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Causes clarification of the soil aggregates stability on mulched soil

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Abstract: Soil aggregates have great effects on soil properties and soil functions. Mulching (organic inputs) has been known as a factor influencing soil aggregate stability. Our study aimed to reveal the causes of the higher stability of soil aggregates under organic mulches. The primary soil characteristics such as organic carbon (C_{ox}), humus quality (E4/E6), potential wettability index (PWI), and aromaticity index (iAR) were determined. The C_{ox} was measured using rapid dichromate oxidation, and E4/E6 was measured using the UV-Vis spectrophotometry. The PWI and iAR were determined according to the intensity of selected bands in diffuse reflectance infrared spectra. Results showed that mulched plots contained higher C_{ox} content in aggregates in comparison with whole soil. This indicates that the carbon was stabilized within the aggregates and sequestrated into the soil. The iAR was significantly higher after using the organic mulches, the aliphatic components of the organic matter thus contribute more to the aggregates stabilization. The PWI of aggregates was found to be higher after applying these mulches than in soil. Organic mulches are therefore able to reduce the wettability of the aggregates and also to protect the aggregate from dispersion with water.

Keywords: Haplic Fluvisol; infrared spectroscopy; organic compounds; soil structure

Soil aggregates are the fundamental core to regulate the soil properties (Wang et al. 2017). A stable aggregates produce favourable conditions for plant growth and soil quality improvement by maintaining the water infiltration, moisture content, nutrient cycle, and especially the C storage (Kumar et al. 2019). Soil aggregates are composed by binding the mineral and organic substances that came from the decomposition of organic matter. The formation of aggregates is developed on the base of various theoretical models. The vital theoretical models are the following: the hierarchical order of aggregates exist in the soil where soil organic matter (SOM) is the major binding agent; microaggregates are formed within the macroaggregates; root-derived organic matter plays an important role in aggregate dynamics; the activity of earthworm has a decisive role in micro and macroaggregates formation; SOM is predominantly stabilized in stable microaggregates; and changes in the rate of macroaggregate turnover influence SOM stabilization across soil types and disturbance regimes (Six et al. 2004). The decrease and increase of aggregation stability depend mainly on the soil organic matter (SOM) content. Many researchers reported a strong correlation between SOM content and aggregation stability (e.g. Jakšík et al. 2015; Fan et al. 2020). However, aggregate stability is based on contents of fine sand, silt and clay particles, polyvalent metals (Fe, Al, Ca), and organic matter complexes, which could restrict the accessibility of microorganisms into them (Six et al. 2004).

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Organic mulches have been known as a material useful in soil structure stability and soil organic carbon improvement (Kader et al. 2017; Pavlů et al. 2021). The most common organic mulches used to improve crop production are straw, bark or wood chips, leaves, hyacinth, and grass (Amare & Desta 2021). Organic mulches play crucial roles in soil chemical, biological and physical properties, which subsequently affect soil aggregation and soil structure stability (Adekiya et al. 2017). With chemical properties, mulches help to enhance more organic matter and raise the plant nutrients content in the soil, especially in the uppermost soil layer (Qu et al. 2019; Jamir & Dutta 2020). Jamil et al. (2005) also reviewed that mulched soil contributes to more nutrient N, P, K uptake than unmulched soil. Considering biological properties, mulches can diversify the soil microorganisms by providing shelter and food (Yang et al. 2003). Mulched soil contains higher nitrogen amount, which microorganisms require for their metabolism during breaking down organic matter (Sharma et al. 2010; Zhang et al. 2020). With regards to physical properties, mulches could maintain the soil structure, soil temperature, and moisture content by preventing water from evaporation (Ranjan et al. 2017; Kader et al. 2019). The effects of mulches on soil aggregate stability are different according to particular mulch characteristics and mulches quantity (Alharbi 2015; Qu et al. 2019).

