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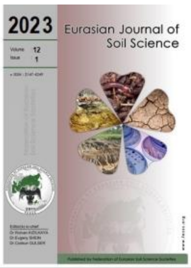

Evaluation of thermal properties of soils amended with microplastics, vermicompost and zeolite using experimental and modeling data

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Abstract

The thermal properties of soils can be influenced by additives of different origins (non-organic, organic and mineral) and roles in soil quality. This study aims to evaluate the effects of microplastics, vermicompost, and zeolite on the thermal properties of two soil types using a combination of experimental data and modeling approaches. Laboratory experiments were conducted using surface layer samples of a clay soil (Vertic Phaeozem) and a loam soil (Haplic Cambisol). Each additive was applied at a mass ratio of 10% to the soil samples. The thermal conductivity (λ), thermal diffusivity (D) and volumetric heat capacity (C_v) were measured with the SH1 sensor of a KD2Pro device during the drainage process of the soil samples at different matric potentials. The relationships between λ, C_v, D, gravimetric water content, and matric suction (h) were analyzed using linear and polynomial regression models (for C_v and D) and a closed-form equation (for λ). The fitted models exhibited small errors, such as a root mean square error (RMSE) of 0.03-0.06 W m^{-1} K^{-1}, and high coefficient of determination R^2>0.9. The effects of the different additives on water retention, λ, C_v and D were found to be specific to each soil type and depended on the properties of both the soil and the additives. These findings highlight the significance of additives in modifying soil thermal properties and emphasize the importance of considering the interactions between soil characteristics and additive properties. The combination of experimental data and modeling approaches provides valuable insights into understanding the complex dynamics of soil thermal properties and the potential impacts of additives on soil functionality and quality.

Keywords: Microplastics, thermal conductivity, thermal diffusivity, vermicompost, volumetric heat capacity, zeolite.

Introduction

The additives in soils can be purposely applied for improvement of soil quality or casually disposed which can cause soil contamination and deterioration of soil properties. Most popular soil ameliorants which are used in agricultural practice are the vermicompost, biochar, zeolites, etc. Unlike the ameliorants, the microplastics (MPs) (plastic fragments <5 mm) are principally non-degradable, inactive pollutants.The MPs can occur in soil due to improper storage of packages and other plastic materials during the agricultural operations. The distribution and migration of the MPs in soils, their extraction from soils, and the ecological effects of the microplastic pollution were subject of an increased scientific interest (Rubio et al., 2016; Qi et al., 2020 etc.; He et al., 2018). The heat transfer in semicrystalline and amorphous polycarbonate (PC) polymers was studied by direct measurement with a KD2Pro device (Rubio et al., 2016; Rubio and Rodríguez, 2017; Wiśniewska and

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Rubio, 2020). The obtained results (Rubio et al., 2016) indicated that the semicrystalline polymers transferred the heat flow better than the amorphous polymers. The addition of the polymer (Moplen polypropylene homopolymers with filler of Scott pine shavings) into a Fluvisol provoked a decrease of its thermal conductivity (λ) (Doneva and Rubio, 2015).

The zeolites and vermicompost are applied in soil as conditioners. The application of zeolites to the soil acts as slow release fertilizers, heavy metal removers, soil conditioners, and leads to increasing of the nutrient and water use efficiency and crop yield (Jakkula and Wani, 2018). Dilkova et al. (1982) found that the natural zeolite had significant quantity of micropores of size less than <0.2 μm and the effect of 10% and 20% applications on plant available water capacity (PAWC) of a silty clay loam soil (Kastanozem) depended on the size of the zeolite fractions. The fragments with sizes less than 0.5 mm had a positive effect on PAWC, while the larger fragments (0.5-5 mm) provoked a reduction in PAWC and an increase of the aeration pores. Such effect of increased air-filled large pores was observed when applying a single fraction of biochar, especially of large (>5 mm) fraction of biochar, while the mix of different size fractions had higher bulk density, λ and D (Usowicz et al., 2016). Katsarova (2021) reported a positive effect of 10% zeolite concentration on the plant available water holding capacity of a loam soil (Fluvisol).

Goswami et al. (2017) reported that the vermicompost amendment shifted the soil pH toward neutrality and the presence of organic matter increased the soil total porosity. The organic matter eventually increased the water holding capacity and aggregation of soil particles (Song et al., 2015). The results (Shein and Mady, 2016) showed that the lowest values of λ and D were at the highest value of organic matter, because organic matter leads to increase of macro pores volume and soil total porosity.

The additives can change the soil bulk density and water retained at different suctions and correspondingly can influence the soil thermal properties. Usowicz et al. (2016) studied the effect of biochar derived from wood off cuts on the soil bulk density and soil thermal properties. They found that the increase in λ and D with the soil water content was greater in soil with higher rather than lower bulk density. Shein and Mady (2016) also found that the largest values of λ and D were corresponding to the largest values of soil bulk density.

The dependence of thermal properties on the varying volumes of soil constituents can be described by experimental data and models (de Vries, 1963; Campbell et al., 1994; Ochsner et al., 2001a; Usowicz, 1992; Lu et al., 2019). According to Lu et al. (2019) the use of soil matric suction rather than volumetric water content (θ) enables more robust and transferable comparisons across soils of different textures. Some models allowed to derive an inverse information on the soil bulk density by the measured data of the volumetric heat capacity or thermal conductivity and water content (Ochsner et al., 2001b; Lu et al., 2016). The soil thermal diffusivity at different water content was estimated from easily available data on soil texture, bulk density, and organic matter content (Mady and Shein, 2018). It was concluded that the best results for D were received when was taken into account the percentage of sand, silt, and clay (soil texture). Wessolek et al (2023) validated ten well established pedo-transfer functions for predicting λ by using easily available soil information such as soil texture, bulk density, and water content. The authors compared measured vs. predicted results and concluded that reliable pedo-transfer models are the de Vries model, and the Brakelmann approach.

