7 |
| NF | 0.6 | 9.9 | 0.68 | 6.91 | 13 |
| NF | 0.9 | 7.3 | 0.37 | 5.01 | 12 |
| VR | 0.2 | 11.0 | 0.12 | 1.07 | 7 |
| VR | 0.3 | 12.0 | 0.23 | 1.91 | 9 |
| VR | 0.6 | 10.0 | 0.16 | 1.63 | 8 |
| FG | 0.2 | 7.1 | 0.21 | 2.90 | 10 |
| FG | 0.3 | 8.7 | 0.36 | 4.16 | 11 |
| FG | 0.6 | 7.9 | 0.51 | 6.42 | 13 |
| FG | 0.9 | 6.7 | 0.56 | 8.28 | 14 |
| FG | 1.1 | 7.1 | 0.78 | 10.92 | 15 |

$^a$ W: bulk of water at field capacity ($-30$ to $-20$ kPa).
$^b$ V: soil water content from $-30$ to $-200$ kPa.
$^c$ Z: caption water zone.
$^d$ r: radius of soil sphere influence

extraction of water in this zone modifies the natural flux,[33,35] although this modification is less pronounced if an individual burst of suction is applied instead of continued suction.[36] Under conditions of individual bursts of suction, the zone of water uptake is restricted to the proximity of the ceramic cup.[32]

Assuming that the soil is at field capacity, the soil tension varies from $-30$ to $-200$ kPa (pF from 2.5 to 3.2) and if the water volumes inside the ceramic cup are known the water uptake zone (Z, $dm^3$) can be defined by the relationship (Table 3):

$$Z = V*100/W \qquad\qquad\qquad (Eq. II)$$

where V is the volume of water extracted ($dm^3$) and W is the percentage (in volume) of soil water content at $-200$ kPa.

The idealized volume of water uptake would consist of a sphere surrounding the ceramic-cup, with a radius varying between 6 and 15 cm (Table 3). Here, the values of the water uptake zone were sufficiently small to prevent zone overlapping (Table 1).

## Filling Time of Soil-Water Samplers

From the water volumes sampled during the two hydrologic cycles and the hydraulic conductivity values obtained with formula (I) it was possible to determine the time required for the samplers to fill. The results are summarized in Table 2 and range from 1 to 2 hours.

## Soil-Water Extraction Conditions and Soil Water Content

Three cases of soil-water extraction were defined, as a function of the soil water content. 1) Soil matricial water retained with lower tensions than inside the sampler. In this situation, soil water extraction is possible; this period was from the middle of autumn to the beginning of summer. 2) Soil matricial water retained with tensions similar to inside the sampler. In this situation, the extraction of soil-water is not possible, although no loss of suction pressure in the samplers occurred. This period lasted between one and two weeks during the wet period (at the beginning of autumn) and also at the beginning of the dry period (late spring-early summer). 3) Soil matricial water retained with tensions higher than inside the sampler may reach (and possibly exceed) the bubble point of the ceramic cup ($-200$ kPa). In this situation (summer),

soil-water extraction is not possible and only a loss of suction in the samplers was observed (corresponding to the dry months, in the middle of summer).

The water volume values obtained during two hydrological periods ranged between 0.094 and 1.26 L (0.15 m and 1.1 m sampler depth, respectively). If the soil water content is similar at all the sites and the same initial suction is applied, the internal volume of the sampler will be directly related to the water volume obtained,[35] although not all authors agree with this.[33] Other authors[37] have argued that the volume of the solution recovered decreases with time due to obstruction of the ceramic by colloids and oxides of iron. This was seen at the VR plot.

In the present study of natural forest soils, clear differences were seen in the water volume obtained in both hydrological cycles studied (Table 4). The first hydrological year was dryer (829 mm total annual rainfall) than the second one (1.464 mm total annual rainfall) and hence an increase occurred in the volume of the soil-solution in the wet period of the second cycle, although a decrease also occurred in the volume of the soil-solution from the first to second cycle in the dry period. The latter was probably due to progressive obstruction of the ceramic of the cup due to the precipitation of colloids and oxides of iron, more pronounced in dry periods. Hysteresis phenomena (stronger soil water retention during dry periods) could be the most important cause of higher volumes in wet periods with respect to dry ones.

