Geoderma 436 (2023) 116526

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Quartz contents derived from particle density measurements improve the accuracy of soil thermal conductivity estimates

Lijie Li [a], Yili Lu [a,*], Tusheng Ren [a], Robert Horton [b]

[a] College of Land Science and Technology, China Agricultural University, Beijing 100193, China
[b] Agronomy Department, Iowa State University, Ames, IA 50011, USA

ARTICLE INFO

Handling Editor: Morgan Cristine L.S.

Keywords:
Quartz content
Particle density
Thermal conductivity
Model
Mineral composition

ABSTRACT

Quartz content (f_{quartz}) is a key value used to estimate soil thermal conductivity (λ) in land surface models. Due to the difficulties in measuring f_{quartz} directly, many studies use sand content (f_{sand}) to approximate f_{quartz} in λ models, causing large uncertainties in λ estimates. The existing methods for determining f_{quartz} are quite limited and complicated, and it is still desired to derive f_{quartz} values with simple parameters. Here, we present an empirical equation to estimate f_{quartz} values from soil particle density (ρ_s). The empirical equation was developed from two published datasets including laboratory measurements on 56 soils, and its performance was evaluated by comparing measured λ values to estimated λ values. Four models were used to estimate λ using inputs of f_{sand}, actual measures of f_{quartz}, and the new empirical equation estimates of f_{quartz}. The root mean square errors, RMSEs, of modeled λ values (based on the empirical equation estimated f_{quartz}) were less than 0.27 W m^{-1} K^{-1}, which were similar to the RMSEs (< 0.26 W m^{-1} K^{-1}) when actual f_{quartz} values were used as model inputs. The new empirical equation estimates of f_{quartz} led to much lower RMSEs in modeled λ values than the RMSEs (< 0.39 W m^{-1} K^{-1}) obtained when f_{sand} values were used to represent quartz content. The new empirical equation provides a simple and easy approach to estimate f_{quartz} as an input to λ models.

1. Introduction

Quartz content (f_{quartz}) is a prerequisite to accurately estimate soil thermal conductivity (λ) and ground heat fluxes (Peters-Lidard et al., 1998; Tarnawski et al., 2021). Because f_{quartz} is not measured in routine soil inventories, it is commonly assumed to be equal to the percentage of sand in soil solids (f_{sand}). While quartz is a predominant primary mineral existing in the sand fraction of deeply weathered soils, it can also exist in the silt and clay particles of some mineral soils (Schönenberger et al., 2012). Therefore, substituting f_{quartz} with f_{sand} can produce erroneous λ results,which has long been identified in λ modeling studies (Bristow, 2002; Lu et al., 2007; He et al., 2020). Mitchell (2002) assigned specific f_{quartz} values for nine soil types ranging from coarse soils to organic soils in the land surface models. Rough approximations of f_{quartz} values, however, have been reported to cause large uncertainties in λ estimations, surface energy balance partitioning and soil temperature predictions (Bristow et al., 1994; Peters-Lidard et al., 1998; Tong et al., 2016; He et al., 2020).

Several techniques (e.g., chemical analysis and the combined analysis of X-ray diffraction (XRD) and X-ray fluorescence (XRF)) have been used to measure f_{quartz} directly. For chemical analysis, soil minerals are treated with acidic and alkaline solutions, and yet quartz remains as the residue (Trostel and Wynne, 1940). Chemically obtained f_{quartz} values are subject to errors because the treatment may not completely separate the quartz from the mineral soils (Trostel and Wynne, 1940). In addition, chemical analysis is judged unreliable in that feldspar and mica (present as minor components) are recorded in part as quartz (Rowse and Jepson, 1972).

The development of XRD and XRF techniques enables quick and nondestructive measurements of mineral compositions. XRD determinations in particular are accurate and fast to identify and quantify the absolute amounts of minerals existing in soils (Hardy, 1992; Schönenberger et al., 2012). The method involves a monochromatic X-ray pointing at a powdered soil sample, and the diffraction pattern is recorded with a photographic film by measuring the diffracted beam at a specific angle (Whittig and Allardice, 1986). The mineral concentration is obtained by adjusting the peak of the angles of glancing diffraction between the X-ray source, detector, and powder slip (Whittig and Allardice, 1986; Schönenberger et al., 2012). To further identify chemical compositions of minerals accurately, the XRF technique works

* Corresponding author.
E-mail address: luyili@cau.edu.cn (Y. Lu).

https://doi.org/10.1016/j.geoderma.2023.116526
Received 28 January 2023; Received in revised form 15 May 2023; Accepted 16 May 2023
Available online 23 May 2023

with secondary and characteristic X-rays, of which the intensity is proportional to the concentration of the chemical element (Schönenberger et al., 2012). Thus, the XRF technique, along with the XRD technique, provide precise information on the mineral composition of multiphase rocks and soil samples. However, special care for mineral sample preparations as well as accurate calibration of the equipment are needed, including correcting angle position and impulse height distribution. Although combined XRD and XRF techniques measure f_{quartz} directly, they are somewhat complicated to apply.

Indirect approaches have also been used to estimate f_{quartz} from easily measurable soil properties. Tarnawski et al. (2009) estimated f_{quartz} values by measuring λ under entire water range and making reverse calculations using the normalized λ models. They found that the estimated f_{quartz} values had fairly good correlations with the measured values, but this approach requires λ values on the entire water content range, which is time consuming. Calvet et al. (2016) proposed a pedotransfer function that estimated f_{quartz} by using gravimetric or volumetric fractions of soil particles as input parameters. They showed that for grassland soils, the ratio of sand-to-OM fraction and the gravimetric fraction of sand were suitable estimators of f_{quartz}. Though this approach was relatively simple to use, the pedotransfer function for f_{quartz} was only valid for the ratio of sand-to-OM fraction lower than 40%, and it had not fully been validated on other soils as well as on λ modelling. Therefore, it is still desired to determine f_{quartz} values using easily measurable parameters.

It is commonly recognized that the mineral composition significantly influences λ values of soil solids, but it is difficult to obtain accurately (Tarnawski et al., 2009). The thermal conductivity of soil solids (λ_{solid}), a required parameter used in normalized λ models, is calculated using a geometric mean method involving f_{quartz}, which is commonly assumed to equal the sand fraction. The, λ_{solid} data can have large errors because quartz has a λ value (7.7 W m^{-1} K^{-1}) almost twice that of other soil minerals (2.13 W m^{-1} K^{-1}). Thus, the knowledge of quartz in soil is vital for accurate λ estimates. Good estimates of λ using the Johansen's method were obtained when using f_{quartz} as an input (Peters-Lidard et al., 1998). For the de Vries (1963) model, much better accuracy was achieved when accurate soil mineral composition and fraction were used for λ_{solid} estimation (Tarnawski et al., 2021). Thus, a quick and efficient way to solve the quartz conundrum is still lacking, and a comprehensive evaluation of λ model performances regarding f_{quartz} is needed.

