CHAPTER 3

LABORATORY TECHNIQUES AND DEVELOPMENT

Soil samples collected in the field were examined with regard to various physical and chemical properties as described in the following chapter 4. In addition, some technique development and verification was required, and some novel approaches investigated to obtain pore water from soils for isotopic analysis from gypseous samples. The techniques employed will be described, and the verification and investigative trials detailed and discussed in this chapter. Where only a few samples were analysed for a particular property, the results immediately follow the methodology.

3.1 GENERAL SOIL PROPERTIES

Gravimetric water content, approximate maximum gypsum content, and chloride content of the soil solution were determined on all field samples. Due to the presence of gypsum in many of the samples, water content (mass of water per unit mass of dry soil, $g\ g^{-1}$) was determined gravimetrically by drying aliquots of about 10 to 30g, held in small plastic containers (chippettes), to constant weight under vacuum with continuous pumping in a large glass desiccator. This took at least one and up to three months for the quantities involved. For the samples taken in April 1989, a column of silica gel was inserted in the vacuum line. This indicated no back-flow of water vapour into the desiccator from the vacuum line and assisted in assessing when the drying was complete.

Water contents so determined are likely to be underestimates in clayey samples, since some strongly held water will not be removed. Where samples from an entire hole were known to be free of gypsum, such as with holes 19 to 21, water contents were determined by conventional oven dying at 105°C overnight. The method used is referred to when quoting gravimetric water contents in appendix 1. For use in convection-diffusion calculations, volumetric water contents ($m^3\ m^{-3}$) are required. These were calculated from gravimetric data by multiplying by soil bulk density, assuming a density of water of 1.00 Mg m^{-3}.

Maximum gypsum content was determined following Nelson *et al.* (1978), by oven drying at 105 to 110 °C for 16 to 36 hours the same sample aliquots vacuum dried to determine water content. The longer time is preferable, as trials showed some samples of pure gypsum lost a small amount of additional weight after the second night of drying. The amounts of water lost show that initially there was partial dehydration of gypsum ($CaSO_4.2H_2O$) to bassanite ($CaSO_4.1/2H_2O$), before completely dehydrating to anhydrite ($CaSO_4$). When drying is complete, all the weight loss is assumed to be due to gypsum water of crystallisation and the gypsum content calculated knowing that pure gypsum looses 20.5% of its mass on complete dehydration. The gypsum content obtained is however a maximum one as there are many clay minerals that lose some moisture under the same conditions. Gypsum contents by this method are considered significant when above about 10% in the clayey samples comprising the bulk of the field samples. This difficulty in estimating the quantity of gypsum was shown by the running of an X-ray diffractogram on a sample calculated to hold 7.5% gypsum by the method of Nelson *et al.* (1978). No gypsum nor other calcium sulphate minerals were found (section 4.4.1). Where gypsum was visible in a sample but calculated as less than 10%, the calculated figure is retained as a maximum value. The error is less at high gypsum contents.

Chloride was determined colorimetrically (Taras *et al.*, 1975) on the same aliquots of sample as above on (approximately) 1:2 soil:water extracts, as milligrams of chloride per kilogram of soil. All of the analyses and some of the water extractions were carried out by the C.S.I.R.O. Division of Soils, Analytical Services Laboratory. The concentration of chloride in soil water was calculated by dividing the chloride concentration in the soil by the gravimetric water content, with the assumption that the solution density may be approximated as 1.00 Mg m^{-3}. As the chloride determinations are only accurate to one percent or more, and the water contents to perhaps 5%, this is not unreasonable.

Matric suction was measured on selected holes using the filter paper technique described by Greacen *et al.* (1987, 1989). Results are approximate only, but of good qualitative use. Dry bulk density was determined on pieces of core of weathered Bulldog Shale, by coating with the sealant saran resin and weighing in air and water, then oven dried and weighed to enable a correction for water content. Results are given below.

TABLE 3.1.1

Dry Bulk Density Measurements on Weathered Bulldog Shale Core

Sample number	1	2	3	4	5	
ρ_b , Mg m^{-3}	1.59	1.59	1.60	1.58	1.58	
Sample number	6	7	8	9	10	Average
ρ_b , Mg m^{-3}	1.57	1.60	1.61	1.50	1.58	1.58±0.03

X-ray diffractograms were run in conjunction with C.S.I.R.O. Division of Soils, Mineralogy Section, on selected samples of flood plain sediment and Bulldog Shale. Particle size analysis was by the pipette method (Lewis, 1983).

Cation Exchange Capacity (CEC) was determined by Analytical Services using a standard NH_4^+ leaching technique. Two samples were submitted, weathered and fresh Bulldog Shale from hole 14. Total exchangeable cations was greater than CEC, probably due to incomplete initial flushing of NaCl from the highly saline samples; the individual ions and CEC are determined separately. Results are given in table 3.1.2. The values are high, but comparable to those obtained from soils developed on the same shale near Andamooka, 100 km south (Milnes *et al.*, 1987), although poorer in calcium.

TABLE 3.1.2

Cation Exchange Capacity of Bulldog Shale

	mmol(+) kg^{-1}					
Sample	Ca	Mg	Na	K	Total	CEC
weathered	14.1	78.0	390	8.9	491	379
fresh	16.1	79.0	364	7.5	467	355

Water chemistry was usually determined by Analytical Services of the Division of Soils. Chloride was determined colorimetrically, and major cations and sulphur by inductively coupled plasma spectrophotometry (i.c.p.s.). All sulphur was assumed to be present as sulphate.

Measurement of pH and electrical conductivity (EC) were performed in the laboratory, and for some samples, in the field, using portable instruments, a Jenco digital pH meter 609 and CHK Engineering PTI-10 $\mu S.cm^{-1}$/ °C meter, respectively. Laboratory pH measurements were higher than field measurements by 0.1 to 0.6 pH units except for the alkaline sample from hole 12 where the difference was 1.25. Field ECs were not corrected for temperature and were 5 to 20% greater than laboratory measurements. Both are listed when available (appendix 2). Alkalinity was determined by the author, by anion-cation balance for trip 1 samples, manual titration with HCl for trips 2, 3 and 4, and automated titration with HCl using an Orion 960 Autochemistry System for trip 5. For the calculation of total dissolved solids, alkalinity was assumed to consist of bicarbonate ion as the pH was always less than 10.3, the value at and above which carbonate is the dominant ion (Drever, 1982). Silicon was measured by Analytical Services by atomic adsorption spectrometry on some samples, and assumed to exist as the neutral $H_4SiO_4{}^{o}{}_{(aq)}$ species.

3.2 EXTRACTION OF WATER FROM SOILS AND BRINES FOR ISOTOPIC ANALYSIS

3.2.1 REVIEW OF EXISTING METHODS

The removal of isotopically representative water from porous media for analysis has sometimes been difficult, particularly in situations where not all the pore spaces are filled with water (in the unsaturated zone). Presses have been used to collect samples for chemical analysis (e.g. Kalil & Goldhaber, 1973), but also for isotopic analysis (Jusserand, 1980). Centrifugation may be successful if the soil or sediment may be further consolidated. The addition of an immiscible liquid with a specific gravity greater than that of water will often improve the yield from centrifugation (e.g. Navada, 1982). Water for chemical analysis has been removed from porous media by suction devices (Stewart, 1972) or absorbed into hydrophilic media (Shimshi, 1966, Tadros & McGarity, 1976). A recent review of soil solution sampling and problems involved is given by Litaor (1988). If these approaches were to be used for an isotopic sample, extreme care would have to be taken to avoid fractionation (essentially, a change in isotopic composition) by evaporation, condensation or exchange with atmospheric water vapour. Yields may be small, and in the case of absorbent materials the water must still be recovered for analysis.

Probably the most widespread method of water extraction from porous media for isotopic analysis is vacuum distillation (Stewart, 1972). The sample is evacuated and the water that vaporises is collected in a cold trap, typically cooled by liquid nitrogen (-196^{0}C) or dry ice-ethanol (-80^{0}C; section 3.2.4). Significant fractionation effects occur where recovery is less than about 99%, although in some cases correction has been successful for lower yields (Hobbs, 1988). Two or even three cold traps may by required to achieve such yields and the sample must be heated (50^{0}C, Fontes *et al.*, 1986; 70^{0}C, Jusserand, 1980; 110^{0}C, Stewart, 1972; 200°C, Navada, 1982). If gypsum is present in a soil or sediment the waters of hydration will contaminate pore water obtained by this method, and the effect is more pronounced at higher temperatures. Vacuum distillation can also be used specifically to collect crystallisation water from hydrated minerals such as gypsum (at 400°C, Gonfiantini & Fontes, 1963; 450°C, Sofer, 1978; 300°C by the author, sect. 3.2.6)

In a novel approach Kalisz *et al.* (1988) heated soil and foliage in a microwave oven and collected condensate for tritium analysis. This approach is highly unlikely to yield good results for D or ^{18}O. The stable isotopes are much more sensitive to fractionation effects caused by incomplete yield; the absolute variations in concentration measured are much less than for tritium, where fractionation effects of phase changes are usually negligible compared to the range of concentration found in nature.

The desiccant molecular sieve (a zeolite) was employed by Thoma *et al.* (1979) and Saxena and Dressie (1984; see also Saxena, 1987) to quantitatively sample water vapour, withdrawn from the soil through a tube of molecular sieve. Water was recovered from the zeolite by vacuum distillation for isotope analysis, tritium in the case of Thoma *et al.*, and tritium and oxygen-18 by Saxena. The former workers also analysed for oxygen-18 but found the results "completely off", but Saxena achieved reasonable results.

Some "direct" methods have been reported. For deuterium analysis, single step distillation-reduction over zinc, suitable for very small samples of porous material (Turner & Gailitis, 1988) and gypsum (Coleman *et al.*, 1982) have been published. It is also possible to analyse for oxygen-18 using CO_2 directly equilibrated with brines, or water retained within a porous medium (e.g. Jusserand, 1980).

Azeotropic distillation with hydrocarbons has been the preferred method of the CSIRO Division of Soils (later Water Resources) laboratory where this work was carried out. The technique was apparently first applied to extract water for stable isotope analysis from porous media by R.M. Brown and G.B. Allison working in Canada in the 1970s (Leaney *et al.*, 1985; G.B. Allison, pers. comm.). Although the technique has been used in many studies, such as Hendry (1983), Allison and Hughes (1983), and Shatkay and Margaritz (1987), it has only recently been documented in detail (Revesz & Woods, *in press*). At present, the method provides good results in a wide variety of soil types, with the important (as far as much arid zone work is concerned) exception of gypseous soils. In addition it has proved useful for extracting water for isotopic analysis from body fluids (Werbin *et al.*, 1959; Cuthbertson *et al.*, 1989), brines (Horita & Gat, 1988; Dighton & Allison, *in prep.*), and plant matter (Leaney *et al.*, 1985: Allison *et al.*, 1985). Unpublished work of G.B. Allison and J.C. Dighton in the early 1980s (pers. comm., included in table 3.2.1) suggested that the hydrocarbon hexane might be of use with gypseous samples.