The aim of this study was to assess the impact of additives of varying origins (non-organic, organic, and mineral), characteristics, and purposes on the thermal properties of clay and loam soils. This was achieved by comparing experimental data obtained at different matric suctions with model outputs. Additionally, the study aimed to investigate the changes in thermal properties of soils following the addition of microplastics, vermicompost, and zeolite.

Material and Methods

The soil samples were taken in May 2020 from the surface 0-20 cm horizon of - a Vertic Phaeozem (S1), under grassland from the experimental field Gorni Lozen (42.63°N, 23.46°E, 585 m a.s.l) and - a Haplic Cambisol (S2), arable land, from the experimental station of potatoes in Samokov (42.34°N, 23.54°, 945 m a.s.l.). After the bulk soil samples were air-dried, grounded and sieved through 2 mm openings, these soil samples were used for the basic soil analyses and for preparing the studied variants. The soil particle-size distribution was determined by sieving and the pipette method (ISO 11277: 2009). The texture classes and soil names were determined according to IUSS Working Group WRB (2022). The total soil organic carbon content (SOC, %) was determined by the modified Tjurin's method (Kononova, 1963; Filcheva and Tsadilas, 2002). The estimate of soil organic matter (SOM) content was done by multiplying of SOC with the Van Bemmelen's conventional factor of 1.724. The acidity of soil was measured by a pH meter in a 1:2.5 soil-water suspension. The mineralogical composition of the soil fractions >63 μm and <63 μm were determined after organic matter removal by X-ray diffraction analysis (XRD) by D2 PHASER (Bruker).

The investigation of soil thermal properties at different matric water suctions was conducted on the intact soil cores in metal rings of 100 cm^3 taken from the fields and on the artificially repacked in laboratory conditions soils and mixtures. The mixtures were maintained for 6 months at 75% of Field Capacity (FC) by periodically wetting of the samples in order to facilitate the aggregates formation between the soil particles and the additives. Then the repacking of the air-dried samples (soil and mixtures) in metal rings of 100 cm^3 volume (d=5.1 cm, h=4.9 cm) was done with 1.2 cm increments and compacting in order to achieve uniform bulk density. The mass of the samples was estimated to achieve a desired soil bulk density (ρ_b) taking into account the bulk densities of the intact soil cores sampled under grassland for S1 (1.47 g cm^{-3}) and in the arable soil layer for S2 (1.15 g cm^{-3}). The laboratory experiment comprised four variants for soils S1 and S2 each performed in two replicates: controls (repacked soil, no additive), mixtures of soil plus 10% by mass of: Polycarbonate (PC) polymer, product Makrolon 2407 produced by Bayer Material Science; Polymethyl methacrylate (PMMA) polymer, product PLEXIGLAS 8N produced by Evonik Industries; vermicompost (V), produced by "Biotor" Ltd; and zeolite (Z), produced by "Bentonite" JSC, respectively. The particle size of PC and PMMA was about 2 mm and for the zeolite it was between 0.8-2.5 mm. The natural zeolite was obtained from the Beli plast deposit, Kardjali region. The density values were 1.20 and 1.19 g cm^{-3} for PC and PMMA, respectively. The measured particle density (ρ_s) of vermicompost was 1.98 g cm^{-3} and of zeolite 2.37 g cm^{-3}.

The particle densities of additives and soils were measured in pycnometers filled with water. The total porosity (*Pt*, %) was calculated using the measured ρ_b and ρ_s ($Pt=[(\rho_s-\rho_b)/\rho_s]\times 100$).

The samples in the 100 cm^3 rings were preliminary capillary wetted at suction 0.25 kPa (pF0.4) on a sand bath during more than 20 days. The gravimetric water content (*W*) at suctions less than 33 kPa (pF 2.5) was determined during drainage of the wetted samples using a suction type apparatus (Shot filters G5 with diameters of pores 1.0-1.6 μm) connected with a hanging column for suctions 1, 5, 10 kPa and with a vacuum chamber for 33kPa. The method is similar to the methods described in ISO 11274: 1998. Equilibrium for each suction was established for 5–7 days. Then the samples were left for air-drying by natural evaporation at room temperature and periodically weighed for determining the soil wetness reduction and corresponding soil thermal properties measurements. At the end of the analyses the soil cores were oven dried at 105°C in order to estimate the mass of dry samples and calculate *W* and ρ_b. A similar procedure was applied in other studies (Usowicz et al., 2013; Markert et al., 2017; Lu et al., 2019). The gravimetric water content at suction 1500 kPa (pF 4.2 – Wilting Point, WP) and the hygroscopic soil water content (*Wh*), corresponding to pF 5.6 were determined on fine earth samples in three replicates using correspondingly the pressure membrane apparatus (ISO 11274:1998) and the vapour-pressure method in desiccators containing saturated solution of NaCl for maintaining 75% relative air humidity. The measurements of thermal properties of the studied samples were conducted with the SH-1 sensor of a KD2Pro device (Decagon Devices Inc., Pullman, USA). The sensor was placed vertically in the center of the metal cylinders and after 15 minutes interval for achieving equilibrium the thermal properties were measured. The thermal conductivity (λ), volumetric heat capacity (C_v), and thermal diffusivity (*D*) were measured at each suction pF (pF=$\log_{10}$(|-cm H_2O|) with parallel gravimetric measuring of the soil water content. The conducted measurements were 7 to 12 for each sample.

The water retention experimental data at different suctions were approximated by the closed-form equation of van Genuchten (1980) in order to assess the water potentials corresponding to the water contents measured during the air-drying stage of the experiment:

$$W=(W_{sat}-W_{res})\times(1+(\alpha\times h)^{n}]^{-(1-1/n)}+W_{res} \qquad (1)$$

where *W* is the gravimetric water content (kg kg^{-1}), *h* is the suction (hPa), W_{sat} is the water content at saturation, W_{res} is the residual water content (h→∞), α (hPa^{-1}), and *n* are the fitted parameters.