The objectives of this study are (1) to develop a new empirical equation to estimate f_{quartz} vales from measurements of soil particle density, and (2) to evaluate the usefulness of the estimated f_{quartz} values as λ models inputs to provide accurate estimations of λ.

2. Materials and methods

2.1. Measurements and datasets

We used published datasets reported by Rühlmann et al. (2006), Schönenberger et al. (2012), and Tarnawski et al. (2015) to develop and test a new empirical approach to estimate f_{quartz} values from measured values of particle density. The datasets included comprehensive soil physical measurements with a wide-range of soil textures. Complete information on the soil physical and chemical properties (e.g., particle density (ρ_s), texture, mineral composition, soil organic matter (OM) content, sampling locations, porosity (n), and water content (θ)), are presented in the original articles. Here we provide a brief description.

Soils data reported by Rühlmann et al. (2006) and from Schönenberger et al. (2012) were used to develop an empirical equation to estimate f_{quartz}. For the 17 soils reported by Rühlmann et al. (2006), mineral compositions were obtained by using XRD analysis (diffractometer URD 63, SEIFERT/FMP). For the 39 soils reported by Schönenberger et al. (2012), samples were ground to grain sizes smaller than 150 μm, and oven-dried at 105 °C for 16 h (loss-on-drying, LOD, mass%) to determine the dry weight. Soil OM content was determined by using the loss-on-ignition (LOI, mass%) method in a ceramic vessel at 1050°C more than 1.5 h. Soil OM fraction (mass%, on the basis of dry soil matter) was calculated by subtracting LOD from LOI. Following the LOI measurements, the mineral composition (mass%) of each soil was identified with the XRD and XRF methods. Soil particle size distributions were determined with a laser diffraction particle size analyzer, and the f_{sand}, f_{silt}, and f_{clay} values were determined as mass fractions of the soil solid particles. The ρ_s values were obtained by using the pycnometer method (Culley, 1993).

The λ values of 39 Canadian soils reported by Tarnawski et al. (2015) were used to evaluate the usefulness of the empirical equation estimates of f_{quartz}. A thermal conductivity probe was used to measure room temperature λ values on repacked soil cores at degrees of saturation (S_r) of 0, 0.25, 0.50, 0.70, and 1. The details of the experiment setup and measurement procedures are presented in Tarnawski et al. (2015). We used 39 mineral soils reported by Tarnawski et al. (2015), but excluded the pure quartz sand because the thermal behavior of pure quartz differs distinctively from mineral soils.

Finally, the usefulness of the newly developed empirical equation to estimate f_{quartz} was also evaluated with field measured soil λ values. We performed in-situ λ measurements on a bare loamy sand soil (78% sand, 7% clay, and 0.2% OM) at the Experimental Farm of China Agricultural University in Beijing, China during a 14-d wetting and drying event (from day of year 272 to 285, 2019). To facilitate sensor installation, the soil surface was carefully leveled and kept bare during the entire observation period. A heat pulse sensor was installed horizontally into the 0–50 mm soil layer, and λ measurements were made every 1.5 h. A datalogger (CR3000, Campbell Scientific, Logan, UT) was used to control the heating process and collect heat pulse data, and λ values were estimated from the heat pulse data following the pulsed infinite line source model (Kluitenberg et al., 1993). Following the final λ measurement, soil cores were collected near the sensor locations to determine the actual soil bulk density (ρ_b) and n values. The θ values of the 0–50 mm soil layer were determined from soil heat capacity (C) and ρ_b values according to the de Vries (1963) mixing model. The XRD method was used to determine the f_{quartz} value of the field soil.

Fig. 1 shows the textual triangle for the 56 laboratory soils and the field soil involved in this study. These soils exhibited a wide range of f_{sand} (0–93%) and f_{clay} (1.1%–41.8%) values, which made this dataset appropriate to determine the sensitivity of λ models to sand and quartz fractions.

2.2. Applications in modeling soil thermal conductivity

The ability of the new empirical equation to provide f_{quartz} values useful for estimating λ values was evaluated by the performance of four popular λ models with f_{quartz} as inputs, including the modified-de Vries model and three normalized models developed by Côté and Konrad (2005), Balland and Arp (2005), and Lu et al. (2007). Here we provide a brief description of these λ models.

2.2.1. Modified-de Vries model

The original de Vries (1963) model was developed from the Maxwell equation for electrical conductivity of a mixture of granular materials dispersed in a continuous fluid, which considered air or water as a continuous medium and soil particles as a mixture of ellipsoidal particles. Soil λ is estimated with the following formula,

$$\lambda = \frac{\theta\lambda_w + k_{air}f_{air}\lambda_{air} + k_{solid}f_{solid}\lambda_{solid}}{\theta + k_{air}f_{air} + k_{solid}f_{solid}} \tag{1}$$

where λ_{solid}, λ_{w} and λ_{air} are thermal conductivities of soil solids, water and air, respectively; θ, f_{solid}, and f_{air} are the volume fractions of water, solids, and air, respectively; k_{air} and k_{solid} are the weighting factors of air and soil solids, respectively, which are defined as follows,

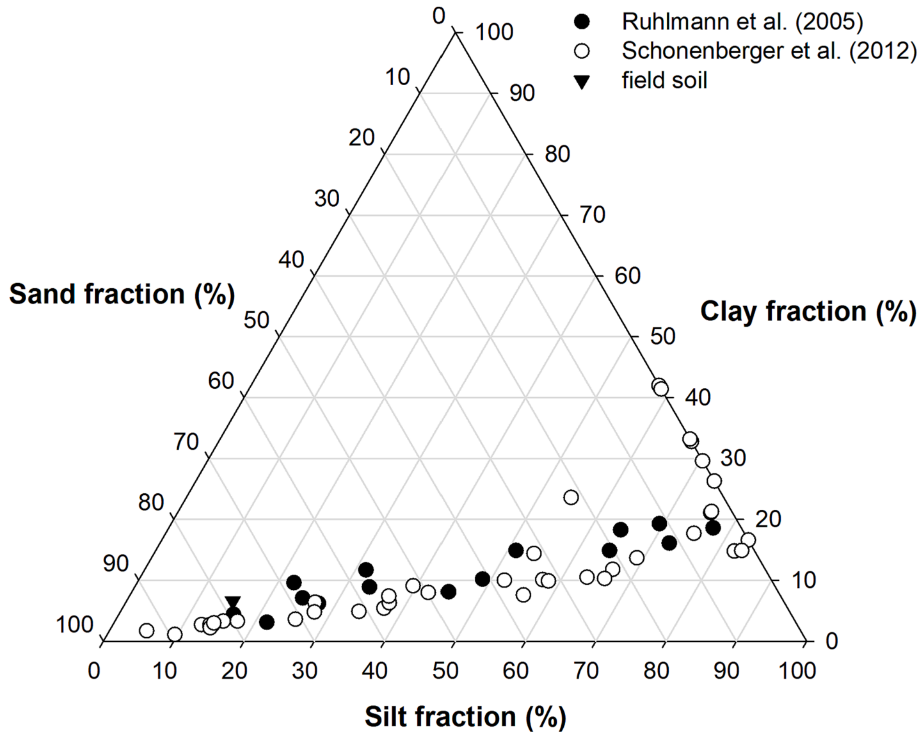

Fig. 1. Soil textural triangle for the 56 soils and one field soil used in this study.

