

Overview of selected soil pore water extraction methods for the determination of potentially toxic elements in contaminated soils: operational and technical aspects

*M. Di Bonito**, *N. Breward*¹, *N. Crout*², *B. Smith*¹ and *S. Young*²

**Environment Agency, Trentside Offices, Scarrington Road, West Bridgford, Nottingham, NG2 5FA, e-mail: marcello.dibonito@environment-agency.gov.uk*

¹ *British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham, NG12 5GG.*

² *School of Biosciences, University of Nottingham, University Park, Nottingham, NG7 2RD*

Abstract

Chemical elements that are either present naturally in the soil or introduced by pollution are more usefully estimated in terms of 'availability' of the element, since it is this property that can be related to mobility and uptake by plants. A good estimation of 'availability' can be achieved by measuring the concentration of the element in soil pore water. Recent achievements in analytical techniques allowed to expand the range of interest to trace elements, which play a crucial role both in contaminated and uncontaminated soils and include those defined as potentially toxic elements (PTE) in environmental studies. A complete chemical analysis of soil pore water represents a powerful diagnostic tool for the interpretation of many soil chemical phenomena relating to soil fertility, mineralogy, and environmental fate. This chapter describes some of the current methodologies used to extract soil pore water. In particular, four laboratory-based methods, i) high speed centrifugation-filtration, (ii) low (negative-) pressure Rhizon™ samplers, (iii) high pressure soil squeezing and (iv) equilibration of dilute soil suspensions, are described and discussed in detail. A number of operational factors are presented: pressure applicable (i.e., pore size involved), moisture pre-requisites of the soil, pore water yielding, efficiency, duration of extraction, materials and possible contaminations for PTE studies. Some consideration is then taken to assess advantages and disadvantages of the methods, including costs and materials availability.

1. Introduction

1.1. Soil pore water and the concept of (bio)availability

Many studies have examined the concentration and retention of metals in soils and the effect of various parameters on their adsorption and solubility, including pH (McBride and Blasiak, 1979; Cavallaro and McBride, 1980; Harter, 1983; Robb and Young, 1999; Green *et al.*, 2003), redox conditions (Davranche and Bollinger, 2001; Davranche *et al.*, 2003; Qafoku *et al.*, 2003), amount of metals (Garcia-Miragaya, 1984; Basta and Tabatabai, 1992; Sauvé *et al.*, 2000), cation exchange capacity (Ziper *et al.*, 1988), organic matter content (Gerritse and Vandriel, 1984; Elliot *et al.*, 1986; Benedetti *et al.*, 1996a, 1996b; Kinniburgh *et al.*, 1999; Kashem and Singh, 2001), soil mineralogy (Tiller *et al.*, 1963; Jenne, 1968; Kinniburgh *et al.*, 1976; Cavallaro and McBride, 1984; Kuo, 1986; Lindroos *et al.*, 2003), biological and microbial conditions (Gerritse *et al.*, 1992; Dumestre *et al.*, 1999; Warren and Haack, 2001) as well as developing assemblage models to mechanistically predict these processes (Dzombak and Morel, 1987; Haworth, 1990; McBride *et al.*, 1997; Celardin, 1999; Weng *et al.*, 2002; Impellitteri *et al.*, 2003, Tye *et al.*, 2003). From these studies it has emerged that total soil metal content alone is not a good measure of short-term bioavailability and not a

very useful tool to determine potential risks from soil contamination (Tack *et al.*, 1995; Sauvé *et al.*, 1998). In fact, since plants take up most nutrients from the soil pore water, it is often assumed that the dissolved potentially toxic elements (PTE) are readily available to organisms (Barber, 1984; Vig *et al.*, 2003). The definition of bioavailability (or phytoavailability) as given by Sposito (1989) suggests, “a chemical element is bioavailable if it is present as, or can be transformed readily to, the free-ion species, if it can move to plant roots on a time scale that is relevant to plant growth and development, and if, once absorbed by the root, it affects the life cycle of the plant”. It is clear that the concentration and speciation of metals in the pore water may provide more useful information on metal bioavailability and toxicity than total soil concentration (Hani, 1996; Knight *et al.*, 1998; Cances *et al.*, 2003; Percival, 2003; Prokop *et al.*, 2003; Shan *et al.*, 2003). Traditionally, however, the soil pore water has not been utilized as a means of assessing bioavailability. This has probably been due to analytical and technical difficulties related to sampling of the soil pore water. Instead, most assessments of metal availability have involved chemical extractants (e.g. EDTA, acetic acid) intended to remove the entire reservoir of reactive metal. This pool may involve a total amount of metal which is several orders of magnitude greater than that found in the soil pore water.

1.1.1. Soil pore water definition

The soil liquid phase has a composition and reactivity defined by the properties of the incoming water and fluxes of matter and energy originating from the local (neighbouring) soil solid phase, biological system, and atmosphere (Fig. 1).

The current view is that in a porous medium, two liquid-phase regions can be identified on functional grounds (Yaron *et al.*, 1996). The first is near the solid phase and is considered the most important surface reaction zone of the porous medium system. This near-surface water also controls the diffusion of the mobile fraction of the solute in contact with (sorbed on) the solid phase. The second region covers the ‘free’ water zone, which governs the water flow and solute transport in soils (Fig. 2). Both phases represent what can be defined as ‘soil pore water’: this term is preferred to the more specific ‘soil solution’ and will be used throughout this chapter.

1.1.2. Bioavailability and soil pore water sampling

To assess the environmental bioavailability, mobility and geochemical cycling of trace elements in soil, analyses of soil pore water composition are frequently more instructive than those from whole soil or soil extracts. The validity of this concept has led to the development of several models that attempt to predict solid solution partitioning of elements and their solution speciation. These ‘assemblage models’ include an increasing number of variables as they develop greater mechanistic capability. Soil pore water analysis can be used to model the nature, direction, extent, and rate of chemical reactions. In fact we can assume that:

1. if soil pore water represents the natural medium for plant growth, then soil pore water analysis allows for prediction of plant response to chemicals occurring in the soil environment (plant uptake prediction);
2. if soil pore water can be related to mobile water in the soil environment, then soil pore water composition can be used to predict the forms and amounts of chemical that may reach ground and surface water through transport from the soil environment (pollutant fate);

3. if soil pore water approaches a steady state relative to the soil solid phase, then soil pore water composition can be used to predict solid phase components controlling chemical distribution in soil (solid-solution processes).

The validity of these assumptions depends on the way that soil pore water is conceptualised, i.e. defined and sampled, and how that concept is translated into an operational method or model whereby soil pore water can be obtained and its composition expressed in a meaningful way. Too often, however, studies skim over a proper definition of soil pore water opting for ‘simulating’ or bypassing the problem.

2. Methods for sampling soil pore water

A range of methods are available for obtaining and analysing ‘unaltered’ soil pore water, with consideration of ion speciation and complexation, and expression of soil pore water composition in thermodynamic terms. Unfortunately, none of them have been adopted as ‘the standard procedure’, leading to a rather confused situation. This is particularly disquieting in environmental studies, where standardization is desirable to achieve highly reliable data. One of the main obstacles to standardization, however, is that sampling of soil pore water often presents conceptual ambiguity as well as technical problems, especially if one tries to characterize the liquid phase in terms of its origin within the soil system. In fact, soil porosity generally represents a limiting factor in defining the ratio between the solid, aqueous and gaseous phases of the soil medium (Yaron *et al.*, 1996) due to the open boundaries between these different phases leading to a pattern of continuously changing processes. In addition, solute concentrations in sampled pore water may depend on a number of technical factors, including,

- method of extraction,
- imposed tensions,
- flow rate to the sampler,
- relation of the soil volume sampled versus the scale of heterogeneity in solute concentration (scaling factor).

This situation is made even more complicated by the wide range of methods of pore water extraction used (see Reeder *et al.*, 1998). For this reason a number of pore classifications have been suggested in the past, as demonstrated in Table 1. In fact, soil pore water sampling can be approached from different angles, where no single methodology is appropriate to all applications. The choice of method will depend on the particular aim of the study in question. In fact, it is arguable that soil pore water is operationally defined by the methodology employed for its acquisition and subsequent analysis. It is therefore very important to describe the methodology and the assumptions employed. A first distinction to make is between field-based and laboratory-based methods. In general, most field sampling methods have been used to interpret soil pore water chemistry from both static and dynamic perspectives, without sufficient consideration of which soil water is being sampled and its chemical reactivity in soils (Wolt, 1994). This possibly makes field-based sampling more suitable than laboratory methods for consideration of chemical transport, provided the solutions obtained represent mobile water in the soil environment. By contrast, considerations of biologically important processes relating to plant nutrient availability, phytotoxicity and soil metabolism are probably best related to chemical composition of diffuse soil water as reflected in the composition of displaced soil pore water.

2.1. Field-based methods

Field methods for sampling pore water are generally grouped under the general term *lysimetry*. This definition usually comprises a range of types of samplers (Wolt, 1994):

- Monolith – any device using an undisturbed soil block or column;
- Filled-in – devices containing soil where the natural soil structure has been disrupted;
- Tension – also called vacuum, suction, point or mini - lysimeters;
- Passive – also called capillary samplers, zero-tension – lysimeters;
- Ebermayer – any lysimeter installation where, by access from a trench, a trough, pan, funnel, plate, or wick is placed under undisturbed soil.

Of these, tension and passive samplers are the most widely used and are discussed below.

2.1.1. Tension samplers

In general, the approach employed for extracting pore water *in situ* is to use tension samplers such as porous cups (for a complete review see Litaor, 1988; Grossmann and Udluft, 1991). Porous cups are designed to replicate the function of a plant root, by applying suction to the soil. The method however is replete with inadequacies that need to be considered in the acquisition and interpretation of data. Principal limitations are the non-representative sampling of soil water occurring above the capillary fringe, and potential artefact effects arising from the reaction of lysimeter materials with the surrounding soil environment. In the first instance, changing the applied vacuum (from 0 to – 40 kPa) was observed to generate little effects on the concentrations of chemical species collected (Beier and Hansen, 1992; Beier *et al.*, 1992). Additionally to this, water will flow from the soil into the porous cup if the capillary pressure in the cup is lower than that in the soil. With a single pump, a vacuum of – 90 kPa can be easily generated and applied to the samplers. Sampling seepage (i.e. slowly percolating) water is therefore possible only as long as the capillary pressure in the soil lies above this value. As a result of the low sampling rates at capillary pressures below – 70 kPa, the use of this system is limited in the majority of soils (Grossmann and Udluft, 1991).

The other problem connected with the use of these samplers is the sorption of solutes from the pore water. Depending on the cup material (materials used include aluminium oxide, glass sinter, ceramic, teflon, acrylic copolymer with internal nylon support, stainless steel, plastic ‘organic’ polymers – PVC, PP, PVDF) additional reactions may take place leading to absorption, precipitation or even release of chemical substances, resulting in pronounced effects on the final composition of the water sampled (Litaor, 1988). Several studies have investigated these effects and questioned the validity of results given by these kinds of samplers (e.g., Hansen and Harris, 1975; Levin and Jackson, 1977; Nagpal, 1982; Guggenberg and Zech, 1992; Goyne *et al.*, 2000). Siemens and Kaupenjohann (2003) found that between 0.8 and 63 mg L⁻¹ of dissolved organic carbon (DOC) was released from sealing and glues of pore water samplers. They concluded that samplers should be designed without glues or elastomers, presenting a suction plate entirely made from borosilicate glass that did not release organic C. Interaction with organics may be particularly significant in the case of PTE adsorption on the surface of the samplers (Shendrikar *et al.*, 1975; Masee and Maessen, 1981; Grossmann *et al.*, 1990; Wenzel and Wieshammer, 1995; Wenzel *et al.*, 1997). Different

materials have been tested to minimize metals sorption effects. For example, McGuire *et al.* (1992) found that metal adsorption on samplers decreased on porous cups made of materials in the sequence ceramic > stainless steel > fritted glass = poly(tetrafluorethene) (PTFE), with PTE being adsorbed in the sequence Zn >> Co > Cr > Cd. These authors also pointed out the importance of the total metal concentration as well as cleaning method (water vs acid solution) and rinse volumes, which affected the extent of the adsorption. Adsorption was between 2 to 15 times higher for water-cleaned samplers, but also increased on acid-cleaned samplers with decreasing volumes utilised. A later study by Andersen *et al.* (2002) found that cups made of PTFE affected the concentrations of Cd, Cu, Ni and Zn, which were adsorbed at pH > 4.5 for low pore water concentrations. Results on adsorption showed that plastic cups may have some advantage over conventional ceramic cups. With increasing sample volume the concentration of a trace metal recorded by the suction cup comes closer to the concentration in the pore water because of the equilibration of the cation exchange surface of the suction cup with the solution. However, the extraction of large sample volumes can cause a significant disturbance of the system (Grossmann and Udluft, 1991). More recently, ceramic cups were found to adsorb PO₄³⁻, DOC, major and minor cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe³⁺, Al³⁺, Mn²⁺, and Zn²⁺) and SO₄²⁻ and NO₃⁻ anions. They release H₄SiO₄ and, in addition to this, relative low pH values (5.1 – 6.2) favoured anion and DOC adsorption, the latter increasing the exchange capacity and cation adsorption of the material (Menendez *et al.*, 2003).

Despite the potential problems, this remains an area of great opportunity for innovation, as illustrated by the development of new types of sampler, such as the soil moisture Rhizon samplers (www.eijkelkamp.com), which will be described later.

2.1.2. Passive samplers

Passive samplers have no tension applied to them. Consequently, they only sample that fraction of the soil water flux occurring under saturated soil conditions or during macropore flow. These devices result in samples of soil water which may represent a combination of bypass water (recent rainfall, irrigation events, i.e. water moving *via* preferential flow), and “internal catchment water” (Booltink and Bouma, 1991), i.e. water moving by diffusion and/or conduction and exhibiting a range of contact times with the soil matrix. The proportion of bypass water compared to internal catchment water will depend on soil structure, soil moisture conditions prior to and during percolate sampling, and features of the design and operation of the lysimeter. As a result, compositional analysis of ‘passive’ lysimeter solutions and pore water obtained by laboratory displacement may substantially differ (Zabowsky and Ugolini, 1990).

