

cessity for a greater number of samples. Present results indicate that NIRS is a nondestructive technique capable of predicting total C and N concentrations in soil size fractions and that improvements to increase the applicability of the method are possible.

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## PROBE FOR MEASURING SOIL SPECIFIC HEAT USING A HEAT-PULSE METHOD

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### Abstract

Temperature rise, measured a short distance from a line heat source, can be used to determine the volumetric specific heat of soil and other materials. Volumetric specific heat is linearly related to the inverse of the temperature rise. The purpose of this note is to describe the construction and performance of a device for measuring specific heat using the line source method. The device was constructed from two hypodermic needles, 0.813 mm in diam. and 28 mm long, and spaced 6 mm apart. One needle contained a heater and the other a thermocouple. The temperature rise from heat pulses given to the heater were measured with the thermocouple. The coefficient of variation (CV) of specific heat on replicate samples was around 1%. Since water is the main variable component of the specific heat in nonswelling soil, changes in water content might be resolved to 0.01 or better in nonswelling soils.

THE SPECIFIC HEAT of the soil is an important parameter for models of soil temperature and heat flow. While calorimetric methods for measuring specific heat are well known (Taylor and Jackson, 1986), they are subject to substantial error (Fritton, 1974). A fast and accurate method is needed for measuring the specific heat of soils and soil constituents. If such a method were available, it might also be used to meas-

ure changes in volumetric water content of nonswelling soils, since changes in water content are primarily responsible for changes in specific heat in such soils.

### Methods

If an instantaneous heat pulse is injected into an infinite medium by a line source, the maximum temperature rise at a distance  $r_m$  from the source is directly related to the quantity of heat liberated at the source, and inversely related to the volumetric specific heat of the medium. A derivation of this relationship is given in the Appendix. Inverting the relationship gives volumetric specific heat as a function of heat input and maximum temperature rise (Eq. [A3]). Equation [A4] in the Appendix shows the maximum radius of influence of the heat pulse to be about  $2.4 r_m$ , thus defining the minimum sample diameter for accurate measurements.

A probe was built using two no. 21 hypodermic needles to provide the information required for the solution of Eq. [A3]. The probe approximates a line source and allows measurement of the temperature rise near the source. Each needle is 28 mm long and 0.813 mm in diam. The metal fittings of the needles were soldered together so that the needles were parallel and spaced 6 mm apart. A heater made from 133 mm of 75- $\mu$ m-diam., enameled Evanohm wire (Wilbur B. Driver, Co., Newark, NJ) (doubled over twice) was pulled into one of the needles, and a thermocouple made from

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Evanohm and constantan wire (same output as Cu-constantan) was pulled into the other. The needles were then filled with epoxy glue. The resistance of the finished heater was 38  $\Omega$ . The resistance per unit length of probe, calculated from the Evanohm resistance, was 1141  $\Omega/m$ .

The heat pulse was generated by applying approximately 10.5 V to the heater for 8 s. This gave a nominal value for  $q$  of 700 J/m [(10.5 V/38  $\Omega$ )<sup>2</sup>  $\times$  1141  $\Omega/m$   $\times$  8 s]. A data logger (Model CR7X, Campbell Scientific, Inc., Logan, UT) controlled the heat pulse, monitored the current through the heater, measured the temperature of the thermocouple, and recorded the average power and the maximum temperature.

The performance of the probe was verified using water immobilized with 2 g agar L<sup>-1</sup>. This small amount of agar was assumed to have a negligible effect on specific heat, but prevented natural convection in the water. The specific heat of water was taken as 4.18 kJ kg<sup>-1</sup> C<sup>-1</sup> and the density as 1 Mg m<sup>-3</sup>.