Extensive trials run on the azeotropic distillation technique and others thought to be of possible use in gypseous soils are documented in the following sections.

3.2.2 AZEOTROPIC DISTILLATION

3.2.2.1 General

The technique of azeotropic distillation is based on the principle that for most mixtures of liquids, the boiling point of the mixture is below those of the pure liquids, and that the vapour produced is also a mixture. When the mixed vapour is cooled, the collected condensate will separate into two layers if the liquids are immiscible and of different densities. The lighter liquid, in this case a hydrocarbon, is refluxed, but all of the other liquid, water, is removed from the material being treated. Any dissolved solids in either liquid remain behind.

Early studies using azeotropic distillation employed benzene to remove water for tritium analysis from body fluids (Werbin *et al.*, 1959), and toluene to determine the water content of silage (Langston *et al.*, 1958; Witter *et al.*, 1958; Dewar & McDonald, 1961). To extract water from soils and plant material for stable isotope analysis, toluene was used by Allison *et al.* (1985), Leaney *et al.* (1985), and various others, while Shatkay and Margaritz (1987) used petroleum ether (boiling point 100-120°C). Hendry (1983) used xylene to obtain water from glacial till for tritium analysis.

At the Adelaide laboratory more recent practice has been to use kerosene, which is cheaper and safer than toluene or benzene. Revesz and Woods (*in press*) demonstrate the similarity in results using kerosene and toluene. For most gypsum-free soil materials the uncertainty in isotopic composition of extracted waters is only a little greater than the external precision of most current mass spectrometers (about ±0.5‰ for δD and ±0.05‰ for $\delta^{18}O$). Figures quoted by Allison and Hughes (1983) are ±2‰ and ±0.5‰ for δD and $\delta^{18}O$ respectively, while Revesz and Woods quote ±2‰ and ±0.2‰. In more amenable media such as sand, Leaney *et al.* (1985) quote uncertainties of ±1.1‰ and ±0.1‰ using toluene.

Azeotropic distillation is also used to recover water from brines for isotopic analysis (e.g. Horita & Gat, 1988; Dighton & Allison, *in prep.*). If the brine is high in divalent cations, particularly magnesium, those ions should first be precipitated out by the addition of sodium fluoride to prevent the formation of hydrated minerals in the residue that affect the isotopic composition of the distillate.

The procedure is as follows. The Dean-Stark apparatus (Fig. 3.2.1) consists of a laboratory heating element, a flask (commonly 250 or 500ml, but 100 ml and one holding several litres have been used), a specially designed receiving trap, and a straight condenser. A bank of six heaters, traps and condensers is used, operated in a fume cupboard. Knowing the water content of the soil, the appropriate amount of soil containing at least 3 ml of water after distillation is measured into a flask (without weighing if the yield does not need to be checked). Water quantities as low as 0.5 ml can be distilled, but may be difficult to

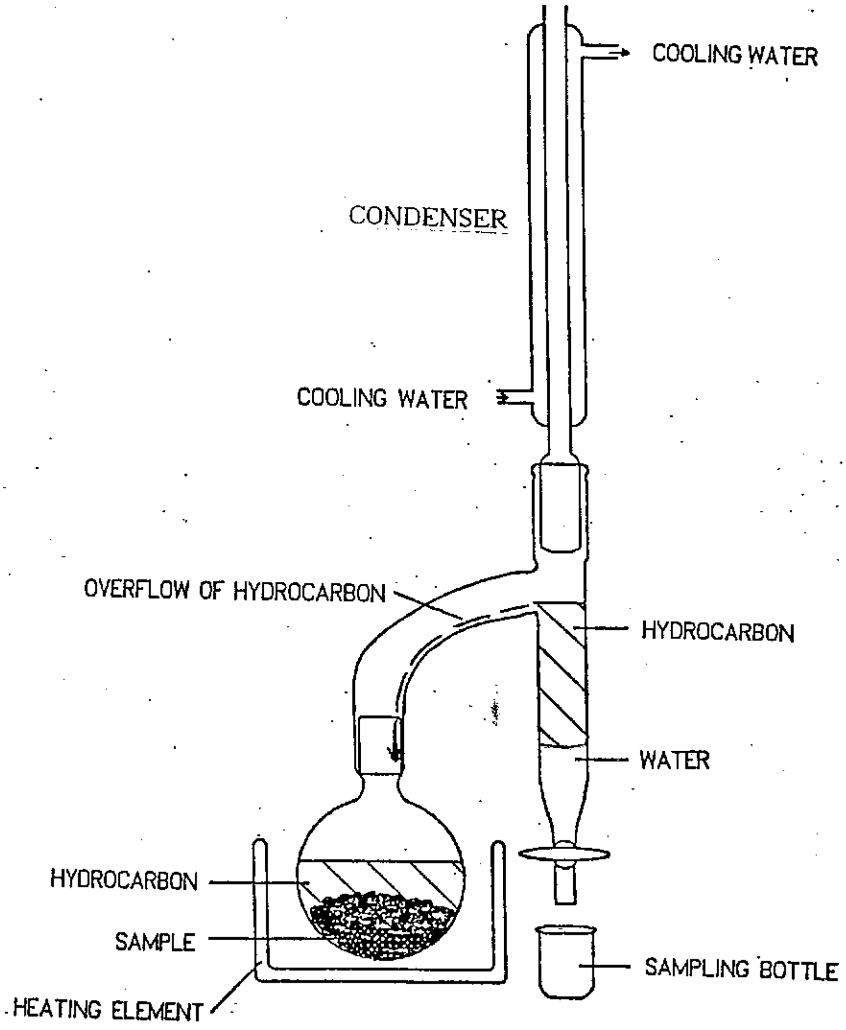

FIGURE 3.2.1 Dean-Stark Apparatus for Azeotropic Distillation of Soil Water. After Revesz & Woods, in press.

analyze for ^{18}O. Enough hydrocarbon is added so that the soil remains covered throughout the entire distillation process. The hydrocarbon must be water free, which is ensured by adding sodium metal to the stored hydrocarbon. At the beginning of the distillation, water and hydrocarbon evolve together with a cloudy appearance. The distillation should continue until the condensate turns clear, and no water drops remain on the glass walls of the entire apparatus. It seems important that the distillation continue at least 10 to 15 minutes after the first clear drops begin to appear, and no further droplets of water are observed being added to the condensate. During this time the hydrocarbon overflow will drip back to the flask through the collector, and the hydrocarbon vapour will remove the water drops from the walls of the glass. Often a few drops of water will adhere to the inside of the condenser; if possible these are pushed down into the trap with a fine spray of hydrocarbon from a squeeze bottle, or with a glass rod.

The entire amount of water is collected in a glass bottle with sealing cap, and any supernatant hydrocarbon pipetted off. Any last trace of hydrocarbon is removed by adding paraffin wax (enough to solidify after dissolving the hydrocarbon, typically about one gram) to the water and warming it up in the closed sample bottle to the melting point of the wax (60 - 70°C). This is shaken and allowed to cool. The solidified wax on the top of the water also helps prevent evaporation during storage and handling. The apparatus is rinsed with acetone or ethanol and allowed to dry between distillations Acetone is preferred, as ethanol has a molecular mass of 48, the same as $C^{16}O^{18}O$, and may interfere with the determination of ^{18}O (pers. comm. Fontes, 1990).

Since the end of this part of the study, Revesz (in Revesz & Woods, in press) has recommended treating the condenser and the trap with a solution of dimethyldichlorosilane compound (Sylon-CT) to render the surface hydrophobic. However, results using untreated glassware reported here compare favourably with those using treated glassware. The treatment would be particularly useful for small samples where the few drops remaining in the condenser constitute a significant proportion of the total distillate, and so contribute to greater errors than with for larger samples.

All the hydrocarbons used previously in published studies (benzene, toluene, xylene, petroleum ether and kerosene) have boiling points over 80°C and will extract at least some crystal water from gypsum. Following the suggestion of J.C. Dighton, referring to the unpublished data of Allison and Dighton (Table 3.2.1), the use of hexane (boiling point 64°C) was extensively investigated for use with gypseous soils such as those collected in the field by the author. Trials also incorporated a brief investigation of the use of diesel fuel (boiling point about 240°C), and are reported in the following pages.

3.2.2.2 Laboratory Trials

A summary of early verification trials at the Adelaide laboratories of the C.S.I.R.O. Divisions of Soils and Water Resources are given in Table 3.2.1, with acknowledgement of source; those by the author are not presented elsewhere but were preliminary runs. Where no standard deviation is given, not enough replicates were made to justify the calculation. Since a much greater range of porous media were being treated by azeotropic distillation in the laboratory, at water contents from 0.5 to 40% by mass, the more comprehensive set of trials were initiated.

These more extensive laboratory trials prompted by the successful preliminary results compiled in table 3.2.1 were carried out on a variety of materials. All techniques for the extraction of water from porous

TABLE 3.2.1

Early Azeotropic Distillation Verification Results from CSIRO Divisions of Soils and Water Resources, Adelaide Laboratory

hydrocarbon	$\Delta\delta D$ ‰ [**]	$\Delta\delta^{18}O$ ‰	Worker; date given only if figures are published
Sand (at high water content)			
Toluene	0.0±1.1	−0.07±0.1	Leaney *et al.* (1985)
Kerosene	−0.7±1.0	−0.13±0.1	Woods
Hexane	+0.5±0.5	+0.35±0.1	Woods
"a range of soil materials"			
Toluene	0 ±2 [*]	0.0 ±0.5 [*]	Allison & Hughes (1983)
Coarse/ Sandy Gypsum (at high water content)			
Hexane	−1.5±1.5	−	Allison & Dighton
Hexane	−1.0	+1.05	Woods

[*] the actual trial results were not stated, only the estimated total error and that "no fractionation ... was observed".

[**] $\Delta\delta = \delta(\text{extract}) - \delta(\text{added water})$

media are sensitive to the nature of the material used, therefore some physical properties of those materials used are given in Table 3.2.2. The tabulation includes those materials used in trials of the other methods covered in this chapter. The results are shown in Table 3.2.3. Most measurements involved eight replicates, except shale and toluene with six, and water and hexane and the remaining shale trials, with four.

A large number of comparisons of hexane and kerosene distillations were carried out to investigate the consistency of the difference between the two (Table 3.2.4). They include some involving replicates, and the average difference between many paired samples of natural, gypsum-free materials from the project area.