Unlike Lu and Dong (2015) who used the closed-form equation for approximating the relationship λ-θ, we used this type of equation to describe λ-*h* relationship:

$$\lambda=(\lambda_{sat}-\lambda_{dry})\times(1+(\alpha^{*}\times h)^{\ n^{*}}]^{-(1-1/n^{*})}+\lambda_{dry} \qquad (2)$$

where λ is the thermal conductivity (W m^{-1} K^{-1}), *h* is the suction (hPa), λ_{sat} is λ at saturation, λ_{dry} is the dry soil thermal conductivity (h→∞), α^* (hPa^{-1}), and n^* are the fitted parameters.

The parameters of the closed form equations W_{sat}, W_{res}, α, n, λ_{sat}, α^*, and n^* (Eqs. 1, 2) were fitted with statistical non-linear regression analysis method of the OriginPro 6.1. Stable results for the parameters were obtained when the parameter W_{res} in Eq. 1 was fixed to zero in cases with estimated negative values. The parameter λ_{dry} in Eq. 2 was calculated by a linear relationship proposed by (Lu et al., 2007) between dry soil thermal conductivity (λ_{dry}) and soil total porosity (Pt).

$$\lambda_{dry} = -0.56\times Pt + 0.51 \tag{3}$$

The volumetric heat capacity (C_v) was modeled by the additive model of de Vries (1963):

$$C_v = C_s \times \rho_b/\rho_s + 4.18 \times \theta/100 \tag{4}$$

where ρ_b and ρ_s are the soil bulk and particle densities; θ is the volumetric water content $\theta = W \times \rho_b$; W – gravimetric water content, C_s – volumetric heat capacity of the solids. C_s was calculated according to de Vries (1963) taking into account the proportions of solid constituents (minerals, soil organic matter, and additives), their specific heat capacity c_s and the soil particle density.

The variability of soil bulk density due to the effect of expansion and shrinkage at different water contents was estimated based on the heat capacity approach (Ochsner et al., 2001b):

$$\rho_{b\ calc} = C_{ve}/(C_s/\rho_s + 4.18 \text{ x } W/100) \tag{5}$$

The measured thermal diffusivity ($D=\lambda/C_v$) is compared with the ratio of modeled λ and C_v.

The performance of the models was estimated by the coefficient of determination R^2 and the root mean square error (RMSE):

$$\text{RMSE} = (\Sigma(x_e - x_m)^2/\text{N})^{1/2} \tag{6}$$

where N is the number of data points, x_e and x_m are the estimated and measured values, respectively.

Results and Discussion

The studied soils differed with respect to their soil texture. Nearly half of the particles of the Vertic Phaeozem (S1) had the size of clay (<0.002 μm) while the Haplic Cambisol (S2) was dominated by the sand fraction (>0.063 mm) (Table 1).

Table 1. Soil texture fractions, soil organic carbon content (SOC) and hygroscopic water content (*Wh*)

Soil variety	Sand (2-0.063 mm), %	Silt (0.063-0.002 mm), %	Clay (<0.002 mm), %	Texture class	SOC, %	*Wh*,%
Vertic Phaeozem (S1)	12	40	48	clay	0.92	6.63±0.03
Haplic Cambisol (S2)	46	32	22	loam	1.10	2.81±0.03

The finer texture of S1 explained the higher hygroscopic water content (*Wh* at pF5.6) compared to S2. The soil organic carbon content (SOC) was 0.92% and 1.10%, respectively for S1 and S2 (Table 1), which corresponded to 1.6% and 1.9% soil organic matter content. The main minerals determined by XRD are presented in Table 2.

Table 2. XRD mineralogical composition (%) of sand (>0.063 mm) and silt+clay (<0.063 mm) fractions and volumetric heat capacity of the minerals (C_v) after de Vries (1963)

Minerals	S1		S2		C_v,
	>0.063 mm	<0.063 mm	>0.063 mm	<0.063 mm	MJ m^{-3} K^{-1}
Quarz (SiO_2)	18.0	24.6	29.2	13.2	2.13
Plagioclase [$(Na,Ca)(Si,Al)_4O_8$]	29.5	29.9	32.7	26.8	2.64
K-feldspar ($KAlSi_3O_8$)	22.6	14.7	13.2	16.9	2.08
Muscovite {$KAl_2[AlSi_3O_{10}](OH)_2$}	23.2	20.4	19.2	31.7	2.52
Amphibol {$Ca_2[Mg_4(Al,Fe)]Si_7AlO_{22}(OH)_2$}	6.8	4.9	1.4	5.2	2.61

The content of quartz was differently distributed among the particles' fractions in S1 and S2. Taking into account the proportions of the sand in the bulk soil, it can be estimated that S1 and S2 contained correspondingly 2% and 13% quartz in the sand-sized particles. As the XRD analyses were not performed separately on the clay fraction, the quartz content in the fraction below 0.063 mm for S1 may be overestimated, but the presence of this mineral in all particle size fractions has to be taken into consideration.

The clay soil (S1) was slightly acidic while the loam soil (S2) was strongly acidic. The vermicompost had very slightly alkaline reaction (pH 7.42) and zeolite had slightly alkaline reaction (pH 7.79) which explained the increase of pH of the mixtures (Table 3).

The soil particle densities (ρ_s) are typical for the mineral soils with low organic matter content (Table 3). The particle densities of the vermicompost (1.98 g cm^{-3}) and zeolite (2.37 g cm^{-3}) caused decrease of ρ_s of the mixtures. The target bulk density (ρ_b) of the repacked soils was close to the intact soil cores taken from the field, which was 1.47 g cm^{-3} under grassland for S1 and 1.15 g cm^{-3} in the arable soil layer for S2. This resulted in about 10% higher *Pt* of S2 than of S1 at the time of repacking of the air dried soil samples (Table 3).