This work is a follow-up to the previous research (Pavlů et al. 2021). Within it, the effect of mulches on chemical and hydraulic soil properties was evaluated. Eight different mulch materials (bark chips, wood chips, wheat straw, cardboard, paper foil, decomposable matting, nonwoven fabric covered by bark chips, and crushed basalt) and a control without any mulch were studied during the 4-year period. The most significant effect of mulching was found in the case of the organic carbon content and aggregate stability under organic mulches (straw, bark chips, and wood chips). These materials differ in their chemical composition. All of them contain holocellulose with variable portion of cellulose and hemicellulose, lignin, proteins, and ash. The literature mentions relatively wide ranges of contents of these substances. The straw contains 28–40% cellulose, 21–26% hemicelluloses, 12–25% lignin, and low amount of ash and proteins (Saleem Khan & Mubeen 2012; Lu et al. 2014; Plazonić et al. 2016). The chemical components of bark chips are mainly of holocellulose (37–64% respectively 25–33% hemicellulose), lignin (18–49%), and ash (8–15%) (Mota et al. 2017; Ferreira et al. 2018; Hamad et al. 2019). However, the chemical composition of wood chips is: hemicellulose (34–38%), cellulose (32–35%), lignin (24–37%), and ash (1–4%) (Abdul Khalil et al. 2010; Chen et al. 2010; Waliszewska et al. 2019). A significant difference in the stability of aggregates (index of water stable aggregates (WSA) measured using the procedure of Nimmo and Perkins (2002)) was confirmed (Pavlů et al. 2021). Specifically, aggregates from plots mulched with bark and wood chips were the most stable (WSA – 0.92, respectively 0.91), aggregates from plots under straw were also stable (WSA – 0.84), on the contrary aggregates from the control plots were the least stable of all studied variants (WSA – 0.67). The increase in carbon content was well correlated with the increase in aggregate stability.

The aim of this work is to try to reveal the cause of the higher stability of soil aggregates under organic mulches. A detailed study of separated aggregates and their qualitative properties, among others with the help of infrared spectroscopy (diffuse reflectance infrared spectroscopy with Fourier transformation – DRIFT), can bring new knowledge about stabilization processes, about the role of individual components of organic matter or some mineral soil components.

MATERIAL AND METHODS

Site description. The study site was carried out at the university experimental field in Troja, Prague, Czech Republic. The locality is situated along the Vltava River at an altitude of 196 m. The average annual precipitation is 470 mm, and an annual average temperature is 11 °C. The soil is characterized as Haplic Fluvisol (IUSS Working Group WRB 2014) with sandy loam texture. The experimental design and soil sampling descriptions were described in detail by Pavlů et al. (2021). Twenty-seven plots (each with an area of 4.5 m^2) were prepared. Mulches were applied to 24 plots, eight mulch types (bark chips, wood chips, wheat straw, cardboard, paper foil, decomposable matting, nonwoven fabric covered by bark chips, and crushed basalt) in three replications and 3 plots remained as control without mulch. The plots were planted with six perennials, always in the same area scheme (*Geranium sanguineum*, *Hemerocallis*, *Salvia nemorosa*, *Echinacea purpurea*, *Coreopsis verticilata*, and *Heuchera sanguinea*) and without adding of any fertilizers.

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Soil sampling. For basic soil characteristic measurements, grab soil samples from 4 punctures per each plot were collected from the surface layer (0–10 cm) using a gouge auger. Samples for aggregate extraction were carefully collected separately using a plastic shovel. Soil sampling was carried out after perennials cutting in October 2018 (last year of experiment). Only the samples from plots mulched with straw, bark, and wood chips were selected and used for this study, because of the significant effect of these mulches on WSA index (Pavlů et al. 2021). Samples from the same year and from control plots were selected and used for a comparison.

Grab soil samples were prepared by the standard procedure for fine earth preparation including drying at 40 °C in the oven, crushing, and then sieving. through the 2-mm sieve. They are referred to soil in the following text. Samples for aggregate extraction were air-dried and aggregates of diameter 2–5 mm were extracted by sieving. The size of the aggregates was chosen in accordance with WSA measuring procedure (Nimmo & Perkins 2002). These aggregates were then crushed for chemical analysis.

