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THE SOIL HEAT OF HYDRATION MEASUREMENT

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Key words: bound soil water, soil property measurement

Abstract

A new soil physical property is identified, the Soil Heat of Hydration (Soil HoH), and a method for its measurement is described and evaluated. The method represents a calorimetric measurement of the energy released on the addition of water to dry soil. Measurement of the incremental change in Soil HoH with incremental drying of soil is used to estimate the amount of bound water in soil and the level of energy release from water associated with this binding.

Introduction

This paper identifies a new physical measurement on soils, the Soil Heat of Hydration (Soil HoH), that is associated with the adsorption of water on soil materials such as clay and organic matter. Soil HoH is determined by calorimetric measurement of the energy released on the addition of water to dry soil. The energy release is calculated from the changes in temperatures and the weights and specific heats of the water and soil.

The level of energy release per unit of water associated with Soil HoH can be determined from the marginal change in Soil HoH with the incremental drying of a dry soil. The amount of bound soil water can be calculated from the Soil HoH and the energy release per unit of water.

Soil HoH differs from Cation Exchange Capacity (CEC) in the nature of the bonds and possibly also their location on clay minerals. Standards and instruments exist for determining the heat of hydration of concrete but the chemical reaction is different from Soil HoH.

A cost effective and practical method for routinely measuring Soil HoH is described and evaluated. This is used to estimate the energy release per unit of water and the bound soil water content.

Methods & Results

The method is designed to be simple and cost-effective and addresses potential errors. The following factors are addressed.

Temperature Probe: Temperature resolution, Response time, Probe thermal capacity (Cp), Spatial averaging.

Soil Sample Preparation: Soil drying, Temperature equilibration, Soil specific heat (Cs)).

Water Preparation: Water quality, Salinity of water.

Temperature Measurements: Soil-Water ratio, Dry soil temperature, Water temperature, Equilibrium temperature of the soil-water mixture.

HoH Calculation: Calculation of HoH from the temperature changes, Assessment of errors.

Temperature Probes

Several configurations of temperature probe were investigated. The main probe used was constructed with two micro-bead 50K NTC thermistors linked in series and glued with epoxy resin in a channel formed in brass shim 0.2mm thick and 40 long and 20mm wide (Fig.1). The 'paddle' containing the thermistors was silver soldered to a stainless steel tube 3.5 mm in diameter and 100mm long. The construction was designed to provide good spatial averaging while minimising thermal capacity and inertia.

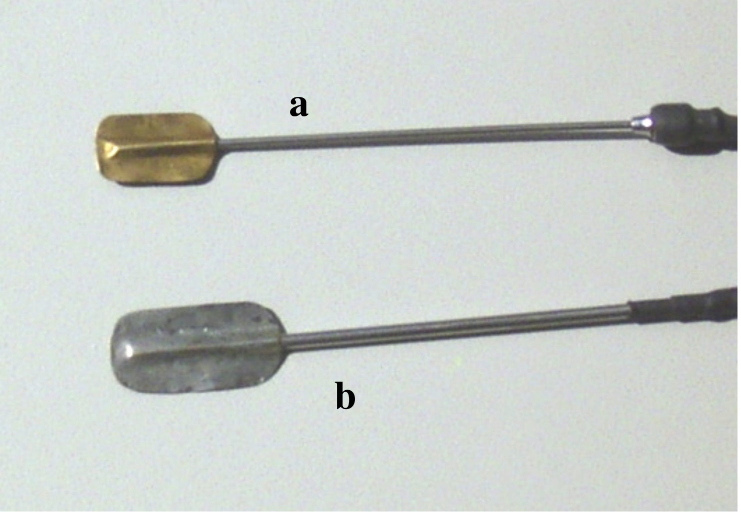

Fig. 1 Photo of temperature measurement probes

The temperature probes were calibrated to an accuracy better than 1 degree and the R^2 for all calibrations was better than 0.998. The resolution was 0.02C at 25C. The response time in water was 15 seconds.

