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Diurnal changes of mineral and organic compounds in the rhizosphere soil of plants growing in sites with different soil parameters

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ABSTRACT

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There is a growing demand for efficient identification of different compounds in the rhizosphere soil. The main aims of this work were to conduct field experiments to identify possible differences in the composition of bulk soils in different sites, as well as in the rhizosphere soil, arising as a result of plant growth in sites with different soil characteristics and to study short-term (during daylight hours) variability in the composition of the rhizosphere soil. Soil samples were collected several times during the day at three sites characterized by different soil parameters. The soil taken from the roots of a widespread weed, nettle, and bulk soil (taken from the top layer of soil in the sites) were analyzed by Raman spectroscopy. The soil spectra showed bands of various organic and mineral compounds. The pH of bulk soils collected in the sites varied and depended on the type of soils and their composition, primarily on the amount of carbon and some minerals in the soils. This was observed even when the differences between the soil parameters in the sites were small. The content of different compounds in the rhizosphere soil was not constant but changed during the day. These changes were regular and varied across the three sites. It was assumed that the main factors influencing these variations were circadian fluctuations of root exudates and soil characteristics. Given the short-term variability of different compounds in the rhizosphere soil, sampling time should be chosen carefully to ensure correct interpretation of experimental data.

Contribution/Originality: Raman spectroscopy has been effectively utilized for the identification of mineral and organic compounds in soil. This experimental study demonstrated that the content of various compounds in the rhizosphere soil changes quite regularly over a short period. These fluctuations in the plant rhizosphere can occur even when soil parameters at different sites are similar.

1. INTRODUCTION

Chemical composition of soils is variable and influenced by many factors. Compared to bulk soil, the rhizosphere soil (the soil at the root-soil interface, the place where plant roots constantly release various organic compounds) is more variable. Root exudates act as chemical signals that lead to changes in the rhizosphere by enhancing the weathering of soil minerals and the transformation of soil organic matter (Lu et al., 2025). Root exudation of primary and secondary metabolites largely depends on plant species and environmental conditions. This is one of the main mechanisms for transferring plant-derived carbon to the soil (Moran & McGrath, 2021). Plants are able to control the quantity and quality of the root exudation (Maurer et al., 2021) and change the properties of the soil to adapt and ensure their survival (Vives-Peris, De Ollas, Gómez-Cadenas, & Pérez-Clemente, 2020). Thus, the chemical composition of the rhizosphere soil can change along with changes in the composition of root exudates.

Our knowledge of the processes controlling root exudation and relationships between rhizosphere soil and plants is still insufficient (Williams et al., 2022; Zhuang et al., 2024). This is particularly relevant for the temporal variability of root exudation and its impact on the surrounding soil. It is expected that daily fluctuations in soil physicochemical parameters may be related to temperature and rhizosphere activity (Fu, Weng, Fujii, & Zhou, 2018). In addition, short-term (diurnal) variations may be due to circadian changes in plants and in the rhizosphere soil (Shtangeeva, Bērtiņš, Vīksna, & Surzhik, 2020).

There is a growing need for efficient identification of various organic and mineral compounds present in soils. Today, routine laboratory methods of soil analysis are time-consuming and often involve the use of different chemical reagents (Demattê, Dotto, Bedin, Sayao, & e Souza, 2019). This requires the development of rapid, high-quality, multi-component analytical techniques. Raman spectroscopy (RS) is a promising non-destructive technique that allows fingerprinting at the molecular level (Yogurtcu, Cebi, Koçer, & Erarslan, 2024). This method has great potential for soil analysis. However, to date, RS in this area remains largely understudied (Sowoidnich, Maiwald, Ostermann, & Sumpf, 2023). The main reason for the infrequent use of RS in soil analysis is fluorescence interference, which occurs mainly due to the complex organic and mineral composition of soils and spectral interference (Li et al., 2024; Nkebiwe et al., 2022; Xing, Du, Zeng, Ma, & Zhou, 2016; Zarei et al., 2023). Raman spectra of soils often show high background signals that can mask weak Raman peaks (Theurer, Maiwald, & Sumpf, 2021).

In this study, we explored the potential of RS in the identification of organic and mineral compounds in bulk soil and in the rhizosphere soil of the widespread plant, nettle. The main objectives of the research were as follows:

- To identify possible differences in the composition of the rhizosphere soil of nettle that arise as a result of plant growth in sites with different soil characteristics.
- To assess how the root activity can change properties of the rhizosphere soil.
- To study short-term (within a day) variability in the composition of the rhizosphere soil.
- To evaluate the effect of differences in soil characteristics on the temporal fluctuations of various compounds in the rhizosphere soil.