$$k_{solid} = \frac{2}{3}\left[1+\left(\frac{\lambda_{solid}}{\lambda_w}-1\right)g_{a(solid)}\right]^{-1}+\frac{1}{3}\left[1+\left(\frac{\lambda_{solid}}{\lambda_w}-1\right)\left(1-2g_{a(solid)}\right)\right]^{-1} \tag{2}$$

$$k_{air} = \frac{2}{3}\left[1+\left(\frac{\lambda_{air}}{\lambda_w}-1\right)g_{a(air)}\right]^{-1}+\frac{1}{3}\left[1+\left(\frac{\lambda_{air}}{\lambda_w}-1\right)\left(1-2g_{a(air)}\right)\right]^{-1} \tag{3}$$

where $g_{a(solid)}$ is the shape factor of soil solid particles, which is set as 0.144 for sandy grains, and 0.125 for silty and clayey grains; $g_{a(air)}$ is the shape factor of air, which depends on soil moisture conditions. In the modified de Vries model, Tarnaswki et al. (2021) assumed that the soil field capacity was equal to half of the saturated water content as follows.

For $\theta_{FC} < \theta < \theta_{sat}$, $g_{a(air)}$ is computed by using the following equation,

$$g_{a(air)} = 0.333 - (0.333 - 0.035)(\theta_{sat} - \theta)/\theta_{sat} \tag{4}$$

For $0 < \theta < \theta_{FC}$, $g_{a(air)}$ is given by,

$$g_{a(air)} = 0.013 + \left(\frac{\theta}{\theta_{FC}}\right)\left[g_{a(FC)} - 0.013\right] \tag{5}$$

where θ_{sat} is the volumetric soil water content at saturation, which is normally set as being equal to the n; θ_{FC} is the soil field capacity, which is assumed to equal $0.5\theta_{sat}$ (Tarnawski et al., 2021), i.e., $\theta_{FC} \approx 0.5\theta_{sat} \approx 0.5n$; $g_{a(FC)}$ is the $g_{a(air)}$ factor corresponding to the field capacity, which is obtained with Eq. (4) by assigning θ to θ_{FC}.

In Eq. (1), λ_{solid} is calculated as the geometric mean of quartz and other minerals in the soil solids, which can be expressed as,

$$\lambda_{solid} = \lambda_{quartz}^{f_{quartz}}\lambda_{other}^{1-f_{quartz}} \tag{6}$$

where f_{quartz} is the volumetric fraction of quartz in the solid particles; λ_{other} refers to the thermal conductivity of minerals other than quartz, which is 2.0 W m^{-1} K^{-1} for $f_{quartz} > 0.2$ and 3.0 W m^{-1} K^{-1} for $f_{quartz} < 0.2$ (Johansen, 1975).

For dry soils, air is considered as the continuous medium with uniform soil particles distributed in air. Accordingly, to calculate the thermal conductivity of dry soils (λ_{dry}), Eq. (1) is given as,

$$\lambda_{dry} = \frac{f_{air}\lambda_{air} + k_{solid(air)}f_{solid}\lambda_{solid}}{f_{air} + k_{solid(air)}f_{solid}} \tag{7}$$

where $k_{solid(air)}$ is the weighting factor of soil solids in continuous air in this case, which can be calculated as,

$$k_{solid(air)} = \frac{2}{3}\left[1+\left(\frac{\lambda_{solid}}{\lambda_{air}}-1\right)g_{a(solid)}\right]^{-1}+\frac{1}{3}\left[1+\left(\frac{\lambda_{solid}}{\lambda_{air}}-1\right)\left(1-2g_{a(solid)}\right)\right]^{-1} \tag{8}$$

where $g_{a(solid)}$ is set as 0.144 for sandy grains, and 0.125 for silty and clayey solids in the moist soil.

Thus, for the modified-de Vries model, the required inputs are volume fractions of water, air, soil solids, f_{quartz} and n (Table 1).

2.2.2. Côté and Konrad (2005) model

Johansen (1975) presented normalized λ values as a function of soil texture, n, θ, and thermal conductivities at saturated and dry conditions. The normalized thermal conductivity (K_e) is expressed as follows,

$$K_e = \frac{\lambda - \lambda_{dry}}{\lambda_{sat} - \lambda_{dry}} \tag{9}$$

where λ_{sat} is the thermal conductivity of saturated soil.

Côté and Konrad (2005) improved the Johansen (1975) model by

Table 1
The input parameters for the four soil thermal conductivity models involved in this study, where f_{air}, f_{solid}, f_{sand}, f_{quartz}, and f_{OM} represent the volume fractions of soil air, solids, sand, quartz, and organic matter, respectively; θ is the water content; and n is the total soil porosity.

Models	Input parameters
Modified-de Vries	θ, f_{sand} (or f_{quartz}), n, f_{air} (or f_{solid})
Côté and Konrad (2005)	θ, f_{sand} (or f_{quartz}), n
Balland and Arp (2005)	θ, f_{sand} (or f_{quartz}), n, f_{OM}
Lu et al. (2007)	θ, f_{sand} (or f_{quartz}), n

introducing an empirical relation of K_e and degree of saturation (S_r),

$$K_e = \frac{kS_r}{1 + (k-1)S_r} \tag{10}$$

where k is a texture-related parameter, which is set as 4.60, 3.55, 1.90, and 0.60 for gravel and coarse sand, medium and fine sand, silty and clayey soils, and organic fibrous soils, respectively (Côté and Konrad, 2005).

Côté and Konrad (2005) established the following relationship between λ_{dry} and n,

$$\lambda_{dry} = \chi 10^{-\eta n} \tag{11}$$

where χ and η are 1.70 W m^{-1} K^{-1} and 1.80 for crushed rocks, 0.75 W m^{-1} K^{-1} and 1.20 for mineral soils, and 0.30 W m^{-1} K^{-1} and 0.87 for organic fibrous soils.