Specific heat was measured on samples of five soils, three from Eastern Washington, one from Western Washington, and one from Alaska. Clay contents ranged from 14 to 47%. The soil series from which the samples were taken are described as follows:

Royal:	Coarse-loamy, mixed, mesic Xerollic Camborthid from Franklin County, Washington.
Palouse:	Fine-Silty, mixed, mesic Pachic Ultic Haploxeroll from Whitman County, Washington. Samples were taken from both A and B horizons. The B horizon has 47% clay.
Walla Walla:	Coarse-silty, mixed, mesic Typic Haploxeroll from Adams County, Washington.
Volkmar:	Coarse-silty over sandy or sandy-skeletal, mixed Aquic Cryochrept from Delta, AK.
Salkum:	Clayey, kaolinitic, mesic Xeric Haplohumult from Lewis County, Washington.

Soil samples, which were either air dry, or wet to a predetermined water content and mixed, were packed into a cylinder 32 mm in diam. by 40 mm long, with the heat probe at the center. Measurements were taken with the heat probe, and then the soil was weighed and dried at 105 °C for 24 h to determine bulk density and water content. A subsample of the Palouse B horizon was kiln-dried at 500 °C, removing all water, to see what effect water retained in clays at oven dryness (105 °C) has on specific heat.

Equation [A3] is based on the assumption of an infinitely long line heat source of infinitesimally small diameter, placed in an infinite medium and activated by a heat pulse of infinitesimal duration. A numerical model similar to Program 4.2 of Campbell (1985), but with 40 nodes and a 0.8-mm-diam. heated probe at the center, was used to investigate the effects of longer heat-pulse duration and larger heater size on the maximum temperature rise.

## Results and Discussion

The results of the numerical simulations, using heat pulses of 1- to 8-s duration, showed maximum variation of  $\Delta T_m$  with pulse width <0.2% and a variation of time to reach maximum temperature (measured from the center of the pulse) <2%. These variations may have been the result of the numerical approximations rather than a failure of Eq. [A3] for longer pulses. In any case, the error from using an 8-s pulse for heating was considered negligible. The minimum sample diameter, calculated from Eq. [A4], was 29 mm, so the 32-mm sample diameter used for these measurements was considered adequate. Our one-dimensional radial model could not be used to check for

errors from having a noninfinite source and sample length, but the results of measurements, presented later, indicate that our sample length was probably adequate.

Measurements on six samples of agar-immobilized water gave a mean specific heat of 4.00  $\pm$  0.039 MJ m<sup>-3</sup> C<sup>-1</sup>. By changing the  $r_m$  value in Eq. [A3] from 0.006 m to 0.00587 m, the measured specific heat value changed to 4.18 MJ m<sup>-3</sup> C<sup>-1</sup>, the accepted value for water. Since the uncertainty in  $r_m$  is larger than the uncertainty in the specific heat of water, we used 0.00587 m as the actual value for  $r_m$  in subsequent measurements, thus, in effect, calibrating the probe to the specific heat of water. This exercise shows the extreme sensitivity of this method to probe spacing: a 2% uncertainty in  $r_m$  results in a 4% error in specific heat.

Table 1 presents measurements of specific heat on several soil samples. All measurements were made on air-dry samples, and then corrected to oven-dry condition using

$$c_s = \rho c / \rho_b - w c_w \quad [1]$$

where  $c_s$  and  $c_w$  are the specific heats of soil and water, respectively,  $w$  is the air-dry water content of the soil, and  $\rho_b$  is the bulk density of the soil. The average CV is about 1%, or roughly the same as for the water sample. For the soil samples, this variation comes both from uncertainty in  $\rho_b$  and  $w$  measurements, and uncertainty from probe measurements. For the water, all of the variation comes from uncertainty in the probe measurement, but the signal from the probe is much smaller than that for soil, and therefore more subject to effects of noise and drift. From the measurements on water and on dry soil, it appears that the measurement precision of this method is 1% of the reading or better. The measurement accuracy is limited by the accuracy of the measurement of probe spacing. If the spacing is determined by calibration with water, and is not altered by the sample, then accuracy is comparable to precision. Slight changes in  $r_m$ , however, will substantially reduce the accuracy of the measurement.