Table 3. Characteristics of the studied variants at repacking: clay soil (S1), loam soil (S2) and mixtures with additives: microplastics (PC and PMMA), zeolite (Z) and vermicompost (V)

Parameter	S1	S1+PC	S1+PMMA	S1+V	S1+Z	S2	S2+PC	S2+V	S2+Z
Bulk density (ρ_b, g cm^{-3})	1.46	1.43	1.43	1.47	1.51	1.15	1.16	1.19	1.21
W at repacking, %	4.90	4.40	4.70	6.70	5.20	2.30	2.00	3.50	2.60
Particle density (ρ_s, g cm^{-3})	2.71	2.56	2.56	2.64	2.68	2.69	2.50	2.58	2.62
Total porosity (*Pt*, %vol.)	46.10	44.00	44.10	44.10	43.40	56.50	53.80	54.00	53.90
pH in H_2O	6.38	6.43	6.41	6.68	6.64	4.49	4.50	5.92	4.77

The approximated by Eq. 1 soil water retention curves of the intact soil cores as taken from the field and on the repacked control samples are presented in Figure 1.

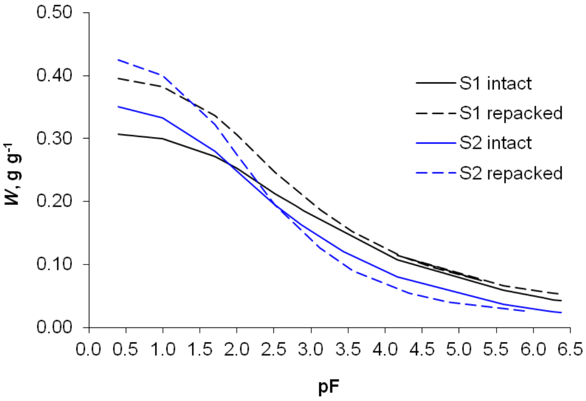

Figure 1. Approximated by Eq. 1 soil water retention curves (SWRC) of the intact soil cores taken from the field and of the repacked soils used as control variants in the laboratory experiment

The water held in micropores was similar for the intact and repacked soil samples, while the water held in the mesopores at suctions less than pF 2.5 depended on the aggregates arrangement and compactness and differed significantly between the intact and repacked samples. The finer textured S1 was characterized with a higher content of capillary pores (pF>2.5) than the medium textured S2. The fitted parameters of the van Genuchten equation (Eq. 1) for the repacked controls and mixtures are presented in Table 4 and the SWRCs are drawn in Figure 2.

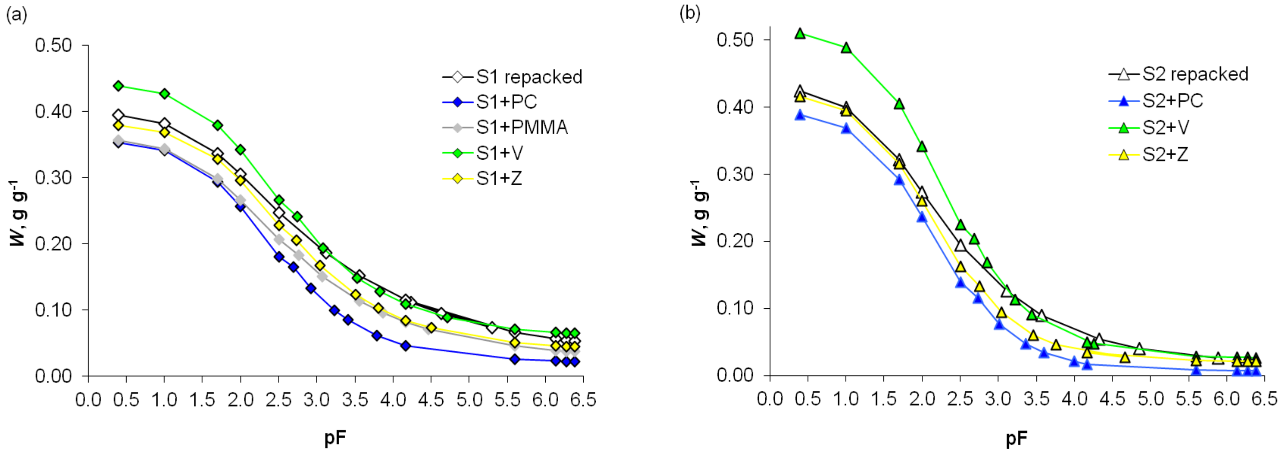

Figure 2. Soil water retention curves (SWRC) approximated by van Genuchten model (Eq. 1) for the studied repacked variants of Vertic Phaeozem, S1 (a) and Haplic Cambisol, S2 (b)

The addition of the microplastics (PC, PMMA) to the studied soils decreased *W* values throughout the whole range of suctions (Figure 2). At the wet end (pF<2.5) the relative decrease of W was better pronounced for S1+PC and S1+PMMA (from 8% to 14%) than for S2+PC (from 2% to 8%). The zeolite addition did not change significantly the water retained at pF<2.5 for both soils. The largest increase of *W* was observed in the variants with vermicompost. At field capacity (pF 2.5) the relative increase of *W* was 27% for S1+V and 44% for S2+V. These results corresponded to Khosravi Shakib et al. (2019) who concluded that the addition of vermicompost to the substrate improved the water retention capacity.

The calculated volumetric heat capacity of soils solids *Cs* for S1 and S2 (Table 5) were close to the often cited value of 2.4 MJ m^{-3} K^{-1} (Campbell and Norman, 1998).