Johansen (1975) used a geometric mean equation to estimate λ_{sat} for unfrozen soils,

$$\lambda_{sat} = \lambda_{solid}^{1-n}\lambda_w^n \tag{12}$$

2.2.3. Balland and Arp (2005) model

The Balland and Arp (2005) model uses Eqs. (9) and (12) to obtain K_e and λ_{sat}. By including OM as a factor, λ_{solid} and λ_{dry} are reformulated as the following equations,

$$\lambda_{soild} = \lambda_{quartz}^{f_{quartz}}\lambda_{OM}^{f_{OM}}\lambda_{other}^{1-f_{quartz}-f_{OM}} \tag{13}$$

where f_{OM} is the volume fraction of soil OM in solid particles, and λ_{OM} is thermal conductivity of soil OM. It should be noted that in Eq. (13), f_{quartz} and f_{OM} are calculated on the basis of soil solid particles.

Balland and Arp (2005) estimated λ_{dry} by using the following relationship,

$$\lambda_{dry} = \frac{0.053(\lambda_{soild} - \lambda_{air})\rho_b + \lambda_{air}\rho_s}{\rho_s - (1-0.053)\rho_b} \tag{14}$$

They used the following equation to calculate K_e for unfrozen soils,

$$K_e = S_r^{0.5\left(1+f_{OM}-af_{sand}-f_{cf}\right)}\left[\left(\frac{1}{1+\exp(-bS_r)}\right)^3 - \left(\frac{1-S_r}{2}\right)^3\right]^{1-f_{OM}} \tag{15}$$

where f_{cf} represents the volume fraction of coarse fragments. a and b are parameters equal to 0.24 and 18.3, respectively.

2.2.4. Lu et al. (2007) model

The Lu et al. (2007) model has been used widely in soil science, engineering, remote sensing, and hydrology studies (Lu et al., 2009; Ghanbarian and Daigle, 2016; Lu et al., 2018). In this model, λ_{solid}, K_e, and λ_{sat} are calculated by using Eqs. (6), (10), and (12), respectively. The K_e-S_r relationship for moist soils is as follows,

$$K_e = \exp\left\{\varphi\left[1 - S_r^{\varphi-1.33}\right]\right\} \tag{16}$$

where φ is a texture dependent parameter, which is set at 0.96 and 0.27 for coarse-textured ($f_{sand} > 40\%$) and fine-textured ($f_{sand} < 40\%$) soils, respectively.

Lu et al. (2007) used a linear equation to estimate λ_{dry} from n,

$$\lambda_{dry} = -0.56n + 0.51 \tag{17}$$

Table 1 lists the input parameters for the four λ models. θ, n, and sand or quartz fraction are the common factors among the four λ models. These models use slightly different values for the constants λ_{quartz}, λ_{other}, λ_w, λ_{air}, and ρ_s (Table 2). Additionally, the ρ_s values (used to estimate n) vary among the four models: 2.65 Mg m^{-3} in the modified-de Vries model and the Lu et al. (2007) model, 2.70 Mg m^{-3} in the Balland and Arp (2005) model, and soil specific values are used in the Côté and Konrad (2005) model.

Table 2
Values of constants included in the four thermal conductivity models used in this study, where ρ_s is the particle density; λ_{quartz}, λ_{other}, λ_w, λ_{air}, and λ_{OM} are the thermal conductivities of quartz, other soil minerals, water, air, and organic matter, respectively; and f_{quartz} represents the quartz fraction in soil solid particles.

Models	ρ_s	λ_{quartz}	λ_{other}	λ_w	λ_{air}	λ_{OM}
	Mg m^{-3}	W m^{-1} K^{-1}				
Modified-de Vries	2.65	7.7	2.0 ($f_{quartz} > 0.2$) 3.0 ($f_{quartz} < 0.2$)	0.57	0.025	–
Côté and Konrad (2005)	Soil specific	7.7	2.0 ($f_{quartz} > 0.2$) 3.0 ($f_{quartz} < 0.2$)	0.60	–	–
Balland and Arp (2005)	2.70	8.0	2.5	0.57	0.024	0.25
Lu et al. (2007)	2.65	7.7	2.0 ($f_{quartz} > 0.2$) 3.0 ($f_{quartz} < 0.2$)	0.594	–	–

The Balland and Arp (2005) model applies Eq. (13) to estimate λ_{solid} from f_{quartz} (or f_{sand}) and f_{OM} values of the soil solid particles. For this purpose, we corrected f_{quartz} (or f_{sand}) and f_{OM} of the Tarnawski et al. (2015) datasets on the basis of the soil solid particles, i.e., by considering OM as a part of the solid particles. To convert mass% to volume%, the density of soil OM was taken as 1.30 Mg m^{-3}, and ρ_s was taken as 2.65 Mg m^{-3} (Hillel, 1982). The other three models ignored soil OM content, so that the soil solid particles only included sand, silt, and clay particles.

To evaluate the usefulness of the new empirical equation estimates of quartz content, we compared measured λ values to model estimated λ values for three model input scenarios: actual measured f_{quartz} values, f_{quartz} values set equal to f_{sand} values, and new empirical equation estimated f_{quartz}. Besides the various f_{quartz} inputs, all other specifications in model calculations remained the same as described previously. Root mean square errors (RMSE) for the λ estimations were calculated to evaluate the performance of the four models with the various f_{quartz} inputs,

$$RMSE = \sqrt{\frac{\sum(\lambda_m - \lambda_e)^2}{m}} \tag{18}$$

where m is the number of data points, λ_m and λ_e is measured and estimated λ with the models.

3. Results and discussion

3.1. The relationship between soil particle density and quartz content

Although f_{quartz} is typically set equal to f_{sand} as an input to λ models, f_{quartz} and f_{sand} do not always correlate well with each other (Tarnawski et al., 2012). In general, quartz exists in sand, silt, and clay particles but with a relatively larger portion in sand particles (Buckman and Brady, 1969; Balland and Arp, 2005). There is evidence that for soils and sediments, ρ_s depends highly on soil mineral and organic components, and ρ_s can act as a strong indicator for the geochemistry of alluvial sediments (Rühlmann et al., 2006; Di Giuseppe et al., 2016). Generally, ρ_s is a bulk property representing the average density of all solids composing the soil, including soil OM (Ruehlmann and Körschens, 2020). Because quartz is often a dominant mineral in soil, the average ρ_s value for mineral soils is similar to the value for quartz, 2.65 Mg m^{-3}. Rühlmann et al. (2006) observed a negative correlation between ρ_s and f_{sand} when

ρ_s was larger than 2.63 Mg m^{-3}, i.e., ρ_s of mineral soils decreased with increasing f_{sand}. For an alluvial soil, it was found that when OM was removed, ρ_s correlated positively with SiO_2, MgO, CaO, and Na_2O contents, but negatively with K_2O, TiO_2, Al_2O_3, and Fe_2O_3 contents (Di Giuseppe et al., 2016). McBride et al. (2012) showed that for clay-rich mineral soils, ρ_s exhibited a positive linear relationship with clay content, but displayed a negative correlation with OM content for soils with diverse mineralogy.