The values in Table 1 are in agreement with some published values for specific heat. For example, Eckert and Drake (1972) give values of 0.88 kJ kg<sup>-1</sup> C<sup>-1</sup> for clay and concrete, and 0.81 kJ kg<sup>-1</sup> C<sup>-1</sup> for marble. Hodgman (1959) gives values of 0.92 kJ kg<sup>-1</sup> C<sup>-1</sup> for clay and 0.79 kJ kg<sup>-1</sup> C<sup>-1</sup> for quartz. The values given by de Vries (1963), however, are 10 to 15% smaller than those shown in Table 1.

Table 1. Means, standard deviations, and coefficients of variation of specific heat ( $c_s$ ) for mineral soil samples, measured with the dual probe.

Soil	Specific heat*	CV (%)
	kJ kg <sup>-1</sup> C <sup>-1</sup>	%
Royal	0.864 $\pm$ 0.0185	2.1
Palouse	0.876 $\pm$ 0.0073	0.8
Walla Walla	0.876 $\pm$ 0.0118	1.3
Volkmar	0.880 $\pm$ 0.0078	0.9
Salkum	0.900 $\pm$ 0.0054	0.6
Palouse B	0.939 $\pm$ 0.0160	1.7

\* Means of three samples.

The specific-heat values for Volkmar, Palouse, Walla Walla, and Royal soils are all similar, around  $0.87 \text{ kJ kg}^{-1} \text{ C}^{-1}$ . Salkum and Palouse B horizons have more clay than the other soils (23 and 47%, respectively), and have significantly higher specific heats. In order to determine whether these higher specific heats might be the result of moisture being retained by the clay at oven dryness, we kiln dried samples of Palouse B horizon at  $500^\circ \text{C}$  and measured the specific heat of these samples. The mean specific heat of two samples was  $0.86 \text{ kJ kg}^{-1} \text{ C}^{-1}$ , nearly identical to the values for the soils with lower clay content. The increased specific heat of the oven-dry soil with high clay content, therefore, appears to be the result of water retention by the clay rather than a difference in the specific heat of the mineral fraction.

The specific heat of the water remaining in the Palouse B horizon sample at oven dryness was calculated from  $c_w' = (c_{sw} - c_{sd})/w$ , ( $c_{sw}$  and  $c_{sd}$  are specific heats for the oven- and kiln-dry samples, respectively, and  $w$  is the mass of water removed by kiln drying oven-dry soil per unit mass of kiln-dry soil). The specific heat of this water was found to be around  $2 \text{ kJ kg}^{-1} \text{ C}^{-1}$ , or about one-half that of free water.

Figure 1 shows results of measurements with the heat probe in samples of Royal sandy loam, where volumetric specific heat was varied by varying water content and bulk density. Volumetric specific heat was calculated from

$$\rho c = c_w \rho_w \theta + c_s \rho_b \quad [2]$$

where  $\theta$  is the volumetric water content and  $\rho_w$  is the density of water. The specific heat of the soil was taken from Table 1 for the Royal soil.

A least-squares fit of a straight line through the data has a slope of  $1.00 \pm 0.02$ , an intercept of  $-0.04 \text{ MJ m}^{-3} \text{ C}^{-1}$ , an  $r^2$  of 0.984, and a standard error of estimate ( $S_{y,x}$ ) of  $0.066 \text{ MJ m}^{-3} \text{ C}^{-1}$ . Departures from the 1:1 line are random, and result from errors in  $\rho_b$  and  $w$  measurement (variation within the sample) as well as errors in the heat-probe measurement.