The thermal capacity of the probes was determined by placing them in a known quantity of water at higher temperature than the initial temperature of the probe. The thermal capacity of the probe was determined from the initial temperatures of the probe and water and the equilibrium temperature. The thermal capacity was 4.8 J/C for the above probe.

Soil Sample Preparation

Factors addressed were the type of soil material, particle size, sample size, sample moisture and soil specific heat. The general characteristics of the soil material analysed are given in Table 1. The red and grey clay samples were obtained from boreholes. The humus represented the layer above the mineral soil where the leaf litter had broken down but was not fully decomposed.

Table 1. Characteristics of the soils analysed.

RA	Red Clay A1	Medium heavy-clay, appreciable organic matter.
RA2	Red Clay A2	Medium-heavy clay, low organic matter
RB	Red Clay B2	Heavy clay, effectively zero organic mater.
GA	Grey Clay A1	Medium heavy clay, appreciable organic matter
GB	Grey Clay B2	Medium heavy clay, no organic matter or structure
Hu	Humus	Humic soil layer developed from acacias
Sa	Sand	Washed river sand

Soil Particle Size

The particle size for clay and humus did not affect the Soil HoH measurement within the range of sieving and the sensitivity of the measurement (Table 2). This is to be expected provided the coarser particles represent aggregations of the finer material and the water mixes completely. However, coarser particles provide greater insulation than fine particles and this increases the difficulty of measuring the dry soil temperature. The standard adopted was passing a 2mm sieve.

Soil Sample Size

The sample size should be sufficient to limit potential errors arising from thermal losses to the surrounds and to buffer against the thermal capacity of the probe. However, large samples are undesirable for sample preparation and for obtaining an average temperature measurement. The sample size was varied depending on the nature and availability of material but 60g of soil was generally used for soils with low HoH and 50g for soils with high HoH. A 20g humus sample was found to be most efficient and consistent.

Table 2. Soil HoH (J/g) for different size fractions of different soils.

	Soil		
Particle Fraction	**RA**	**Hu**	**Sand**
Coarse	8.35	21.08	0.60
Medium	8.15	27.09	0.75
Fine	8.40	24.68	0.70

Soil Moisture Content

A strong effect of the initial sample moisture content on the measured Soil HoH is illustrated by results for humus (Fig. 2). The drained upper limit (DUL) for the moisture content of the humus was 133%.

Initial measurements were conducted on sun dried samples to avoid the possible occurrence of erroneous results through sample preparation. Sun dried soils reached temperatures just over 50C and this can arise naturally for surface soils. As the sun drying produced high variability the standard used was oven drying at 105°C.

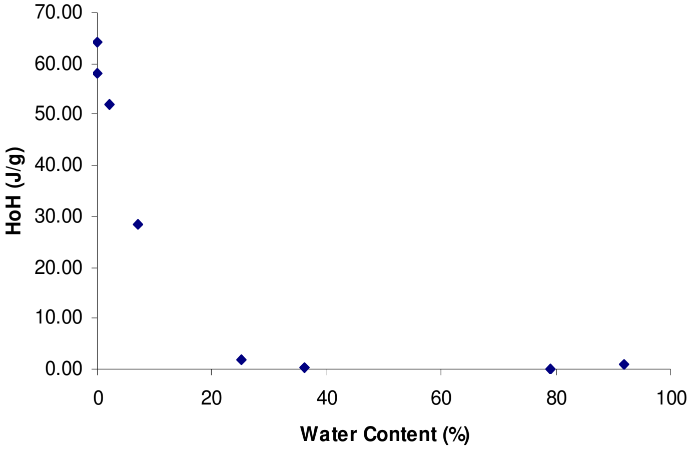

Fig. 2 HoH for humus across a range of water contents.