The previous studies suggest that although quartz is often a dominant soil mineral and an average ρ_s of 2.65 Mg m^{-3} is acceptable for many soils, ρ_s does vary with relative fractions of quartz, OM, and clay minerals: (1) For soils with relatively large OM contents, the ρ_s values tend to be < 2.65 Mg m^{-3}, because the density of OM (1.30 Mg m^{-3}) is only about half that of quartz; (2) For soils with relatively large clay contents, the ρ_s values tend to be > 2.65 Mg m^{-3}, because fine clays usually contain minerals with greater particle densities than that of quartz. Inspired by this information, in Fig. 2 we present ρ_s values versus f_{quartz} values for the 56 soils reported by Rühlmann et al. (2006) and Schönenberger et al. (2012). The ρ_s versus f_{quartz} values segregated into two distinct groups. For the group with ρ_s values larger than 2.63 Mg m^{-3}, ρ_s decreased as f_{quartz} increased; for the group with ρ_s values smaller than 2.63 Mg m^{-3}, ρ_s increased as f_{quartz} increased.

Further analysis showed that there existed two significant linear correlations between f_{quartz} and ρ_s, which can be expressed as,

$$f_{quartz} = \begin{cases} -3.26\rho_s + 9.27 \quad \rho_s > 2.63 \quad R^2 = 0.60^{**} \\ 4.07\rho_s - 9.89 \quad \rho_s \leqslant 2.63 \quad R^2 = 0.84^{**} \end{cases} \tag{19}$$

where R^2 is the coefficient of determination, and the asterisks ** indicate a significance level of 0.01. Here, the dividing density is 2.63 Mg m^{-3}, less than the quartz ρ_s value of 2.65 Mg m^{-3}, which is due to the presence of soil OM.

3.2. Evaluating the ability of the newly developed f_{quartz}-ρ_s equation to provide useful inputs for λ model estimations

For the 56 soils used to develop the new empirical equation, f_{quartz} ranged from 0.17 to 0.84, while f_{sand} ranged from 0 to 0.93 (Fig. 2). Note that f_{sand} exhibited a wider range than f_{quartz}, which will introduce errors in λ model results if f_{sand} values are substituted for f_{quartz} values. Next, we evaluate the performance of four thermal conductivity models by comparing the measured λ values for the 39 Canadian soils from Tarnawski et al. (2015) versus λ model estimated values based on three different model inputs, i.e., using actual f_{quartz} values, using the new empirical equation estimates of f_{quartz}, and using f_{sand} values as a direct substitute for f_{quartz}.

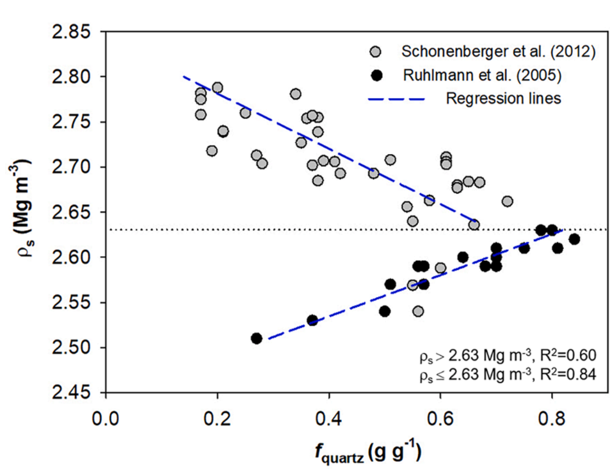

Fig. 2. Soil particle density (ρ_s) plotted against quartz content (f_{quartz}) for the 56 soils reported in Rühlmann et al. (2006) and Schönenberger et al. (2012). The blue dashed lines represent the linear regression equation fitted to the black and gray dots. R^2 values represent the coefficients of determination.

When f_{quartz} values were set equal to f_{sand} values, relatively large errors occurred in the model estimated λ values (see the blue dots in Fig. 3). The RMSEs were 0.22, 0.23, 0.23, and 0.31 W m^{-1} K^{-1} for the modified-de Vries model, the Côté and Konrad (2005) model, the Lu et al. (2007) model, and the Balland and Arp (2005) model, respectively (Table 3). The errors were especially obvious in the wet range where all models overestimated λ values (Fig. 3a, Table 3). It was unexpected that the Balland and Arp (2005) model, which included OM as a key factor influencing λ_{soild} (Eq. (13)), only produced reliable λ estimates for soils with OM ranging from 2.7% to 23.3% (volume% in soil dry matter), with RMSEs < 0.27 W m^{-1} K^{-1} (data not shown). For high OM soils, e.g., the silt loam soil with an OM content of 46.6% (from Manitoba), the Balland and Arp (2005) model estimated λ values were significantly lower than the measured values.

Significant improvements in λ estimations were obtained when the actual f_{quartz} values were used in the models (see the black dots in Fig. 3). For the modified-de Vries, Côté and Konrad (2005) and Lu et al. (2007) models, the RMSEs were < 0.16 W m^{-1} K^{-1} (Table 3). The Balland and Arp (2005) model, however, still exhibited significant negative bias with an average RMSE of 0.26 W m^{-1} K^{-1} (Table 3).

Compared to the λ model estimates made with f_{quartz} equal to f_{sand}, the λ estimates (see the red dots in Fig. 3) obtained when f_{quartz} values were determined by Eq. (19) agreed well with the measured λ values. For the modified-de Vries, Côté and Konrad (2005), and Lu et al. (2007) models, the RMSE values ranged from 0.15 to 0.18 W m^{-1} K^{-1} (Table 3), very close to RMSE values when the actual f_{quartz} values were used as model inputs (Table 3). This was also true for the Balland and Arp (2005) model, although the RMSE value was 0.27 W m^{-1} K^{-1}. Thus, the new empirical equation estimates of f_{quartz} effectively reduced the errors in λ model estimated values.

It is noteworthy that the errors in the estimated λ values were saturation dependent. For example, the modified-de Vries, Côté and Konrad (2005), Balland and Arp (2005), and Lu et al. (2007) models provided excellent λ estimates of the measured values in relatively dry soils with S_r values < 0.25, with RMSEs in the range of 0.12–0.17 W m^{-1} K^{-1} (Table 3). However, discrepancies were observed in wet soils (Fig. 3). Compared to the λ estimates based on f_{sand}, using the new empirical equation to estimate f_{quartz} reduced RMSEs of λ model estimates by 13%-35% for the four models, and the reduction in model errors was most significant in wet soils. Lu et al. (2007) reported that when f_{sand} was used as a model input, λ was overestimated at $\theta > 0.20$ m^3 m^{-3}. This is caused by the fact that in the geometric means of Eqs. (6) and (12), λ_{soild} and λ_{sat} are functions of f_{quartz}, thus it is vital to have accurate f_{quartz} values for reliable λ estimations, especially for wet soil conditions.