2. MATERIALS AND METHODS

2.1. Sampling Sites and Protocol

Three sites were selected for the experimental study. Site 1 was located in the southeast of St. Petersburg, Russia (59°52′40″N, 29°51′00″E), site 2 was in St. Petersburg, 26 km from site 1 (59°50′57″N, 30°22′18″E), and site 3 was located 96 km north of St. Petersburg (60°42′59″N, 30°03′24″E). Each site was approximately 2.5 x 2.5 m in size. Sites 1 and 2 had similar soil characteristics, while soil parameters in site 3 differed from those in the first two sites (Table 1). Soils in sites 1 and 2 have undergone anthropogenic transformation; in site 3, the anthropogenic load was expressed to a lesser extent. At the end of May 2024, rhizosphere soil (soil adjacent to roots of widespread plant species nettle (*Urtica dioica* L.) and bulk soil from the upper (0–10 cm) horizon were collected from the sites simultaneously during the day at 9:30, 15:00, and 20:30. A completely randomized design was used for sampling. Each time, soil was taken from roots of at least three plants. To collect rhizosphere soil samples, soil was gently shaken from plant roots. The soil residues adhering to the roots were then collected. Soil samples were air-dried to constant weight and sieved through a 1 mm sieve to remove non-soil materials, including plant debris, and then stored in a fridge until analysis.

Table 1. Parameters of bulk soils collected from three experimental sites.

Sites	Texture	Sand, %	Silt, %	Clay, %	C, %	pH
Site 1	Sandy loam	59.47	39.25	1.28	5.75	7.55
Site 2	Sandy loam	59.36	39.07	1.57	5.26	7.63
Site 3	Loamy sand	80.88	18.91	0.21	1.27	6.78

2.2. General Analysis of Soil Samples

The pH (1:2.5 H_2O) of the soil samples was determined, and a modified Tyurin's method (Rastvorova, Andreev, Gagarina, Kasatkina, & Fedorova, 1995) was used to measure the total carbon in the soils. The granulometric composition of the soil samples was determined using the small-angle laser diffraction method on a laser granulometer Shimadzu SALD-2201 (Japan). The data were processed using the WingSALD software.

2.3. Raman Spectroscopy. Measurement Conditions and Instrument Parameters

To obtain Raman spectra of the samples, an OPTEC-785Video-M confocal Raman micro-spectrometer and an OPTEC-785TRS-2700 confocal THz Raman micro-spectrometer were used. The OPTEC-785Video-M micro-spectrometer included a CT-RAMAN-785-S703 OEM spectrometer for the spectral range of 100…3300 cm^{-1} (spectral resolution of 7 cm^{-1}), a BAC151B microscope platform (BWTEK Inc., USA) connected via a fiber-optic probe to the CT-RAMAN-785-S703 OEM spectrometer, and a laser with an excitation wavelength of 785 nm/CCTX-RAMAN-785-FI (Horiba Jobin-Yvon). The laser power was regulated within 10...420 mW. The laser beam was focused using a 20X objective (Plan Achromatic). Spectra were acquired with an exposure of 3 seconds. The average number of measurements for each spectrum was 100. Data processing, including baseline removal using a multi-polymodal method optimized to compensate for diffuse fluorescence bands, was performed using the OPTEC-Mobile Raman System software package (Software Registry for the Russian Federation No. 13217 (11.04.2022)). For spectral analysis of samples in the terahertz region, a confocal THz-Raman micro-spectrometer OPTEC-785TRS-2700 was applied (spectral range -200…+2700 cm^{-1}, anti-Stokes region of the Raman spectrum -200 cm^{-1}…-7 cm^{-1}, Stokes region - +7 cm^{-1}…+2700 cm^{-1}, spectral resolution 3.5 cm^{-1}).

The OPTEC-785TRS-2700 micro-spectrometer included a high-resolution spectrometer BTS162-785H (BWTEK, USA), a single-mode laser at a wavelength of 785 nm with an adjustable power of 5...100 mW, SureLock, an optical dispersing module with a volume holographic diffraction grating (VHDG) XLF-MICRO-785 (Ondax Inc., USA), and a Leica microscope platform DM2700M. The number of measurements for each spectrum was 64. The Savitzky-Golay algorithm (Savitzky & Golay, 1964) was applied to smooth the spectral contour. Measurements were performed three times per sample. The replicates were averaged to produce one spectrum per sample. Preliminary processing of the spectrum was carried out by adjusting the baseline using an iterative polynomial approximation. Processing of data obtained from the spectrometer was carried out using algorithms with the BWSpec4 and OPTEC-Raman version 1.2 software packages.

2.4. Statistical Analysis

STATISTICA for Windows 8.0 Software package (StatSoft, Tulsa, OK, USA) was used for the interpretation of the experimental results. The objective was to determine whether the Raman spectra of soils could be effectively distinguished from each other. Variables were compared using the t-test. For all statistical tests, the significance level was set at $P < 0.05$.

The normal distribution of the data set was verified with the Shapiro-Wilk test. Principal component analysis (PCA) was applied to better understand the distribution of different compounds in the rhizosphere soil, as well as to assess the contribution of various factors that may influence soil-plant interactions. For PCA, the original data were standardized.