Soil Specific Heat

Specific heat is used to calculate the energy change associated with a temperature change. The specific heat of sand was estimated from the equilibrium temperature when mixing equal quantities of sand and water at different initial temperatures taking the HoH of the sand into account. The specific heat of soils was similarly determined but by mixing the soil with dry sand rather than water. The specific heat of the soil (Cs) can be calculated from the equilibrium temperature provided the specific heat of the sand is known according to:

$$Cs = (Tw - Te) * Cf * Wf / (Te - Ts) * Ws \qquad (1)$$

Cs	soil specific heat (J/g .K)
Tw	initial temperature of water or sand (C)
Ts	initial temperature of soil (C)
Te	equilibrium temperature of mixed water and soil (C)
Cf	specific heat of water or sand (J/g .K)
Cs	specific heat of soil (J/g .K)
Wf	weight of water or sand (g)
Ws	weight of soil (g)

The steps in estimating the specific heat of sand using water were:

- Estimating the HoH of the sand using water at the same initial temperature as the sand assuming a specific heat for sand of 1J/g.K.
- Estimating of the specific heat of sand by determining the equilibrium temperature following addition of water around 10C warmer or cooler than the soil using the initial estimate of the sand HoH.

- Iterative recalculation of the Soil HoH with the revised specific heat, and then the specific heat using the revised estimate of the Soil HoH.

Different mixing routines were investigated. One involved no mixing and just sufficient water to wet the sand. The mixing regime adopted increased the temperature of the wet sand by 0.1C.

The measurements of the specific heat of the sand averaged 0.96 J/g.K (quartz sand is generally assigned a specific heat around 0.74 J/g.K). The specific heat determinations for soil (Table 3) are similar for all mineral soils, ranging from 1.04 to 1.16 J/g.K. The specific heat of humus is appreciably higher at 1.65 J/g.K.

Table 3. Specific heat measurements for soils determined by mixing with dry sand (J/g.K).

	Average	**Individual Measurements**
GA	1.16	1.25, 1.10, 1.14, 1.14
GB	1.04	1.05, 1.12, 1.02, 0.95
RA	1.12	1.12,1.10, 1.13, 1.11
RA2	1.06	1.02, 1.02. 1.11, 1.09
RB	1.10	1.19, 1.19, 1.03, 0.99
Hu	1.65	1.74, 1.62, 1.54, 1.69
Saline Clay	1.20	1.21, 1.19

Water Quality

Possible effects of water quality on the Soil HoH measurement were investigated by using water from diverse sources and different salinities (Table 4). The conditioned water derived from a commercial system that reduces the size of the clusters of molecules in liquid water. Initial observations on all soils indicated no significant effect of water quality. The same result also arose with more detailed measurements on the RA1 soil despite the use of a high 5M salt concentration (Table 4). Tap water was used unless otherwise specified.

Table 4. Average HoH (J/g) for the RA2 soil for different water sources (3 replicates).

Water Treatment	**Mean**	**SE**
Tap	5.93	0.180
Deionised	6.10	0.185
Distilled	5.88	0.201
Conditioned	5.63	0.110
Spring	5.42	0.556
Microwaved	6.09	0.344
1M NaCl	6.00	0.367
2M NaCl	5.72	0.366
5M NaCl	5.62	0.299

Measurement Methods

Initial observations on sand and humus indicated that variability in the measurement could arise from sample mixing with the magnitude of the frictional heat depending on the nature of the material and the level of mixing. Sand produced the greatest temperature increase with mixing, either wet or dry. Shaking produced more heat than when using a tumbling action to mix dry samples. The procedure employed involved comprehensive mixing of the dry sample prior to temperature measurement and minimal mixing thereafter.

Soil – Water Ratio

The Soil HoH was constant over a wide range of ratios of soil to added water for all mineral soils. Humus performed similarly at low soil:water ratios but samples at 1:1 provided a lower HoH than with a 1:2 soil:water ratio. The drained upper limit for the humus was 133% hence the soil:water ratio does not significantly influence the HoH measurement provided sufficient water is added to saturate the sample. The wetting characteristics of mineral soils make the achievement of complete wetting readily apparent but this does not arise with humus.

A minimum amount of water was initially used to maximise the temperature increase. However, to facilitate mixing the amount of added water was adjusted to provide a more fluid mixture (slurry). The ratio of soil to water generally used was 1:1.43 for soils with a HoH below 10 J/g and 1:2 for others.