2.2. Laboratory-based methods

Laboratory methods of pore water displacement are designed to approximate diffuse water in quasi-equilibrium with the soil solid phase. Methodologies for obtaining “unaltered” soil pore water in a laboratory setting may be broadly defined as **displacement techniques** and comprise:

- Column displacement (pressure or tension displacement, with or without a displacing head solution);
- Centrifugation (with or without immiscible liquid displacement);
- Saturation extracts (including saturation pastes);

- Water extracts;
- Complexation and exchange techniques (e.g., DGT technique, Hooda *et al.*, 1999);
- Lysimetric methods (both tension and passive, including Rhizon samplers - see also field methods)

The various column displacement methods are the most widely applicable and reliable techniques, although require a high degree of operator experience. However, of the methods listed above, four different extraction methods were chosen for a more detailed description and discussion:

- 1) low (negative-) pressure Rhizon samplers (or ‘Soil Moisture Samplers’ - SMS);
- 2) high speed centrifugation-filtration or drainage centrifugation;
- 3) high pressure soil squeezing or ‘pressure filtering’ (squeezing).
- 4) equilibration of dilute soil suspensions

These methods were selected for different reasons, but mainly for their flexibility and novelty. Rhizon samplers represent the current equivalent of porous cups, widely used in the recent past; centrifugation is possibly the current most widely used method due to the ease and the ready availability of the requisite equipment in most laboratories; squeezing is a novel alternative, since it has been used on soils recently (Di Bonito, 2005) and has the potential to access water contained in small pores; soil suspension or saturation extracts constitute a valid alternative, especially when batch experiments are carried out (Degryse *et al.*, 2003). Furthermore, these methods are capable to perform ‘fractionated’ extraction on the soil, whereby a combination of the methods can be used to provide soil water originating from a wider range of pores, which can present a variety of interactions with the soil matrix and possibly different chemistry.

3. Description and discussion of selected methods

3.1. Rhizon Soil Moisture Samplers (SMS)

Rhizon samplers are a hybrid device, which can be used in the laboratory, e.g. pot experiments, as well as in the field (Knight *et al.*, 1998; Cabrera, 1998). They represent one of the latest developments in terms of tension samplers, where it is necessary to apply a suction to withdraw pore water, either with a syringe, a vacuum tube or a pump. In this chapter Rhizon samplers obtained from Rhizosphere Research Products (Wageningen, Holland), later acquired by Eijkelkamp (www.eijkelkamp.com), are described. Using this device, a pore water sample is obtained by inserting the sampler into a wet soil, and applying a suction from a vacuum tube or syringe. According to the manufacturer, the yield in water with 100 kPa pressure differential is greater than 1 ml min⁻¹.

For the soil pore water sampling, the procedure described by Knight *et al.* (1998) and Tye *et al.*, (2003) can be normally followed. Samplers are inserted into soil containers and soil pore water extracted by connecting a syringe to each sampler and applying a suction.

3.1.1. Materials

Standard Rhizon samplers (Fig. 3) consist of a length of porous, chemically-inert hydrophilic polymer plastic (2.5 mm outer diameter, 1.4 mm inner diameter, average

pore diameter ca. 0.1 μm), namely polyethersulphone (PES – G.P.J.P. van Dijk, pers. comm.). This is capped with nylon at one end, and attached to a 5 or 10 cm length of polyethylene tubing, with a Luer-Lock (L-L) male connector at the other end. The tubing is double walled, the inner sleeve is polyethylene (PE) because it is highly inert, the outer wall (for strength) is polyvinylchloride (PVC). The porous polymer and part of the PVC tube is strengthened by a stainless steel wire. The Bubble Point (BP) of the sampler, i.e. the minimum pressure needed to overcome the capillary action of the fluid within the largest pores, which are then emptied¹, is greater than 200 kPa. The dead volume (or void volume i.e., the total of the volume of the porous material and the inner volume) is relatively low, ~0.5 ml.

Nominal data for physical characteristics and dimensions of the Rhizon samplers are given in Table 2.

3.1.2. Theoretical basis of method

When suction is generated within the sampling system, water is sucked inwards through the pores of the sampler until a corresponding capillary pressure occurs in the pores. If the capillary pressure in the sampler is lower than that in the soil, water flows from the soil into the sampler until the capillary pressure in the sampler and in the soil are equal. The maximum capillary pressure in a pore can be calculated by the following equation (Schubert, 1982):

$$p_c = \frac{-2\gamma(T) \cos \theta}{rgD_1} \times 10^{-9} \quad (1)$$

where

p_c = capillary pressure (MPa);

γ = surface tension (N m^{-1});

T = temperature;

θ = contact angle;

r = radius of the pore (m);

D_1 = density of the liquid (kg dm^{-3});

g = gravitational constant (m s^{-2}).

This equation is valid for pores with a circular cross-section. For other shapes an empirical adjustment factor must be considered. Surface-active substances that are dissolved in the water, for example humic substances, can decrease the surface tension. Materials that are not completely hydrophilic (e.g. plastic) need a smaller pore size.

The time required for sampling depends directly on the actual unsaturated hydraulic conductivity (\mathbf{k}) of a soil. Soil pore water will be extracted when $\mathbf{k} > 10^{-3} \text{ m day}^{-1}$ and when there is a good hydraulic contact between the soil and the sampler.

3.1.3. Zone of influence

The zone of influence of the sampler is the zone where sampler installation and operation affect solute flow, the region of the soil from which rhizon water is drawn, and the fraction of soil water that is represented in rhizon solutions. According to the supplier (Eijkelkamp, www.eijkelkamp.com), a Rhizon sampler with 10 cm length

¹ Bubble Point tests are usually carried out to characterize a membrane or porous material consistency or quality; they are also a common procedure to determine the maximum pore size.

porous polymer producing a 7 ml sample, will have removed a water cylinder of 1 cm diameter. Following this approach, it was concluded that a generic zone of influence, extending to a radius of 5 cm in all directions from the edge of the porous sampler, should be considered. The assumption of a 5 cm radius of influence however is not supported by any consideration of properties such as hydraulic conductivity or porosity and was only to advise users to space samplers at 5-10 cm distance between each other. Nevertheless, the recharge area of these samplers (the space in which the water flows towards the sampler) will necessarily depend upon the capillary pressure in the soil, the tension applied, the diameter of the sampler and the pore size distribution of the soil.

Warrick and Amoozegar-Fard (1977) presented an equation that theoretically described the maximum radius of influence (r_m). The former can be estimated in stationary conditions (steady state flow) for a point in an infinite medium around the sampler as follows:

$$r_m = \sqrt{\left(\frac{q}{\pi \cdot K_s}\right) \times 10^{(-\alpha \cdot h_1)}} \quad (2)$$

where

q = volumetric flow rate into the sampler ($\text{cm}^3 \text{s}^{-1}$);

K_s = saturated hydraulic conductivity (cm s^{-1});

α = fitted parameter of hydraulic conductivity function (kPa^{-1});

h_1 = pressure head at r_m (outside the sphere of influence of sampler, kPa).

An alternative expression for the maximum radius of influence is that given by Morrison and Szecsody (1985), which was derived from equation (2) but with \mathbf{k} (unsaturated hydraulic conductivity) expressed as a function of the hydraulic head (see also Hart *et al.*, 1994 and Hart and Lowery, 1997):

$$k(h) = K_s^{(\alpha \Delta h)} \quad (3)$$

where

$\Delta h = h_0 - h_1$

h_0 = suction head at the sampler (kPa)

Therefore r_m will be calculated as:

$$r_m = \sqrt{\left[\frac{4r_0}{\alpha} e^{\frac{\alpha r_0}{2}} (1 - e^{\alpha(\Delta h)})\right]} \quad (4)$$

where

r_0 = radius of the sampler

The constant α is empirically derived and is a measure of the relative importance of gravity and capillarity for water movement in the particular soil (see Bresler, 1978 and Morrison and Szecsody, 1985). Fine soils, where capillarity dominates, have small α -values; coarse soils where gravity effects control water transport have larger α -values (Phillip, 1968).

3.1.4. Uses and limitations for soil pore water extractions

Rhizon samplers are becoming increasingly popular, especially for studies on bioavailability. Knight *et al.* (1998) were one of the first groups of researchers to apply these devices to extract pore water for metal availability studies (Cd, Zn) on soil pore water. Applications on nutrient properties and distribution in different media are also found (e.g. Cabrera, 1998). The methodology has been compared with centrifugation for microbial ecotoxicity testing on soil amended with Cd and Zn (Tiensing *et al.*, 2001). Luo *et al.* (2001, 2003) studied Cu and Zn in polluted soil as influenced by γ -radiations, monitoring the changes in metal concentration over time. More recently, the same authors evaluated the use of a multi-layer column device, with installation of Rhizon samplers, to collect soil pore water for study on nitrate leachability in sludge-amended soils. Rhizon samplers were also used by Tye *et al.* (2002, 2003) to extract pore water to predict As solubility in contaminated soils and to study Cd^{2+} and Zn^{2+} activities in soil pore water on a range of soils.

Figure 4 shows r_m as calculated by equation (4), varying the pressure head (Δh) and the type of soil (α -value). The real diameter of a Rhizon sampler and optimal sampling conditions ($h_0 = -200$ kPa) were assumed for the calculations. The two vertical lines, FC (Field Capacity) and 'syringe suction', enclose the expected conditions for any soil in these conditions. According to Cabrera (1998), 10 ml plastic syringes applied to Rhizon samplers are likely to generate an average suction of -48.1 ± 0.5 kPa.

As expected, the radius of influence is greater for finer (clayey) soils, and smaller for coarser soils. The α -values shown in Fig. 4, range through most of the published α -value for soils (0.01 kPa^{-1} to 1.01 kPa^{-1}). However, there is a considerable variation in α and K_s , therefore more accurate r_m calculations can be made if those two parameters are determined experimentally for a particular soil. In general, the calculation showed that the overall axial-radial influence of this type of sampler is very small, confirming the findings of Hart and Lowery (1997). This could result in a limitation of the method especially when the soil is not homogeneous (or it has not been homogenised) causing preferential flow conditions to prevail.

Samples collected with these devices may inadequately represent the pore water in its natural occurrence because of problems inherent in the technique (Litaor, 1988). This limitation may be additionally influenced by the complex nature of the soil, whose heterogeneity highly affects the chemical concentrations in pore water. Hence rhizon samplers, with their small cross-sectional area, may not adequately integrate for spatial variability (England, 1974; Amoozegar-Fard *et al.*, 1982; Haines *et al.*, 1982), and may represent 'point samples' with qualitative rather than quantitative attributes (Biggar and Nielsen, 1976).

Furthermore, as these devices are produced from organic materials (polysulphone fibres), samplers may add some organic matter to a sample. A recent study (Di Bonito, 2005) posed questions in these areas, and found that after several applications porosity would decrease due to a combination of wearing and organics building up. In addition, as the PVC tubes contains a plasticizer and stabilizers of which producers do not give information, this needs to be taken into account particularly when PVC additives may give problems in analytical methods. In this case, other materials may constitute a better choice. The supplier also informs the users that decaying organic material may influence N-NH_4 analysis in auto-analyser systems. Another important consideration on polysulfone fibres application for soil solution sampling is the apparent retention of

colloidal Fe at the fibre interface (Jones and Edwards, 1993b) which is not entirely clear and should not to be overlooked, due to the high retention of colloidal Fe and its role in the translocation of PTE in soil.

3.2. Centrifugation

Centrifugal extraction of pore water is a relatively routine and well-established method. Its use started early in the 20th century (Cameron, 1911), but was little used until its reintroduction by Davies and Davies (1963). Since then few modifications have been applied to the method. Generally, one can distinguish between three main kinds of centrifugation: low-pressure centrifugal displacement or high-pressure centrifugal displacement and centrifugation with immiscible liquid (Fig. 5).

The first two types are based on free drainage of the pore water, through a porous plate supporting the sample, into a collecting cup. The third, now mostly in disuse, is based on the displacement of pore water by a dense, immiscible liquid followed by subsequent collection of the displaced water after it has floated to the top (Mubarak and Olsen, 1976; Batley and Giles, 1979; Whelan and Barrow, 1980; Kinniburgh and Miles, 1983).

Centrifugation has been widely applied to the extraction of pore waters from various materials including sediments, chalks, sandstones and clayey soils (e.g. Shaffer *et al.*, 1937; Richards and Weaver, 1944). Drainage centrifugation was reported as a method for the removal of fluids from various saturated and partially saturated geological materials in the early soil science literature. These early studies were aimed at measurements of the physical properties of the rocks rather than the characterisation of extracted pore waters. Jones *et al.* (1969) and Sholkovitz (1973) later reported the use of centrifugation, to extract pore water from basin sediments for chemical characterisation. Much of the sampling of pore water in hydrochemical investigations in UK aquifers follows the approach developed and tested in the pioneering work of Edmunds and Bath (1976). The same high-speed centrifugation technique adopted by these authors was later used by Wheatstone and Gelsthorpe (1982) and others for the extraction of pore waters from Triassic sandstones. The technique gradually became the preferred method in soil science. Adams *et al.* (1980) reported that centrifugal displacement at low pressures (< 500 kPa) represented the most widely employed approach to obtaining soil pore water.

The direct centrifugation drainage technique is often preferred as a simple way of obtaining pore water that minimises risks of contamination (Tyler, 2000). Centrifugation allows the quick and easy removal of soil water at precise intervals in time at matric suctions greater than 100 kPa, the upper limit of most of the porous ceramic samplers (Jones and Edwards, 1993a). The pressure applied can go up to 1500 kPa with the highest centrifugal speeds.

3.2.1 Materials

Various centrifuges exist on the market to accommodate the vessels required by the method. For example, a Beckman J21C high-speed refrigerated centrifuge, fitted with a 6 x 500 cm³ Beckman JA-10 fixed-angle rotor is a common choice. In particular, the study we refer to (Di Bonito, 2005) utilised specially designed polyoxymethylene

(Acetal) tubes provided with 316 stainless steel, 20 μm mesh filters, which were manufactured in-house to adapt the rotor available with the centrifuge (Fig. 6).