3.3. Evaluation of the usefulness of the newly developed f_{quartz}-ρ_s empirical equation using field λ data

Fig. 4 shows comparisons between model estimated λ values and field measured λ values, where f_{sand} values (blue dots) and new empirical equation estimates of f_{quartz} (red dots) were used in the four λ models. During the 14-day period, λ varied from 0.85 to 1.50 W m^{-1} K^{-1} in response to the wetting and drying periods with θ variations of 0.04–0.36 m^3 m^{-3} in the 0–50 mm soil layer. All of the models underestimated λ slightly during the dry period and overestimated λ slightly during the wet period. This might be due in part to λ values determined with the heat-pulse sensor being affected by heterogeneous θ distributions in the 0–50 mm soil layer: More heat (released by the heating sensor) moved into the top soil section during wetting, but less heat moved into the top section during drying. In contrast, the models assumed that θ distribution and heat transfer was uniform in the the 0–50 mm soil layer. Even so, when the new empirical equation estimates of f_{quartz} were used in the models, the RMSE errors (0.09–0.12 W m^{-1} K^{-1}) of λ model estimates were reduced by 64–70% as compared to

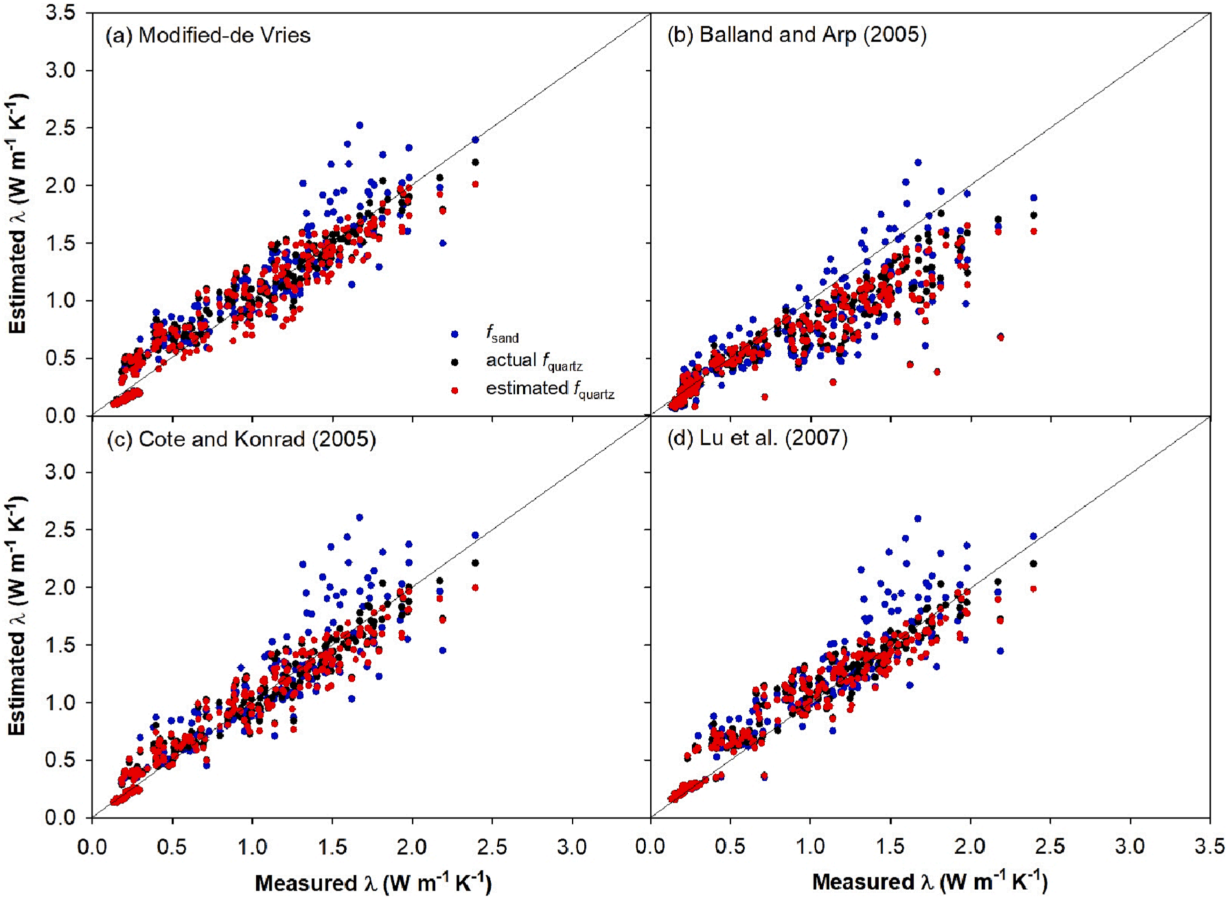

Fig. 3. Comparison between the measured thermal conductivity (λ) and the estimated λ values using the modified-de Vries, Côté and Konrad (2005), Balland and Arp (2005), and Lu et al. (2007) models for the 39 repacked soils with the input parameters of f_{sand} (blue dots), actual f_{quartz} (black dots), and estimated f_{quartz} (red dots) in λ models, respectively. The solid lines are the 1:1 lines.

Table 3
The root mean square errors (RMSE, W m^{-1} K^{-1}) of estimated thermal conductivity values at various degrees of saturation (S_r) using four models (modified-de Vries, Côté and Konrad (2005), Balland and Arp (2005), and Lu et al. (2007)) with the following inputs for quartz content (f_{quartz}): f_{sand} set equal to f_{quartz}, actual measured f_{quartz} values, and empirical equation estimated f_{quartz} values.

Models	S_r	f_{sand}	Actual measured f_{quartz}	Empirical equation estimated f_{quartz}
Modified-de Vries	0–0.25	0.17	0.17	0.16
	0.25–1	0.25	0.15	0.19
	0–1	0.22	0.16	0.18
Côté and Konrad (2005)	0–0.25	0.15	0.12	0.13
	0.25–1	0.29	0.15	0.18
	0–1	0.23	0.13	0.15
Balland and Arp (2005)	0–0.25	0.17	0.13	0.13
	0.25–1	0.41	0.34	0.36
	0–1	0.31	0.26	0.27
Lu et al. (2007)	0–0.25	0.17	0.14	0.14
	0.25–1	0.28	0.16	0.19
	0–1	0.23	0.15	0.16

those obtained with f_{sand} as the model input (Fig. 4a–d). Using the new empirical equation estimates of f_{quartz} as inputs to λ models can accurately estimate dynamic λ values in field soil.