## Chemical Calibration of Solution Passing
## Through the Ceramic Cup

Linear regression equations were obtained to compare the results of the chemical analyses of the water obtained with the zero-tension lysimeter (blank test solution, BTS) and those obtained with the solution passing through the ceramic cup (TCS). From each equation, a concentration correction factor was deduced (Table 5) (using geometric means) and this factor was further applied to the soil water sample analyses (except for $PO_4^{3-}$ and $Cu^{2+}$, which were below the limit of detection; Table 6a,b).

The chemical composition of the ceramic cup (constructed with kaolinite, talc, alumina, and other feldspar minerals)[20] modifies the composition of the soil solution due to exchange phenomena. Many works have addressed the sorption-leaching capacity of ceramics,[10,24,26,27,38-45] but there is little consensus about the behavior of these ions (Table 7). Some works[43] have shown that the concentrations of $Ca^{2+}$ and $Mg^{2+}$ increase when they pass through ceramic cups while other authors[38] have indicated that major cation concentrations remain unaltered under such conditions or that they are

*Table 4.* Mean values of volume of soil water obtained by suction cups, and percentage of change (from 100%) in different periods (wet and dry) in the hydrological cycles analysed (I and II).

| Plot | Depth (m) | Volume[a] (L) Ia[b] | Volume[a] (L) Ib[c] | Volume[a] (L) IIa[d] | Volume[a] (L) IIb[e] | % of change a[f]/b[g] |
|---|---|---|---|---|---|---|
| SM | 0.3 | 0.45 (3) | 0.41 (23) | 0.44 (8) | 0.32 (56) | 98 / 77 |
| | 0.6 | 0.82 (9) | 0.79 (13) | 0.81 (10) | 0.71 (35) | 98 / 90 |
| | 0.9 | 1.22 (5) | 1.12 (13) | 1.17 (6) | 0.91 (43) | 96 / 81 |
| | 1.1 | 1.24 (39) | 1.53 (9) | 1.48 (11) | 0.91 (58) | 119 / 59 |
| NF | 0.15 | 2.00 (39) | 0.21 (40) | 0.17 (52) | 0.11 (97) | 87 / 51 |
| | 0.3 | 0.05 (34) | 0.05 (55) | 0.09 (54) | — | 173 / — |
| | 0.6 | 0.59 (39) | 0.60 (35) | 0.80 (11) | 0.70 (29) | 135 / 118 |
| | 0.9 | 0.15 (34) | 0.21 (21) | 0.40 (49) | 0.16 (57) | 260 / 77 |
| VR | 0.15 | 0.09 (71) | 0.16 (37) | 0.14 (46) | 0.15 (50) | 152 / 94 |
| | 0.3 | 0.07 (67) | 0.21 (44) | 0.36 (39) | 0.28 (48) | 497 / 132 |
| | 0.6 | 0.09 (51) | 0.18 (52) | 0.22 (75) | 0.15 (77) | 248 / 85 |
| FG | 0.15 | 0.23 (29) | 0.26 (9) | 0.25 (26) | 0.20 (52) | 108 / 74 |
| | 0.3 | 0.40 (33) | 0.44 (25) | 0.44 (19) | 0.30 (47) | 112 / 69 |
| | 0.6 | 0.59 (51) | 0.72 (21) | 0.57 (39) | 0.32 (78) | 97 / 45 |
| | 0.9 | 0.33 (55) | — | 0.81 (41) | 0.39 (98) | 244 / — |
| | 1.1 | 0.46 (95) | — | 1.19 (34) | 0.65 (78) | 259 / — |
| | | | | | Mean | 174 / 81 |

[a] Volume: Mean water volume and standard deviation, in brackets.

[b] Ia: Wet period of first hydrological period.

[c] Ib: Dry period of first hydrological period.

[d] IIa: Wet period of second hydrological cycle.

[e] IIb: Dry period of second hydrological cycle.

[f] a: Wet period.

[g] b: Dry period.

adsorbed on passing through ceramic cups.[41] Here, the major cations studied showed a tendency towards ion sorption when they passed through the ceramic cups (Tables 5 and 7).