One obvious application of the heat probe is the

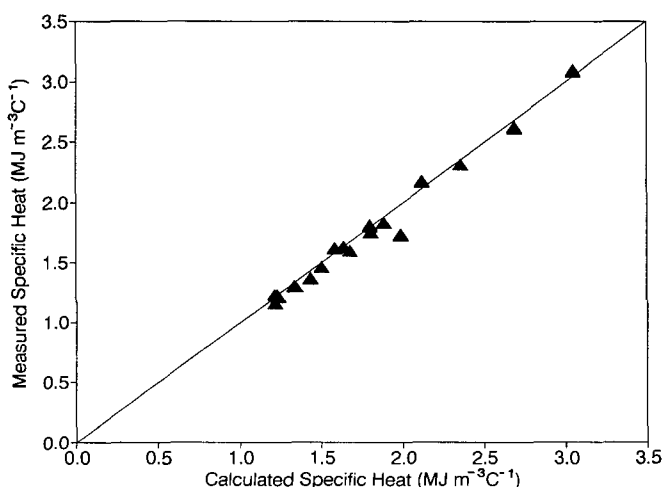


Fig. 1. Measured volumetric specific heat of Royal sandy loam as water content and bulk density vary, as a function of predicted specific heat using Eq. [2].

measurement of  $\theta$ . Solving Eq. [2] for water content gives

$$\theta = (\rho c - \rho_b c_s) / \rho_w c_w \quad [3]$$

Errors in  $\theta$  will result primarily from uncertainties in  $\rho c$  and in  $\rho_b$ . If we assume mid-range values for  $\rho c$  and  $\rho_b$  of  $2 \text{ MJ m}^{-3} \text{ C}^{-1}$  and  $1.3 \text{ Mg m}^{-3}$ , a 1% uncertainty in  $\rho c$  and  $0.1 \text{ Mg m}^{-3}$  uncertainty in  $\rho_b$ , then the uncertainty in water content from the measurement is 0.025 (0.005 from  $\rho c$  and 0.021 from  $\rho_b$ ). If, however, we are only interested in water-content changes (measurements made without changing probe location), and  $\rho_b$  does not change with water content, then the resolution in water content should be around 0.005.

### Appendix

When a finite quantity of heat,  $Q$ , is instantaneously liberated in a line source placed in an infinite medium, the temperature change ( $\Delta T$ ) at a distance  $r$  from the line, at time  $t$  after the instantaneous heat pulse, is given by (Carslaw and Jaeger, 1959, p. 258)

$$\Delta T = \frac{Q}{4\pi\kappa t} \exp(-r^2/4\kappa t) \quad [A1]$$

Here,  $\kappa$  is the thermal diffusivity ( $\text{m}^2 \text{ s}^{-1}$ ) of the medium. Equation [A1] can be differentiated with respect to time to find the time of maximum temperature change at a fixed distance,  $r_m$ , from the line source. This gives  $t_m = r_m^2/4\kappa$ . Substituting this into Eq. [A1] gives the maximum temperature rise ( $\Delta T_m$ ) at distance  $r_m$  as

$$\Delta T_m = Q/e\pi r_m^2 \quad [A2]$$

Information about the specific heat of the medium comes from the fact that the heat input,  $Q$ , used by Carslaw and Jaeger (1959) to obtain Eq. [A1], is the measured heat input to the line source,  $q$  (J/m), divided by the volumetric specific heat of the medium ( $\rho c$ ). Thus,  $q = \rho c Q$ . Substituting this into Eq. [A2] and solving for volumetric specific heat gives

$$\rho c = q/(e\pi r_m^2 \Delta T_m) \quad [A3]$$

Volumetric specific heat is therefore linearly related to the inverse of  $\Delta T_m$ .

The temperature rise at any distance  $r_o$  from the heater at time  $t_m$  is obtained by substituting  $t_m$  into Eq. [A1]. The ratio of this equation to Eq. [A2] gives  $\Delta T_o/\Delta T_m = \exp[1 - (r_o/r_m)^2]$ . We can use this equation to find the distance to the effective outer boundary at  $t_m$ :

$$r_o = r_m [1 - \ln(\Delta T_o/\Delta T_m)]^{1/2} \quad [A4]$$

If we take  $\Delta T_o/\Delta T_m = 0.01$  as the outer boundary, then  $r_o = 2.37 r_m$ .

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