Soil analysis. The same chemical parameters were measured for soil and for aggregates. The organic carbon content (C_{ox}) was determined using the rapid dichromate oxidation technique (Sparks 1996). The humus quality (E4/E6) was analysed according to the spectrophotometric method. The soil samples were extracted using sodium pyrophosphate (0.05 M $Na_4P_2O_7$) and measured by the absorbance ratio at 400 and 600 nm (Sparks 1996, Agilent 8453 UV-Visible spectrophotometer, Santa Clara, USA).

DRIFT spectra were recorded by the infrared spectrometer (Nicolet iS10, Waltham, USA). The spectra with a range of 2.5 to 25 μm (4 000 to 400/cm) were used. The gold mirror was used as a background reference. The 64 scans with resolution 4/cm and Kubelka-Munk units were applied. OMNIC 9.2.41 software (Thermo Fisher Scientific Inc., Waltham, USA) was applied for spectra analysis. The potential wettability index (PWI) and index of aromaticity (iAR) were determined using DRIFT spectra (Figure 1). The bands of the alky C-H groups – A (2 948–2 920/cm and 2 864–2 849/cm) were assumed to indicate the hydrophobicity and bands of the C=O groups – B (1 710 and 1 640–1 600/cm) indicate hydrophilicity. The ratio of hydrophobicity and hydrophilicity was used to determine the potential wettability index (Ellerbrock et al. 2005).

$$PWI = A/B \quad (1)$$

The aromaticity index was calculated according to reflectance of aliphatic bands ranging from

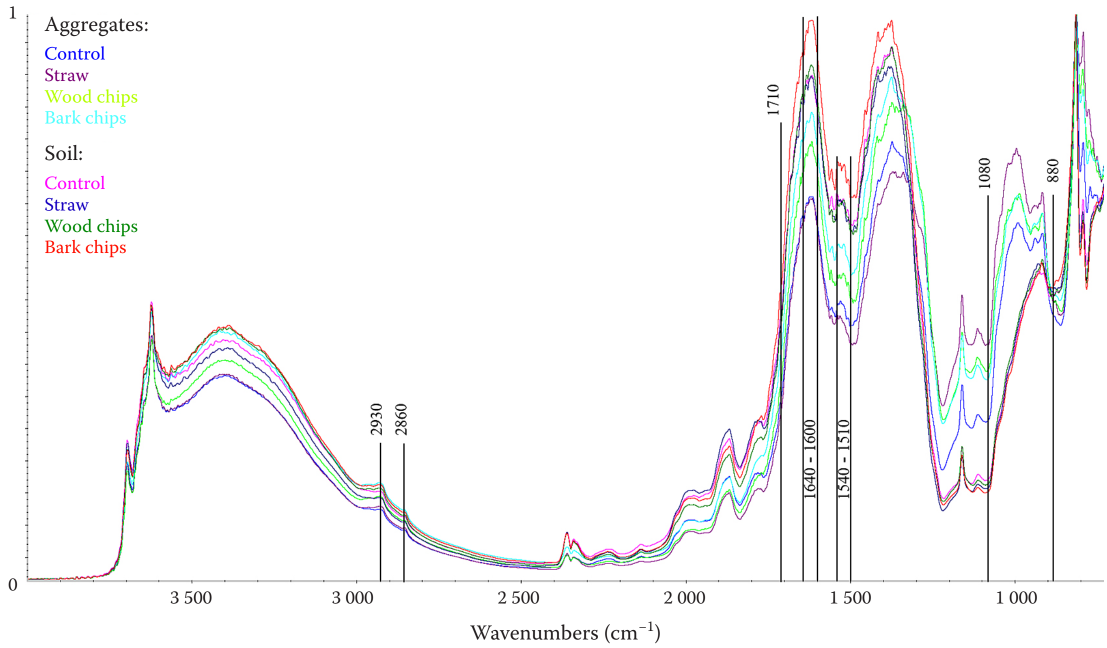

Figure 1. Average diffuse reflectance infrared spectroscopy with Fourier transformation (DRIFT) spectra of studied treatments normalized to the maximum intensity (800/cm)