The time dependence of yields using toluene and kerosene during distillation from water, sand and shale are shown in figure 3.2.2, and those with hexane in figure 3.2.3. These were obtained by distilling a known mass of medium and contained water in a Dean-Stark apparatus with a volume-calibrated collector (Dewar & McDonald, 1961). Five to eight grams of water were involved in these trials, in about 50g of porous medium. Figure 3.2.2 suggests that for quantities of porous medium of about 10 to 100g, at least 30 minutes boiling time is required using kerosene, and about 90 minutes for toluene to obtain effectively 100% yields. In practice two to three hours were allowed. Using hexane on porous media, no yield improvement past about 95% can be obtained from fine grained material after about 5 hours (Fig. 3.2.3). The distillation of water alone by hexane took over 12 hours to complete, however this is probably due to the small contact area between the two phases compared to that within a porous medium; isotope results are further out than for extraction from soil.

In the special case of gypseous samples, relative yield may exceed 1.0 indicating that gypsum crystallisation water is being extracted as well as pore water. Also, as distillation proceeds most slowly with

TABLE 3.2.2

Brief Description of Materials Used in Trials.

Sand: graded industrial quartz sand, 0.3 -0.6 mm diameter.

Shale 1 : weathered Bulldog Shale (Freytag, 1966), montmorillonitic, from near Lake Eyre, South Australia.

Shale 2 : weathered Tapley Hill Formation shale, brown-grey, slightly calcareous, collected from a road cutting at Flinders University, South Australia.

Lunette : aeolian gypsum dune, 70% gypsum (silt to sand size grains), 27% fine quartz sand, 3% calcite sand, total organic carbon 0.3%, collected from south-western New South Wales by G.B. Allison.

Gypsum : crushed, coarsely crystalline agricultural gypsum.

Clay : heavy black vertisol, from O'Hallaran Hill, South Australia, collected by J.C. Dighton and G.R. Walker.

Silty Sand : flood plain sediment from near Lake Eyre, South Australia.

A.R. Gypsum : Analytical grade gypsum, as a finely divided powder.

TABLE 3.2.3

Deviations from the Known Isotopic Composition of Waters Azeotropically Distilled with Various Hydrocarbons

Deuterium ΔδD ‰

	θ_g	Hydrocarbon used			
	g g^{-1}	Hexane	Toluene	Kerosene	Diesel
Water	-	−2.6±1.9	+0.2±0.6	−0.8±1.4	−1.3±1.8
Sand	.03	+2.3±1.2	+2.6±0.6	+1.4±0.8	-
Shale 2	.38	−2.4±0.6	−1.7±0.3	−0.4±0.7	-

Oxygen-18 $\Delta\delta^{18}O$ ‰

	θ_g	Hydrocarbon used			
	g g^{-1}	Hexane	Toluene	Kerosene	Diesel
Water	-	−0.53±0.42	+0.05±0.09	−0.16±0.29	−0.4±0.4
Sand	0.03	+0.49±0.15	+0.56±0.21	+0.43±0.13	-
Shale 2	0.38	−0.11±0.22	−0.29±0.11	−0.06±0.09	-

TABLE 3.2.4

Comparison of the Isotopic Composition of Waters Extracted by Azeotropic Distillation with Kerosene and Hexane

Deuterium δD_{smow} ‰

Material	n	θ_g	Hydrocarbon used		Difference
		$g\ g^{-1}$	Kerosene	Hexane	(Hex-Kero)
Clay	9	0.391	-16.8	-20.0±1.5	-3.2
Shale 1	3	0.288	-2.7	-6.9±0.6	-4.2
Shale 2	17	0.189	-35.9	-39.0±0.8	-3.1
Mixed Field	25	0.09-0.22			-3.3±1.9*

Oxygen-18 $\delta^{18}O_{SMOW}$ ‰

Material	n	θ_g	Hydrocarbon used		Difference
		$g\ g^{-1}$	Kerosene	Hexane	(Hex-Kero)
Clay	9	0.391	-1.67	-3.0±0.4	-1.3
Shale 1	3	0.288	+6.40	+5.3±0.2	-1.1
Shale 2	17	0.189	-4.53	-5.6±0.15	-1.1
Mixed Field	15	0.09-0.22			-1.14±0.31

n = number of replicates

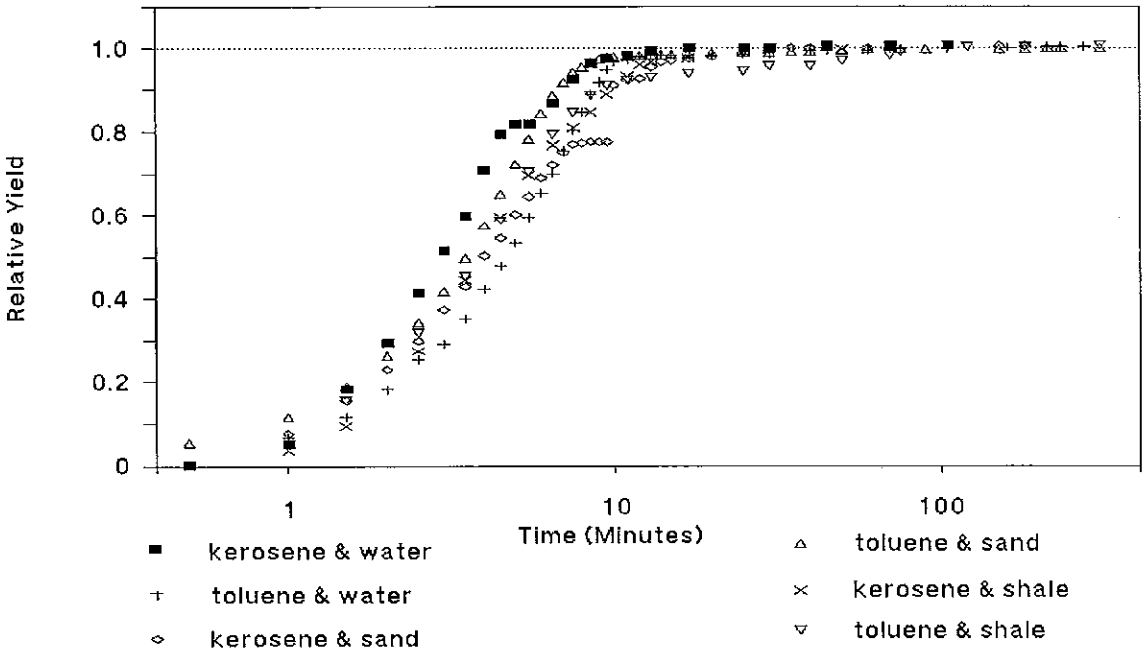

FIGURE 3.2.2 Relative Yield versus Time Curves for Azeotropic Distillation of Water and Soil Water Using Toluene and Kerosene from Revesz & Woods, in press

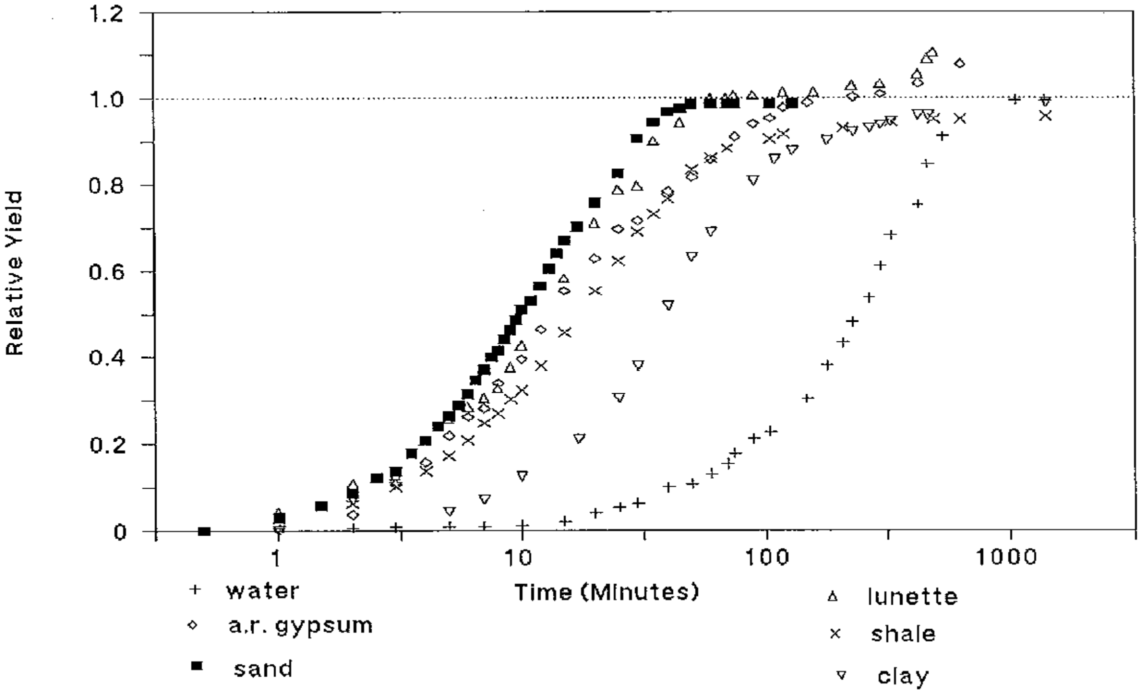

FIGURE 3.2.3 Relative Yield versus Time Curves for Azeotropic Distillation of Water and Soil Water using Hexane

hexane, the isotopic composition of distillate from shale at different times were taken, and are compared to a separate kerosene distillation in Table 3.2.5. These two pieces of information need to be taken together, as will be discussed shortly.

The hydrocarbons used have a range of boiling points, namely hexane (b.p. 64 to 68°C), toluene (b.p. 111°C), kerosene (b.p. 160-230°C), and diesel fuel (b.p. about 240°C), recorded during the yield time trials. The progressive nature of the extraction is shown in a plot of vapour temperature versus relative yield (Fig. 3.2.4). These show the truly azeotropic part of the process, with a vapour temperature less than the boiling point of water, while there is enough water present to provide the proportion required for the azeotrope. As the water remaining becomes small, the temperature of the mixed vapour rises until the boiling point of the hydrocarbon is reached. This behaviour is well known, following the typical pattern of most azeotropic mixtures (Vogel, 1956).

3.2.2.3 Discussion

The trials verify that azeotropic distillation of soils and water using toluene and kerosene are generally satisfactory, particularly at high water contents. Toluene gives better results for the distillation of water alone, while kerosene gives better results for porous media. The accuracy for sand is generally not as good for either as that reported by Leaney *et al.* (1985), by Revesz and Woods (*in press*), and early work by the author (Table 3.2.1), which were all carried out at higher water content, and thus lower soil matric suction (pore water potential). Results may be expected to be less accurate at high suction, as the fraction of water held at very high suction, and not removed by

TABLE 3.2.5

Effect of Distillation Time on the Isotopic Composition of Soil Water Extracted by Azeotropic Distillation with Hexane, Compared to a Separate Distillation with Kerosene

material : Shale 2, θ_g = 0.205 g/g, 5 replicates each. Expressed as difference between hexane and kerosene extracted waters, permil.