Overall, our evaluation on the usefulness of the newly developed empirical equation estimates of f_{quartz} on λ model estimations confirmed the effectiveness of the new approach to approximate f_{quartz}. When soil mineral information is unavailable, a simple soil-specific ρ_s measurement can be used in Eq. (19) to estimate f_{quartz}, which can be used as a model input to estimate λ with acceptable accuracy. However, the Balland and Arp (2005) model is not recommended for use in high OM soils.

3.4. Limitation and uncertainty of the empirical equation

First, it should be pointed out that the published ρ_s datasets in Rühlmann et al. (2006) and Schönenberger et al. (2012) were determined on samples with OM. OM would lower ρ_s values but has no significant on f_{quartz}. Further study should test the feasibilities of the proposed equation on soils with high OM content. Second, it should be pointed out that the ρ_s values increase with f_{clay} (McBride et al., 2012). For clay-rich mineral soils with relatively low f_{quartz} values or soils with heavy mineral elements, the ρ_s values are considerably higher than 2.65 Mg m^{-3} (e.g., 2.80–3.20 Mg m^{-3} for biotite and 4.80–5.30 Mg m^{-3} for hematite according to Skopp (2012)). Thus, further work is required to examine the relationship between f_{quartz} and ρ_s on a wider range of soils and varying conditions.

4. Conclusion

Using published data on 56 soils we developed an empirical equation to relate f_{quartz} to ρ_s. This relationship could be used to estimate f_{quartz} from ρ_s. The performance of the new approach was confirmed by comparing λ data estimated by four thermal conductivity models versus measured values on 39 Canadian soils and one field soil from China. The

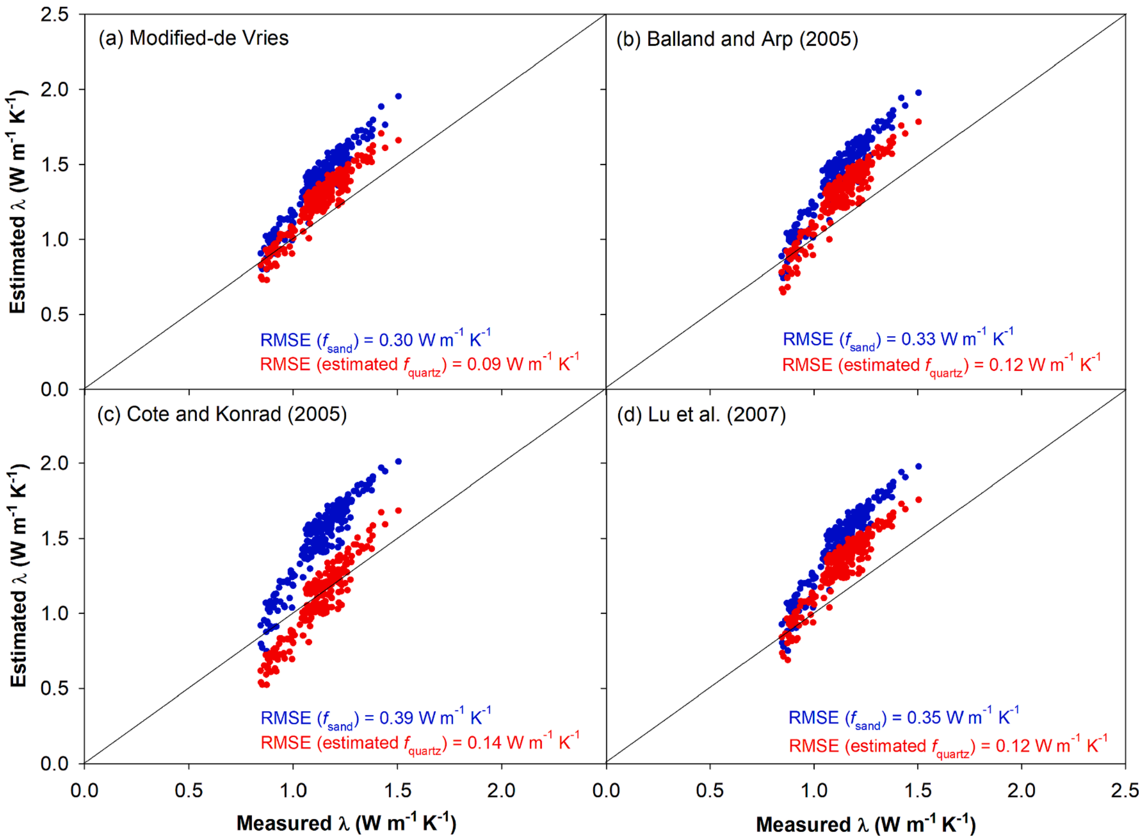

Fig. 4. Comparison between the measured thermal conductivity (λ) and the estimated λ values using the modified-de Vries, Côté and Konrad (2005), Balland and Arp (2005), and Lu et al. (2007) models on the field soil with the input parameters of f_{sand} (blue dots) and estimated f_{quartz} (red dots), respectively. The root mean square errors (RMSE) are presented. The solid lines are the 1:1 lines.

results showed that when f_{sand} was replaced with estimated f_{quartz} values, the errors in modeled λ data were reduced significantly over the entire saturation range, and the λ results that were comparable to those when the actual f_{quartz} values were used. The new approach can be integrated into models and algorithms where f_{quartz} is required. Additional studies are required to test the new appraoch in a wide range of soil types and mineral compositions.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Tusheng Ren reports financial support was provided by National Natural Science Foundation of China. Robert Horton reports statistical analysis and writing assistance were provided by U.S. National Science Foundation. Robert Horton reports statistical analysis and writing assistance were provided by USDA-NIFA Multi-State Project.

Data availability

Data will be made available on request.

Acknowledgements

This work was funded by National Natural Science Foundation of China (41977011), U.S. National Science Foundation under Grant 2037504, and USDA-NIFA Multi-State Project 4188.

References

Balland, V., Arp, P., 2005. Modelling soil thermal conductivities over a wide range of conditions. J. Environ. Eng. Sci. 4, 549–558. https://doi.org/10.1139/S05-007.

Bristow, K.L., White, R.D., Kluitenberg, G., 1994. Comparison of single and dual-probes for measuring soil thermal properties with transient heating. Aust. J. Soil Res. 32, 447–464. https://doi.org/10.1071/sr9940447.

Bristow, K.L., 2002. Thermal conductivity. In: Dane, J.H., Topp, G.C. (Eds.), Methods of soil analysis. Part 4. SSSA, Madison, WI, pp. 1209–1226.

Buckman, H.O., Brady, N.C., 1969. The Nature and Properties of Soils. MacMillan, p. 653.

Calvet, J.C., Fritz, N., Berne, C., Piguet, B., Maurel, W., Meurey, C., 2016. Deriving pedotransfer functions for soil quartz fraction in southern France from reverse modeling. Soil 2, 615–629. https://doi.org/10.5194/soil-2-615-2016.