Position of bands mentioned in paper and used for potential wettability index (PWI) and index of aromaticity (iAR) were marked

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3 000–2 800/cm (AL) and aromatic band at 1 520/cm (AR) (Cunha et al. 2009).

$$iAR = AL/(AL + AR) \quad (2)$$

Data analysis. The data were analysed using the software IBM SPSS (Ver. 26). ANOVA was used to define the differences of the primary soil characteristics, potential wettability index, and aromaticity index among the various mulch types (straw, wood chips, and bark chips) and control treatment. *T*-test was used to determine the differences between the two groups (soil and aggregates). Tukey test was performed to express the statistical differences among the treatments.

RESULTS

Figure 1 shows DRIFT spectra of all studied treatments. Each line represented the average of three replications. The spectra were normalized to the maximum intensity that belongs to the quartz band around 800/cm. There were visible differences between soil spectra and powdered aggregate spectra in the wavenumbers range 1 080–880/cm. This part of spectra appertains to bands of secondary silicates located mainly in the clay fraction of soil. Based on the normalized spectra, we can conclude the aggregates contain a higher amount of clays compared to the soil. However, confirmation of this finding by direct texture measurement was not possible due to the small amount of separated aggregates.

The effects of various mulches on soil properties. Table 1 shows that the soils under the wood and bark chips had a higher organic carbon content than the soil under straw and soil on the control plot. Regarding the distribution of humus quality (E4/E6) in the soil, there were no significant differences among the mulch types ($P > 0.05$). The effects of mulches on the potential wettability index were statistically different in various mulch types. Soils from bark and wood chips treatments had higher PWI compared to the straw and control treatment. The index of aromaticity showed a remarkable difference at $P < 0.05$. Soils from wood chips treatment had the highest iAR, followed by bark chips, straw, and control treatments. If we evaluate soils from mulched plots together and compare their properties with the control plot, a difference can be seen only in the organic carbon content.

Table 2 shows that the content of C_{ox} in aggregates was higher under bark chips and wood chips, than under straw and on control plots. The influence of all studied mulches on humus quality and PWI in aggregates was not found. The iAR of aggregates was significantly different among the various mulch treatments. Aggregates from wood chips, bark chips, and straw treatments had a higher iAR than the control treatment. If we evaluate aggregates from mulched plots together and compare their properties with the control plot, a difference could be seen not only in the C_{ox} content, but also in both evaluated indexes.

The comparison of soil and aggregates. Figure 2 shows the differences between soil and aggregates. There was no significant difference in C_{ox} content between soil and aggregates on control, straw, and wood chips treatment, while the bark chips and a combination of all mulches types showed a statistical difference between soil and aggregates (A). Regarding the humus quality (E4/E6), there were no obvious differences in all treatments (control, straw, wood chips, bark chips, and combination of all mulches) (B). The effects of mulches on the PWI of aggregates were observed in straw, bark chips, and a combination of all mulch

Table 1. The various effects of different mulch types on soil properties

Mulches	C_{ox}	*CV*	E4/E6	*CV*	PWI	*CV*	iAR	*CV*
Control	*1.52 ± 0.102*^{b}	6.68	3.67 ± 0.303^a	7.36	0.024 ± 0.002^b	2.08	0.045 ± 0.005^b	8.89
Straw	*1.64 ± 0.199*^{b}	12.10	3.87 ± 0.106^a	3.44	0.023 ± 0.002^b	14.35	0.043 ± 0.004^b	6.98
Wood chips	*2.33 ± 0.280*^{a}	12.03	3.73 ± 0.400^a	10.35	0.029 ± 0.002^a	15.86	0.054 ± 0.006^a	9.26
Bark chips	*2.47 ± 0.092*^{a}	3.71	3.77 ± 0.066^a	4.83	0.027 ± 0.003^a	20.00	0.050 ± 0.006^{ab}	10.00
All mulches	2.14 ± 0.42*	19.63	3.78 ± 0.21	5.56	0.026 ±0.003	11.54	0.049 ± 0.006	12.24