The minor cations $Fe^{3+}$, $Mn^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ were adsorbed by the ceramic cups (Table 5). Other authors[44] reported the absence of sorption behavior for $Cu^{2+}$, and $Zn^{2+}$ at pH = 4. In the present study, minor cations showed a tendency to be sorbed by the ceramic cups (Table 7; pH range 5.7–6.9). The metal load influences the effect of pH on ion sorption, but this is only evident at concentrations much higher than those found in nature.[46] Thus, at a moderate metal load of $Zn^{2+}$ (45 mmol g$^{-1}$; 46; from 2 to 20 mmol g$^{-1}$ in our study, figures commonly found in the soil environment)

*Table 5.* Chemical calibration results: regression equations between blank test solution and passage through ceramic solution; regression coefficient ($r^2$); number of data (n): 64.

| Parameter | Regression equation | ($r^2$) | TCS[a] values respecting 100% of BTS[b] | | | |
|---|---|---|---|---|---|---|
| | | | Geometric mean | Error (+/−) | Corrected factor | Tendency |
| $H^+$ | $TCS^a = 0.601BTS^3 + 2.41$ | 0.566 | 102 | 6 | 0.98 | L[c] |
| $\alpha^d$ | $TCS = 0.877BTS + 3.744$ | 0.933 | 92 | 9 | 1.09 | R[e] |
| DOC | $TCS = 0.748BTS + 0.683$ | 0.892 | 84 | 18 | 1.19 | R |
| $Na^+$ | $TCS = 0.657BTS + 0.604$ | 0.525 | 93 | 40 | 1.08 | R |
| $K^+$ | $TCS = 0.855BTS + 0.219$ | 0.899 | 87 | 17 | 1.15 | R |
| $Ca^{2+}$ | $TCS = 0.783BTS + 0.12$ | 0.922 | 84 | 21 | 1.19 | R |
| $Mg^{2+}$ | $TCS = 0.842BTS + 0.109$ | 0.784 | 91 | 34 | 1.10 | R |
| $Si(OH)_4$ | $TCS = 0.934BTS + 0.247$ | 0.936 | 139 | 144 | 0.72 | L[f] |
| $Al^{3+}$ | $TCS = 0.878BTS + 0.048$ | 0.828 | 90 | 63 | 1.11 | R |
| $Fe^{3+}$ | $TCS = 0.407BTS + 0.014$ | 0.495 | 69 | 40 | 1.45 | R |
| $Mn^{2+}$ | $TCS = 0.729BTS + 0.004$ | 0.932 | 83 | 112 | 1.21 | R |
| $Zn^{2+}$ | $TCS = 0.746BTS + 0.14$ | 0.676 | 69 | 37 | 1.45 | R |
| $Cu^{2+}$ | $TCS = 19.49BTS + 0.005$ | 0.280 | N.d.[g] | N.d. | N.d. | N.d. |
| $Cl^-$ | $TCS = 0.887BTS + 0.399$ | 0.993 | 101 | 29 | 0.99 | I[h] |
| $NO_3$ | $TCS = 0.968BTS + 0.047$ | 0.987 | 88 | 31 | 1.14 | R |
| $PO_4^=$ | $TCS = 0.708BTS + 0.042$ | 0.473 | 6 | 3 | 16.67 | R[i] |
| $SO_4^=$ | $TCS = 0.873BTS + 0.225$ | 0.094 | 76 | 14 | 1.32 | R |

[a] TCS: passage through ceramic solution.
[b] BTS: blank test solution.
[c] L: low leachage.
[d] $\alpha$: electric conductivity, in $\mu S\,cm^{-2}$.
[e] R: low retention.
[f] L: leachage.
[g] N.d.: Not determined.
[h] I: inalterated.
[i] R: retention.

the effect of pH on metal adsorption is low and this sorption decreases with acidity. A maximum of metal sorption has been reported for pH values of between 6.3 and 7.0,[46] these values being quite similar to those found in our samples.

The values of $Cu^+$ before and after passing through the ceramic were not correlated ($r^2 = 0.28$; Table 5). Possibly, the low concentrations of this micronutrient (few $\mu g\,L^{-1}$) could be responsible for this.