Dry Soil Temperature Measurement

Bulk oven dry samples were stored in sealed containers. Samples for measurement were weighed and placed in zip-top plastic bags, generally 80 mm wide and 120 mm deep, and equilibrated at room temperature. Prior to temperature measurement the samples were thoroughly mixed by tumbling, facilitated by entrapping a large volume of air when sealing the bag. The bag was then placed in a polystyrene cup to provide thermal insulation.

The probe temperature was established to be close to the expected soil temperature prior to measurement. The sample was laid horizontally and the probe placed centrally in the soil with an appreciable length of the probe stem being covered by soil. The probe was repositioned at least once, either by rotating the container or by shifting the probe. Relocation was continued until the temperature change between readings was positive and less than 0.1C.

Water Temperature Measurement

The water temperature measurement is straight forward due to the high specific heat and thermal conductivity of water. The measurement was obtained when stirring the water with the probe immediately before addition to the soil to ensure identical probe and water temperatures.

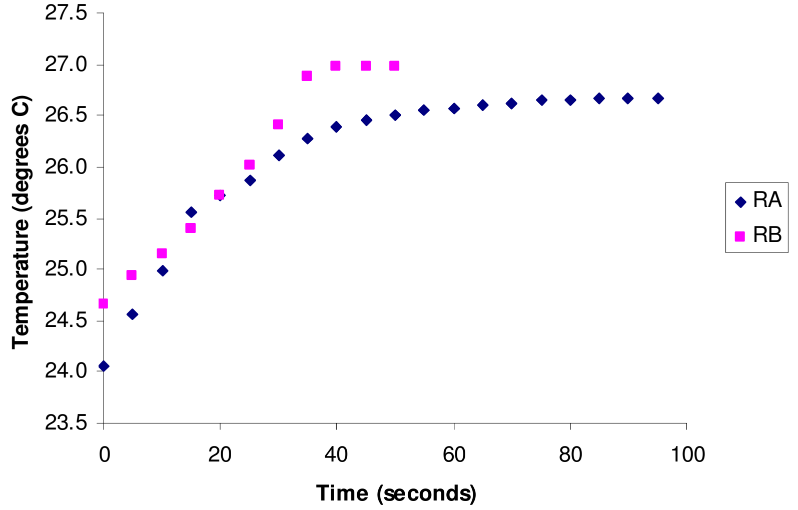

Fig. 3a Temperature response curves for RA and RB soils obtained without mixing.

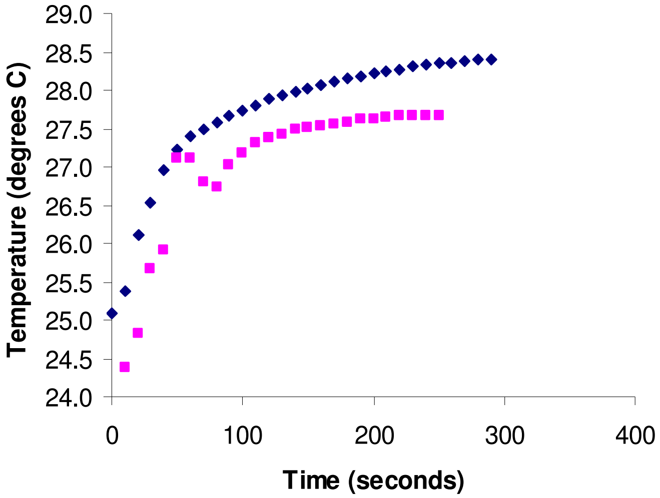

Fig. 3b Temperature response curves for humus soils obtained with and without mixing. The smooth curve is unmixed.

Mixed (equilibrated) Temperature Measurement

An initial mixing was used too ensure rapid distribution of water through the dry soil. The type and level of mixing depended on the nature of the soil.