Table 4. Fitted parameters of Eq. 1, RMSE - root mean square error

Parameter	S1	S1+PC	S1+PMMA	S1+V	S1+Z	S2	S2+PC	S2+V	S2+Z
W_{sat} (g g^{-1})	0.400	0.357	0.361	0.443	0.383	0.434	0.396	0.519	0.425
W_{res} (g g^{-1})	0.030	0.021	0.027	0.058	0.039	0.017	0.007	0.026	0.021
α (hPa^{-1})	0.022	0.010	0.018	0.011	0.01	0.024	0.011	0.011	0.012
n	1.255	1.511	1.324	1.394	1.396	1.387	1.713	1.595	1.657
RMSE (g g^{-1})	0.021	0.021	0.010	0.017	0.014	0.019	0.035	0.036	0.033

Table 5. Calculated volumetric heat capacity of solids (C_s, MJ m^{-3} K^{-1})

Variant	Vertic Phaeozem (S1)	Haplic Cambisol (S2)
S	2.361	2.345
S+10% PC	2.258	2.245
S+10% PMMA	2.275	
S+10% vermicompost	2.508	2.491
S+10% zeolite	2.338	2.324

The addition of both types of microplastics (PC, PMMA) decreased this value by 0.1 MJ m^{-3} K^{-1}, the vermicompost increased it by 0.15 MJ m^{-3} K^{-1}, while the zeolite almost did not influence it. The C_v at given soil moisture content differed between the studied soils due to the difference in the initial soil bulk density observed under the grassland in case of S1 and of the arable soil (S2). The estimated bias between S1 and S2 of the predicted C_v (Eq. 4) was 0.23 MJ m^{-3} K^{-1} (Figure 3).

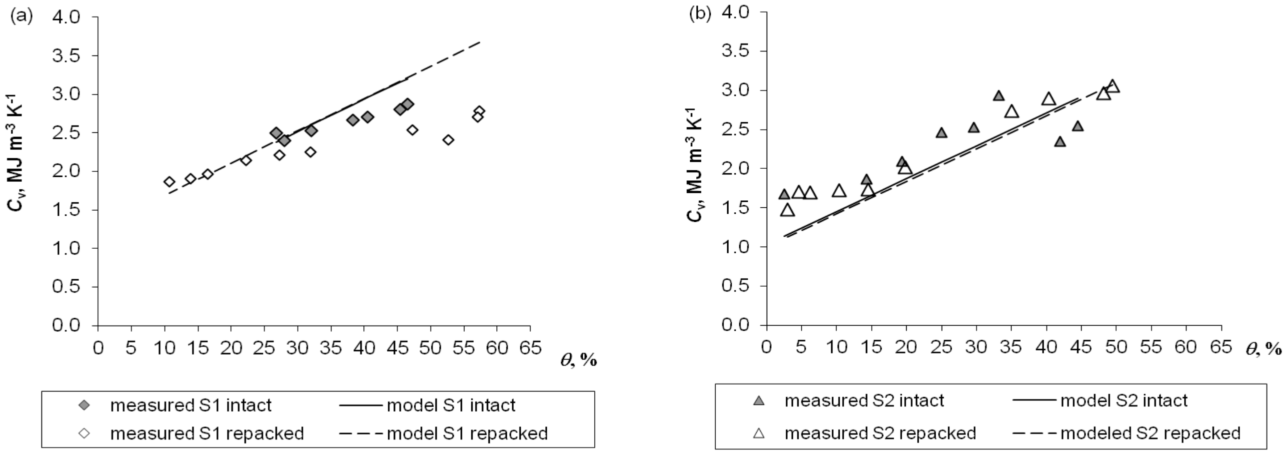

Figure 3. Measured and estimated (Eq. 4) volumetric heat capacity (C_v, MJ m^{-3} K^{-1}) versus volumetric fraction of water content (θ, % vol.) for S1 (a) and S2 (b)

The experimental data obtained on the intact and repacked samples scattered around the model predictions in a different manner for both soils (Figure 3). In the clay soil (S1) the measured C_v values were lower than predictions at soil water content above 22%vol. for the repacked samples and above 32%vol. for the intact samples. The experimental data for S2 were higher than predicted values except at near saturation. Kodešová et al. (2013) reported variable line slopes of the linear regressions between the measured C_v and θ. The authors obtained mostly higher slopes for this relationship than the value of 4.18 MJ m^{-3} K^{-1} (heat capacity of water, Eq.4) for the representative soils of the Czech Republic. In our experiment this can be explained with changes of soil bulk density of the samples during the wetting and air drying processes. This hypothesis was tested by the reverse calculation of ρ_b, so-called the C-approach (Ochsner et al., 2001b) using the measured C_v (Eq. 5) and C_s of solids as determined by the solid constituents (Table 5). The calculated ρ_{bcalc} are presented in Figure 4.

The decreasing of calculated ρ_{bcalc} with increasing of the soil water content in S1 was less pronounced on the intact samples and most evident in the mixture with PMMA (Figure 4a). The other mixtures and the control (repacked soil) were between these cases. Due to the unstable structure, the medium textured arable soil S2 showed a tendency for slaking as shown by the increased bulk density (Figure 4b). The exception was the variant with the vermicompost which prevented such slaking (Figure 4b). A lot of studies pointed out that the soil bulk density has significant influence on the volumetric heat capacity (Abu-Hamdeh, 2003; Usowicz at al., 2016; Tong et al., 2020). The varying ρ_b (Figure 4) and some uncertainties of the parameters C_s hindered the use of Eq. 4 for describing the relationship between C_v and the volumetric water content. We applied a simple linear regression between the measured C_v and the gravimetric water content W (g g^{-1}) (Figure 5).