C_{ox} – soil organic carbon (in %); E4/E6 – humus quality; PWI – potential wettability index; iAR – index of aromaticity; average values ± standard deviations, *CV* – coefficient of variation (in %); small letters indicate the significant differences among the mulches types at $P < 0.05$; *significant difference between control and mulched variants computed together; values written in italics were adopted from Pavlů et al. (2021)

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Table 2. The different effects of various mulches on soil properties in aggregates

Mulches	C_{ox}	*CV*	E4/E6	*CV*	PWI	*CV*	iAR	*CV*
Control	1.45 ± 0.254[b]	14.22	3.75 ± 0.219[a]	6.30	0.025 ± 0.006[a]	8.00	0.048 ± 0.000[b]	2.08
Straw	1.9 ± 0.156[b]	6.86	3.70 ± 0.794[a]	19.33	0.033 ± 0.006[a]	4.85	0.063 ± 0.006[ab]	11.11
Wood chips	2.69 ± 0.211[a]	6.35	3.92 ± 0.052[a]	5.26	0.035 ± 0.006[a]	5.14	0.074 ± 0.025[a]	24.32
Bark chips	3.07 ± 0.435[a]	11.65	4.01 ± 0.525[a]	10.83	0.035 ± 0.006[a]	6.86	0.065 ± 0.015[ab]	15.39
All mulches	2.55 ± 0.57*	22.35	3.87 ± 0.45	11.63	0.034 ± 0.005*	14.71	0.067 ± 0.014*	20.90

C_{ox} – soil organic carbon (in %); E4/E6 – humus quality; PWI – potential wettability index; iAR – index of aromaticity; average values ± standard deviations, *CV* – coefficient of variation (in %); small letters indicate the significant differences among the mulches types at $P < 0.05$; *significant difference between control and mulched variants computed together

types. Higher PWI was found in the aggregates than in the soil. In the wood chips and control treatment no significant difference between soil and aggregates was found (C). The comparison of iAR showed significant differences in straw treatment and in the case of all mulch combination between soil and aggregates. Aggregates were found to have higher iAR than soil.

DISCUSSION

The soil organic carbon (C_{ox}) is more pronounced after mulching. Wood and bark chips showed the highest content of C_{ox} followed by C_{ox} content under straw. The higher C_{ox} content under bark and wood chips was probably due to the quality of organic mat-