3.2.2. Theoretical basis of method

Although the exact force distribution is difficult to determine, the physics of fluid removal from porous geological materials by drainage centrifugation is fairly well understood (Edmunds and Bath, 1976). Given a column of soil under centrifugation, the tension applied, p_a , can be derived as:

$$p_a = \frac{\omega^2}{2g} (r_1^2 - r_2^2) \quad (5)$$

where:

p_a = tension applied developed at a generic point r_2 of column (cm water);

ω = angular velocity (rad sec^{-1});

g = gravitational constant (cm s^{-2});

r_1 = distance from base of column to centre of rotation (cm).

The applied force is therefore a function only of distance from the rotor and the centrifugal speed, i.e. it has the same magnitude irrespective of the density and nature of the material tested, and the pattern of water removal will depend on the pore size distribution of the material. At equilibrium, p_a will be everywhere balanced by a capillary pressure, p_c , which can also be expressed as follows (Washburn, 1921):

$$p_c = \frac{2\gamma \cos \theta}{\rho \cdot r} \quad (6)$$

where

p_c = capillary pressure in a pore (N m^{-2});

γ = surface tension (N m^{-1});

ρ = specific gravity;

θ = contact angle between porous solid and liquid;

r = radius of pore (m).

The extent of interstitial water removal is therefore a function of the centrifuge dimensions and rotation speed, but it is also governed by the weight of sample used, the degree of initial saturation as well as the material's pore size distribution.

3.2.3. Pore water extraction

The centrifugation drainage procedure described by Edmunds and Bath (1976) and Goody *et al.* (1995) can normally be applied for this method. The relationship between the distance to the centre of rotation and speed (hence pressure) applied as well as the optimal choice of centrifuge speed, centrifugation time, and sample weight can be established in relation to the particular sample and volume of interstitial water required (see also Kinniburgh and Miles, 1983).

A known quantity of soil is placed into weighed centrifuge buckets. After the samples are spun at the chosen speed, any pore water extracted can be collected using disposable

syringes, weighed and filtered through adequate filters for chemical analysis. If only small volumes of pore water were extracted, replicate samples can be used to bulk the extracts. Distilled water blanks is normally passed through the extraction steps to minimize any contamination by materials or handling.

During centrifugation a soil sample is spun at a specific speed, which corresponds to a relative centrifugal force (RCF) and, according to equation (5), a corresponding pressure. The pressure on each point within the soil column can be represented depending on the distance to the axis of rotation and speed. Fig. 7 shows the variation of the applied pressure within a single bucket, as calculated by using equation (5). The radius varies between 5 (top of the column) and 9 cm (base of the column) depending on the position of the point inside the bucket, which is inclined at 45° with respect to the axis of rotation. In this situation we considered the maximum speed achievable as ca. 7000 rpm, which was calculated according to a reduction factor for the rotor in use with the centrifuge, in case of materials having density higher than water (Beckman instruments, 1988).

The mean distance from the axis of rotation is 7 cm, which is the midpoint at which we can calculate the relationship between the varying speed and the pores drained according to equation (6). Fig. 8 shows the resulting pressure profile at the midpoint with varying centrifugal speed.

3.2.4. Uses and limitations for soil pore water extractions

Many researchers have tested and reported the yield (defined also as “extraction efficiency” – Entwisle and Reeder, 1993, see later in this chapter) for different materials and using a range of rotation speeds and lengths of operation. As a general principle, the volume of solution extracted is a function of the initial weight of the sample, the pore size distribution (PSD) of the soil, the degree of initial saturation, the centrifuge dimensions, and rotational speed (Edmunds and Bath, 1976). In the study of Edmunds and Bath (1976), extraction yields of 20-30% were obtained at low speeds, compared with up to 85-95% of the available pore water using the high-speed centrifuge. In the study of Wheatstone and Gelsthorpe (1982), the moisture content of the samples tested varied between 6 and 15% and the percentage of water extracted increased with increasing speed from 3000 to 12000 rotations per minute (rpm). At the optimum speed of 12000 rpm, tests showed that only a marginal increase in the amount of fluid extracted was observed after an initial 30 minutes operation. In the work of Kinniburgh and Miles (1983), yields were typically 20 to 50% for soils of moisture content 10 to 40%, but up to 90% for some chalks with 20% initial moisture content. Di Bonito (2005) found that centrifugation achieved an efficiency of 28% (measured on a single tube), and very little pore water was collected at low speeds (1000 and 2000 rpm). This was due to the initial moisture content of the soil used and the low pressure differential between the matric potential of the soil (representing the strength at which water is held in the soil), equivalent to FC (-10kPa), and the corresponding potential applied during these steps (respectively 18 and 70 kPa). When centrifuging, pore water is lost from the sample when positive pressures exerted by centrifugal force are greater than the matric suction exerted by the solid phase (Jones and Edwards, 1993a). A significant amount of water (up to 40% of the total) remained in the samples at the end of the 5-step centrifugation extraction.

During centrifugation compaction of the soil occurs, the effect being more significant for finer textures (Gamerding and Kaplan, 2000). In a recent study (Di Bonito, 2005) from an initial bulk density (ρ_b) of 0.67, a final ρ_b of 1.01 g cm³ was measured, therefore affecting the nominal pore distribution. Although this is a predictable drawback of the methodology, it could lead to misinterpretation of the possible sources of the water in terms of porosity if not carefully considered. According to Jones and Edwards (1993a), a moisture content gradient also develops through the sample. As water migrates down through the sample, the base of the soil, from which the solution is released, will be in excess of its water-holding capacity (0 kPa) during part of the centrifugation process, indicating that centrifugation may also yield solution from pores of all sizes at the one time (Lorenz *et al.*, 1994).

Studies comparing different centrifugation methods and other techniques in providing soil pore water have been reported by many authors (e.g. Menzies and Bell, 1988; Zabowski and Ugolini, 1990; Sheppard *et al.*, 1992; Dahlgren, 1993; Lorenz *et al.*, 1994; Giesler *et al.*, 1996; Chapman *et al.*, 1997). Most studies are fairly consistent in their illustration of the differences among methods in terms of element concentrations in pore water, partly due to different fractions of pore waters considered. Moreover, centrifugation can be used to fractionate the pore water by selecting several centrifugation rates, i.e. pore water can be extracted using a number of steps, with an increment of centrifugal speed. When increasing the centrifugal speed, and therefore the relative centrifugal force (RCF) value, during the various stages of soil centrifugation, less available water may gradually be released and collected (Tyler, 2000), thereby extracting water from a range of pore size distributions. Centrifugal speed has been shown to influence significantly the composition of the extracted soil pore water, which, depending on the specific soil considered, can display an effective increase in metal concentrations (Pérez *et al.*, 2002). In the simplest case of piston and preferential flow (Beven, 1989), water is considered to have a bimodal distribution in velocity, corresponding to 'mobile' and 'immobile' phases (Coats and Smith, 1964). In an unsaturated soil medium with a given degree of heterogeneity, piston flow tends to be dominant at higher water contents and preferential flow at lower water content (Padilla *et al.*, 1999).

3.3. Pressure filtering (Squeezing)

The squeezing method represents an approach where it is possible to modify the pressure during the extraction. This technique has been proved to be effective with various structured materials (coherent sediments and rocks) and has also been used for incoherent materials, including peat, clay, till, sand, silt, chalk, sea sediments (Entwisle and Reeder, 1993), but only recently has been used on soils (Di Bonito, 2005).

The squeezing technique was originally developed to obtain pore water samples mainly from unconsolidated marine silts and clays. Manheim (1966) developed a heavy duty squeezer capable of applying a stress up to 150 MPa based on the early designs of a number of Soviet workers, most notably Kriukov (1971). Similar designs have been used by Morgenstern and Balasubramonian (1980), Brightman *et al.* (1985), and Krahn and Fredlund (1972) to evaluate change in salinity with increased pore water extraction and increased pressure. The methodology has been used to extract pore fluid from materials with moisture content slightly below 7%. The method is often unsuccessful on highly

cemented, hard material. In comparative studies, squeezing has been found to have a lower potential for contaminations and artefacts, partly because pore water extraction and filtration can be conducted in-line (Bufflap and Allen, 1995b). Very little direct contamination of the pore water resulted from clay studies using this extraction method (Entwisle and Reeder, 1993). In contrast differences in ionic strength and major components were found with increasing pressure applied and decreasing moisture contents (Cave *et al.*, 1998; Reeder *et al.*, 1998).

3.3.1. *Materials*

The squeezing apparatus described here is the one in use at the British Geological Survey (BGS) and utilises a hydraulic pump (Wykeham Farrance Engineering Ltd., Slough) which has a maximum output stress of 70 MPa and hydraulic hoses and fittings (Fig. 9). The main body of the cell and other metal parts in contact with the test sample or pore water are manufactured from Type 316 stainless steel, selected for its resistance to corrosion and its high tensile strength.

The cell body sample chamber is 75 mm in diameter and 100 mm high (Fig. 10). The outside of the cell has a spiral trough through which temperature controlled fluid circulates inside a plastic insulation jacket. Temperature control of the cell is achieved by a heater/chiller, which is capable of temperature control between -10° and 50°C. The pore water collection pipe screws into the top plate. Pore fluid is collected directly into disposable polypropylene syringes.

Two syringe taps (which can have a 0.45 µm Acrodisc filter in between) are pushed onto the pore water pipe allowing flexibility of pore water collection: taps can be opened and closed when multiple samples are collected and syringes need to be replaced. The metal filter, which has a diameter of 90 mm, is also made of Type 316 stainless steel (see Entwisle and Reeder, 1993 for further details).

3.3.2. *Theoretical basis of method*

The squeezing process involves the expulsion of pore water from the material being compressed. In general the material consists of solid particles (mineral phase), and spaces (voids), which in an unsaturated environment such as a soil, contain both air and water. When a squeezing stress is applied to a water-saturated material, its volume decreases by three main mechanisms:

- compression of the solid phase;
- compression of the pore water between the solid phase; and
- escape of water from the voids.

In most circumstances, the compression of the solid and liquid phases is negligible and most of the change in volume is caused by the escape of pore water. This may be illustrated by a hydromechanical analogy for load changing and squeezing as shown in Figure 11 (after Lambe and Whitman, 1979). The resistance of the solid phase during compression is represented by a spring and the rate at which the pore fluid flows is dependent upon the size of the valve aperture. In (a) the valve is closed and in equilibrium. When a pressure is added (b) the piston load is apportioned by the water and the spring in relation to the stiffness of each. There is little movement in the piston because the water is relatively incompressible. Most of the load is carried by the water and this increases the water pressure. If the valve is now opened (c) the excess pore pressure dissipates by water escaping through the valve (d). The piston drops and the volume of the chamber decreases until there is a new equilibrium when the applied load

is carried by the spring and the water pressure has returned to the original hydrostatic condition (e). The gradual transfer of load from the water to the spring is shown in (f). The dissipation of the pore water is called primary consolidation.

The rate at which the pore fluid is expelled is related to the length of the sample and the pore size. A typical graph of the rate of settlement, and therefore pore fluid extraction, after the addition of a load (Fig. 12) shows both primary and secondary consolidation.

Most of the excess pore pressure dissipates during primary consolidation. Secondary consolidation involves the movement of particles as they adjust to the increase in effective pressure and the dissipation of excess pore pressure from very small pores. The pore water extracted during squeezing is mainly due to primary consolidation.

3.3.3. Pore water extraction

Soil is placed into the clean dry cell. A 90 mm diameter Whatman filter paper is then placed on to the shoulder of the sample chamber and a clean steel filter placed on top of the filter paper. The top plate is screwed into the cell to contact the metal filter; the temperature control unit cooler is then switched on. A small nominal stress (<1 MPa) needs to be applied to remove most of the air from the cell and to allow the sample and the components to bed in. When the selected temperature ($\pm 2^\circ\text{C}$) is attained, the pressure can be increased and water collected.

The squeezing test may take from 1 hour to in excess of 2 or more weeks, depending on the set up and the physical properties of the material, producing either a single bulk sample or a number of “sequential” water samples (Ross *et al.*, 1989). When sufficient volume of pore water had been obtained (~ 15 mL to allow chemical analysis), the syringe is removed and the sample filtered as soon as collected through appropriate filters and treated for analysis. This process can be repeated by continuing squeezing, using a new syringe assemblies as necessary, until no further pore water is obtained (Cave *et al.*, 1998).

After the extraction is completed, typically the specimen is removed and measured to calculate its volume, weighed and oven dried at 105°C for density and moisture content determinations.

3.3.4. Extraction Efficiency

The percentage of the available pore water extracted, E , (Entwisle and Reeder, 1993) is determined as:

$$E = \frac{W_p}{W_{si} - W_{sd}} 100 \quad (7)$$

where

W_p = weight of pore water collected;

W_{si} = weight of sample initially tested;

W_{sd} = weight of sample post squeezing (centrifuging) after oven drying.

This can be written as:

$$E = \frac{W_p}{W_s \cdot \theta_w} 1000 \quad (8)$$

where

θ_w = moisture content with respect to initial wet sample weight. This concept is applied both to centrifugation and squeezing, where moisture contents are normally

reported with respect to the dry weight. A known mass (at least 50 g, in triplicates) of the original sample is tested by determining its weight before and after heating at approximately 105 to 110°C for a minimum of 24 h.

The percentage moisture content with respect to the initial wet sample weight, θ_w , can be determined as:

$$\theta_w = \frac{W_w - W_d}{W_d} 100 \quad (9)$$

where

W_w = wet sample weight;

W_d = dry sample weight.

3.3.5. Uses and limitations for soil pore water extractions

This methods was recently tested on three different soil types (Di Bonito, 2005): a Brown sand from the Newport region, a Calcareous pelosol from the Hanslope region and a sandy silt with high organic matter content (LOI 27.1 %, OC 15.7 %) from the Nottingham region. Extraction efficiency, $\%E$, for the three soils were calculated and resulted to be 27.4% for a sandy soil. This is due to the initial low moisture content (11.1%) and the sandy texture of the soil. Previous tests on different materials (Entwisle and Reeder, 1993) showed that samples with an initial moisture content of less than 10% present a low extract efficiency and that there is an apparent cut-off of about 7-8% below which no water is collected. Furthermore, the sandy texture of the soil suggests that solid particle repacking, which is one of the main mechanisms through which pore water is displaced, will be limited during squeezing. The rate of settlement and therefore the pore water extraction by primary consolidation are also related to the change in volume (i.e., voids ratio) that the sample suffers during the process; this is related to the texture of the sample, with sand giving lower porosity. $\%E$ for the other two soil, respectively organic and a clayey, were 68.3% and 67.4%.