Time (hours)	1.5	2	3	6
$\Delta\delta D_{hex-kero}$	-4.0±1.1	-3.8±0.5	-3.7±0.6	-3.3±0.5
$\Delta\delta^{18}O_{hex-kero}$	-1.42±.19	-1.20±0.15	-1.12±0.15	-0.88±0.13
average yield(%)	82	89	92	92

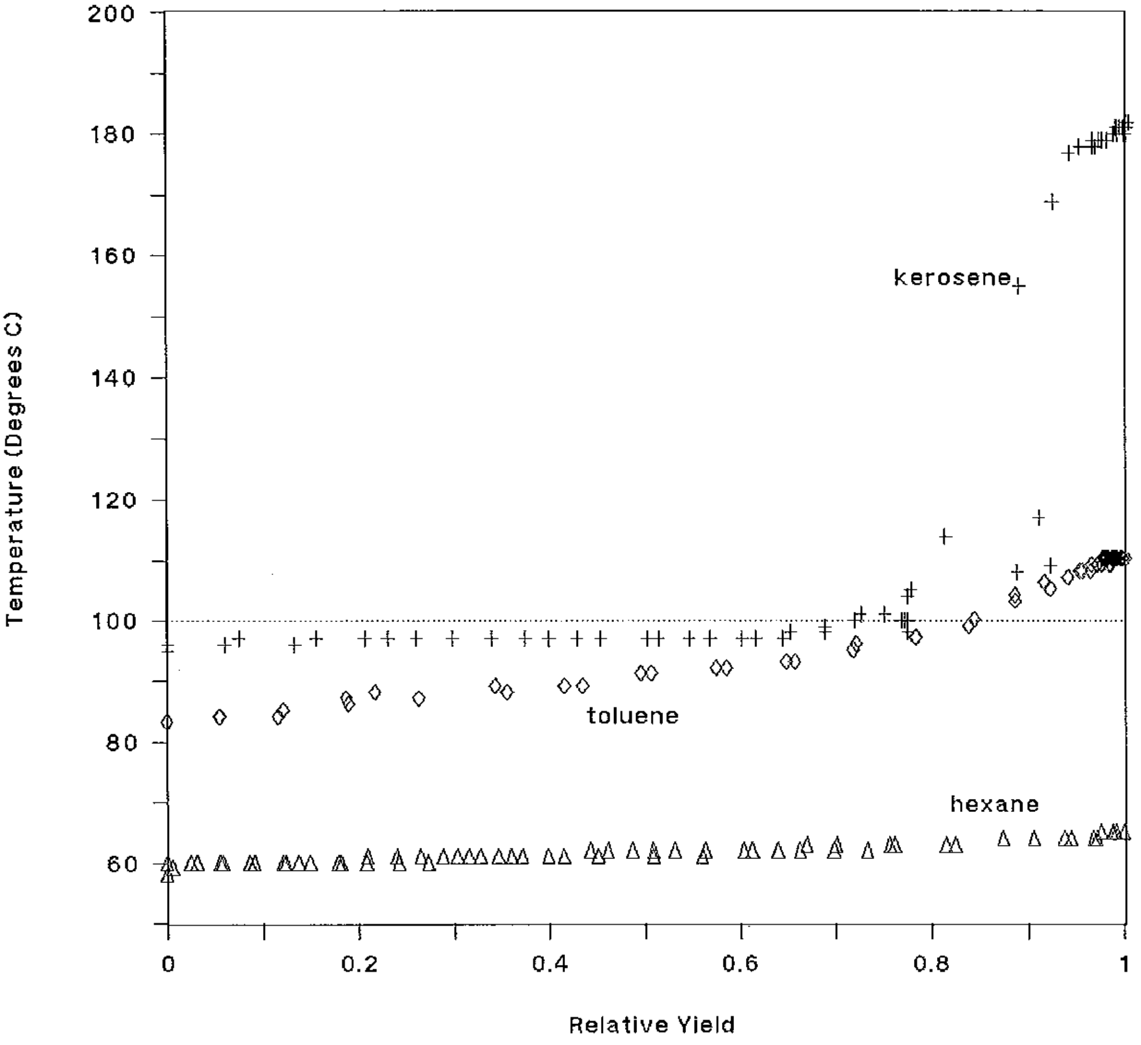

FIGURE 3.2.4 Temperature Versus Relative Yield Curves for Azeotropic Distillation of Water from Sand Using Hexane, Toluene and Kerosene Two runs per hydrocarbon

the treatment, becomes significant at low water content. The higher temperatures involved with the three hydrocarbons, and hence ability to extract a greater proportion of water at high suction, is reflected well in the results for shale (Table 3.2.3), a fine-grained material that holds a large portion of its water in fine pores.

The results using hexane are not as satisfactory as those with kerosene and toluene for any of the materials, except perhaps for shale at high water content (saturation). The results using diesel to purify water alone were unsatisfactory, and so the use of that hydrocarbon was not pursued. This poor result may be caused by the "bumpy" nature of the early part of the distillation, when surges of vapour may partially escape from the top of the condenser, or possibly the relatively large (compared to other hydrocarbon-water distillations) amount of water observed adhering to the inside of the condenser.

Gypsum crystallisation water was removed after long boiling times with every azeotrope. However, if boiling time is restricted to two to three hours, the contribution of gypsum water to the total amount extracted by hexane is very small, and for materials with coarse-grained gypsum (sand size and above) a pore water sample can be obtained (the results of Tables 3.2.1 and 3.2.4 were obtained in this fashion). Although for gypsum-free soil samples a more representative water sample would be obtained by longer boiling, the value obtained after only two to three hours gives nearly as good value as six hours (Table 3.2.5), and is quick enough to prevent large contamination by gypsum water (Fig. 3.2.3).

As a general rough guide, the isotope value of a hexane distillate is lighter than an equivalent kerosene distillate by about -3 and -1.1 permil for δD and $\delta^{18}O$ respectively. The magnitude of the bias apparently depends on both the grain size and water content of the material, being greater for fine grain size and lower water content (or more strictly, higher suction). This reflects the difficulty the low temperature process has in removing water held at high suctions within the porous media, the proportion of this obdurate water being greater compared to that comfortably extracted in fine grained materials and at low water content. For a given material a water-content or suction corrected bias could be determined and used to remove the bias for a particular soil type. However, the heterogeneity of natural soil profiles means that allowing for the "average" bias is probably the best correction to make, remembering that the precision of the result is probably two or three times worse than that of a straight kerosene-distilled result. The magnitude of this bias would be best determined for the soil type of a particular field study. The values are obtained by hexane distillation are therefore accurate enough to be of use in most circumstances, though perhaps not for precise studies.

3.2.3 MASS BALANCE APPROACH

3.2.3.1 General

There are two ways to determine the isotopic composition of pore water in a gypseous sample by using mass balance. The first is to extract the combined pore and gypsum waters by an established method, then the crystallisation water alone from gypsum in another aliquot (methods for gypsum are discussed in section 3.2.6). The isotope balance of the system is

$$\delta_t(\theta + G) = \delta_p\theta + \delta_g G, \tag{3.1}$$

so that the pore water isotope composition is

$$\delta_p = \frac{1}{\theta} G\,(\delta_t - \delta_g) + \delta_t, \qquad (3.2)$$

where
δ_p = isotope content of pore water, permil
δ_t = isotope content of "total", combined pore and gypsum waters
δ_g = isotope content of gypsum water alone
θ = gravimetric water content of the soil, g/g
G = gravimetric gypsum water content, g/g,
i.e. G = 0.205 x (mass gypsum / mass dry soil).

Both θ and G must be expressed per mass of dry soil including gypsum (not per mass of oven dry soil including bassanite or anhydrite!). The error of an isotope value obtained by this method may be estimated as follows. Considering the error in each term to be $\Delta\delta_t$, ΔG etc.,

$$\delta_p + \Delta\delta_p = \frac{1}{\theta + \Delta\theta}(G+\Delta G)\Big((\delta_t - \delta_g) + \Delta(\delta_t - \delta_g)\Big) + \delta_t + \Delta\delta_t. \qquad (3.3)$$

Using the relation

$$\frac{1}{1+\Delta x/x} \cong 1 - \Delta x / x \quad \text{for} \quad \Delta x \ll x, \qquad (3.4)$$

then multiplying out and dropping second order terms, we find that

$$\Delta\delta_p = \frac{G}{\theta}\left(\Delta(\delta_t - \delta_g) + (\delta_t - \delta_g)\left(\frac{\Delta G}{G} + \frac{\Delta\theta}{\theta}\right)\right) + \Delta\delta_t. \qquad (3.5)$$

Since the signs of the errors are unknown, and noting that $|\Delta\delta_t| \cong |\Delta\delta|$, and $|\Delta(\delta_t - \delta_g)| \cong \sqrt{2}\ |\Delta\delta|$, where $|\Delta\delta|$ is the routine precision of the mass spectrometer used,

$$|\Delta\delta_p| \le \frac{G}{\theta}\left(\sqrt{2}|\Delta\delta| + |(\delta_t-\delta_g)|\left(\left|\frac{\Delta G}{G}\right| + \left|\frac{\Delta\theta}{\theta}\right|\right)\right) + |\Delta\delta|. \tag{3.6}$$

The error is greater at high gypsum and low pore water contents, as well as being dependent on the relative errors of gypsum water (and hence gypsum itself) and water contents, and is less if the pore water happens to be similar to the gypsum water. The relative errors in gypsum and water content are usually a few percent, so that the error in δ_p will be several times the routine precision of the mass spectrometer used.

The second mass balance approach is by dilution, adding enough water of known isotopic composition to an aliquot of sample to make it moist enough to remove water for analysis by physical means such as centrifugation. The added and pore waters must be allowed to equilibrate (at least one hour, Revesz and Woods, *in press*, but preferably longer) in a sealed container. The centrifuged water is analysed and the pore water isotope composition calculated from the water and isotope balance;

$$\delta_p = \frac{V}{W}(\delta_t - \delta_a) + \delta_t \tag{3.7}$$

where W = mass of water in the soil aliquot = $M\theta_g / (1+\theta_g)$

M = mass of damp soil in aliquot

V = mass of water added to system

and δ_a = isotope content of added water.

Considering the errors in the various terms to be $\Delta\delta_p$, ΔV etc., we have

$$\delta_p + \Delta\delta_p = \frac{(V+\Delta V)((\delta_t-\delta_a) + \Delta(\delta_t-\delta_a))}{W + \Delta W} + \delta_t + \Delta\delta_t. \tag{3.8}$$

The mass of water added V is known very accurately if several grams are involved weighed to an accuracy of 10 mg or less, so that $V+\Delta V \cong V$.