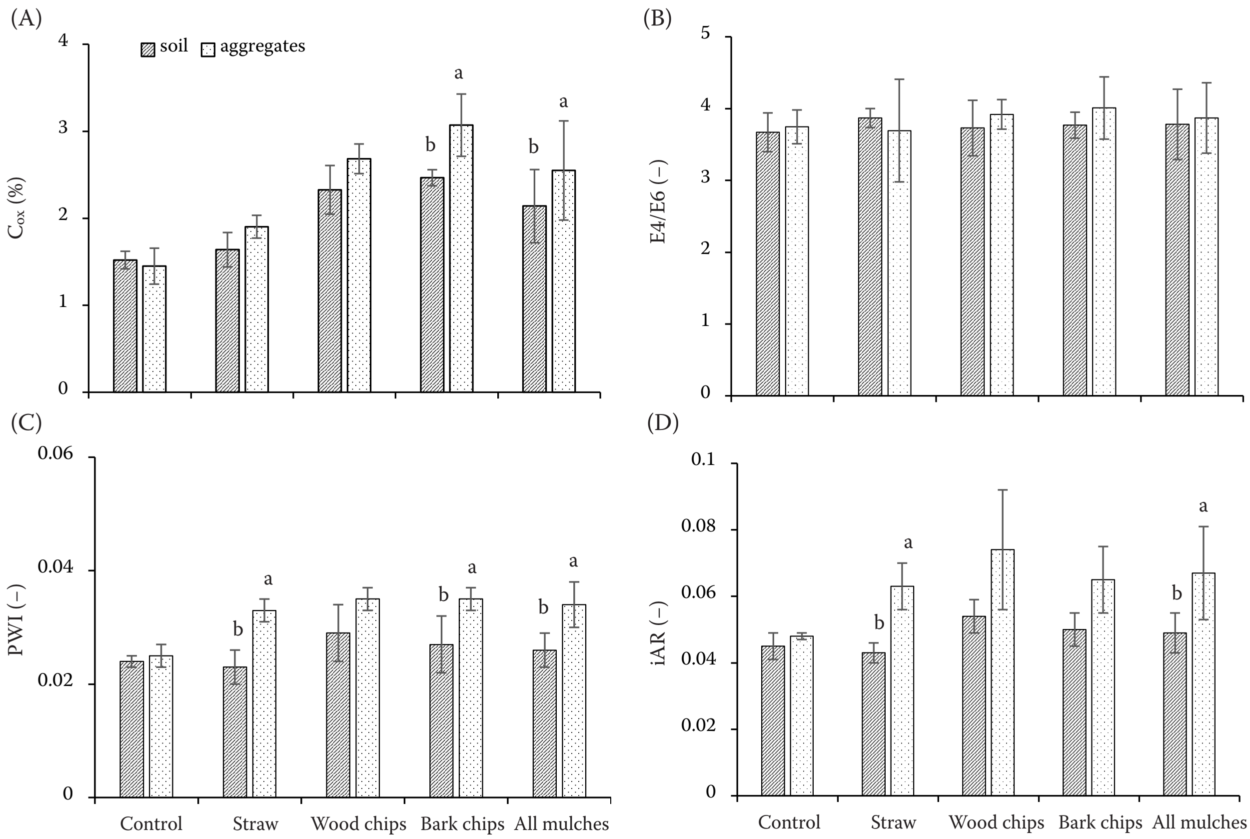

Figure 2. Average values of soil organic carbon (C_{ox}) (A), humus quality (E4/E6) (B), potential wettability index (PWI) (C), and index of aromaticity (D) separately for treatments

All mulches – a combination values of straw, wood and bark chips; the error bars correspond to the ± standard deviation values; columns followed by different letters indicate significant differences between soil and aggregates according to the significant difference *t*-test, $P \leq 0.05$

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ter and a higher content of recalcitrant in bark and wood. It was agreed with the findings of Luna et al. (2016) confirming that the higher concentration of C_{ox} could result from the quality and quantity of organic residues, and probably due to hardly decomposable materials (recalcitrant) as e.g. lignin, litter decaying and root exudate from the plant species in the experimental field. Contrary, a lower C_{ox} content in straw treatment than wood and bark chips ones could be possible due to less lignin content and higher content of easier decomposable cellulose in straw (Tozluoğlu et al. 2015). Straw provided more water-soluble substances (pectin, organic acids, free amino acids, and mineral elements) into the soil solution, which was the source of nutrients and energy for microbial growth and decomposition (Gao et al. 2016). Rapid decomposition of organic materials caused the C_{ox} loss through CO_2 volatilization, C leaching, and plant uptake (Turmel et al. 2015). In addition, a comparison between the soil and aggregates showed that the concentration of C_{ox} was higher in aggregates than in the soil (Figure 2). This could indicate that aggregates were stabilized and improved due to the binding agents through organic materials adsorbed, together with an electronic binding between negative charges of clay minerals and positive charges of oxides, and a coat of oxides on the surface of mineral forms bridged from one particle to the others (Six et al. 2004; Tivet et al. 2013). Nonetheless, once aggregates were stabilized, they could protect the C_{ox} from leaching, dissolving, reducing the accessibility for microbial decomposition, and for interacting between pores insides and outside of the aggregates (Goebel et al. 2005; Leue et al. 2015; Zhao et al. 2021).