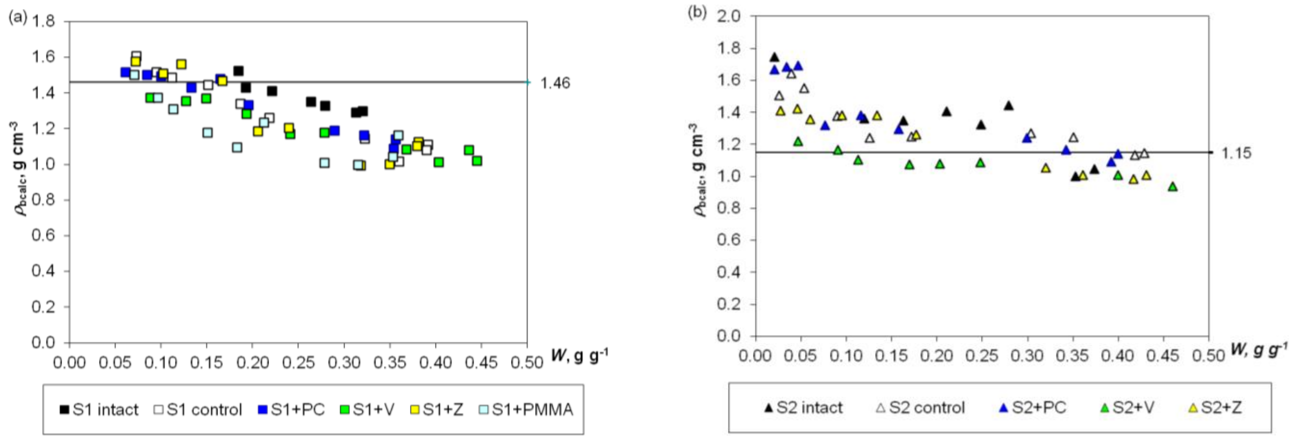

Figure 4. Calculated soil bulk density (ρ_{bcalc}, g cm^{-3}) (Eq. 5) versus gravimetric water content (W, g g^{-1}) for S1 variants (a) and for S2 variants (b)

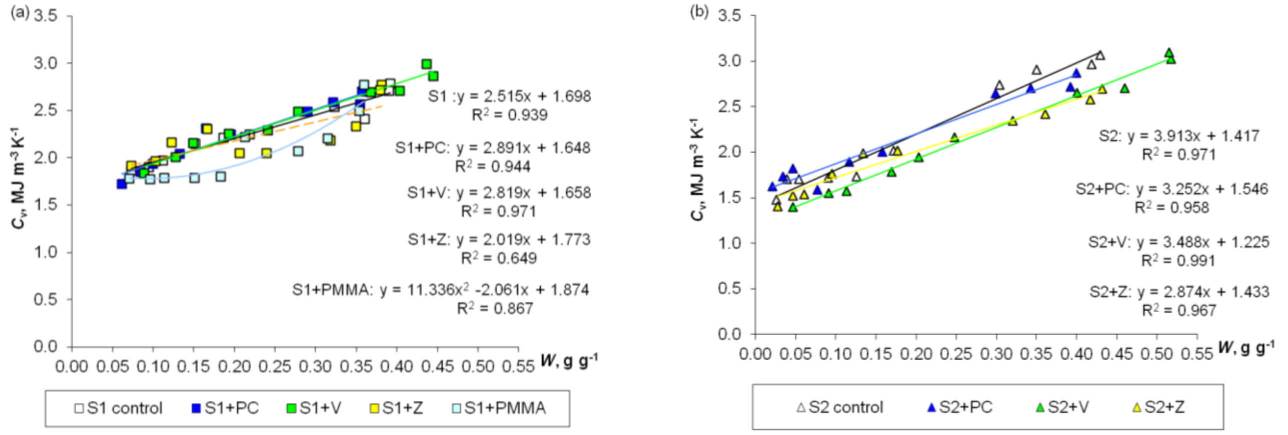

Figure 5. Regression relationships between measured volumetric heat capacity (C_v, MJ m^{-3} K^{-1}) and gravimetric water content (W, g g^{-1}) for variants with S1 (a) and S2 (b)

In most cases the coefficients of determination were very high (R^2=0.93÷0.99). The exceptions were S1+Z (R^2=0.649) and S1+PMMA where a better fit was achieved by a second order polynomial (R^2=0.867), which can be due to the non-linear relations of ρ_b and W in these cases.

The intercepts of the obtained linear regression models confirmed the higher volumetric heat capacity of the clay soil S1 than of the loam soil S2 at dry conditions (Figure 5). While the addition of PC almost did not influence C_v in both soils, the addition of vermicompost decrease C_v in S2 (Figure 5b) by preventing of slaking (Figure 4b) and did not affect C_v of S1 (Figure 4a). The zeolite also decreased C_v at the higher W more pronouncedly in S2 than in S1. We tested PMMA only in the clay S1 and obtained a decrease of C_v at the intermediate W. The models which are most cited for describing the relationship between λ and h (McCumber and Pielke, 1981; Lu et al., 2019) did not fit well our data as it is shown in Figure 6.

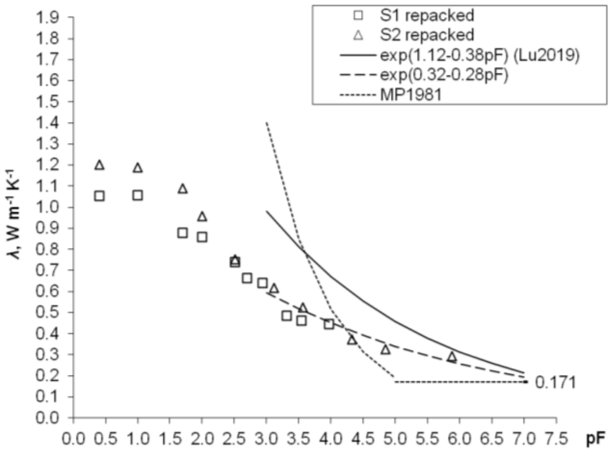

Figure 6. Relationships between λ and pF for the repacked controls of S1 and S2. Symbols – measured data; lines - models: MP model of McCumber and Pielke (1981); Lu et al. (2019) for dry end (pF>3); fitted exponential equation to the current experimental data

The thermal conductivity at not-wet region (pF>3) is considered less dependent on the soil texture and ρ_b and Lu et al. (2019) proposed a universal exponential equation for describing λ-pF relation. We compared the predicted with the measured data for the repacked S2 and obtained RMSE of 0.224 W m^{-1} K^{-1}. A better result (RMSE=0.032 W m^{-1} K^{-1}) was obtained when the exponential equation was fitted with the measured data. Both exponential models tended to the value λ=1.171 W m^{-1} K^{-1} which was fixed by McCumber and Pielke (1981) for pF>5.1. Another option, also used by Tong et al. (2020), was the empirical equation found by Lu et al. (2007) for estimation of λ_{dry} by the *Pt* data (Eq. 3). We estimated λ_{dry} and then performed the non-linear regression analyses for fitting the rest of the parameters of the closed-form equation (Eq. 2). The obtained values of the parameters are shown in Table 6 and the simulated λ-pF curves are drawn in Figure 7.