The retention (or release) of $Al^{3+}$ by ceramics depends on the degree of $Al^{3+}$ saturation of the soils, and is related to the presence of gibbsite in the
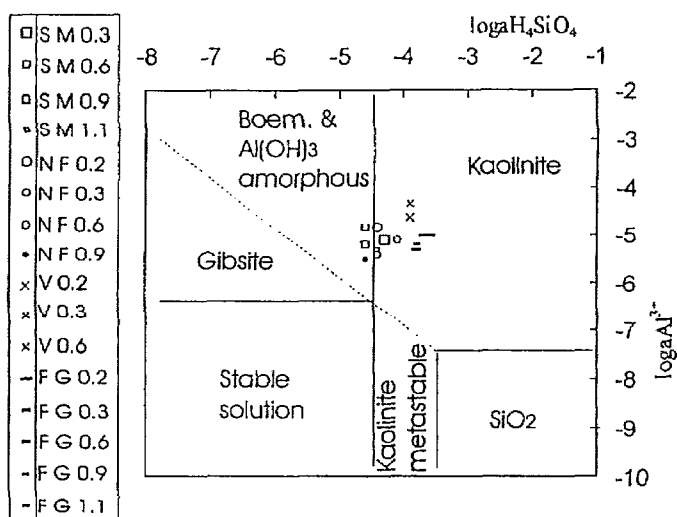
Figure 1. Mineral stability of soil-solution samples [Al(OH)₃-bohemite-kaolinite-opal system].[48] Legend: Plot site and depths (in m).

soil.[42,47] This is partly in agreement with the present results, because in some—but not all—samples (plots SM 60, SM 90, and NF 90; Fig. 1) the soil-solutions studied were saturated in gibbsite. Raulund-Rasmussen[45] has remarked that with increasing pH $Al^{3+}$ cations are released by the ceramic cup; the interpretation was that protons replace the $Al^{3+}$ of the ceramic, leading to the formation of amorphous gibbsite close to the ceramic. Thus, in our case a depletion of $Al^{3+}$ in the solution from the ceramic cup was accompanied by an increase in $H^+$ (lower pH). Several authors[45,46] have related low pH to the sorption of $Al^{3+}$.

The pH value increases when solution passes through the ceramic, due to elimination of $CO_2$ and other volatiles from the soil solution,[49,50] although in this work this phenomenon was not observed.

As in other works,[39,43] $H_4SiO_4$ release was detected, although in a highly variable fashion (Table 5). Aluminum (Al) and Fe oxides and hydroxides are effective sorbents of dissolved silica and owing to the presence of Al-chelating organic acids Si sorption in soils is decreased.[51] Soil forest solutions have sufficient DOC (with chelating effects) to permit $H_4SiO_4$ release.

Phosphate sorption has been reported in several works.[26,27,39,41,44] In the present work, phosphate was the ion most adsorbed (Table 5) The Cl⁻ did not

*Table 6.* Soil water composition (mean and error values) as extracted by ceramic cups collected (at different depths) at the SM and NF plots. A correction factor was applied, except for $PO_4^{2-}$ and $Cu^{2+}$, registered under detection limit. Values in $mg\,L^{-1}$ (except for X*).