In our result, the PWI was more pronounced after applying organic mulches to the soil surface. The wood and bark chips treatments had a higher soil PWI compared to straw and control. It is probably due to the less mineralization rate and because the wood and bark chips themselves contain more recalcitrance compounds and reduce microbial decomposition (Goebel et al. 2005). A comparison between the soil and aggregates (Figure 2) showed that straw, bark chips, and a generally organic mulching are able to enhance PWI in aggregates. The secondary metabolites produced from decomposing organic matter can be extremely hydrophobic, particularly from fungal exudates and hyphae (Hallett & Young 1999). Higher PWI values point to lower aggregate wettability, which caused a decrease in infiltration rates (Haas et al. 2018). However, the lower wettability could also result from the accumulation of organic compounds (terpenes and waxes), which came from the root and earthworm activity (Haas et al. 2018). Six et al. (2004) reviewed that high SOM content could lower wettability due to the increasing hydrophobic characteristics of SOM and the formations of various additional intermolecular associations during drying. Many researchers documented that once SOM content and compositions were improved, it could enhance the capacity of absorbing and retaining more moisture in the aggregates (Bajoriene et al. 2013; Hosseini Bai et al. 2014; Leue et al. 2015). Besides that, the clay-organic surface of aggregates is also able to decrease the potential wettability (Leue et al. 2010), which was supported by our result from the infrared spectroscopy showing the high content of clay fractions in the aggregates. Fér et al. (2016) found that the wettability of surface aggregates could be reduced by various mineralogical compositions of the clay (i.e., illite) in coating and interiors. It was also documented by Ellerbrock et al. (2009) that the rate of water and solute mass transfer could be decreased because of the influences of clayey aggregate coatings and lining along the biopores in the surface.

The variation of aromaticity index was significantly higher in the wood, bark chips, and straw treatment than in the control treatment. A comparison between soil and aggregates revealed that the straw and all mulch types showed higher iAR in aggregates than in the soil. This could indicate that mulches, especially straw, enhanced more aliphatic compounds in the aggregates. The greater iAR could result from the increase of SOM mineralization, which contained the aggregated-related aliphatic compounds (Jakab et al. 2019) and could be related to the proportion of aromatic compounds (lignin, phenols, and alkyl-aromatics) in the materials (Laudicina et al. 2015; Wiedemeier et al. 2015). Corvasce et al. (2006) reported that the aromatic compounds exist differently according to the plant residues and could be released into the soil through microbial decomposition. The aromatic compounds are likely to adsorb onto the soil particles rather than dissolve (Corvasce et al. 2006). Moreover, soil disturbance like tillage or soil stirring is expected to increase aromaticity in the aggregates-occluded soil organic matter (Jakab et al. 2019).

CONCLUSION

After applying the organic mulches (straw, wood chips, and bark chips), the content of C_{ox} was found

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higher in the aggregates than in the soil. On the other hand, the infrared spectroscopy showed the aggregate spectra of all variants including control without mulch had higher reflectances of the secondary alumosilicates than in the soil spectra. This indicated that these minerals abundant in clay fraction play an important role in aggregate creation, but differences in aggregate stability are mainly affected by organic compounds. Higher values of the aromaticity index mean a relatively lower proportion of aromatic components, or a higher proportion of aliphatic components of organic matter in stable aggregates than in unstable aggregates from the control plot. These substances are also considered to be hydrophobic and are therefore able to protect the aggregate from dispersion with water, which is confirmed by the higher values of the potential wettability index for stable aggregates from mulched plots.

Another more general result of the article is that infrared spectroscopy can provide useful information about the qualitative parameters of soils, both mineral and organic. In contrast, the E4/E6 ratio, commonly used to evaluate the quality of organic matter, proved to be less sensitive in this case.

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