Côté, J., Konrad, J.M., 2005. A generalized thermal conductivity model for soils and construction materials. Can. Geotech. J. 42, 443–458. https://doi.org/10.1139/t04-106.

Culley, J.L.B., 1993. Density and compressibility. In: Carter (ed.), M.R. (Ed.), Soil sampling and methods of analysis, 1st ed. Canadian Soc. of Soil Sci., Lewis Publ., CRC Press, Boca Raton, FL, pp. 529–539.

de Vries, D.A., 1963. The thermal properties of soils. In: van Wijk (Ed.), Physics of Plant Environment. North Holland, Amsterdam., pp. 210–235

Di Giuseppe, D., Melchiorre, M., Tessari, U., Faccini, B., 2016. Relationship between particle density and soil bulk chemical composition. J. Soils Sediments 16, 909–915. https://doi.org/10.1007/s11368-015-1275-3.

Ghanbarian, B., Daigle, H., 2016. Thermal conductivity in porous media: Percolation-based effective-medium approximation. Water Resour. Res. 52, 295–314. https://doi.org/10.1002/2015WR017236.

Hardy, M., 1992. X-ray diffraction measurement of the quartz content of clay and silt fractions. Clay Minerals 27, 47–55. https://doi.org/10.1180/claymin.1992.027.1.05.

He, H.L., He, D., Jin, J.M., Smits, K.M., Dyck, M., Wu, Q.B., Si, B.C., Lv, J.L., 2020. Room for improvement: A review and evaluation of 24 soil thermal conductivity parameterization schemes commonly used in land-surface, hydrological, and soil-vegetation-atmosphere transfer models. Earth-Sci. Rev. 211, 103419 https://doi.org/10.1016/j.earscirev.2020.103419.

Hillel, D., 1982. Introduction to Soils Physics. Harcourt Brace Jovanovich Publishers, Academic Press Inc, San Diego, California, pp. 155–166.

Johansen, O., 1975. Thermal conductivity of soils. Ph.D. thesis. Norwegian University of Sci. & Tech, Trondheim, Norway.

Kluitenberg, G.J., Ham, J.M., Bristow, K.L., 1993. Error analysis of the heat pulse method for measuring soil volumetric heat capacity. Soil Sci. Soc. Am. J. 57, 1444–1451. https://doi.org/10.2136/sssaj1993.03615995005700060008x.

Lu, Y., Horton, R., Zhang, X., Ren, T., 2018. Accounting for soil porosity improves a thermal inertia model for estimating surface soil water content. Remote Sens. Environ. 212, 79–89. https://doi.org/10.1016/j.rse.2018.04.045.

Lu, S., Ren, T., Gong, Y., Horton, R., 2007. An improved model for predicting soil thermal conductivity from water content at room temperature. Soil Sci. Soc. Am. J. 71, 8–14. https://doi.org/10.2136/sssaj2006.0041.

Lu, S., Ju, Z., Ren, T., Horton, R., 2009. A general approach to estimate soil water content from thermal inertia. Agric. For. Meteorol. 149, 1693–1698. https://doi.org/10.1016/j.agrformet.2009.05.011.

McBride, R.A., Slessor, R.L., Joosse, P.J., 2012. Estimating the particle density of clay-rich soils with diverse mineralogy. Soil Sci. Soc. Am. J. 76, 569–574. https://doi.org/10.2136/sssaj2011.0177n.

Mitchell, K.E., 2002. The community Noah land surface model (LSM)-User's guide. 15th AMS Conf. on Hydrology.

Peters-Lidard, C.D., Blackburn, E., Liang, X., Wood, E.F., 1998. The effect of soil thermal conductivity parameterization on surface energy fluxes and temperatures. J. Atmos. Sci. 55, 1209–1224. https://doi.org/10.1175/1520-0469(1998)055<1209:TEOSTC>2.0.CO;2.

Rowse, J.B., Jepson, W.B., 1972. The determination of quartz in clay materials. J. Therm. Anal. 4, 169–175. https://doi.org/10.1007/BF01911926.

Ruehlmann, J., Körschens, M., 2020. Soil particle density as affected by soil texture and soil organic matter: 2. Predicting the effect of the mineral composition of particle-size fractions. Geoderma 375, 114543.

Rühlmann, J., Körschens, M., Graefe, J., 2006. A new approach to calculate the particle density of soils considering properties of the soil organic matter and the mineral matrix. Geoderma 130, 272–283. https://doi.org/10.1016/j.geoderma.2005.01.024.

Schönenberger, J., Momose, T., Wagner, B., Leong, W.H., Tarnawski, V.R., 2012. Canadian field soils I. Mineral composition by XRD/XRF measurements. Int. J. Thermophys. 33, 342–362. https://doi.org/10.1007/s10765-011-1142-4.

Skopp, J.M., 2012. Physical properties of primary particles. In: Huang, P.M., Li, Y., Summer, M.E. (Eds.), Handbook of Soil Science, 2nd. CRC Press, Boca Raton, FL, pp. 1.1–1.10.

Tarnawski, V.R., Momose, T., Leong, W.H., 2009. Assessing the impact of quartz content on the prediction of soil thermal conductivity. Géotechnique 59, 331–338. https://doi.org/10.1680/geot.2009.59.4.331.

Tarnawski, V.R., McCombie, M.L., Leong, W.H., Wagner, B., Momose, T., Schönenberger, J., 2012. Canadian field soils II. Modeling of quartz occurrence. Int. J. Thermophys. 33, 843–863. https://doi.org/10.1007/s10765-012-1184-2.

Tarnawski, V.R., Momose, T., McCombie, M.L., Leong, W.H., 2015. Canadian field soils III. Thermal-conductivity data and modeling. Int. J. Thermophys. 36, 119–156. https://doi.org/10.1007/s10765-014-1793-z.

Tarnawski, V.R., Wagner, B., Leong, W.H., Mccombie, M., Coppa, P., Bovesecchi, G., 2021. Soil thermal conductivity model by de Vries: Re-examination and validation analysis. Eur. J. Soil Sci. 72, 1940–1953. https://doi.org/10.1111/ejss.13117.

Tong, B., Gao, Z.Q., Horton, R., Li, Y.B., Wang, L.L., 2016. An empirical model for estimating soil thermal conductivity from soil water content and porosity. J. Hydrometeorol. 17, 601–613. https://doi.org/10.1175/JHM-D-15-0119.1.

Trostel, L.J., Wynne, D.J., 1940. Determination of quartz (free silica) in refractory clays. J. Am. Ceram. Soc. 23, 18–22. https://doi.org/10.1111/j.1151-2916.1940.tb14187.x.

Whittig, L.D., Allardice, W.R., 1986. X-Ray diffraction techniques. In: Klute, A. (Ed.), Methods of soil analysis. Part 1. American Society of Agronomy, Soil Science Society of America, Madison, Wisconsin USA.