The time to complete the extractions can vary depending on the approach used and can be of weeks if the aim of the extraction is to go through states of equilibrium with the pressure applied. In general, stiffer materials of low permeability require longer periods of squeezing.

Figure 13 shows the cumulative release of pore water for three soils tested with increasing pressure (Di Bonito, 2005). The dotted line represents the pressure corresponding to the hygroscopic coefficient, i.e. the upper limit for the capillary water. This illustrates the capability of squeezing to reach a wider range of pores. This pressure value should also correspond to most of the available water in the soil. In fact by this stage almost 75% of the total water was extracted for the clayey soil and 60% for the organic soil.

Soil compaction was clearly very marked for the clayey and the organic soils, and to a lesser extent for the sandy one, due to the soils intrinsic characteristics.

3.4. Soil suspensions

Under this umbrella lie a number of different applications, amongst others the batch equilibration and equilibrium soil solution methods. According to the USEPA (1999),

the former represents the most common laboratory method for determining partition coefficients - normally defined as K_d -, both for contaminated sites studies and for predictions of chemicals behaviour in soils (OECD, 2002). The batch equilibration method consists of mixing a soil with a known amount of liquid (background electrolyte), which is then shaken into a slurry and allowed to equilibrate for an adequate time. The solution will be separated from the solids by centrifuging the slurry, resulting in a supernatant and a separated solid phase. The supernatant will therefore be removed, filtered and analysed.

3.4.1. Materials

There is a multitude of choices for shakers (reciprocal or not) and centrifuges with annexed spares, with several variations to the above described general procedure. Widely different soil:solution ratios (R , kg L⁻¹) have been used to investigate the adsorption and desorption behaviour of trace-metals ions by soils, from 1:2 up to 1:200 soil:solution dilutions (Table 3). The background electrolyte solution and ionic strength also vary extensively between reported studies. It is commonplace in many soil and environmental studies to utilise 5 mmol L⁻¹ (0.01 *N*) Ca²⁺ solutions (where the counter ion is NO₃⁻, Cl⁻, or occasionally, SO₄²⁻) for batch equilibration with soil to mimic soil pore water ionic strength and composition (Wolt, 1994). This arises from a historical precedent originating from earlier studies of soil exchangeable cations and dissolved salt content, but is still largely used in many studies (Table 3). However, depending on the value of R , the equilibrating solution may reflect the ionic strength and ion composition of the added electrolyte more than it does that of the *in situ* pore water. Some studies have not made provision for background electrolyte composition that would be comparable to the pore water, sometimes even having an ionic strength (I) that approaches zero (Table 3). However, it is well known that solid:solution equilibria in soils depend significantly on ionic strength (I).

Time is another variable for this methodology, where a 24-48 h extraction time is generally typical for many batch extractions (e.g., Anderson and Christensen, 1988; Yin *et al.*, 2002) but it may also vary and extend into several weeks according to the aim of the study (Jopony and Young, 1994). Longer equilibration times are normally selected to try to take into account the slow kinetics of the organic-metal desorption.

3.4.2. Theoretical basis of method

The method of soil suspensions extracts is based on metal desorption/dissolution processes, which primarily depend on the physico-chemical characteristics of the metals, selected soil properties and environmental conditions. Metal adsorption/desorption and solubility studies are important in the characterization of metal mobility and availability in soils. Metals are in fact present within the soil system in different 'pools' and can follow either adsorption and precipitation reactions or desorption and dissolution reactions (Selim and Sparks, 2001). The main factors affecting the relationship between the soluble/mobile and immobile metal pools are soil pH, redox potential, adsorption and exchange capacity, the ionic strength of soil pore water, competing ions, and kinetic effects (e.g. contact time) (Evans, 1989; McBride, 1994; Sparks, 1995; Impellitteri *et al.*, 2001).

Adsorption equilibria are often summarised by the *distribution or partition coefficient*, K_d , which expresses the relative affinity for a sorbate in solution to be

absorbed or desorbed (Oscarson and Hume, 1998). The distribution coefficient, K_d , is usually defined as the ratio of concentrations in the adsorbed and liquid phase, thus:

$$K_d = \frac{[M_{soil}]}{[M_{solution}]} \quad (10)$$

usually expressed in $L\ kg^{-1}$. However, when reporting K_d values for soils, it is very important that the definitions of $[M_{soil}]$ and $[M_{solution}]$ are given, identifying what form of metals is described. For example, for estimating immediately bioavailable metal in soil pore water, the free ion activity estimated by speciation programs can be used (Jopony and Young, 1994); conversely, if the study focuses on metal transportation to groundwater, it may be more appropriate (pragmatically) to include all species of metals in solution (Impellitteri *et al.*, 2001).

The extent to which a chemical is adsorbed or desorbed can generally be rationalised within the frameworks of solution and surface chemistry. *Internal* and *external* factors affecting sorption and/or desorption can be distinguished (Harter and Naidu, 2001). Examples of the first category are:

- Ionic strength
- Cation, anion and organic ligands
- pH
- Total metal concentration

Examples of the second category are:

- Pressure
- Temperature
- Soil:solution ratio (**R**)
- Experiment technique and sample storage conditions

3.4.3. Uses and limitations for soil pore water extractions

The main advantage of the use of this method is related to the costs, as there is often no need for extra equipment in the laboratory, no chemicals are involved unless trying to reproduce the composition of the natural background electrolyte. The preparation is easy and the use widespread, allowing comparison with results from other studies.

Nevertheless, variations in **R** have been found to influence the aqueous-phase chemistry of trace-metal ions, and thereby affect sorption and desorption processes (O’Conner and Connolly, 1980; Voice *et al.*, 1983; Di Toro, 1985; Celorie, 1989). Generally, K_d values tend to decrease with increasing soil concentration (high **R**), suggesting increased metal solubility. Grover and Hance (1970) suggested that this effect is predominantly caused by higher surface area exposure at high **R**. Another explanation would be that there are simply more particles that pass through a given filter at higher solid concentrations. Therefore, more particles transporting bound metal are erroneously analysed as ‘soluble’ or desorbed metals in a supernatant, yielding lower K_d values (Voice and Weber, 1985; Van Benschoten *et al.*, 1998). A third and more plausible explanation is that K_d increases as labile metal is depleted (stronger sites accessed) and so a small value of **R** (substantial depletion) will produce a greater K_d value. Early studies on this topic revealed that total concentrations of soluble salts generally decreased with an increase in the soil moisture content (increasing dilution)

(Reitemeier, 1946, Khasawneh and Adams, 1967, Larsen and Widdowson, 1968). More recently Yin *et al.* (2002) used a series of R values (from 0.5 to 0.02) in batch experiments to quantify the solubility of Cu, Ni and Zn in soils. Again, greater concentrations arose from larger values of R .

The effect of R on metal concentrations in soil pore water is of interest because it can characterize soil pore water at different water content, and also to explain the effect of different values of R in procedures for extracting equilibrium soil pore water. Water extracts are often used to measure pore water chemistry and thus extrapolating its equivalent composition at FC. However, varying soil:solution ratios showed that this could be an ambiguous exercise if not corroborated by sound speciation models. A major part in the final result can be played by Organic Matter (OM) in the soil, where desorption of OM can render unreliable or inconsistent the values of metal released with varying R (Di Bonito, 2005). On the other hand, there is good evidence that solubility/adsorption equilibria of free divalent metals are maintained reasonably well (relatively constant $[M^{2+}]$ and very limited depletion of labile pool). The significance of this is that it is possible to attain a fairly reliable estimate of bioavailable metal (M^{2+}) even in strongly dilute suspension but poor estimates of M_{soln} (e.g. for leaching studies) since they are hopelessly dependent on operational aspects of the suspension/extraction scheme. USEPA (1999) and Yin *et al.* (2002) drew the conclusions that values of metal dissolved based on this technique conducted with a soil:solution ratio significantly less than those existing in the field would overestimate metal sorption and underestimate metal migration (see also Strandberg and Fortkamp, 2005).

4. Conclusions and recommendations

Rhizon soil moisture samplers, centrifugation, high pressure squeezing and soil water suspensions constitute good laboratory techniques for the recovery of pore water. The functionality, benefits and limitations of these methods can be summarised as follows.

Rhizon samplers should be used preferably as a disposable device, to avoid material modification with time, decrease in porosity and possibly significant variations in solute chemistry; this will inevitably increase the experimental costs in the case of larger designs. Given the nature of the materials, results should be treated cautiously in cases where humic substances are present in the soil. There is no equipment required except syringes (or vacuum tubes), ease of handling/deployment and straightforward use constitute major advantages. There are no 'side-effects' (provided time is allowed for equilibration with the soil) if M^{2+} (free ion activity) were needed as opposed to M_{sol} (total metal in pore water), as often required in environmental studies. The overall geometric mean axial-radial influence of these samplers is very small, suggesting that careful consideration of the samplers' placement and experimental designs as a function of the characteristics of the soil under investigation is required. Rhizon samplers only function when the matric potential is greater than 10 kPa (above FC) otherwise the potential gradient and the hydraulic conductivity are too low to obtain a sample. Rates of solution accumulation by tension samplers can vary in a given soil due to heterogeneity of moisture content and solution flow pathways. Increasing the applied tension increases the non-uniformity of sampling. Hence the more uniform the particle size the more uniform is the sampling rate.

Centrifugation presents fewer material problems compared to Rhizon samplers; however, tubes and other spare parts are not commercially available and often have to be built in-house. The method is optimal for bulk solution studies, or when homogenisation represents a key experimental point; targeted studies are also possible but would necessitate prior examination of the soil water holding capacity and release under varying centrifugal speeds, which could be demanding in terms of time and effort.

Centrifugation covers a wider range of pore sizes compared to Rhizon sampling, but nevertheless will only yield a fraction of the total pore fluids. A consideration when using this methodology is that compaction and pore size reduction may occur during centrifugation. As this effect is more significant for finer textures, therefore these soils would need to be tested for compaction prior to experimentation. Furthermore, a moisture content gradient also develops through the sample. As the water migrates down through the sample, the base of the soil will be in excess of its water-holding capacity (0 kPa) during part of the centrifugation process, resulting in saturation of the sample at its base. This could cause alteration of the chemical composition of the extracted pore water, caused by a mixing process, which would homogenize the composition compared to the heterogeneous *in situ* conditions. Some studies reached similar conclusions, indicating that centrifugation yielded solution from pores of all sizes at the one time. This effect would however be much more evident at soil matric potential increasingly above FC, where preferential flow conditions and gravitational water prevail with respect to capillary water, and for single extractions. In fact, as this method is destructive and produces compaction of the soil sample, capillary conditions are most likely to be established as the extraction would proceed to later fractions, due to the reduction of the total nominal porosity.

Soil squeezing is not as accessible as the other three, at least with the present apparatus required, but there is space for further development and improvement (i.e. simplification of the design and/or reduction of labour required). The rate of pore water collected during squeezing tests shows that sample texture and organic matter content are important variables to consider prior to extraction. In the cases of sandy soils, exceeding FC would be advisable to improve the release of pore water. Conversely, due to the higher range of pressures exerted compared to Rhizon samplers and centrifugation, a greater amount of the total available water was generally extracted. Efficiencies of 67% and 68% were observed for a clayey and a sandy silt with high organic matter respectively. The principal constraint of this methodology is the time involved: if the extractions require ‘multiple-step at quasi-equilibrium’ protocol then a much longer duration, compared to centrifugation and Rhizon samplers, is needed for a complete test. The duration of the extraction constitutes a major limitation, especially when organic matter is a key component of the soil studied. Decomposition of OM and anaerobism can lead to massive variations in chemical composition and speciation. Careful consideration should therefore be made in those circumstances. However, ‘fast’ extractions with high initial pressures may produce good results and minimize the alterations produced by anaerobism.

Batch extractions are very accessible and easy to reproduce. Costs and ease represent the main advantages of this method: often no extra equipment and no chemicals are necessary, unless the aim is to reproduce the composition of the natural background

electrolyte. One of the main drawbacks is related to the actual comparability of results, given the wide range of operating factors used in the literature. In particular, variations in soil:solution ratios (R) have been found to influence the aqueous-phase chemistry of trace-metal ions, and thereby affect sorption and desorption processes. Varying R can show to be an ambiguous exercise if not corroborated by sound speciation models, particularly where a major part in the final result can be played by Organic Matter (OM) in the soil. Batch extractions have proven to be very consistent in estimating the bioavailable fraction of the metal (M^{2+}) even in strongly dilute suspension, whereas they are not always reliable for estimates of M_{soln} (e.g. for leaching studies) since they are hopelessly dependent on operational aspects of the suspension/extraction scheme.

One important conclusion drawn in the literature is that values of metal dissolved based on this technique conducted with a R significantly less than those existing in the field would overestimate metal sorption and underestimate metal migration. As a consequence, suspensions with high solids concentrations should be used for batch experiments extractions to approach more closely natural conditions, unless only estimates of free metal ion activity (M^{2+}) are needed.

In summary, the importance of the method employed for soil pore water extraction should not be underestimated. Experimental design and performance should be chosen to reflect the particular aim of the study, reported in sufficient detail to allow others to make appropriate comparisons and the parameters operationally defined as a function of the method employed.

References

- Adams, F., Burmester, C., Hue, N.V., and Long, F.L. (1980). Comparison of column-displacement and centrifuge methods for obtaining soil solution. *Soil Science Society of America Journal*, **44**, 733-735.
- Amoozegar-Fard, A. D., Nielsen, D.R., and Warrick, A.W. (1982). Soil solute concentration distribution for spacially varying pore water velocities and apparent diffusion coefficients. *Soil Science Society of America Journal*, **46**, 3-9.
- Andersen, M.K., Raulund-Rasmussen, K., Strobel, B.W., and Hansen, H.C.B. (2002). Adsorption of cadmium, copper, nickel, and zinc to a poly(tetrafluorethene) porous soil solution sampler. *Journal of Environmental Quality*, **31**(1), 168-175.
- Barber, S.A. (1984). *Soil nutrient bioavailability: a mechanistic approach*, John Wiley, New York.
- Basta, N.T., and Tabatabai, M.A. (1992). Effect of cropping systems on adsorption of metals by soils. II. Effect of pH. *Soil Science*, **153**, 195-204.
- Batley, G.E., and Giles, M.S. (1979). Solvent displacement of sediment interstitial waters before trace-metal analysis. *Water Research*, **13**(9), 879-886.
- Beckman Instruments, (1988). Instructions for using the JA-10 fixed angle rotor. Beckman J-21 Series, J-6, and J-6B, Spinco Division of Beckman Instruments, INC., Palo Alto, Ca.
- Beier, C., and K. Hansen. (1992). Evaluation of porous cup soil-water samplers under controlled field conditions: comparison of ceramic and PTFE cups. *Journal of Soil Science*, **43**, 261-271.