| Plot | SM | | | | NF | | | |
|---|---|---|---|---|---|---|---|---|
| Depth[a] | 0.3 | 0.6 | 0.9 | 1.1 | 0.2 | 0.3 | 0.6 | 0.9 |
| pH | 5.9 ± 0.20 | 6.0 ± 0.03 | 5.7 ± 0.04 | 5.8 ± 0.13 | 6.6 ± 0.07 | 6.8 ± 0.06 | 6.3 ± 0.05 | 6.6 ± 0.04 |
| X[b] | 21 ± 1 | 20 ± 1 | 29 ± 3 | 19 ± 1 | 26 ± 2 | 34 ± 4 | 17 ± 1 | 13 ± 1 |
| DOC | 5.9 ± 0.5 | 5.9 ± 0.5 | 4.9 ± 0.4 | 4.9 ± 0.4 | 9.8 ± 0.9 | 14.6 ± 1.2 | 12.7 ± 1.9 | 4.9 ± 0.4 |
| $Na^+$ | 2.3 ± 0.2 | 1.9 ± 0.1 | 2.7 ± 0.2 | 2.3 ± 0.2 | 1.9 ± 0.2 | 2.5 ± 0.4 | 1.9 ± 0.1 | 2.0 ± 0.2 |
| $K^+$ | 1.8 ± 0.1 | 1.6 ± 0.1 | 1.0 ± 0.1 | 1.0 ± 0.1 | 1.6 ± 0.1 | 1.8 ± 0.2 | 0.8 ± 0.1 | 0.6 ± 1.0 |
| $Ca^{2+}$ | 0.42 ± 0.05 | 0.43 ± 0.06 | 0.38 ± 0.08 | 0.35 ± 0.04 | 0.98 ± 0.09 | 1.08 ± 0.21 | 0.49 ± 0.08 | 0.29 ± 0.04 |
| $Mg^{2+}$ | 0.66 ± 0.03 | 0.631 ± 0.02 | 0.848 ± 0.11 | 0.532 ± 0.03 | 0.89 ± 0.05 | 0.99 ± 0.15 | 0.69 ± 0.02 | 0.49 ± 0.02 |
| $H_4SiO_4$ | 2.8 ± 0.35 | 1.5 ± 0.21 | 1.6 ± 0.30 | 2.3 ± 0.58 | 2.3 ± 0.4 | 4.7 ± 1,1 | 2.3 ± 0.6 | 1.5 ± 0.2 |
| $Al^{3+}$ | 0.22 ± 0.01 | 0.15 ± 0.02 | 0.41 ± 0.16 | 0.15 ± 0.02 | 0.39 ± 0.02 | 0.22 ± 0.02 | 0.11 ± 0.02 | 0.08 ± 0.01 |
| $Fe^{3+}$ | 0.09 ± 0.03 | 0.10 ± 0.05 | 0.21 ± 0.18 | 0.07 ± 0.03 | 0.09 ± 0.02 | 0.10 ± 0.04 | 0.05 ± 0.02 | 0.03 ± 0.01 |
| $Mn^{2+}$ | 0,19 ± 0.07 | 0,08 ± 0.03 | 0,33 ± 0.11 | 0,19 ± 0.07 | 0,06 ± 0.03 | 0,06 ± 0.03 | 0,07 ± 0.02 | 0,05 ± 0.01 |
| $Zn^{2+}$ | 0.52 ± 0.08 | 0.60 ± 0.11 | 0.78 ± 0.17 | 0.64 ± 0.13 | 1.26 ± 0.27 | 1.07 ± 0.24 | 0.59 ± 0.12 | 0.43 ± 0.05 |
| $Cl^-$ | 1.7 ± 0.2 | 1.6 ± 0.1 | 4.3 ± 0.7 | 2.3 ± 0.2 | 2.3 ± 0.4 | 4.1 ± 1,1 | 1.6 ± 0.2 | 1.1 ± 0.1 |
| $NO_3^-$ | 0.18 ± 0.05 | 0.32 ± 0.12 | 0.35 ± 0.07 | 0.42 ± 0.10 | 0.23 ± 0.04 | 0.68 ± 0.27 | 0.23 ± 0.02 | 0.23 ± 0.03 |
| $SO_4^{2-}$ | 3.0 ± 0.4 | 3.1 ± 0.3 | 2.3 ± 0.3 | 1.3 ± 0.2 | 2.9 ± 0.2 | 5.4 ± 1.1 | 2.7 ± 0.3 | 1.8 ± 0.3 |

[a] in m.

[b] electric conductivity, in $\mu S\,cm^{-1}$.

*Table 7.* Soil water composition (mean and error values) as extracted by ceramic cups collected (at different depths) at the VR and FG plots. A correction factor was applied, except for $PO_4^{2-}$ and $Cu^{2+}$, registered under detection limit. Values in $mg\,L^{-1}$ (except for X*).