- Dry humus initially repels water and initial gentle mixing with the probe is used to ensure uniform distribution of water.
- Water generally distributes quickly throughout well structured, non-hydrophobic soils without mixing.
- Fine textured subsoils generally need mixing to allow penetration of water through the sample.

The initial mixing of clays involved upward displacement of centre of the plastic bag. The centre of the bag was then forced down with the probe and the mixture gently stirred. A second mixing was used after the initial temperature stabilization (45 to 60 seconds with other than humus) to ensure uniform mixing. Gentle and minimal mixing with the probe was used to produce a uniform slurry as the friction produces heat. The equilibrated temperature was confirmed by repositioning the probe in the sample.

The response rate for the clay soils is rapid but soils containing humus take appreciably longer to equilibrate (Fig 3a). Clay subsoils equilibrate within one minute while surface soils containing humus may take over two minutes to reach a maximum. Mixing can increase the response rate and hence decrease the measurement time (Fig. 3b).

HoH Calculation

The HoH is most simply calculated by summing the energy difference between the wet and dry soil, and the added water pre and post mixing. The energy change is given by the weight and specific heat of the sample and the magnitude of the temperature change. For the soil it is:

$$Hs = Ws * Cs * dTs \qquad (2)$$

Hs	energy change in the soil (J)
Ws	weight of soil (g)
Cs	specific heat of soil (J/g.K)
dTs	Difference between the dry soil and equilibrium mixed temperatures (C)

The energy change for the water is:

$$Hw = Ww * Cw * dTw \qquad (3)$$

Hw	energy change in the water (J)
Ww	weight of water (g)
Cw	specific heat of water (J/g ^{o}C) (1.487 J/g.K)
dTw	Difference between the dry soil and equilibrium mixed temperatures (C)

Additional factors that can affect the estimate of HoH include:

- The thermal capacity of the temperature probe (Cp, J/K).
- The thermal capacity of the plastic bag (Cb, J/K).

The change in energy associated with heating of the temperature probe, (Hp) is:

$$Hp = dTw * Cp \qquad (4)$$

The change in energy associated with heating of the plastic bag, (Hb, J) is:

$$Hb = dTs * Wb * Cb \qquad (5)$$

Wb	effective weight of the plastic bag
Cb	specific heat of polythene

The effective weight of the plastic bag was determined from the area of the bag in contact with the sample. For the plastic bags and sample sizes used it was around 0.4g.

The total energy change, dH, is the sum of Hw, Hs, Hp and Hb. The HoH (J/g) for the soil sample is dH divided by the weight of soil:

$$HoH = (Hw + Hs + Hp + Hb) / Ws \qquad (6)$$

The relationship between HoH and the temperature change is linear but the magnitude of the temperature change depends on ratio of soil to water as well as the HoH of the material. Most temperature increases were between 1 and 3C but for humus could be larger than 6C.

Magnitude of Errors

The magnitude of errors depends on the ratio of soil to water and the magnitude of temperature change. The potential error estimates given here represent calculations based on given levels of measurement error for temperatures, weights and specific heats. The realised errors derive from statistical estimates associated with replicate measurements.

Potential Error Levels

The estimate of HoH is higher for an anomalously high equilibrium temperature measurement but lower for erroneously high values for dry soil and added water. The accuracy of the dry soil measurement has least effect on the estimate of HoH, and the equilibrium temperature the greatest due to the thermal capacities. For clay soils the temperature measurement should be accurate to within 0.1C for the error in HoH to be less than 3%.

An error of 0.1 J/g.K in the specific heat estimate gives an error of 2.5% in the estimate of HoH for the soil:water ratios used for mineral soils. The error for humus with the same absolute error in specific heat is lower at 1% due to the lower ratio of material to water.

An error of 5% in estimating the weight of water produces a 3% error in the estimate of HoH. With volumetric measurement of water this error should be less than 1%. It would be negligible with gravimetric measurement of the added water. Errors arising through determination of soil dry weight are negligible when the weight is determined to 0.1g.

The error associated with the thermal capacity of the probe is potentially large but is negligible when the thermal capacity is incorporated in the calculation of HoH.