- Beier, C., Hansen, K., Gundersen, P., and Andersen, B.R. (1992). Long-term field comparison of ceramic and poly(tetrafluoroethene) porous cup soil water samplers. *Environmental Science Technology*, **26**, 2005-2011.
- Benedetti, M.F., VanRiemsdijk, W.H., Koopal, L.K., Kinniburgh, D.G., Gooddy, D.C., and Milne, C.J. (1996a). Metal ion binding by natural organic matter: From the model to the field. *Geochimica et Cosmochimica Acta*, **60(14)**, 2503-2513.
- Benedetti, M.F., VanRiemsdijk, W.H., and Koopal, L.K. (1996b). Humic substances considered as a heterogeneous donnan gel phase. *Environmental Science & Technology*, **30(6)**, 1805-1813.
- Biggar, J.W., and Nielsen, D.R. (1976). Spatial variability of leaching characteristics of a field soil. *Water Resources Research*, **12(1)**, 78-84.
- Booltink, H.W.G., and Bouma, J. (1991). Morphological characterization of bypass flow in well-structured clay soil. *Soil Science Society of America Journal*, **55**, 1249-1254.
- Bresler, E. (1978). Analysis of trickle irrigation with application to design problems. *Irrigation Science*, **1**, 3-17.
- Brewer, R. (1964). *Fabric and mineral analysis of soil*, J. Wiley, New York.
- Brightman, M.A., Bath, A.H., Cave, M.R., and Darling, W.G. (1985). Pore fluids from the argillaceous rocks of the Harwell region. 85-6, British Geological Survey, Keyworth, Nottingham.
- Bufflap, S.E., and Allen, H.E. (1995b). Comparison of pore water sampling techniques for trace metals. *Water Research*, **29(9)**, 2051-2054.
- Cabrera, R.I. (1998). Monitoring chemical properties of container growing media with small soil solution samplers. *Scientia Horticulturae*, **75**, 113-119.
- Cameron, F.K. (1911). *The soil solution: the nutrient medium for plant growth*, Chemical Publishing, Easton, PA.
- Cances, B., Ponthieu, M., Castrec-Rouelle, M., Aubry, E., and Benedetti, M.F. (2003). Metal ions speciation in a soil and its solution: experimental data and model results. *Geoderma*, **113(3-4)**, 341-355.
- Cavallaro, N., and McBride, M.B. (1980). Activities of Cu^{2+} and Cd^{2+} in soil solutions as affected by pH. *Soil Science Society of America Journal*, **44**, 729-732.
- Cave, M.R., Reeder, S., Entwisle, D.C., Blackwell, P.A., Trick, J.K., Wragg, J., and Burden, S.R. (1998). Extraction and analysis of pore waters from bentonite clay. *WI/98/9C*, British Geological Survey, Keyworth, Nottingham.
- Celardin, F. (1999). Semi-empirical correlations between so-called mobilizable and mobile concentrations of heavy metals in soils. *Communications in Soil Science and Plant Analysis*, **30(5-6)**, 843-854.
- Celorie, J.A., Woods, S.L., Vinson, T. S., and Istok, J. D. (1989). A comparison of sorption equilibrium distribution coefficients using batch and centrifugation methods. *Journal of Environmental Quality*, **18(3)**, 307-313.
- Chapman, P.J., Edwards, A.C., and Shand, C.A. (1997). The phosphorus composition of soil solutions and soil leachates: influence of soil:solution ratio. *European Journal of Soil Science*, **48**, 703-710.
- Coats, K.H., and Smith, B.D. (1964). Dead-end pore volume and dispersion in porous media. *Society of Petroleum Engineers Journal*, **4(1)**, 73-84.
- Dahlgren, R.A. (1993). Comparison of soil solution extraction procedures: effect on solute chemistry. *Communications in Soil Science and Plant Analysis*, **24(15-15)**, 1783-1794.
- Davies, B.E., and Davies, R.I. (1963). A simple centrifugation method for obtaining small samples of soil solution. *Nature*, **198**, 216-217.
- Davranche, M., and Bollinger, J.C. (2001). A desorption-dissolution model for metal release from polluted soil under reductive conditions. *Journal of Environmental Quality*, **30(5)**, 1581-1586.

- Davranche, M., Bollinger, J.C., and Bril, H. (2003). Effect of reductive conditions on metal mobility from wasteland solids: an example from the Mortagne-du-Nord site (France). *Applied Geochemistry*, **18**(3), 383-394.
- Degryse, F., Broos, K., Smolders, E., and Merckx, R. (2003). Soil solution concentration of Cd and Zn can be predicted with a CaCl₂ soil extract. *European Journal of Soil Science*, **54**(1), 149-157.
- Di Bonito, M. (2005). Trace Elements in Soil Pore Water: A Comparison of Sampling Methods, Ph.D. thesis, University of Nottingham, Nottingham (<http://etheses.nottingham.ac.uk/archive/00000123/>).
- Di Toro, D.M. (1985). A particle interaction model of reversible organic chemical sorption. *Chemosphere*, **14**, 1503-1538.
- Dumestre, A., Sauve, S., McBride, M., Baveye, P., and Berthelin, J. (1999). Copper speciation and microbial activity in long-term contaminated soils. *Archives of Environmental Contamination and Toxicology*, **36**(2), 124-131.
- Dzombak, D.A., and Morel, F.M.M. (1987). Adsorption of inorganic pollutants in aquatic systems. *Journal of Hydraulic Engineering-Asce*, **113**(4), 430-475.
- Edmunds, W. M., and Bath, A.H. (1976). Centrifuge extraction and chemical analysis of interstitial waters. *Environmental Science and Technology*, **10**, 467-472.
- Elliot, H.A., Liberati, M.R., and Huang, C.P. (1986). Competitive adsorption of heavy metals by soils. *Journal of Environmental Quality*, **15**, 214-219.
- Entwisle, D.C., and Reeder, S. (1993). New apparatus for pore fluid extraction from mudrocks for geochemical analysis. In: *Geochemistry of Clay-Pore Fluid Interaction*, D. A. C. Manning, Hall, P.L. and Hughes, C.R., ed., Chapman & Hall, London, 365-388.
- Gamerding, A.P., and Kaplan, D.I. (2000). Application of a continuous-flow centrifugation method for solute transport in disturbed, unsaturated sediments and illustration of mobile-immobile water. *Water Resources Research*, **36**(7), 1747-1755.
- Garcia-Miragaya, J. (1984). Levels, chemical fractionation, and solubility of lead in roadside soils of Caracas, Venezuela. *Soil Science*, **138**, 147-152.
- Gerritse, R.G., Adeney, J.A., Baird, G., and Colquhoun, I. (1992). The reaction of copper ions and hypochlorite with minesite soils in relation to fungicidal activity. *Australian Journal of Soil Research*, **30**(5), 723-735.
- Gerritse, R.G., and Vandriel, W. (1984). The relationship between adsorption of trace metals, organic matter, and pH in temperate soils. *Journal of Environmental Quality*, **13**(2), 197-204.
- Giesler, R., Lundstrom, U.S., and Grip, H. (1996). Comparison of soil solution chemistry assessment using zero- tension lysimeters or centrifugation. *European Journal of Soil Science*, **47**(3), 395-405.
- Goody, D.C., Shand, P., Kinniburgh, D.G., and Van Riemsdijk, W.H. (1995). Field-based partition coefficients for trace elements in soil solutions. *European Journal of Soil Science*, **46**, 265-285.
- Goyne, K.W., Day, R.L., and Chorover, J. (2000). Artifacts caused by collection of soil solution with passive capillary samplers. *Soil Science Society of America Journal*, **64**(4), 1330-1336.
- Green, C. H., Heil, D. M., Cardon, G.E., Butters, G.L., and Kelly, E.F. (2003). Solubilization of manganese and trace metals in soils affected by acid mine runoff. *Journal of Environmental Quality*, **32**(4), 1323-1334.
- Greenland, D.J., and Hayes, M.H.B. (1981). *The chemistry of soil processes*, John Wiley & Sons, Chichester.
- Grossmann, J., and Udluft, P. (1991). The extraction of soil water by the suction-cup method: a review. *Journal of Soil Science*, **42**, 83-93.
- Grossmann, J., Bredemeier, M., and Udluft, P. (1990). Sorption of trace metals by suction cups. *Zeitschrift für Pflanzenernährung und Bodenkunde*, **153**, 359-364.

- Grover, R., and Hance, R.J. (1970). Effect of ratio of soil to water on adsorption of linuron and atrazine. *Soil Science*, **100**, 136-138.
- Guggenberger, G., and Zech, W. (1992). Sorption of dissolved organic-carbon by ceramic P-80 suction cups. *Zeitschrift Fur Pflanzenernahrung Und Bodenkunde*, **155**(2), 151-155.
- Haines, B.L., Waide, J.B., and Todd, R.L. (1982). Soil solution nutrient concentrations sampled with tension and zero-tension lysimeters: report of discrepancies. *Soil Science Society of America Journal*, **46**, 658-661.
- Hani, H. (1996). Soil analysis as a tool to predict effects on the environment. *Communications in Soil Science and Plant Analysis*, **27**(3-4), 289-306.
- Hansen, E.A., and Harris, A.R. (1975). Validity of soil-water samples collected with porous ceramics cups. *Soil Science Society of America Journal*, **39**, 528-536.
- Hart, G.L., and Lowery, B. (1997). Axial-radial influence of porous cup soil solution samplers in a sandy soil. *Soil Science Society of America Journal*, **61**(6), 1765-1773.
- Hart, G.L., Lowery, B., McSweeney, K., and Fermanich, K.J. (1994). In situ characterization of hydrologic properties of Sparta sand: relation to solute travel using time domain reflectometry. *Geoderma*, **64**, 41-55.
- Harter, R.D. (1983). Effect of soil pH on adsorption of lead, copper, zinc, and nickel. *Soil Science Society of America Journal*, **47**(1), 47-51.
- Harter, R.D., and Naidu, R. (2001). An assessment of environmental and solution parameter impact on trace-metal sorption by soils. *Soil Science Society of America Journal*, **65**(3), 597-612.
- Haworth, A. (1990). A review of the modelling of sorption from aqueous-solution. *Advances in Colloid and Interface Science*, **32**(1), 43-78.
- Hesterberg, D. (1998). Biogeochemical cycles and processes leading to changes in mobility of chemical in soils. *Agriculture, Ecosystems & Environment*, **67**, 121-133.
- Hooda, P.S., Zhang, H., Davison, W., and Edwards, A.C. (1999). Measuring bioavailable trace metals by diffusive gradients in thin films (DGT): soil moisture effects on its performance in soils. *European Journal of Soil Science*, **50**(2), 285-294.
- Impellitteri, C.A., Allen, H.E., Yin, Y., You, S., and Saxe, J.K. (2001). Soil properties controlling metal partitioning. In: *Heavy metals release in soils*, H. M. Selim, and Sparks, D.L., ed., CRC Press LLC, Lewis Publishers, Boca Raton, Florida, 149-165.
- Impellitteri, C.A., Saxe, J.K., Cochran, M., Janssen, G., and Allen, H.E. (2003). Predicting the bioavailability of copper and zinc in soils: Modeling the partitioning of potentially bioavailable copper and zinc from soil solid to soil solution. *Environmental Toxicology and Chemistry*, **22**(6), 1380-1386.
- IUPAC, (2001). Appendix II. Definitions, Terminology and Symbols in Colloid and Surface Chemistry, part I. 57, International Union of Pure and Applied Chemistry, Commission on Colloid and Surface Chemistry Including Catalysis, Washington, DC; available on internet at the URL: http://www.iupac.org/reports/2001/colloid_2001/manual_of_s_and_t.pdf
- Jenne, E.A. (1968). Controls on Mn, Fe, Co, Ni, Cu, and Zi concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *Advances in Chemical Ser.*, **73**, 337-387.
- Jones, B.F., Vandenburg, A.S., Truesdell, A.H., and Rettig, S.L. (1969). Interstitial brines in playa sediments. *Chemical Geology*, **4**, 253-262.
- Jones, D.L., and Edwards, A.C. (1993a). Effect of moisture content and preparation technique on the composition of soil solution obtained by centrifugation. *Communications in Soil Science and Plant Analysis*, **24**(1-2), 171-186.
- Jones, D.L., and Edwards, A.C. (1993b). Evaluation of polysulfone hollow fibres and ceramic suction samplers as devices for the in situ extraction of soil solution. *Plant and Soil*, **150**, 2, 157-175.
- Jopony, M., and Young, S.D. (1994). The Solid=Solution Equilibria of Lead and Cadmium in Polluted Soils. *European Journal of Soil Science*, **45**(1), 59-70.