Again using the relation for $1/(1+\Delta x/x)$ and dropping out second order terms we have

$$\Delta\delta_p \cong V/W\ \Delta(\delta_t - \delta_a) - V/W\ (\delta_t - \delta_a)\ \Delta W/W + \Delta\delta_t. \qquad (3.9)$$

Following the same reasoning as for the first dilution case, and noting that the second term is $\delta_p - \delta_t$, we obtain

$$|\Delta\delta_p| \leq V/W\ \sqrt{2}|\Delta\delta| + |\delta_p - \delta_t||\Delta W/W| + |\Delta\delta|. \qquad (3.10)$$

The error is strongly dependent on V/W, the dilution, hence the amount of added water must be kept to a minimum. In addition, the added water should have an isotopic composition similar to the expected pore water composition. Since $W = M\theta / (1+\theta)$, using similar arguments it can be shown that

$$\Delta W / W \cong \Delta M / M + \Delta\theta / (\theta(1+\theta)), \qquad (3.11)$$

and as the mass of the damp soil can be precisely known, $\Delta M/M \ll \Delta\theta/(\theta(1+\theta))$,

$$\Delta W / W \cong \Delta\theta / (\theta(1+\theta)) \qquad (3.12)$$

so that the error is also strongly dependent on the relative error of the water content. Unfortunately the water content is imperfectly known, since

(a) vacuum and/or desiccant drying does not remove all the water from some clay minerals that is available to exchange with the added water, and

(b) water content may vary between the aliquots used for water and isotope content determination, particularly in coarse grained and inhomogeneous materials, such as where the soil structure is disrupted by growing gypsum crystals.

It is conceptually possible to treat both θ and δ_p as unknowns and calculate both by mass balances from two different dilutions on different aliquots, or successive dilutions on the same aliquot. This was attempted, but gave very unsatisfactory results that can be attributed to water content variation between aliquots, or the large second dilution on a single aliquot.

3.2.3.2 Laboratory Trials

Dilution trials of the second mass balance technique were carried out on a variety of materials where the pore water isotopic composition was known by doping with a known water or azeotropic distillation with kerosene of gypsum free samples. Maximum errors were calculated by equations given above. The error in θ was taken to be 0.005 g/g, verified by replicated determinations on some samples. Gypsum contents were determined by the method of Nelson *et al.* (1978). Damp masses of soil from about 40 to 200g were weighed into 500ml glass jars, and the diluting water weighed in. The jars were then capped and additionally sealed with PVC tape, and occasionally shaken while stored in a constant temperature room (20°C) for at least one week to equilibrate. Storage at constant temperature reduces the formation of condensation. Two aliquots of stirred sample slurry were placed in stainless steel centrifuge tubes with the immiscible heavy liquid trichloroethene and centrifuged for 10 to 20 minutes at 2800 rpm. The water was decanted and purified by azeotropic distillation with kerosene. Samples of the dilutant (δD =

-86‰ , $\delta^{18}O$ = -19.6‰ relative to V-SMOW) were run with each batch of diluted waters on the mass spectrometer, and the batch values used in calculations to improve accuracy. The combined distillation and analysis accuracy ($\Delta\delta$) were taken as 1 and 0.1%. for δD and $\delta^{18}O$ respectively. The five dilution trials of Table 3.2.6 are of the same materials at different dilutions; those in Table 3.2.7 of gypsum-free field samples from various holes drilled for this project.

3.2.3.3 Discussion

While most of the calculated isotope comparisons were within the estimated maximum errors of the known values, the accuracy is quite poor compared to those obtained from gypsum free samples by azeotropic or vacuum distillation. As the equations describing the errors suggest, best results are obtained at low dilutions (higher water content samples). Lesser dilutions would be possible if a more powerful centrifuge were used. In general, a more reliable value can be obtained by azeotropic distillation with hexane.

3.2.4 VACUUM DISTILLATION AT ROOM TEMPERATURE

3.2.4.1 Laboratory Trials

Vacuum distillation is a common technique for the extraction of water from soils for isotopic determination at many laboratories. A typical set-up is shown in figure 3.2.5 (Saxena, 1987). A vacuum line was constructed in the manner of figure 3.2.5, with a single vapour trap cooled by liquid nitrogen, and without any heating coils. A series of trials were run at room temperature (20 - 25°C), to avoid the risk of

TABLE 3.2.6

Results of Dilution Trials to Determine the Isotope Composition of Known Pore Water. Expressed in permil relative to V-SMOW

Soil	θ_g	gypsum content	dilution	known pore water		calculated results	
				δD	$\delta^{18}O$	δD	$\delta^{18}O$
	$g\ g^{-1}$	$g\ g^{-1}$		‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$
1	0.103	0.45	1.945	131	-2.43	126±10	-2.9±0.8
			2.580			135±12	-2.3±1.0
			2.866			126±14	-4.0±1.2
			4.196			116±18	-4.9±2.7
2	0.180	0.0	0.978	-31.6	-3.53	-26.6±2.6	-3.6±0.3
			2.047			-28±4	-3.6±0.6
			3.186			-32±6	-3.9±0.7
			3.995			-29±7	-3.9±0.8
3	0.102	0.28	1.817	-31.6	-3.53	-25±6	-2.9±0.9
			2.737			-28±7	-1.9±1.1
			5.347			-31±9	-2.8±1.4
4	0.159	0.104	1.817	70	-3.2	72±6	-1.5±0.7
			1.955			65±6	-1.8±0.7
			2.246			70±7	-3.5±1.7
			2.535			75±8	-2.6±0.8

Soil Key: 1. Sand + Lunette 2. Shale 2 3. Shale 2 + Lunette
4. Shale 1 + gypsum

TABLE 3.2.7

Results of Dilution Trials to Determine the Isotopic Composition of Pore Water of Field Samples, Compared to Results by Azeotropic Distillation with Kerosene. Expressed in permil relative to V-SMOW.

Soil	θ	dilution	known pore water		calculated results	
	g/g		δD	$\delta^{18}O$	δD	$\delta^{18}O$
			‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$
1	0.186	1.802	8.0	9.45	20±6	12.1±0.8
1	0.064	6.486	9.2	11.45	26±15	12.6±2.9
1	0.117	1.804	25.7	12.40	40±7	16.4±1.3
		4.587			32±10	14.8±1.7
1	0.165	1.773	-3.3	6.57	18±6	10.0±1.0
		2.729			22±7	10.7±1.0
1	0.165	2.185	6.2	5.19	4±6	7.8±0.9
		3.303			12±7	9.9±1.3
1	0.106	4.014	-0.2	7.37	6±10	15.0±1.8
		5.766			-2±11	8.6±1.8
1	0.118	2.215	4.3	9.73	2±7	9.9±1.3
		3.790			3±8	11.3±1.5
2	0.378	0.661	14.0	11.47	16±2	12.1±0.6
2	0.427	0.487	15.3	11.84	14.2±1.1	11.5±0.2

Soil Key: 1. Silty Sand 2. Shale 1

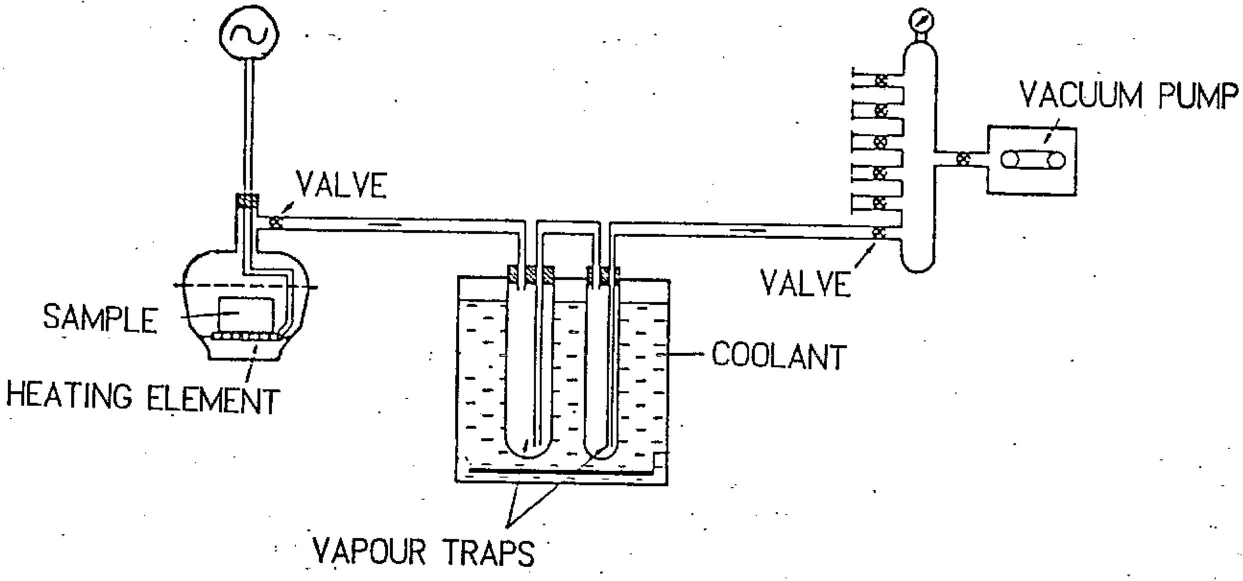

FIGURE 3.2.5 An Example of Vacuum Distillation Apparatus for the Recovery of Soil Water. After Saxena, 1987

removing crystal water. Known water was added to dry sand and lunette samples, while results for shale are compared to kerosene extracted results (Table 3.2.8). The extractions were run for about four hours. Trials left overnight were unsuccessful due to small leaks in the system that could not be eliminated.

TABLE 3.2.8

Results of Trials of Room Temperature Vacuum Distillation. Expressed as difference between known (added) and extracted waters, ‰

Material	θ_g g g^{-1}	n	ΔδD ‰	n	$\Delta\delta^{18}O$ ‰
Sand	0.032–0.085	8	+0.5±0.5	4	+0.17±0.16
Lunette	0.026–0.094	6	-6.2±4.3	4	+0.6 ±1.3
Shale 1	0.327	8	-6.6±1.0	8	-1.49±0.14

n = number of replicates. Maximum yield determined by oven drying several of the samples was 97 to 98%. This does not allow for any water lost to the vacuum line.

3.2.4.2 Discussion

The method was satisfactory for the clean sand used, but gave very poor results for the natural materials. This is not unexpected, as this is the "gentlest" of extractions, and likely to leave behind a small amount of water in the finer pores of most materials, with resulting isotopic fractionation. Although correction for incomplete yield is sometimes applied with apparently favorable results (e.g. Hobbs, 1988); the yields involved there were closer to 100% than these, and the correction was not attempted on the results here.