Realised Error Levels

The standard errors for duplicate observations are typically between 0.2 and 0.5 J/g for mineral soils and around 1.2 for humus respectively (Table 5). These statistics include results obtained with sun dried soils early in the development of the method and therefore contain higher variance than can be routinely achieved. As the variance differs between soil types these values are only indicative.

The statistical evaluations of accuracy incorporate variation between replicate samples as well as measurement errors. It was apparent during measurement that many replicate samples performed differently hence much of the statistical error need not be measurement error.

Measurements on a saline clay provide an indication of the relative magnitude of the measurement error and sample variability. Measurement at its field salinity provided a range of 2 J/g for average HoH values of 7.7 and 15.9 J/g for sun and oven dried samples respectively (Table 6). Measurement for samples where salt had been leached from the soil using a 1:5 soil:water ratio provided an absolute difference between samples of 0.6 (+-0.3)for an average HoH around 24 J/g for oven dried samples.

Table 5. Variability in the measurements of soil HoH (J/g) for soils across all 'treatments'. The standard errors were calculated using analysis of variance and are mainly based on duplicate observations.

Soil	Mean	Mean SE	Min. SE	Max. SE	n
GA	9.8	0.30	0.01	0.80	52
GB	2.4	0.17	0.05	0.38	60
RA	8.9	0.51	0.20	1.47	60
RA2	6.1	0.22	0.07	0.61	52
RB	4.7	0.21	0.05	1.10	88
Hu	25.8	1.16	0.13	3.4	126

The error for thoroughly homogeneous samples is around +-0.3 J/g and is independent of the magnitude of the HoH. The magnitude of this measurement error is less than the difference between most replicate samples and so is not limiting for practical application. In practice the realised magnitude of the error depends on the magnitude of the HoH (Table 5) as most of the variation is due to variation between the replicate samples.

Table 6. HoH (J/g) determinations for naturally saline clay subject to different levels of leaching of salt by water.

Leaching Ratio	EC (mS/cm)	% salt	HoH values	Mean HoH
0 (air)	9.39	4.7	8.9, 6.9, 7.3	7.7
0 (oven)	9.39	4.7	15.9, 16.5, 15.2	15.9
1:5		1.19	24.1, 24.7	24.3
1:5		1.19	23.5, 24.0	23.8

Energy Released from Water with Soil HoH

Knowledge of the energy release per unit of water associated and the Soil HoH allows calculation of the amount of water adsorbed to the soil. This strongly adsorbed water is generally referred to as the bound soil water fraction.

The energy released per unit of water (Hw) was calculated from the marginal increase in HoH with incremental drying. Application of this calculation invokes the assumptions that:

- All water associated with the incremental change in soil water content contributes to the HoH.
- The higher temperatures used to achieve additional drying do not structurally or chemically alter the soil.

The marginal increase in HoH with incremental drying of dry soil was determined by redrying the reference soil material at 150C when it had previously been dried at 105C. Additionally, humus samples were dried at temperatures ranging between 105 and 150, and samples of the GA soil were dried at increasing incremental temperatures to 250C. Four replicates were used for the reference (105C) samples, and duplicates for samples dried at higher temperatures. The HoH calculation used the driest samples as the reference and took account of the thermal capacity of residual water in soil samples dried at lower temperatures.

Humus showed the greatest change in moisture, the GA soil with high organic content was next, and clay subsoils were least. Most samples heated above 150°C were excluded due their low incremental HoH. The highest heating caused obvious loss of organic matter (burning), but there was no such apparent damage in two samples heated between 200 and 250°C.