- Kashem, M.A., and Singh, B.R. (2001). Metal availability in contaminated soils: I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni and Zn. *Nutrient Cycling in Agroecosystems*, **61**(3), 247-255.
- Khasawneh, F.E., and Adams, F. (1967). Effect of dilution on calcium and potassium contents of soil solutions. *Soil Science Society of America Journal*, **31**, 172-176.
- Kinniburgh, D.G., and Miles, D.L. (1983). Extraction and chemical analysis of interstitial water from soils and rocks. *Environmental Science and Technology*, **17**(6), 362-368.
- Kinniburgh, D.G., Jackson, M.L., Syers, J.K. (1976). Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminium. *Soil Science Society of America Journal*, **40**, 796-799.
- Kinniburgh, D.G., van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F., and Avena, M.J. (1999). Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. *Colloids and Surfaces – A - Physicochemical and Engineering Aspects*, **151**(1-2), 147-166.
- Knight, B.P., Chaudri, A.M., McGrath, S.P., and Giller, K.E. (1998). Determination of chemical availability of cadmium and zinc in soils using inert soil moisture samplers. *Environmental Pollution*, **99**, 293-298.
- Krahn, J., and Fredlund, D.G. (1972). On total, matric and osmotic suction. *Soil Science*, **114**(5), 339-348.
- Kriukov, P.A. (1971). Gornye, pochverrye i Ilovye Rastvory (Interstitial waters of soils, rocks and sediments). *Izdatel, stvo Nauka, Moskow*.
- Kuo, S. (1986). Concurrent sorption of phosphate and zinc, cadmium, or calcium by a hydrous ferric oxide. *Soil Science Society of America Journal*, **50**, 1412-1419.
- Lambe, T.W., and Whitman, R.V. (1979). *Soil mechanics, SI Version*, John Wiley & Sons, New York.
- Larsen, S., and Widdowson, A.E. (1968). Chemical composition of soil solution. *Journal of the Science of Food and Agriculture*, **19**, 693-695.
- Levin, M.J., and Jackson, D.R. (1977). A comparison of in situ extractors for sampling soil water. *Soil Science Society of America Journal*, **41**, 535-536.
- Lindroos, A.J., Brugger, T., Derome, J., and Derome, K. (2003). The weathering of mineral soil by natural soil solutions. *Water Air and Soil Pollution*, **149**(1-4), 269-279.
- Lindsay, W.L. (1979). *Chemical equilibria in soils*, John Wiley, New York.
- Litaor, M.I. (1988). Review of soil solution samplers. *Water Resources Research*, **24**(5), 727-733.
- Lorenz, S.E., Hamon, R.E., and McGrath, S.P. (1994). Differences between soil solutions obtained from rhizosphere and non-rhizosphere soils by water displacement and soil centrifugation. *European Journal of Soil Science*, **45**, 431-438.
- Luo, Y.M., Qiao, X. L., Song, J., Christie, P., and Wong, M.H. (2003). Use of a multi-layer column device for study on leachability of nitrate in sludge-amended soils. *Chemosphere*, **52**(9), 1483-1488.
- Luo, Y.M., Yan, W.D., and Christie, P. (2001). Soil solution dynamics of Cu and Zn in a Cu- and Zn-polluted soil as influenced by gamma-irradiation and Cu-Zn interaction. *Chemosphere*, **42**(2), 179-184.
- Luxmoore, R.J. (1981). Micro-, meso- and macroporosity of soil. *Soil Science Society of America Journal*, **45**, 671.
- Manheim, F.T. (1966). A hydraulic squeezer for obtaining interstitial waters from consolidated and unconsolidated sediments. 550-556, USGS, Washington.
- Massee, R., and Maessen, F.J.M.J. (1981). Losses of silver, arsenic, cadmium, selenium, and zinc traces from distilled water and artificial sea-water by sorption on various container surface. *Analytica Chimica Acta*, **127**, 206-210.

- Mattigod, S.V., Sposito, G., and Page, A.L. (1981). Factors affecting the solubilities of trace metals in soils. *Chemistry in the soil environment*, M. Stelly, ed., American Society of Agronomy - Soil Science Society of America, Madison, WI, 203-221.
- McBride, M.B., and Blasiak, J.J. (1979). Zinc and copper solubility as a function of pH in an acid soil. *Soil Science Society of America Journal*, **43**, 866-870.
- McBride, M.B., Sauve, S., and Hendershot, W. (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science*, **48(2)**, 337-346.
- McGuire, P.E., Lowery B., Helmke, P.A. (1992). Potential sampling error - Trace metal adsorption on vacuum porous cup samplers. *Soil Science Society of America Journal*, **56(1)**, 74-82.
- Menendez, I., Gallardo, J.F., and Vicente, M.A. (2003). Functional and chemical calibrates of ceramic cup water samplers in forest soils. *Communications in Soil Science and Plant Analysis*, **34(7-8)**, 1153-1175.
- Menzies, N.W., and Bell, L.C. (1988). Evaluation of the influence of sample preparation and extraction technique on soil solution composition. *Australian Journal of Soil Research*, **26(3)**, 451-464.
- Morgenstern, N.R., and Balasubramonian, B.I. (1980). Effects of pore fluid on the swelling of clay shale. *Forth International Conference on Expansive Soils*, Denver, 190-205.
- Morrison, R., and Szecsody, J. (1985). Sleeve and casing lysimeters for soil pore water sampling. *Soil Science*, **139(5)**, 446-451.
- Mubarak, A., and Olsen, R.A. (1976). Immiscible displacement of soil solution by centrifugation. *Soil Science Society of America Journal*, **40(2)**, 329-331.
- Nagpal, N.K. (1982). Comparison among, and evaluation of, ceramic porous cup soil water samplers for nutrient transport studies. *Canadian Journal of Soil Science*, **62**, 685-694.
- OECD, (2002). OECD Guidelines for the testing of chemicals revised, Proposal for a new guideline 312, Leaching in Soil Columns.
- O'Conner, D.J., and Connolly, J.P. (1980). The effect of concentration of adsorbing solids on the partition coefficient. *Water Research*, **14**, 1517-1523.
- Padilla, I.Y., Yeh, T.C.J., and Conklin, M.H. (1999). The effect of water content on solute transport in unsaturated porous media. *Water Resources Research*, **35(11)**, 3303-3313.
- Percival, H.J. (2003). Soil and soil solution chemistry of a New Zealand pasture soil amended with heavy metal-containing sewage sludge. *Australian Journal of Soil Research*, **41(1)**, 1-17.
- Pérez, D.V., de Campos, R.C., and Novaes, H.B. (2002). Soil solution charge balance for defining the speed and time of centrifugation of two Brazilian soils. *Communications in Soil Science and Plant Analysis*, **33(13-14)**, 2021-2036.
- Phillip, J. (1968). Steady infiltration from buried point sources and spherical cavities. *Water Resources Research*, **4(5)**, 1039-1047.
- Prokop, Z., Cupr, P., Zlevorova-Zlamalikova, V., Komarek, J., Dusek, L., and Holoubek, I. (2003). Mobility, bioavailability, and toxic effects of cadmium in soil samples. *Environmental Research*, **91(2)**, 119-126.
- Qafoku, N.P., Ainsworth, C.C., Szecsody, J.E., Qafoku, O.S., and Heald, S.M. (2003). Effect of coupled dissolution and redox reactions on Cr(VI)(aq) attenuation during transport in the sediments under hyperalkaline conditions. *Environmental Science and Technology*, **37(16)**, 3640-3646.
- Reeder, S., Cave, M.R., Entwisle, D.C., and Trick, J.K. (1998). Extraction of water and solutes from clayey material: a review and critical discussion of available techniques. *WI/98/4C*, British Geological Survey, Keyworth, Nottingham.
- Reitemeier, R. F. (1946). Effects of moisture content on the dissolved and exchangeable ions of soils of arid regions. *Soil Science*, **61**, 195-214.

- Richards, L.A., and Weaver, L.R. (1944). Moisture retention by some irrigated soils as related to soil moisture tension. *Journal of Agricultural Research*, **69**, 215-235.
- Robb, F., and Young, S.D. (1999). Addition of calcareous metal wastes to acid soils: consequences for metal solubility. *Water Air and Soil Pollution*, **111(1-4)**, 201-214.
- Ross, C.A.M., Bath, A.H., Entwisle, D.C., Cave, M.R., Fry, M.B., Green, K.A. and Reeder, S. (1989). Hydrochemistry of porewaters from Jurassic Oxford Clay, Kellaways Beds, Upper Estuarine and Upper Lias formations at the Elstow site, Bedfordshire. *WE/89/28*, British Geological Survey, Keyworth, Nottingham.
- Sauvé, S., Dumestre, A., McBride, M., and Hendershot, W. (1998). Derivation of soil quality criteria using predicted chemical speciation of Pb^{2+} and Cu^{2+} . *Environmental Toxicology and Chemistry*, **17(8)**, 1481-1489.
- Sauvé, S., Hendershot, W., and Allen, H.E. (2000). Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environmental Science and Technology*, **34(7)**, 1125-1131.
- Schubert, H. (1982). *Kapillarität in porösen feststoffsystemen*, Springer-Verlag, Berlin.
- Shaffer, R.J., Wallace, J., and Garwood, F. (1937). The centrifuge method of investigating the variation of hydrostatic pressure with water content in porous material. *Transactions of the Faraday Society*, **33**, 723-734.
- Shan, X.Q., Wang, Z.W., Wang, W.S., Zhang, S.Z., and Wen, B. (2003). Labile rhizosphere soil solution fraction for prediction of bioavailability of heavy metals and rare earth elements to plants. *Analytical and Bioanalytical Chemistry*, **375(5)**, 400-407.
- Shaw, E.M. (1993). *Hydrology in practice*, Chapman & Hall, London.
- Shendrikar, A.D., Dharmarajan, V., Walker-Merrick, H., and West, P.W. (1975). Adsorption characteristics of traces of barium, beryllium, cadmium, manganese, lead, and zinc on selected surfaces. *Analytica Chimica Acta*, **84**, 409/417.
- Sheppard, M.I., Thibault, D.H., and Smith, P.A. (1992). Effect of extraction techniques on soil pore-water chemistry. *Communications in Soil Science and Plant Analysis*, **23(13-14)**, 1643-1662.
- Sholkovits, E. (1973). Interstitial water chemistry of the Santa Barbara basin sediments. *Geochimica et Cosmochimica Acta*, **37**, 2043-2078.
- Siemens, J., and Kaupenjohann, M. (2003). Dissolved organic carbon is released from sealings and glues of pore-water samplers. *Soil Science Society of America Journal*, **67(3)**, 795-797.
- Sposito, G. (1989). *The chemistry of soils*, Oxford University Press, New York.
- Strandberg, J., and Fortkamp, U., (2005). Investigations on methods for site specific, determination of the partition coefficient – K_d , for contaminants in soils, IVL report B1619, available online at: <http://www.ivl.se/rappporter/pdf/B1619.pdf>
- Tack, F.M.G., and Verloo, M.G. (1995). Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *International Journal of Environmental Analytical Chemistry*, **59(2-4)**, 225.
- Tiensing, T., Preston, S., Strachan, N., and Paton, G.I. (2001). Soil solution extraction techniques for microbial ecotoxicity testing: a comparative evaluation. *Journal of Environmental Monitoring*, **3(1)**, 91-96.
- Tiller, K.G., Hogson, J.F., Peech, M. (1963). Specific sorption of cobalt by soil clays. *Soil Sciences*, **15**, 392-399.
- Tye, A.M., Young, S.D., Crout, N.M.J., Zhang, H., Preston, S., Barbosa-Jefferson, V.L., Davison, W., McGrath, S.P., Paton, G.I., Kilham, K., and Resende, L. (2003). Predicting the activity of Cd^{2+} and Zn^{2+} in soil pore water from the radio-labile metal fraction. *Geochimica et Cosmochimica Acta*, **67(3)**, 375-385.

- Tye, A.M., Young, S.D., Crout, N.M.J., Zhang, H., Preston, S., Bailey, E.H., Davison, W., McGrath, S.P., Paton, G.I., and Kilham, K. (2002). Predicting arsenic solubility in contaminated soils using isotopic dilution techniques. *Environmental Science and Technology*, **36(5)**, 982-988.
- Tyler, G. (2000). Effects of sample pretreatment and sequential fractionation by centrifuge drainage on concentrations of minerals in a calcareous soil solution. *Geoderma*, **94**, 59-70.
- U.S.E.P.A., Office of Air and Radiation, (1999). Understanding variation in partition coefficient, K_d values – Volume 1. The K_d model, Methods of Measurements, and Applications of Chemical Reactions Codes. EPA 402-R-99-004A.
- Van Benschoten, J.E., Young, W.H., Matsumoto, M.R., and Reed, B.E. (1998). A nonelectrostatic surface complexation model for lead sorption on soils and mineral surfaces. *Journal of Environmental Quality*, **27**, 24-30.
- Vig, K., Megharaj, M., Sethunathan, N., and Naidu, R. (2003). Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: a review. *Advances in Environmental Research*, **8(1)**, 121-135.
- Voice, T.C., and Weber, J.W.J. (1985). Sorbent concentration effects in liquid/solid partitioning. *Environmental Science and Technology*, **19**, 789-796.
- Voice, T.C., Rice, C.P., and Weber, J.W.J. (1983). Effects of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems. *Environmental Science and Technology*, **17**, 513-518.
- Warren, L.A., and Haack, E.A. (2001). Biogeochemical controls on metal behaviour in freshwater environments. *Earth-Science Reviews*, **54(4)**, 261-320.
- Warrick, A.W., and Amoozegar-Fard, A. (1977). Soil-water regimes near porous cup water samplers. *Water Resources Research*, **13(1)**, 203-207.
- Washburn, E.W. (1921). The Dynamics of Capillary Flow. *The American Physical Society, 2nd series*, **17**, 374-375.
- Weng, L.P., Temminghoff, E.J.M., Lofts, S., Tipping, E., and Van Riemsdijk, W.H. (2002). Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil. *Environmental Science and Technology*, **36(22)**, 4804-4810.
- Wenzel, W.W., and Wieshammer, G. (1995). Suction cup materials and their potential to bias trace-metal analyses of soil solutions - a review. *International Journal of Environmental Analytical Chemistry*, **59(2-4)**, 277-290.
- Wenzel, W.W., Sletten, R.S., Brandstetter, A., Wieshammer, G., and Stingeder, G. (1997). Adsorption of trace metals by tension lysimeters: Nylon membrane vs. porous ceramic cup. *Journal of Environmental Quality*, **26(5)**, 1430-1434.
- Wheatstone, K.C., and Gelsthorpe, D. (1982). Extraction and analysis of interstitial water from sandstone. *Analyst*, **107**, 731-736.
- Whelan, B.R., and Barrow, N.J. (1980). A study of a method for displacing soil solution by centrifuging with an immiscible liquid. *Journal of Environmental Quality*, **9(2)**, 315-319.
- Wolt, J. (1994). *Soil solution chemistry: applications to environmental science and agriculture*, John Wiley & Sons, New York.
- Yaron, B., Calvet, R., and Prost, R. (1996). *Soil pollution - Processes and Dynamics*, Springer - Verlag, Berlin.
- Yin Y.J., Impellitteri C.A., You S.J., and Allen H.E. (2002). The importance of organic matter distribution and extract soil : solution ratio on the desorption of heavy metals from soils. *Science of the Total Environment*, **287 (1-2)**: 107-119.
- Zabowsky, D., and Ugolini, F.C. (1990). Lysimeter and centrifuge soil solutions: Seasonal differences between methods. *Soil Science Society of America Journal*, **54**, 1130-1135.