| Plot | VR | | | FG | | | | |
|---|---|---|---|---|---|---|---|---|
| Depth[a] | 0.2 | 0.3 | 0.6 | 0.2 | 0.3 | 0.6 | 0.9 | 1.1 |
| pH | 6.2 ± 0.07 | 5.8 ± 0.05 | 5.8 ± 0.04 | 6.9 ± 0.05 | 6.5 ± 0.05 | 6.0 ± 0.05 | 5.9 ± 0.06 | 5.9 ± 0.09 |
| X[b] | 26 ± 3 | 37 ± 5 | 39 ± 3 | 58 ± 6 | 44 ± 2 | 29 ± 1 | 37 ± 1 | 37 ± 3 |
| DOC | 29 ± 4 | 82 ± 26 | 78 ± 19 | 30.3 ± 3.2 | 18.5 ± 1.5 | 8.8 ± 0.8 | 8.8 ± 0.8 | 8.8 ± 0.8 |
| $Na^+$ | 2.2 ± 0.2 | 2.5 ± 0.2 | 2.3 ± 0.2 | 2.2 ± 0.1 | 2.3 ± 0.1 | 2.4 ± 0.2 | 2.9 ± 0.2 | 2.9 ± 0.2 |
| $K^+$ | 2.2 ± 0.2 | 3.1 ± 0.6 | 3.3 ± 0.3 | 6.1 ± 0.2 | 6.6 ± 0.2 | 3.0 ± 0.1 | 3.5 ± 0,1 | 2.3 ± 0.6 |
| $Ca^{2+}$ | 0.42 ± 0.05 | 1.08 ± 0.16 | 1.15 ± 0.12 | 2.06 ± 0.31 | 0.69 ± 0.07 | 0.29 ± 0.05 | 0.39 ± 0.05 | 0.29 ± 0.03 |
| $Mg^{2+}$ | 0.74 ± 0.03 | 0.97 ± 0.11 | 1.13 ± 0.09 | 1.87 ± 0.26 | 0.99 ± 0.06 | 0.59 ± 0.02 | 0.69 ± 0.02 | 0.99 ± 0.03 |
| $H_4SiO_4$ | 4.7 ± 0.8 | 5.6 ± 1.1 | 4.8 ± 1.0 | 15.3 ± 2.9 | 10.7 ± 1.5 | 9.2 ± 0.7 | 9.9 ± 0.5 | 9.9 ± 0.6 |
| $Al^{3+}$ | 0.61 ± 0.06 | 1.47 ± 0.22 | 1.33 ± 0.19 | 0.26 ± 0.02 | 0.28 ± 0.02 | 0.13 ± 0.01 | 0.17 ± 0.02 | 0.144 ± 0.01 |
| $Fe^{3+}$ | 0.33 ± 0.17 | 0.40 ± 0.15 | 0.56 ± 0.24 | 0.35 ± 0.15 | 0.28 ± 0.12 | 0.09 ± 0.04 | 0.09 ± 0.03 | 0.06 ± 0.02 |
| $Mn^{2+}$ | 0.26 ± 0.10 | 0.42 ± 0.16 | 0.52 ± 0.16 | 0.13 ± 0.05 | 0.06 ± 0.02 | 0.43 ± 0.15 | 0.33 ± 0.12 | 0.46 ± 0.17 |
| $Zn^{2+}$ | 2.91 ± 0.72 | 1.02 ± 0.21 | 3.00 ± 1.03 | 1.37 ± 0.03 | 0.73 ± 0.15 | 0.52 ± 0.06 | 0.52 ± 0.06 | 0.60 ± 0.07 |
| $Cl^-$ | 1.3 ± 0.3 | 1.2 ± 0.3 | 1.2 ± 0.1 | 2.8 ± 0.5 | 1.6 ± 0,2 | 2.5 ± 0.2 | 3.3 ± 0.1 | 3.7 ± 0.1 |
| $NO_3^-$ | 0.11 ± 0.03 | 0.11 ± 0.02 | 0.23 ± 0.06 | 2.50 ± 0.87 | 2.30 ± 0.32 | 0.30 ± 0.05 | 0.20 ± 0.03 | 0.50 ± 0.06 |
| $SO_4^{2-}$ | 2.0 ± 0.2 | 2.8 ± 0.3 | 2.7 ± 0.1 | 4.7 ± 0.5 | 5.1 ± 0.5 | 3.5 ± 0.5 | 4.8 ± 0.8 | 4.3 ± 0.7 |

[a] in m.
[b] electric conductivity, in $\mu S\,cm^{-1}$

Table 8. Chemical calibration of cup ceramics by other authors and the present work.

| Authors / ions | Na+ | K+ | Ca$^{2+}$ | Mg$^{2+}$ | Al$^{3+}$ | Fe$^{2+}$ | Mn$^{2+}$ | Zn$^{2+}$ | Cu$^{2+}$ | Si | Cl$^-$ | NO$_3^-$ | PO$_4{}^{3-}$ | SO$_4{}^{2-}$ | Observations |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Wolf[43] | L$^a$ | | L$^a$ | L$^a$ | | | | | | L$^a$ | | | | | Woodstock granite, humid-template |
| Hansen & Harris[26] | | | | | | | | | | | | I | R$^b$ | | Laboratory & field test |
| Levin & Jackson[38] | | | I | I | | | | | | | | R | I | | Laboratory test |
| Zimmerman et al.[39] | | | | | | | | | | L$^c$ | | R$^d$ | R$^e$ | | Field test |
| Lindsay[40] | | | | | | R | R | R | R | | | I | | | Laboratory test |
| Nagpal[41] | | R | | | | | | | | | | I-R | R | | Laboratory & field test |
| Botthcer et al.[27] | | | | | | | | | | | | | R | | Laboratory test |
| Driscoll[42] | | | | | R$^f$- L$^g$ | | | | | | | | | | Acid forest USA-Canada |
| Liator[44] | | | | | I$^h$ | | | | | | | R | R | | Alpine watershed (Colorado) |
| Raulund-Rasmussen[45] | | | | L$^i$ | | | | | | | | | | | Acid soil solution |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Grossmann et al.[24] | | | | | | | | P[j] | P[j] | | | | | R | Laboratory & field test | |
| Guggenberger & Zech[10] | | I-R[k] | | | | | I-R[k] | | | | | | I-R[k] | Lab. & field test; old cup ceramic | | |
| Present work | R | R | R | R | R | R | R | R | N.v. | L | I | R | R | R | Lab. & field test; humid mediterran. |