3.2.5 ADSORPTION OF VAPOUR BY DESICCANTS

3.2.5.1 Laboratory Trials

The desiccant molecular sieve (a zeolite) was employed by Thoma *et al.* (1979) and Saxena (1987) to sample water vapour withdrawn from the soil through a tube of molecular sieve. It seemed feasible that such a desiccant might be used to passively adsorb vapour in equilibrium with a source of liquid water, such as in an individual soil sample. Three desiccants were used: molecular sieve 3Å, activated aluminium oxide (alumina), and silica gel. Molecular sieve and alumina were regenerated at 350°C under vacuum, and silica gel at 200°C under vacuum, as recommended by the Merck company (undated booklet "Drying in the Laboratory"). There were three runs, in sealed desiccators at 20 ± 0.3°C, the first over distilled water (relative humidity 100%) and the other two over saturated sodium chloride solution (relative humidity 77%). Regenerated desiccant (10 - 15g) was weighed into small plastic containers and exposed suspended above a large excess of water. In the first two runs the containers were occasionally weighed to constant mass, and in the third left sealed. Waters were recovered by azeotropic distillation of the loaded desiccants with kerosene (180°C) with yields of 67-75% (molecular sieve 3Å), 82-89% (alumina) and 101-102% (silica gel. Results are given relative to the equilibrating water in table 3.2.9.

3.2.5.2 Discussion

Results were scattered, particularly for the distilled water run. At lower humidity (77%), molecular sieve 3Å appeared to reflect fairly well the D content of the underlying water body, while alumina gave the most

TABLE 3.2.9

Results of Trials of Desiccants to Adsorb Equilibrated Water Vapour at 20°C. Expressed as difference between known (added) and extracted waters, ‰. Three replicates each, quoted errors are of the extracts only.

Desiccant		run 1 rh=100% 37 days	run 2 rh=77% 34 days	run 3 rh=77% 24 days
Molecular	$\Delta\delta D$ ‰	-8.9±0.7	-0.9±0.4	-0.9±0.3
Sieve 3Å	$\Delta\delta^{18}O$ ‰	-2.55±0.20	-4.30±0.33	-4.28±0.02
Activated	$\Delta\delta D$ ‰	-5.9±0.6	+4.4±1.2	+4.0±0.6
Alumina	$\Delta\delta^{18}O$ %	+0.29±0.09	-0.48±0.12	-0.59±0.16
Silica	$\Delta\delta D$ ‰	-24.7±1.0	-3.2±0.5	-3.0±0.2
Gel	$\Delta\delta^{18}O$ ‰	-1.53±0.18	+1.15±0.04	+0.67±0.27

r.h. = relative humidity

average isotopic composition of the known water: $\delta D = -19.5$‰ v-smow

$\delta^{18}O = -3.8$‰ v-smow

representative ^{18}O values. The approach was not pursued further.

For deuterium, water vapour at equilibrium is depleted relative to liquid water in a NaCl brine by 67‰ at 6 molar (saturation) and 20°C, compared to 81‰ relative to pure water (Stewart & Friedman, 1975). The water in the desiccants, at equilibrium, would be expected to be 14 ‰ *heavier* than the water in the equilibrating brine. The experimental results show that the water in the desiccants, *as extracted*, is heavier over brine by about 10‰ (molecular sieve 3Å and alumina) and 22‰ (silica gel). With ^{18}O, the equilibrium fractionation is the same between vapour and pure water or NaCl brine (Stewart & O'Niel, 1977, quoting data of Taube, 1954). There may be a problem in using azeotropic distillation to extract water from desiccants, or some equilibrium fractionation difference between water in a desiccant compared to pure water. These aspects were not investigated, but the whole approach may merit further investigation.

3.2.6 RECOVERY OF GYPSUM CRYSTALLISATION WATER

The isotopic composition of the water of crystallisation of gypsum has proved a useful tracer in many studies (e.g. Sofer, 1978; Lyon, 1978; Bath *et al.*, 1987). Crystal water was collected by vacuum distillation at elevated temperatures. For trials here, lunette soil (70% gypsum) was dried by vacuum or by azeotropic distillation with hexane for two to three hours. Subsequently the water of crystallisation was extracted by azeotropic distillation with kerosene. Results are shown in Table 3.2.10, together with a vacuum distillation at 200°C.

It is concluded that azeotropic distillation with kerosene was a suitable means of recovering the crystal water from dry gypsum. Where gypsum is intimately mixed with soil material, gypsum water may be

TABLE 3.2.10

Reproducibility of Azeotropic Distillation with Kerosene of Gypsum Crystallisation Water

results expressed relative to V-SMOW, permil

drying treatment	n	δD_{SMOW} ‰	$\delta^{18}O_{SMOW}$ ‰
vacuum dry	4	−44.7±1.3	+1.83±0.37
after hexane distillation	5	−43.2±0.6	+2.20±0.12

n = number of replicates.

n.b. A vacuum dry sample extracted by vacuum distillation at 200°C had the composition $\delta D = -44.9‰$, $\delta^{18}O = +1.28‰$ relative to SMOW.

recovered after hexane distillation of the same sample has removed pore water. For other samples it is probably better to hand pick and clean coarse (>0.5mm) gypsum crystals from field samples after wet sieving, then washing the gypsum in acetone and air drying. This technique was used for most field samples of this project. Only very small amounts of clinging soil have been observed on samples so treated, so that pore water contributions to the distillate obtained is negligible.

3.2.7 CONCLUSION

Azeotropic distillation is a suitable method to extract water from porous media for isotopic measurement. At low water content (strictly, high suction) the results are not as accurate and have asystematic errors, compared to those at higher water contents, such as have been published in the literature. Toluene gives the best results for distillation of waters, while the cheaper and safer kerosene gives the best results for non-gypseous porous media, and for the hydrated mineral gypsum itself. Errors are about 1.5 and 0.2 ‰ for deuterium and oxygen-18 respectively. Hexane distillation, restricted to two to three hours duration, gives a value for pore water from gypseous material, systematically lower than the (equivalent hypothetical) kerosene values by 3 and 1.1 ‰ for δD and $\delta^{18}O$ respectively, with errors of about 2 and 0.3‰.

Other methods were investigated in the effort to extract pore water from gypseous samples. Mass balance approaches (dilution) proved too sensitive to the natural inhomogeneity of samples, particularly their water content, and gave only inaccurate results. Vacuum distillation at room temperature gave satisfactory results for coarse-grained material only, not for the majority of natural samples that have a fine-grained component. Adsorption of equilibrated water vapour by desiccants gave generally poor results, except for the measurement of deuterium using the desiccant molecular sieve 3Å.

3.3 INTERLABORATORY COMPARISON OF METHODS TO DETERMINE THE STABLE ISOTOPE COMPOSITION OF SOIL WATER

The results of this exercise organized by the author on the suggestion of his supervisors Drs Allison and Walker were not quite complete at the time of writing. The work will be presented as a short paper or technical note when complete (Woods, Allison & Walker, *in prep.*).

3.3.1 INTRODUCTION

Experience over more than a decade at C.S.I.R.O. in Adelaide, South Australia, suggested that the technique employed and nature of the soil involved can cause results scattered by several permil deviation for deuterium, and over one permil for oxygen-18, much greater than the precision available with modern mass spectrometers. With the growing number of studies involving the stable isotope composition of soil water being published, it seemed timely that an intercomparison of representative techniques in a number of active laboratories be done.

The results of such an exercise involving three soil types and four samples are presented here and comments made regarding possible pitfalls of the different techniques.

3.3.2 PREPARATION

A sandy, gypseous and clayey soil were chosen to try and cover the range of soils encountered in most studies. The clayey soil was prepared at high and low water contents, as some initial work suggested this may affect the result (see previous sections).

Bulk samples of soil were crushed and passed through a 2mm sieve, then oven dried at 105°C, except for gypseous soil which was dried at room temperature in a desiccator under vacuum to prevent the dehydration of the mineral gypsum. Soil was then allowed to equilibrate with atmospheric water vapour to air dryness, as it is impractical to handle kilogram masses of soil at oven dryness without some uncontrolled exposure to atmospheric vapour. Bulk samples were divided for use with a geological sample splitter, which has multiple, alternating outlets to two trays either side of the large inlet. This proved suitable for both mixing and dividing the soils. It was very important to homogenize the gypseous soil, prepared as a 50:50 mixture of sand (from hole MAG 15, 1.5 - 2.0 m, near Maggee in the Murray Mallee district of South Australia, Cook *et al.*, 1990) and lunette soil. The efficiency of the sample splitter was demonstrated by splitting an aliquot of the prepared gypseous soil and determining the total oven-dry water content (this includes both pore water and water of crystallisation of gypsum). The average from eight subsamples was 0.0997 ± 0.0012 g g^{-1}(1.2%). Uniformity of air dry sand (from near Borrika in the Murray Mallee, hole BUF 018, 0.8-0.85m, Hughes *et al.*, 1988) and clay (the O'Hallaran Hill vertisol of the previous work) was checked by replicate grab samples:

sand	$n = 4$	$\theta_g = 0.0014 \pm 0.0004$ g g^{-1}
and clay	$n = 4$	$\theta_g = 0.0434 \pm 0.0002$ g g^{-1}.

Split samples were prepared as for the dilution trials of section 3.2.3. The average error in the amount of water added compared to the amount desired was about 0.05g in 10 to 30g total (0.5 to 0.2%). A check oven-drying aliquots from four bottles of one trial gave $\theta_g = 0.118 \pm 0.003$ (2.5%), showing the calculated water contents are replicable to within the experimental uncertainty of determination.

As a check of the variability of stable isotope composition of soils so prepared, two soils, the clay and a loam (Clarendon loam obtained from Dr Keith Smettem of the Division of Soils) were prepared, doped with water to $\theta_g = 0.12$ g g^{-1}, and allowed to equilibrate in a constant temperature room for one week. Each sample was then split into two aliquots, and the pore water removed by azeotropic distillation with kerosene for analysis (Table 3.3.1).

TABLE 3.3.1

Check on Reproducibility of Method for Preparing Soil Samples Containing Isotopically Identical Water

sample type	number of jars	number of determinations	δD	$\delta^{18}O$
clay	6	12	−33.8 ±1.2	−5.58 ±0.48
loam	5	9*	−38.2 ±0.6	−6.40 ±0.31

* One distillation was lost by error.

The results are different from the waters used for doping (δD = -23,‰ δ^{18}O = -3.41‰ for the vertisol, -24‰ and -3.85‰ for the loam) due to the presence of a small amount of water in the air dried bulk samples, about 0.017 and 0.0155 g g^{-1} respectively. The difference between the results is however greater than would be expected from the very similar air-dry and final water contents and similar doping waters. The importance of soil type and (probably) mineralogy will be even more apparent in the results of the main, interlaboratory trial. The scatter of an individual soil type prepared as described is fairly small, so that the preparation technique is considered reliable.

Fourteen laboratories (including CSIRO Adelaide Laboratory) in eleven countries were contacted to take part in the interlaboratory comparison (Table 3.3.2). The list is not exhaustive but covers most of those active in the field and the range of extraction techniques in common use. Samples of sand and gypsum soil at moderate water contents and clayey soil at low and high water content were prepared and distributed. Two out of 52 jars were reported as broken in transit. Laboratories were requested to process the samples by their usual techniques, and if possible return an aliquot of water to the Adelaide laboratory to enable spot checks that all isotope analyses of the water extracted were compatible.