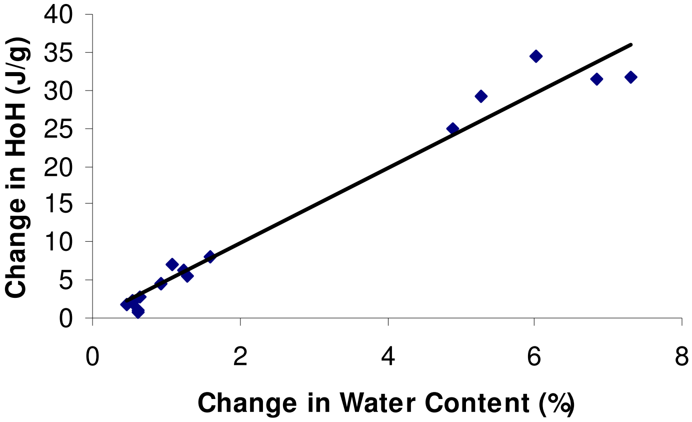

Fig. 4 Change in HoH with change in the water content of oven dried soils. Combined results for mineral soils and humus.

Fig. 4 compares the change in HoH with change in water content. The regression is strong and passes through zero. It indicates that the energy release from water associated with HoH is around 500 J/g (the energy is 100 times that for a 1% moisture change as given by the slope of the regression).

The strength of the regression in Fig. 4 is largely due to the clustering of points at each end of the line. Consideration of results for the mineral soils only, with three outliers removed, produces a similar result but with a higher slope (greater energy release), and the intercept being slightly but significantly different from zero (Table 7). This regression indicates that the energy released from the water is around 547 J/g.

The most comparable measure from the literature relates to the enthalpy of vaporisation which characterises the energy change associated with the phase transition of water from liquid to vapour. This value is given as being 544J/g. The release of energy associated with Soil HoH could derive from the dissociation of hydrogen bonds between water molecules but this does not take account of any energy change associated with the binding of water to the surface of clay and organic matter.

The amount of water that is tightly bound to soil is logically the water that contributes to the Soil HoH. This estimate of bound soil water is given by the Soil HoH divided by the energy released per gram of water. With this procedure active clay with a HoH of 30 J/g is estimated to have 5.5% moisture tightly bound to the clay.

Table 7. Linear regressions relating the incremental change in HoH (J/g) with incremental drying (ΔW as a %). The intercept for mineral soils differs significantly from zero.

	Equation	R^2	SE (m)	Intercept	N
All results	$Hw = 5.01 . \Delta W - 0.339$	0.971	0.215		17
Mineral Soils	$Hw = 5.47 . \Delta W - 0.737$	0.980	0.292	*	9

Conclusions

The Soil Heat of Hydration (Soil HoH) represents the energy release on the addition of water to a dry soil. The energy appears to derive from the dissociation of hydrogen bonds between water molecules. Knowledge of the energy release per unit or water allows calculation of the bound soil water content from Soil HoH.

The determination of Soil HoH depends most critically on:

- The level of drying of the soil.
- The accuracy of temperature measurements.

The Soil HoH measurement does not depend on:

- The soil particle size.
- Provided the soil becomes saturated, the volume of added water.
- The quality or salinity of the added water.

Calculation of Soil HoH should take account of:

- The ratio of soil to water.
- The specific heat of the soil.

- The initial soil and water temperatures.
- The temperature after mixing the soil and water.
- The thermal capacity of the probe

The practicalities of conducting the measurement are:

- Dry soil temperatures are most difficult to determine.
- Wet soil temperatures are most reliably measured when the mixture forms a slurry.
- Identical initial temperatures of the soil and water are not required but the measurement is most readily conducted with the soil and water equilibrated in a stable temperature environment.

The main issues with standardisation of the measurement are:

- Ensuring the soil samples are consistently and uniformly dried.
- Minimising the mixing of samples during measurement.

The main potential sources of measurement error are:

- Variable drying of samples.
- Error in measuring the dry soil temperature.
- Error in measuring the equilibrated temperature.
- Error in the value used for soil specific heat.

Despite the multiple potential sources of measurement error, the errors associated with the measurement method are less than the variations between replicate samples. The variations between replicate samples appear to be primarily due to variations in the composition of the samples.

In batch modes each Soil HoH measurements takes around three minutes hence most time is spent in sample preparation. The measurement procedure is reasonably quick and reliable and hence is suitable for routine use. Applications of the Soil HoH measurement are addressed elsewhere.

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