R: Ions adsorbed by ceramic; R: low adsorption; L: Ions leached from ceramic; I: Unaltered ions; N.v.: Not valid values.

[a] After cleaning with dilute HCl.

[b] At high phosphate concentrations and slow sampling sample.

[c] 111%.

[d] 96%.

[e] 43%.

[f] In gibbsite-rich soils.

[g] In gibbsite-poor soils.

[h] At pH = 5–6.

[i] Related to lower proton activities.

[j] [10] At pH = 4.

[k] [11] Three-year old ceramic cups.

follow any clear trend and only a slight degree of sorption of $NO_3^-$ (similar to that indicated in other research)[38,39,41,43] and of $SO_4^{2-}$ (similar to that indicated in other research)[10,24] was observed.

In general, with the exception of chlorides and silica (which tends to be released), almost all ions showed a tendency to be sorbed.

High sampler filling rates, induced by strong suction in the probes, also lead to a reduction in the sorption effect of ceramic cups.[24] Consistent with this, the flow of water toward the ceramic cup was fairly high in this work (Table 2).

Two main factors (pH and DOC)[24] determine the exchange capacity of ceramics. The cation exchange capacity decreases with low pH values because of the protonization of negative exchange sites and, to a lesser extent, the additional competition of protons for exchange sites.[24] Thus, owing to the relative low soil pH (from 5.1 to 6.2) of the soils studied here the finding of a relatively low cation exchange capacity (resulting in a low cation release or retention) would be reasonable. Moreover, the effects of the DOC are dual.[24] First, DOC is able to form complexes with cations and hence prevents sorption and reduces the cation-filter (sorption) effect of the ceramic. Second, DOC is adsorbed by the ceramic cups, leading to an increase in their exchange capacity; and the potential sorption of cations would therefore be increased (a stronger adsorption of humic substances occurs at low pH-values despite the effect of pH on the exchange capacity). We consider that this second action of DOC is a determinant factor in the adsorption behavior of the ceramic cups used in the present work: relatively low pH values (acid forest soil- solution, pH ranging from 5.1 to 6.2) allow the sorption of anions and DOC, which increases the exchange capacity of the cup and cation adsorption. The result is a generalized (anions, COD, and cations) ceramic cup adsorption and the inhibition of $H_4SiO_4$ sorption.

## CONCLUSIONS

From the above results and discussion, the following conclusions can be drawn:

The time required to obtain a sample of soil solution was relatively short (mean value, 2 h), the sphere of water uptake being small (with a radius from 6 to 15 cm), both overall depending on the length of samplers.

Hydraulic conductivity values were not substantially modified during the sampling period (two hydrologic cycles).

The chemical analyses obtained according to the calibration of the ceramic-cups performed point to a marked adsorption of $PO_4^{3-}$ COD, major and minor ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Al^{3+}$, $Mn^{2+}$, and $Zn^{2+}$), and $SO_4^{2-}$ and $NO_3^-$ anions (except $Cl^-$, which did not show any clear trend) tended to be adsorbed, while $H_4SiO_4$ was released. In any case, sorption values were relatively low and showed considerable variability. A marked sorption of phosphates hampered the validity of the values of this anion obtained in the soil-water samples.

Relatively low pH values (5.1–6.2) favor the adsorption of anions and DOC, which increases the exchange capacity of cup and cation adsorption.

The result is a generalized tendency towards sorption (anions, COD, and cations) on the ceramic cup, excepting silica (with a competitive sorption behavior with respect to DOC), and chloride (considered an ion not strongly involved in soil sorption).

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