Ziper, C., Komarneni, S., Baker, D.E. (1988). Specific cadmium sorption in relation to the crystal of clay minerals. *Soil Science Society of America Journal*, **52**, 49-53.

List of Figures

Figure 1. Biogeochemical cycling of soil contaminants: the soil liquid phase is acting as a regulator of contaminant fate (modified, from Hesterberg, 1998, based on Lindsay, 1979; Mattigod *et al.*, 1981).

Figure 2. Schematic representation of soil water states and their definitions (from Shaw, 1993).

Figure 3. Sketch of a Rhizon sampler (from “Rhizon soil moisture sampler: operating instructions”. www.eijkelkamp.com).

Figure 4. Radius of influence of a Rhizon sampler as a function of the pressure head and the soil type.

Figure 5. Pore water extraction by (a) drainage centrifugation using a swing-out rotor and (b) immiscible liquid displacement using a fixed-angle rotor (after Kinniburgh and Miles, 1983).

Figure 6. Centrifuge tubes for soil separation, designed and manufactured by R&D Workshop BGS, Keyworth; 1 – pore water collector cup; 2 – upper soil container; 3 – screwable acetal top; 4 – screwable acetal filter and support; 5 – stainless steel filter.

Figure 7. Pressure profile depending on distance R from rotation axis at maximum speed (7000 rpm) based on equation (5).

Figure 8. Pressure profile depending on the speed at a midpoint of 7 cm from axis of rotation calculated using equation (6); relationships between speeds of rotation, pressure applied and minimum capillary size drained (radius = 7 cm).

Figure 9. Squeezing apparatus, designed and manufactured by R&D Workshop, BGS Keyworth.

Figure 10. Clay squeezing cell, designed and manufactured by R&D Workshop, BGS Keyworth.

Figure 11. A hydromechanical analogy for load changes during squeezing (after Lambe and Whitman, 1979).

Figure 12. The rate of settlement for increasing stress (modified, from Entwisle and Reeder, 1993).

Figure 13. Cumulative volume of pore water extracted for the three soils tested with increasing pressure; the dotted line represents the pressure corresponding to the hygroscopic coefficient, i.e. the upper limit for the capillary water.

List of Tables

Table 1. Examples of soil pore classifications, with description of equivalent soil water phenomena and matric pressures; a brief illustration of the soil system in those conditions is also given; ‘d’ represents the equivalent diameter of pores and is expressed in μm , unless otherwise stated.

Table 2. Physical characteristics and dimensions of a Rhizon sampler.

Table 3. Some example of the background electrolyte composition and soil:solution ratios used in the literature, ordered by decreasing soil:solution ratio.

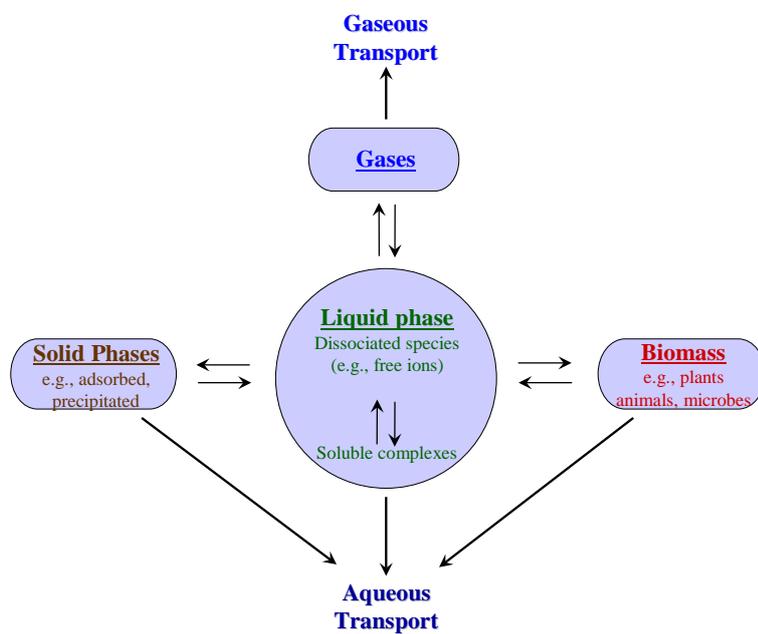


Figure 1. Biogeochemical cycling of soil contaminants: the soil liquid phase is acting as a regulator of contaminant fate (modified, from Hesterberg, 1998, based on Lindsay, 1979; Mattigod *et al.*, 1981).

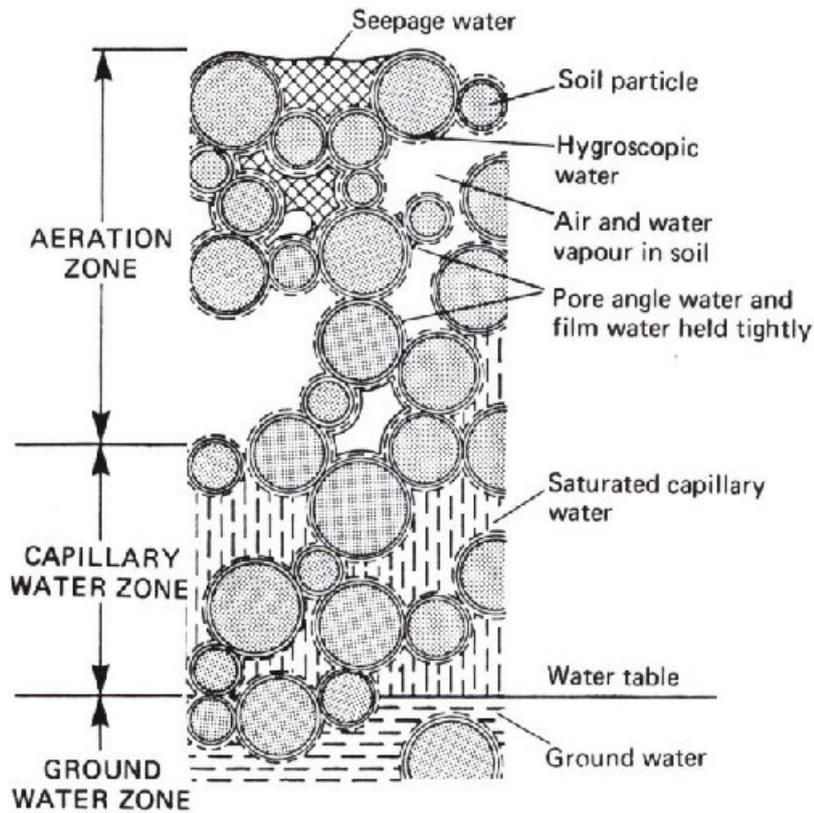


Figure 2. Schematic representation of soil water states and their definitions (from Shaw, 1993).

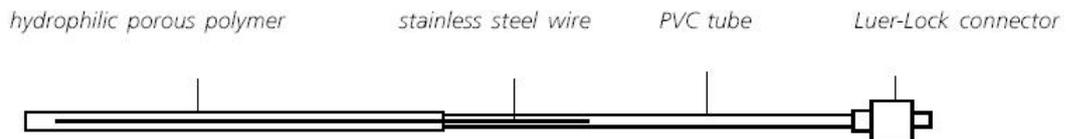


Figure 3. Sketch of a Rhizon sampler (from “Rhizon soil moisture sampler: operating instructions”. www.eijkelkamp.com).

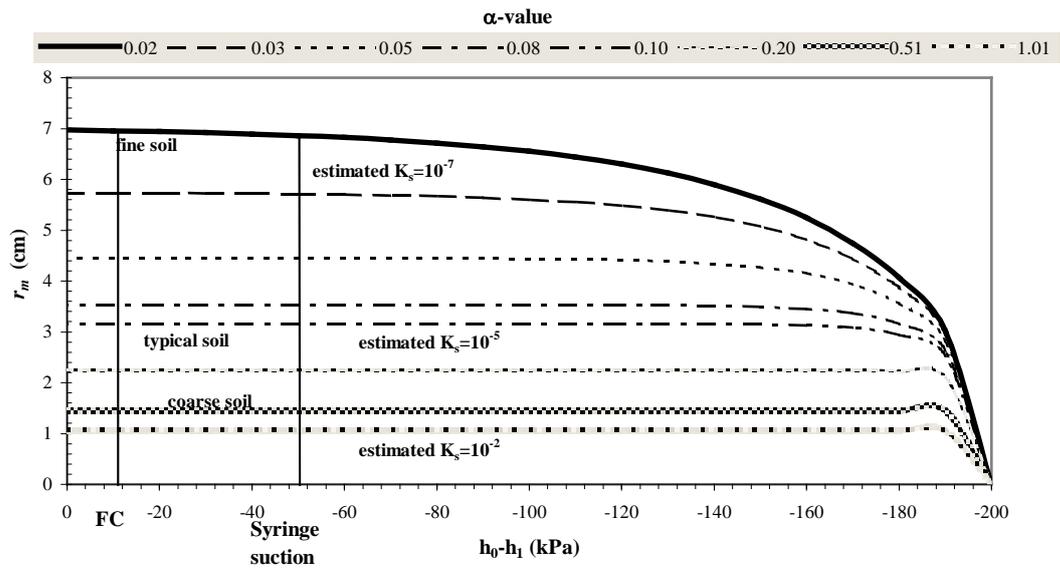


Figure 4. Radius of influence of a Rhizon sampler as a function of the pressure head and the soil type.

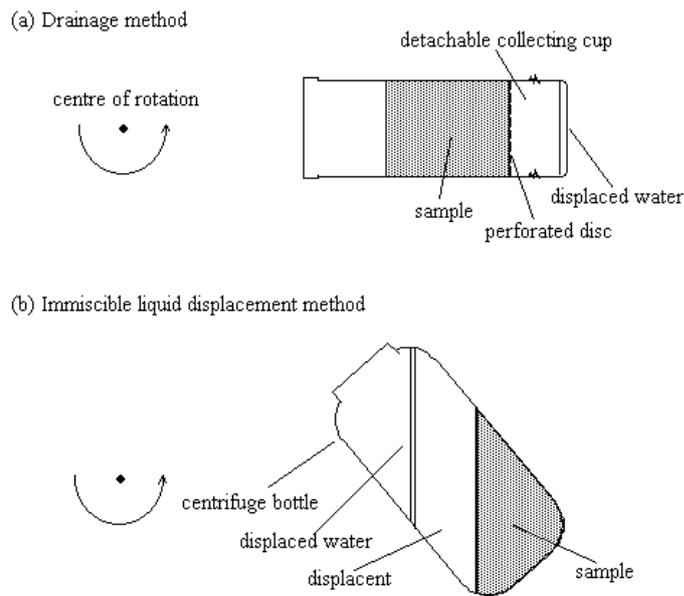


Figure 5. Pore water extraction by (a) drainage centrifugation using a swing-out rotor and (b) immiscible liquid displacement using a fixed-angle rotor (after Kinniburgh and Miles, 1983).

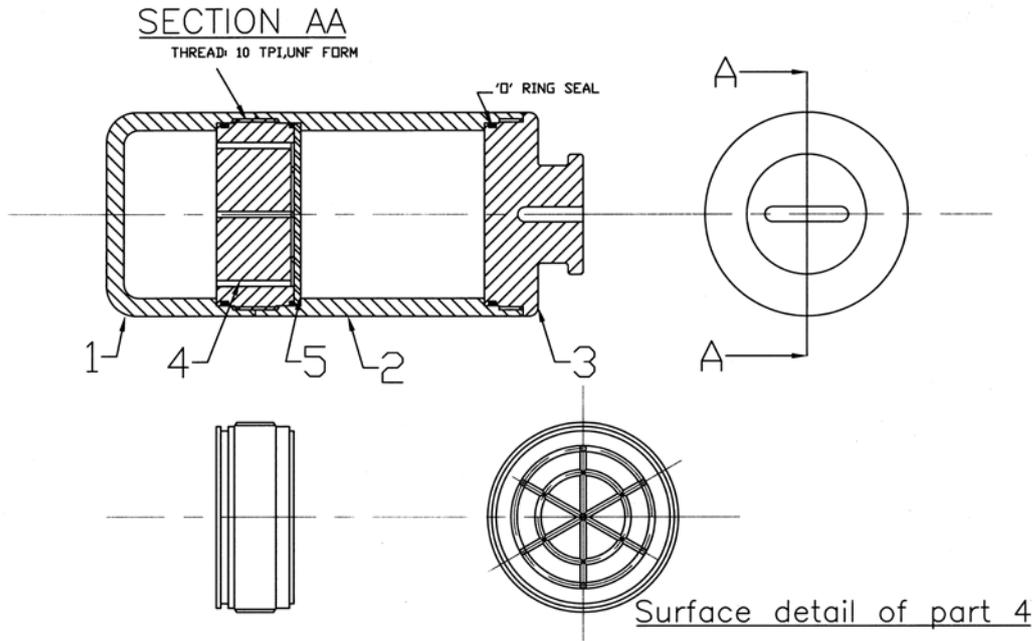


Figure 6. Centrifuge tubes for soil separation, designed and manufactured by R&D Workshop BGS, Keyworth; 1 – pore water collector cup; 2 – upper soil container; 3 – screwable acetal top; 4 – screwable acetal filter and support; 5 – stainless steel filter.