Table 6. Parameters of the closed-form equation $\lambda(h)$ (Eq. 2), RMSE – root mean square error

Parameter	S1	S1+PC	S1+PMMA	S1+V	S1+Z	S2	S2+PC	S2+V	S2+Z
λ_{sat} (W m^{-1} K^{-1})	1.063	0.990	0.875	1.064	1.060	1.216	1.124	1.078	1.232
λ_{dry} (Eq.3), W m^{-1} K^{-1}	0.252	0.263	0.263	0.262	0.266	0.189	0.210	0.208	0.209
$\alpha*$ (hPa^{-1})	0.025	0.004	0.014	0.009	0.054	0.022	0.011	0.012	0.006
$n*$	1.267	1.659	1.344	1.607	1.238	1.270	1.492	1.454	1.492
RMSE (W m^{-1} K^{-1})	0.031	0.049	0.035	0.063	0.042	0.026	0.050	0.056	0.053

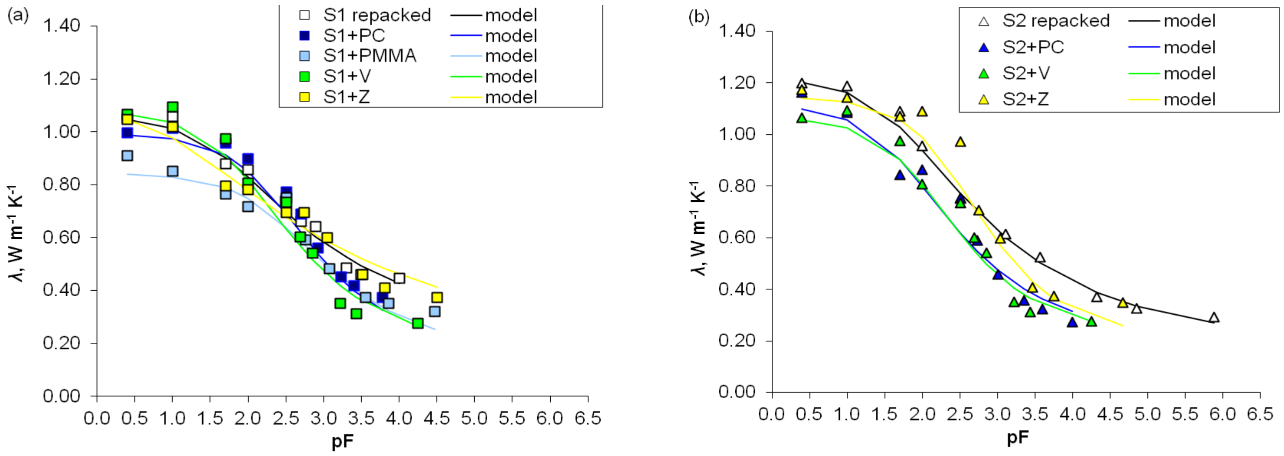

Figure 7. Relationships between measured λ and pF for variants with repacked soils (S1) (a) and S2 (b). Model (Eq. 2)

The RMSE of the predicted λ by Eq. 2 were in the range 0.023÷0.063 W m^{-1} K^{-1} and were lower than the most of the reported RMSE for the dry-end approximation of Lu et al. (2019). We did not found a statistical relationship between the parameters of van Genuchten equation for describing SWRC (*n* and α) and that of λ (*h*) ($n*$ and $\alpha*$).

The estimated higher λ_{sat} of S2 than of S1 can be explained with higher content of sand (46%) and respectively of quartz as discussed above which has higher λ (8.8 W m^{-1} K^{-1}) in comparison with that of clay minerals (2.9 W m^{-1} K^{-1}) (de Vries, 1963). The λ_{sat} of the mixtures with microplastics decreased at water saturation by 7% in S1+PC, 8% in S2+PC and 18% in PMMA+S1 due to the lower λ of the polymers (Table 6).

The decrease of λ in the mixtures with the studied microplastics was observed almost throughout the whole range of suctions (Figure 8), except at pF2.5, and pF2.0 for S1+PC, where λ were close to the control values.

The addition of vermicompost decreased λ_{sat} by 11% in S2+V and also throughout the whole range of suctions, while the decreased of λ in S1+V commenced at pF>3. The addition of zeolite to S2 increased λ values in the whole suction range and more pronouncedly at pF>2.5. In case of S1+Z there was a slight negative effect on λ (-1% to -10%).

The dependence of thermal diffusivity (*D*) on gravimetric water content was described with 2nd order polynomials with high coefficients of determination R^2 (Figure 8). The curvature was better pronounced in all variants of the coarser textured S2 and in the variant S1+PMMA. The thermal diffusivity was higher in S2 and in variants with non-organic additives. The addition of vermicompost decreased *D* at given soil moisture content. The latter corresponded to the results received by Usowicz et al. (2014) who revealed that addition of different organic amendments (biochar, peat, compost) into the soil caused considerable reduction of the λ and *D*. When *D* is presented as a function of matric suctions the variants with clay textured S1 were grouped more closely to the control (Figure 9a), while the increase of *D* in S2+Z at a given suction was well distinguished (Figure 9b).