Some general physical properties of the soils are listed in table 3.3.3. Calcium carbonate and organic carbon were determined by measurement of CO_2(g) evolved on ignition of plain and acid-washed aliquots on a Lico carbon analyser, while chloride, matric suction and gypsum content were determined as described earlier. The water used to dope the samples was Adelaide tap water, with an isotopic composition δD = -16.2‰ ± 0.6‰ (7 replicates), δ^{18}O = -2.73‰ ± 0.12‰ (5 replicates).

TABLE 3.3.2

List of Laboratories Participating in the Interlaboratory Comparison of Methods to Determine the Isotope Composition of Soil Water

Group &/or Organization	City	Country
CSIRO Division of Water Resources	Adelaide	Australia
CSIRO Division of Water Resources	Perth	Australia
CSIRO Division of Water Resources	Canberra	Australia
United States Geological Survey	Reston	U.S.A.
Institute of Hydrology, British Geological Survey	Wallingford,	England
Institute of Nuclear Sciences, DSIR	Lower Hutt,	New Zealand
Weizmann Institute of Science	Rehovot	Israel
Department of Earth Sciences, Waterloo University	Waterloo	Canada
Division of Hydrology, Uppsala University	Uppsala	Sweden
Department of Dynamic Geology, University of Pierre et Marie Curie	Paris	France
Institute of Hydrology, GSF München	Neuherberg,	Germany
Isotope Division, Bhabha Atomic Research Centre	Bombay	India
Laboratory of Isotope Hydrology and Geochemistry, University of South Paris	Paris	France
Division of Research and Laboratories, IAEA	Vienna	Austria

Note : Laboratories are listed in an arbitrary order

TABLE 3.3.3

Some Physical Properties of the Interlaboratory Test Soils.

Soil Type	θ_g g g^{-1} air dry	as doped	Cl^- mg kg^{-1}	Gypsum g g^{-1}	$CaCO_3$ g g^{-1}	Organic Carbon mg g^{-1}	Matric Suction kPa
1 Sand	0.001	0.051	900	0.00	0.000	1.3	160
2 Gypseous	0.002	0.102	160	0.35	0.037	2.2	47
3 Clay	0.043	0.147	100	0.00	0.000	2.9	5000
4 Clay	0.043	0.252	100	0.00	0.000	2.9	150

3.3.3 RESULTS

Laboratories other than that of the author are identified by letter and method only. The techniques were:

-azeotropic distillation with hydrocarbons,

-vacuum distillation,

-microdistillation with zinc, and

-centrifugation with an immiscible liquid.

At the organising laboratory (N), five or six jars of each sample were prepared and distilled in dual aliquots to evaluate the reproducibility of distributed, prepared soils. Averages are also presented with those of other laboratories. The jars were stored for six to eight weeks before treatment to be comparable with those arriving at other locations. The results are shown in table 3.3.4.

TABLE 3.3.4

Reproducibility of the Isotopic Composition of Pore Water in Prepared Samples by a Single Method - Azeotropic Distillation.

Sample	Hydrocarbon	Reps.	δD ‰ ± s.d.	$\delta^{18}O$ ‰ ± s.d.
N1 Sand	kerosene	10	-24.6 ± 1.0	-3.81 ± 0.30
N2 Gypseous	kerosene	2	-28.7	-0.75
N2 Gypseous	hexane	10	-23.2 ± 1.2	-3.75 ± 0.20
N2 Gypseous	kero.after hex.	6	-35.5 ± 1.1	+2.92 ± 0.24
N3 Clay	kerosene	10	-28.1 ± 0.5	-3.61 + 0.13
N4 Clay	kerosene	10	-24.0 ± 0.8	-3.43 ± 0.18

The techniques employed by the laboratories are listed in table 3.3.5, the results of all analyses shown in table 3.3.6 and illustrated in figures 3.3.1 and 3.3.2.

3.3.4 DISCUSSION

The most consistent results are those for pore water extracted from sand, with a spread of 7‰ (excluding one outlier, J1) for δD and 1.2‰ for $\delta^{18}O$. This is considerably greater than the precision claimed by most workers in their studies, although few details have been published. On a $\delta^{18}O$-δD plot, the reported values fall in a cluster rather than along a well defined line (Fig. 3.3.3).

Gypseous soils have proved difficult to deal with in the past, as gypsum gives up some or all of its crystallisation water on heating past about 45 °C (Hardie, 1967), so that most methods will extract a mixture

TABLE 3.3.5

Methods Employed by Participating Laboratories in the Interlaboratory Comparison of Methods to Extract Soil Water for Isotopic Analysis

Laboratory	Method	Maximum extraction temperature °C
A	azeotropic, kerosene	185
B	azeotropic, toluene	110
C		
D,a	microdistillation	150-200
D,b	vacuum distillation	150
D,c	centrifugation with Arklone	room temperature
E	vacuum distillation	50
F	vacuum distillation	80
G	azeotropic, petroleum ether	120
H	vacuum distillation	
I		
J	microdistillation	200
K	microdistillation	110
L		
M	Vacuum	200
N,a	azeotropic, kerosene	185
N,b	azeotropic, hexane	65
N,c	azeotropic, kerosene after hexane	185

TABLE 3.3.6

Results Summary, Intercomparison of Methods to Determine the Isotopic Composition of Soil Water

results relative to V-SMOW, ‰

Lab.	1. Sand		2. Gypseous		3. Clayey, dry		4. Clayey, wet	
	δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD	$\delta^{18}O$
	‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$	‰$_{SMOW}$
A	-27.8*		-31.0*		-30.3*		-25.0*	
B	-24.7	-4.23	-29.1	-2.31	-33.1	-4.84	-27.2	-4.30
C								
D,a	-31.0		-39.5		-43.1		-34.5	
D,b	-30.8	-4.30	-30.2	-1.42	-41.6	-4.93	-30.2	-3.55
D,c			-20.0	-3.27*				
E	-32.7	-4.51	-29.2	-3.73	-48.6	-6.30	-38.3	-4.90
F	-26.8	-4.58	-32.1	-3.20	-38.1	-6.00	-36.6	-5.76
G	-28.3*	-4.76*	-26.3*	-3.72*	-34.3*	-5.21*	-30.0*	-4.68*
H	-27.4*	-5.03*	-32.0*	-4.88*	-57.1*	-8.02*	-44.2*	-6.57*
I								
J	-41.9							
K	-26.1		broken		-34.7		-36.4	
L	-32.0		-28.0		broken		-40.0	
M	-22.5*						-27.0*	
N,a	-24.6	-3.81	-28.7	-0.78	-28.1	-3.61	-24.0	-3.43
N,b			-23.2	-3.75				
N,c			-35.5	+2.92				

* Analysis by lab. N (author) of supplied aliquot.

Dope water composition δD = -16.2‰, $\delta^{18}O$ = -2.73‰

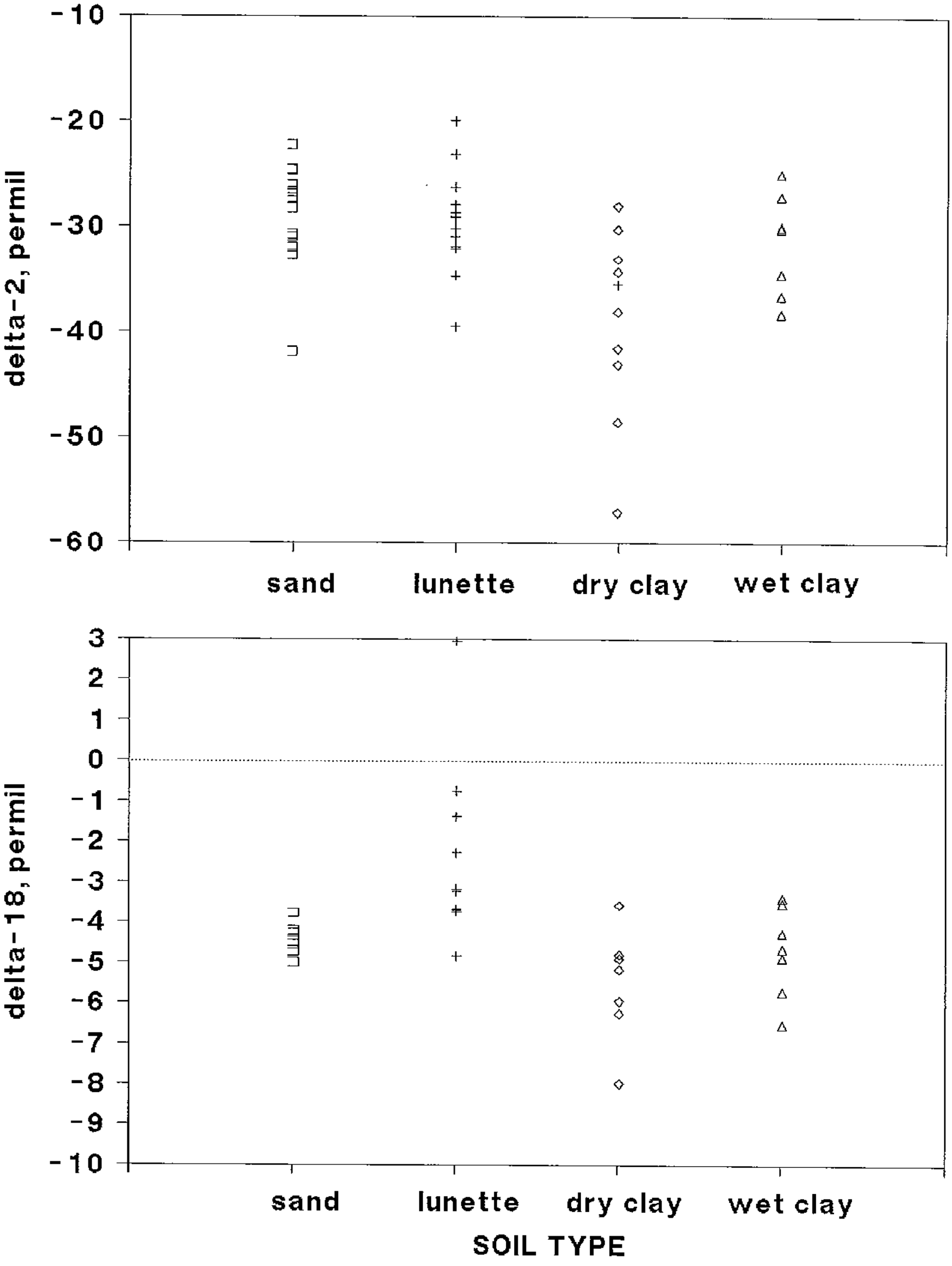

FIGURE 3.3.1 Results of Interlaboratory Comparison of Methods to Determine the Isotopic Composition of Soil Water, by Sample Type, to Dec. 1989