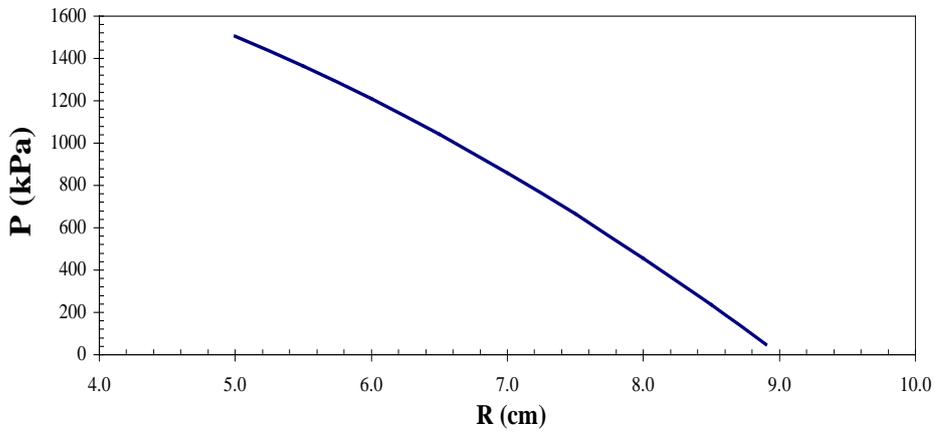


Figure 7. Pressure profile depending on distance R from rotation axis at maximum speed (7000 rpm) based on equation (5).

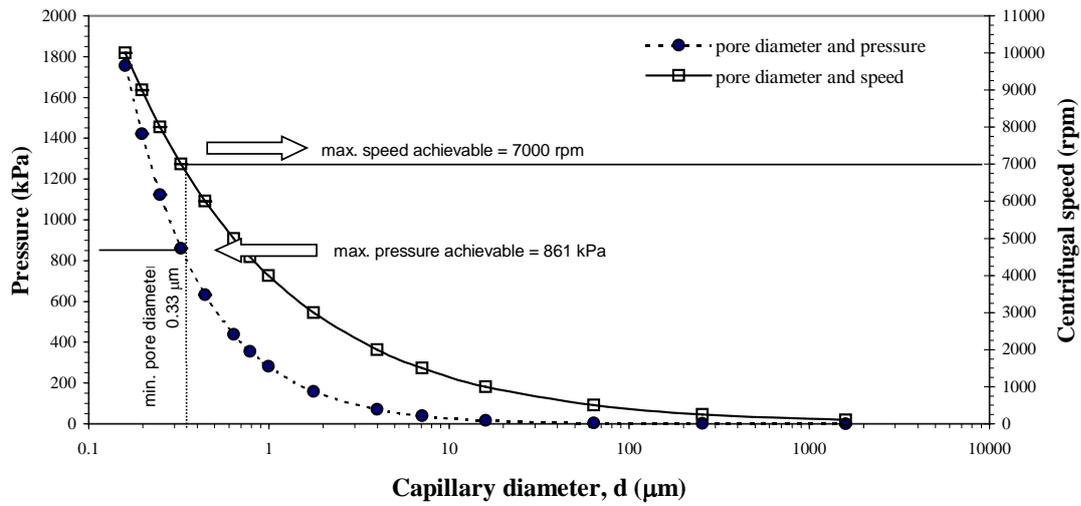


Figure 8. Pressure profile depending on the speed at a midpoint of 7 cm from axis of rotation calculated using equation (6); relationships between speeds of rotation, pressure applied and minimum capillary size drained (radius = 7 cm).

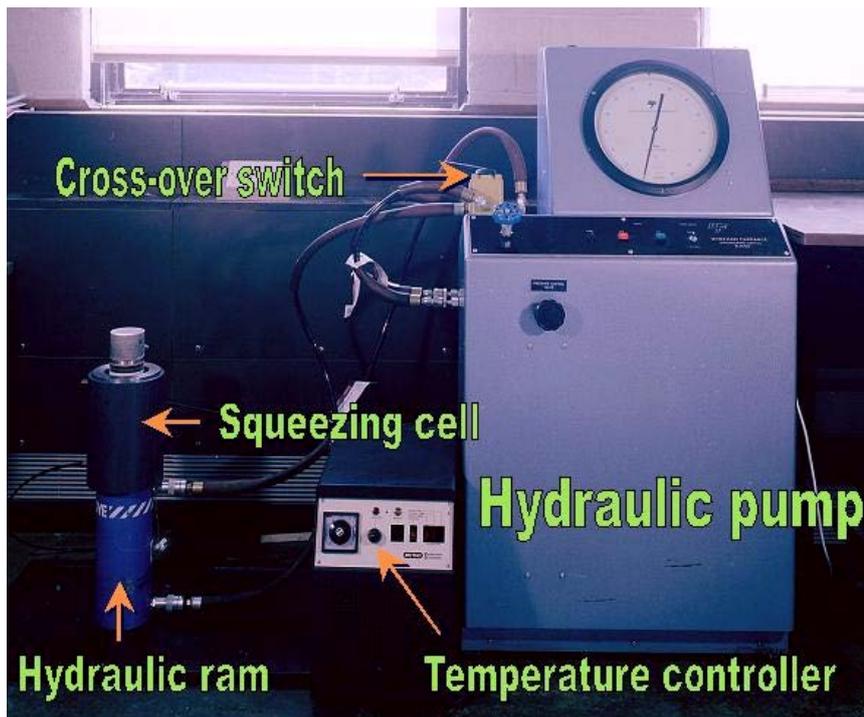


Figure 9. Squeezing apparatus, designed and manufactured by R&D Workshop, BGS Keyworth.



Figure 10. Clay squeezing cell, designed and manufactured by R&D Workshop, BGS Keyworth.

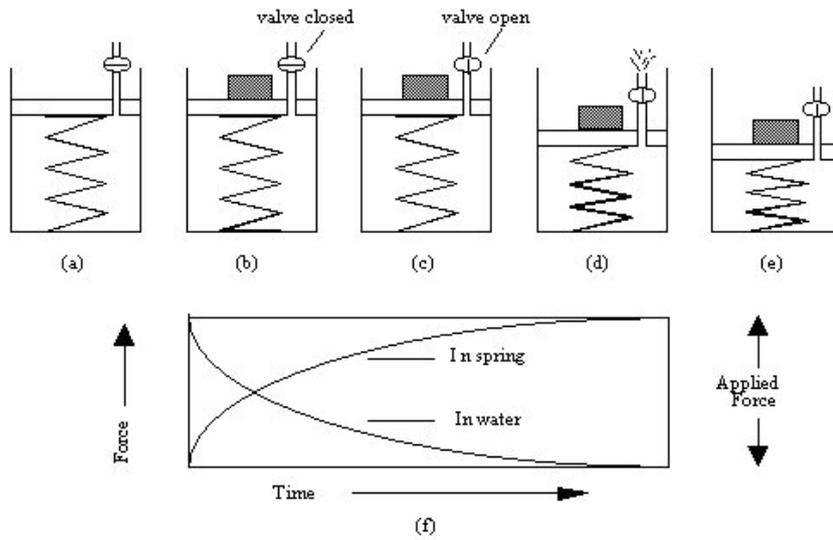


Figure 11. A hydromechanical analogy for load changes during squeezing (after Lambe and Whitman, 1979).

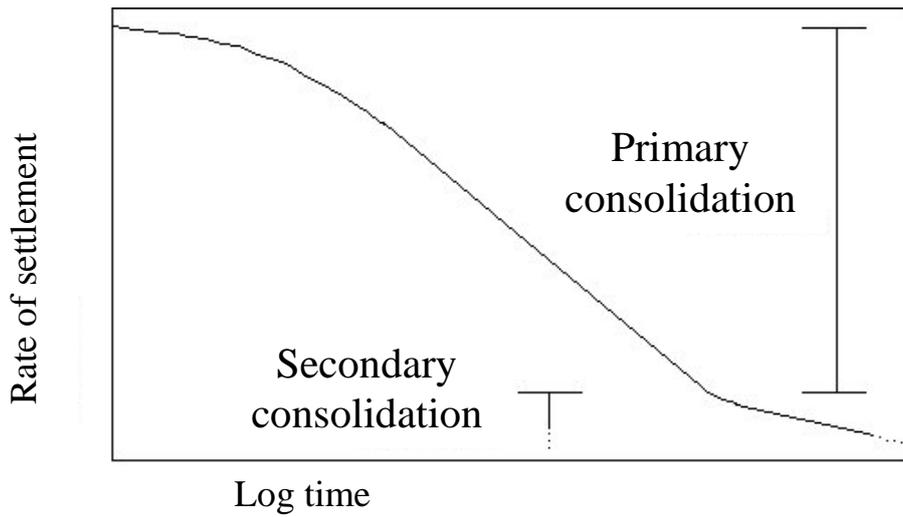


Figure 12. The rate of settlement for increasing stress (modified, from Entwisle and Reeder, 1993).

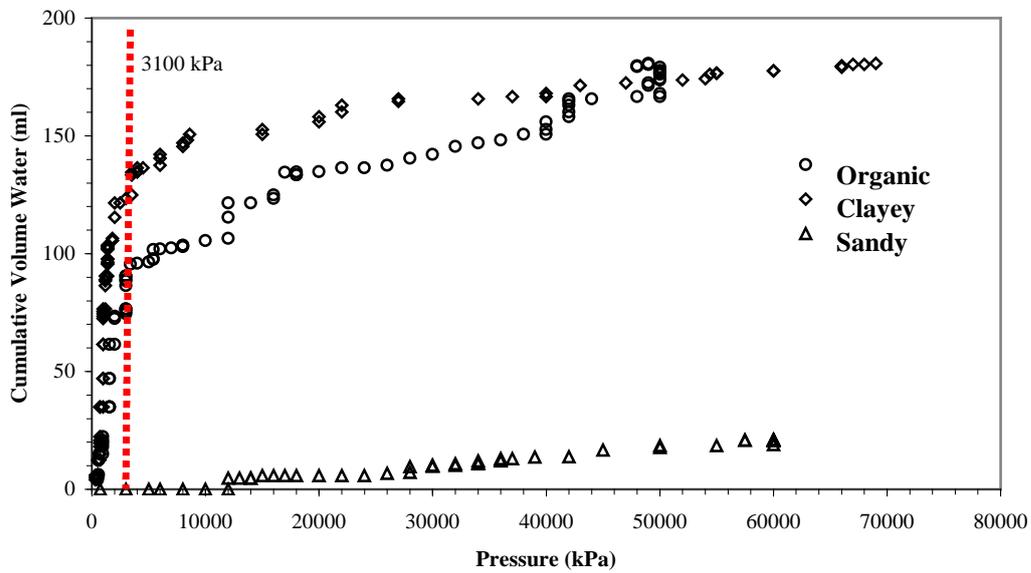


Figure 13. Cumulative volume of pore water extracted for the three soils tested with increasing pressure; the dotted line represents the pressure corresponding to the hygroscopic coefficient, i.e. the upper limit for the capillary water.

Table 1. Examples of soil pore classifications, with description of equivalent soil water phenomena and matric pressures; a brief illustration of the soil system in those conditions is also given; ‘d’ represents the equivalent diameter of pores and is expressed in μm , unless otherwise stated.

Soil system	Functional classification (μm)	Physical classification		Predominant water phenomena	'd' (μm)	[†] Equivalent water pressure (kPa)
	<i>Greenland and Hayes, 1981</i>	<i>Brewer, 1964</i>	<i>Luxmoore, 1981</i>			
Spaces as large as these are commonly formed between the clods of newly ploughed soil. Cracks in dry clay soils can reach widths of this order of magnitude.	Transmission pores: air movement and drainage of excess water $d > 50$	Macropores	Macropores	Channel flow through profile from surface ponding and/or perched water table	10000	- 0.015
Pores of about this size and smaller are formed between aggregates of finely tilled soil as for a seed-bed.					1000	
Pores between spherical particles 0.65 mm in diameter in closest packing have this size (Dallavalle, 1948). Roots will not extend into rigid pores smaller than this (Wiersum, 1957).		Fine Macropores	Mesopores	Drainage; hysteresis; gravitational driving force for water dynamics	(1 mm)	
Pores larger than about 15 μm (corresponding to 9.8 kPa) are drained in most soils that can be said to be at Field Capacity.			100		- 1.5	
Pores down to this size are accessible to bacteria.	Storage pores: retention of water against gravity and release to plant roots $0.5 < d < 50$	Mesopores	Micropores	Evapotranspiration; matric pressure gradient for water distribution	10	- 15
Water in pores of about this size or larger is available to plants in non-saline soil (correspond to 1500 kPa).						
When micropores are treated as slits between parallel plates, about half the pore space in dried aggregates of clay soil can commonly be attributed to plate separations of 10 nm or less (Sills <i>et al.</i> , 1974).		Micropores	Physico-Chemical classification (adsorption) <i>IUPAC, 2001</i>		1	- 150
	Residual pores: retention and diffusion of ions in solution $0.005 < d < 0.5$		Macropores	Capillary condensation; transport	0.1	- 1500 (PWP [#])
		Ultramicropores				
				Mesopores		0.01
Roughly corresponding to the thickness of 3 layers of water molecules on a clay surface.	Bonding spaces: support major forces between soil particles $d < 0.005$	Cryptopores	Micropores	Physisorption; adsorbate-adsorbate and adsorbant-adsorbate interactions	0.001 (1 nm)	- 150000*

Table 2. Physical characteristics and dimensions of a Rhizon sampler.

q m³ s⁻¹ (10⁸)	BP kPa	Porous area cm²	Length cm	Internal diameter cm	Outer diameter cm	Internal Volume cm³	Dead Volume ml
1.7	200	7.90	10	0.14	0.25	0.15	0.5

BP: Bubble point

q : volumetric flow rate into the sampler

Table 3. Some example of the background electrolyte composition and soil:solution ratios used in the literature, ordered by decreasing soil:solution ratio.

Potentially toxic elements studied	R kg L⁻¹	Background electrolyte	Ionic strength mmol L⁻¹
Cr	1:1; 1:20	NaNO ₃	100
Cd, Cu	1:4	CaCl ₂	15-150
Cd	1:10	(Ca,Na)(Cl,NO ₃)	30
Zn	1:10	CaCl ₂ , Na(Cl,NO ₃ ,SO ₄)	5-300
Cu, Zn	1:10	Mg(NO ₃) ₂	10
Cd	1:20	NaNO ₃ , Ca(NO ₃) ₂	30
Cd, Cr, Cu, Ni, Pb, Zn	1:30	Na-acetate	10
Cd	1:40	H ₂ O	-
Cd	1:40	Ca(NO ₃) ₂	10
Co, Cu, Ni	1:100	CaCl ₂	0.5
Cu, Ni, Pb, Zn	1:100	H ₂ O	-
Cu	1:200	Ca(NO ₃) ₂	30

Source: Harter and Naidu (modified), 2001 and references thereafter.