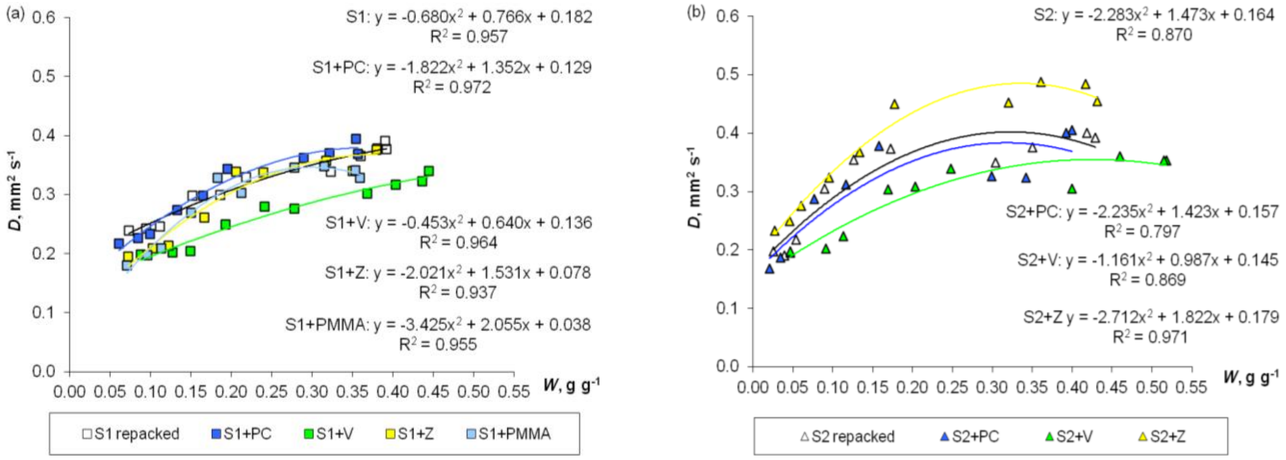

Figure 8. Regression relationships between soil thermal diffusivity (D, mm^2 s^{-1}) and gravimetric water content (W, g g^{-1}) for variants with S1 (a) and S2 (b)

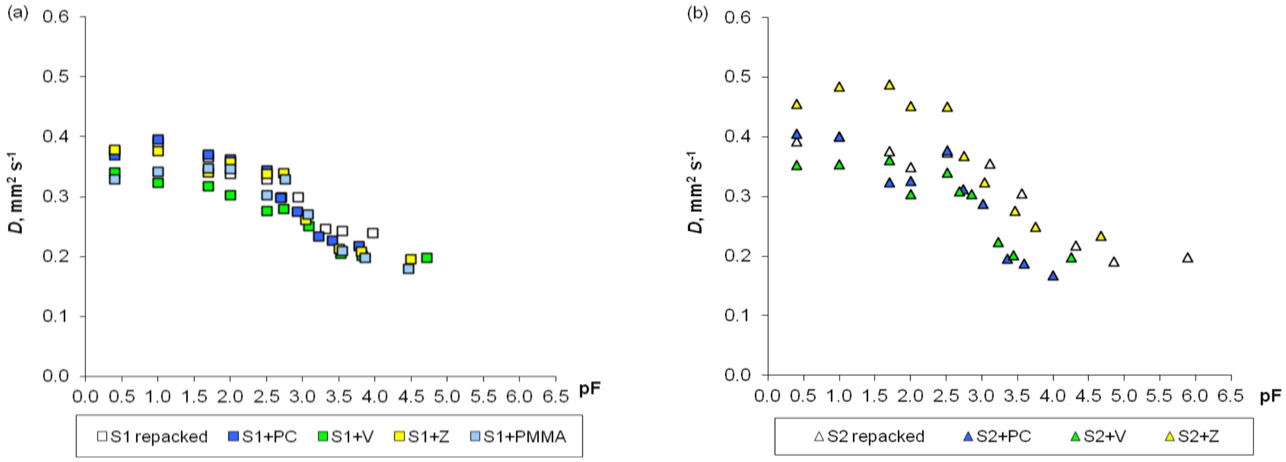

Figure 9. Soil thermal diffusivity (D, mm^2 s^{-1}) versus matric suction (pF) for variants with S1 (a) and S2 (b)

Conclusion

The effects of microplastics (PC, PMMA), vermicompost, and zeolite on soil water retention and thermal properties of clay (S1) and loam (S2) soils were evaluated by comparing experimental data with models' outputs. The main conclusions drawn from this study are as follows:

1. The use of gravimetric water content is recommended over volumetric water content when direct measurements are taken and when the repacked soil cores are susceptible to expansion or slaking during wetting-drainage cycles.

2. Closed-form equations, such as the van Genuchten equation (1980), were successfully applied to describe the soil water retention characteristics (SWRC) (as well as the relationship between thermal conductivity (λ) and water suction (h), yielding satisfactory results with a root mean square error (RMSE) ranging from 0.03 to 0.06 W m^{-1} K^{-1}.

3. The addition of microplastics (PC, PMMA) led to a decrease in water retention capacity across the entire range of suctions. The reduction in soil thermal properties was more pronounced for PMMA compared to PC in S1. The addition of PC had minimal influence on volumetric heat capacity (C_v) in both soils. The decrease in thermal conductivity (λ) and thermal diffusivity (D) was more significant in S2 due to decreased pore space and the lower λ of the polymers.

4. Vermicompost increased water retention capacity, C_s and λ_{dry} in both soils by preventing slaking of water saturated soils it caused a reducing of soil thermal properties, especially in S2.

5. Zeolite exhibited a more pronounced decrease in C_v at higher water content levels in S2 compared to S1. The effects on λ were opposite in both soils, with an increase in λ observed at pF>2.5 in S2 and a slight decrease in S1. The increase in thermal diffusivity (D) in S2+Z was distinct from the other variants at a given suction.

These findings provide valuable insights into the effects of microplastics, vermicompost, and zeolite on soil water retention and thermal properties, contributing to our understanding of their potential impacts on soil functionality and environmental sustainability.

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