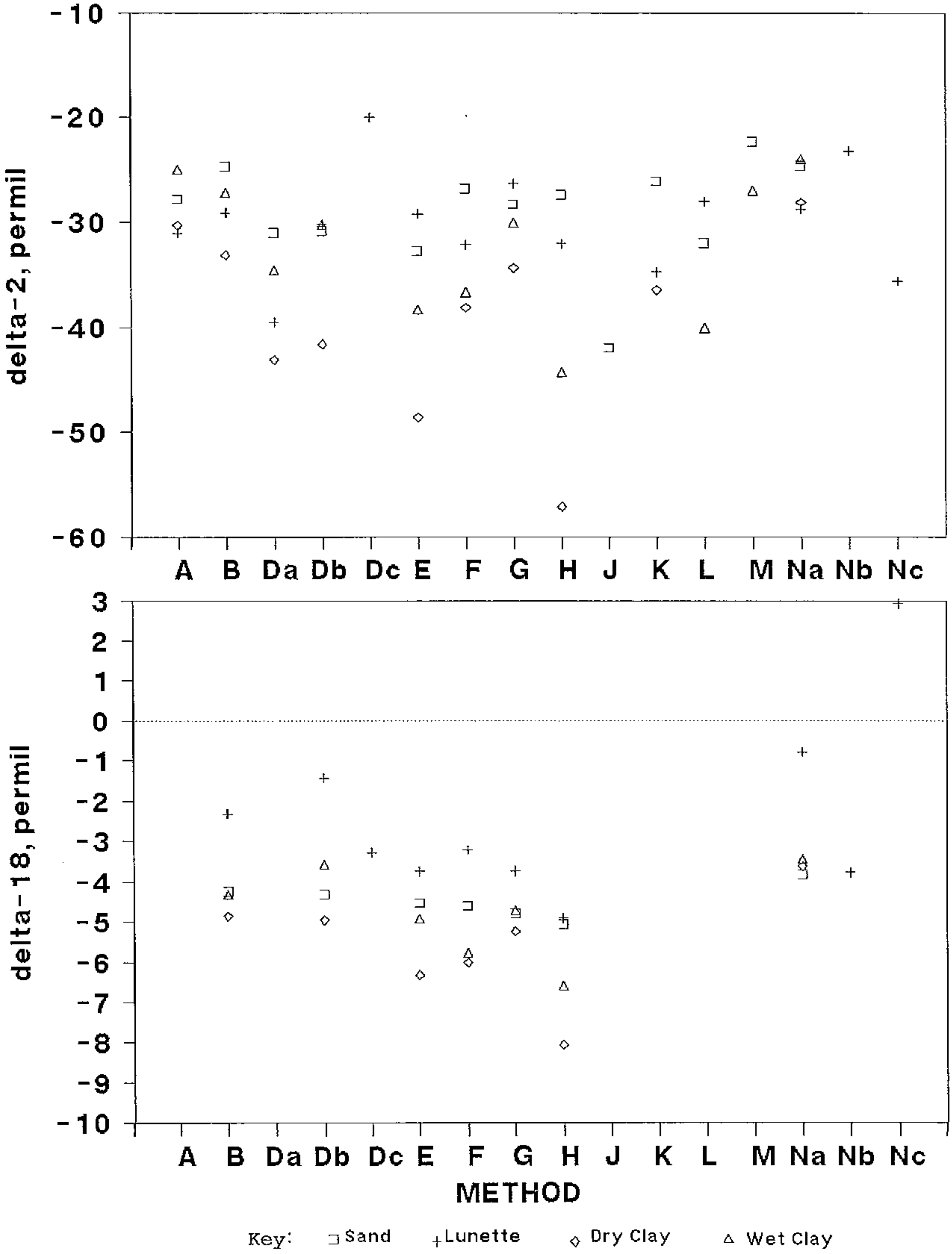

FIGURE 3.3.2 Results of Interlaboratory Comparison of Methods to Determine the Isotopic Composition of Soil Water, by Method. to Dec. 1989

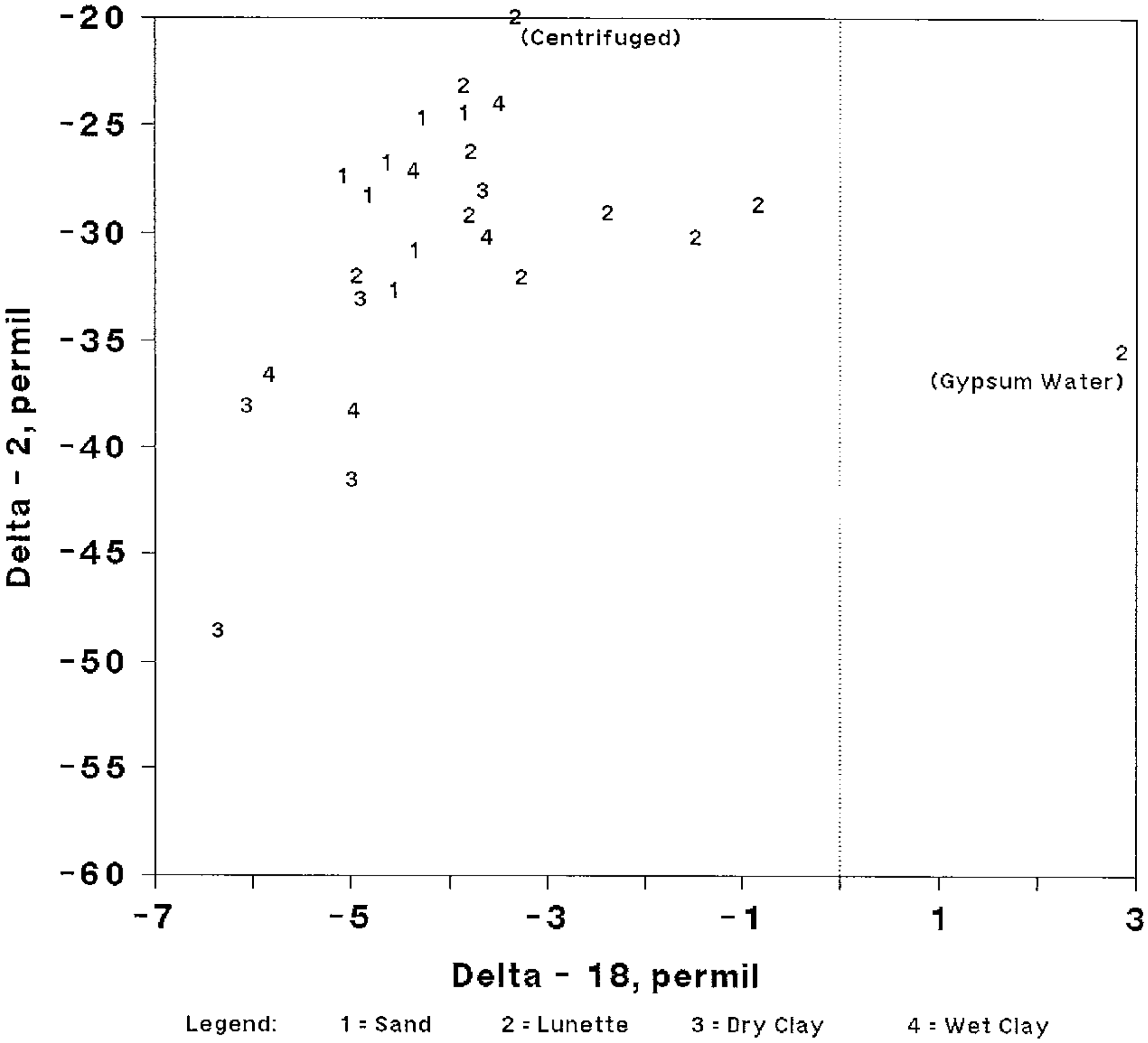

FIGURE 3.3.3 Results of Interlaboratory Comparison of Methods to Determine the Isotopic Composition of Soil Water. O-18 - D plot, to Dec. 1989

of pore and crystal water from a gypseous medium. The results for extraction from the gypeous soil using vacuum distillation and azeotropic distillation (except with hexane) give consistent results for δD, and the yields reported by various workers (0.143 to 0.176) indicate of extraction of both waters, as the (pore) water content was 0.102. The most representative sample of pore water is expected to be that obtained by centrifugation, and the best sample of gypsum water alone that obtained by azeotropic distillation with kerosene after hexane (see section 3.2.6). These form end members of the set, with the other results in between. Taking the end members as correct, the expected composition of a mixture of pore and gypsum waters would be

$$\delta(\text{both}) = (\delta(\text{pore}) \times \theta_g + \delta(\text{gypsum}) \times G) / (\theta_g + G) \qquad (3.13)$$

where G is the water contained in the gypsum per unit mass of soil. At 35% gypsum content, $G = 0.35 \times 0.205 = 0.123$, (0.205 being the water content of pure gypsum) so that δ(both) = – 28.5‰, close to the observed values. Azeotropic distillation with hexane gave a value closest to that determined by centrifugation, with the 3‰ lighter bias discussed in section 3.2.2.

The oxygen-18 results for the gypseous soils are not as easy to explain. The value for crystal water is quite distinct, but several methods obtain a $\delta^{18}O$ close to the centrifugation value. The expected mixture would have a composition of +0.11‰, and reported values lie between this and the centrifugation value or beyond. This inconsistency is also apparent on the $\delta^{18}O$–δD plot (Fig. 3.3.3).

Results for the clayey soil at "low" and "high" water contents show a large scatter about different means, with ranges of 29 and 20‰ for δD and 4.4 and 3.1‰ for $\delta^{18}O$ respectively. Results fall about a line of approximate slope 8 on the $\delta^{18}O$-δD plots (Fig. 3.3.3), suggesting various extraction efficiencies in a Rayleigh-like distillation process. Extractions at higher temperatures (vacuum at 150°C and azeotropic distillations not using hexane) tend to give the heavier results, and vacuum distillation at lower temperatures lighter results. The result obtained at the lowest temperature are not the isotopically lightest of the full set of results however, suggesting other factors such as the length of time the collection is performed over (which affects yield), or the presence of leaks, may also be important.

3.3.5 CONCLUSIONS

Each of the techniques involved in this intercomparison has its own advantages and drawbacks. Azeotropic distillation is fast, but the sample is rendered useless for many further analyses. Its distillate may be fractionated by incomplete collection (light result) or escape of some vapour out of the condenser (heavy result), as well as occasional spill-overs. Also, trace hydrocarbon in the distillate even after treatment with wax appears to be a problem in some mass spectrometers (Hobbs, 1988). While the use of hexane, with boiling time restricted to two to three hours, removes pore and not crystal water from gypseous samples, the result is biased (section 3.2.2).

Vacuum distillation is slow, but the dried sample may be used for other analyses. The system must be free from leaks for (often) unattended periods of several hours, and the result appears to be very sensitive to incomplete yields. The sample must be at least gently heated to avoid this, room temperature extractions by the author gave good results only for clean sand, but not for naturally occurring soils (section 3.2.4).