3. RESULTS AND DISCUSSION

Air and soil temperatures varied slightly between sites during the sampling day, but they were always highest at 15:00 (Figure 1). The carbon concentrations and pH of the bulk soils in sites 1 and 2 were statistically significantly higher than in site 3 (Table 1).

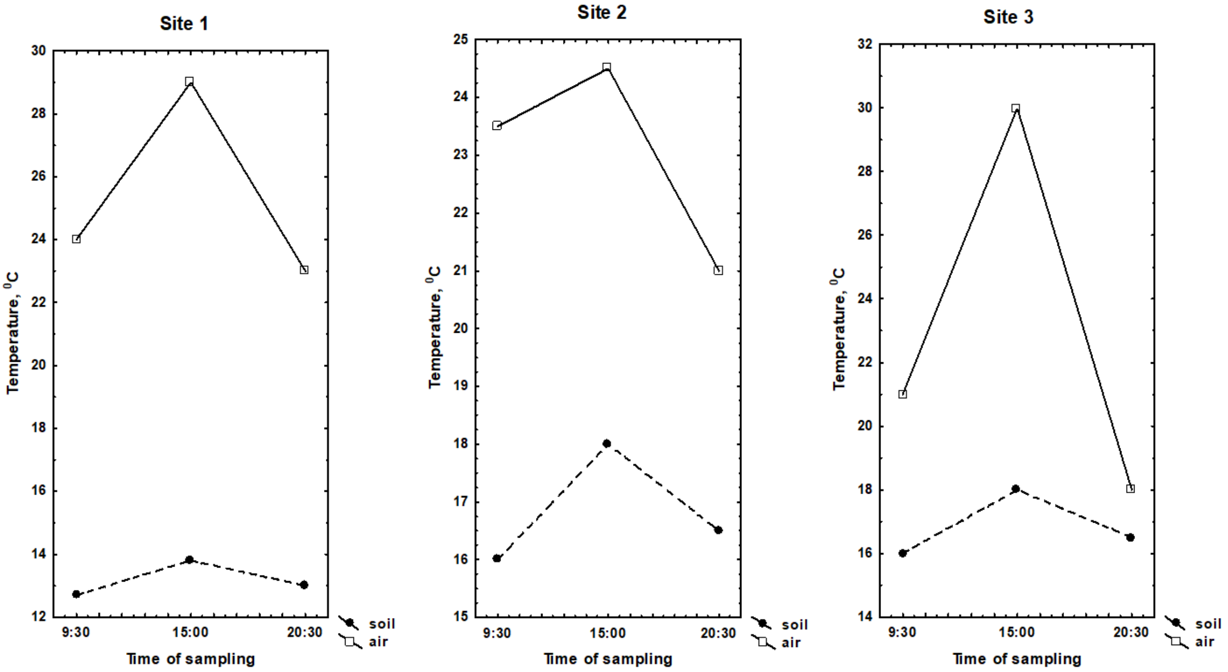


Figure 1. Variations of soil and air temperature in the experimental sites.

3.1. Comparison of Raman Spectra and pH of Bulk Soils of Three Experimental Sites

Figure 2 shows the Raman spectra of bulk soils from the experimental sites revealed vibrational bands attributable to various minerals and organic compounds. The mineral groups identified include feldspars (507 cm^{-1}), clay minerals (248, 335-340, 423 cm^{-1}), muscovite (259-261 cm^{-1}), carbonate minerals (1079, 1102 cm^{-1}), hematite (215-218 cm^{-1}, 324-326 cm^{-1}), hydroxyapatite (962 cm^{-1}), and quartz (467 cm^{-1}). Organic compounds detected encompass aliphatic compounds (1447 cm^{-1}), carotenoids (1005, 1218, 1513, 1525 cm^{-1}), carbohydrates (747, 915 cm^{-1}), cellulose (380, 1096, 1379 cm^{-1}), chlorophyll (740, 1196, 1325 cm^{-1}), lipids (1307 cm^{-1}), pectin (479, 850 cm^{-1}), and phenylpropanoids (1263, 1632 cm^{-1}). These findings provide insights into the mineralogical and organic composition of the soils, which are essential for understanding soil properties, fertility, and potential environmental interactions.

The Raman spectra of the bulk soils from the three sites demonstrated distinct mineralogical and organic features. The signal intensities of most bands in the bulk soils collected from sites 1 and 2 were 2-3 times higher than those in the bulk soil collected from site 3. In many cases, these differences were statistically significant. This can be explained by variations in the concentration of carbon in the soils collected from sites 1 and 2 compared to site 3 (Table 1). The one exception was quartz. Its signal intensity in the bulk soil collected at site 3 was higher than in the bulk soils taken from two other sites. This fact correlates with the sand content in the soils 82% in the soil of site 3 and 59% in the soils of sites 1 and 2. It is also known that the presence of calcite and dolomite in the soil can increase the pH of the soil (Huang et al., 2014). Therefore, the distinctions between the bulk soil pH values of site 3 and those of sites 1 and 2 can be attributed to differences in the availability of carbonates in the soils.

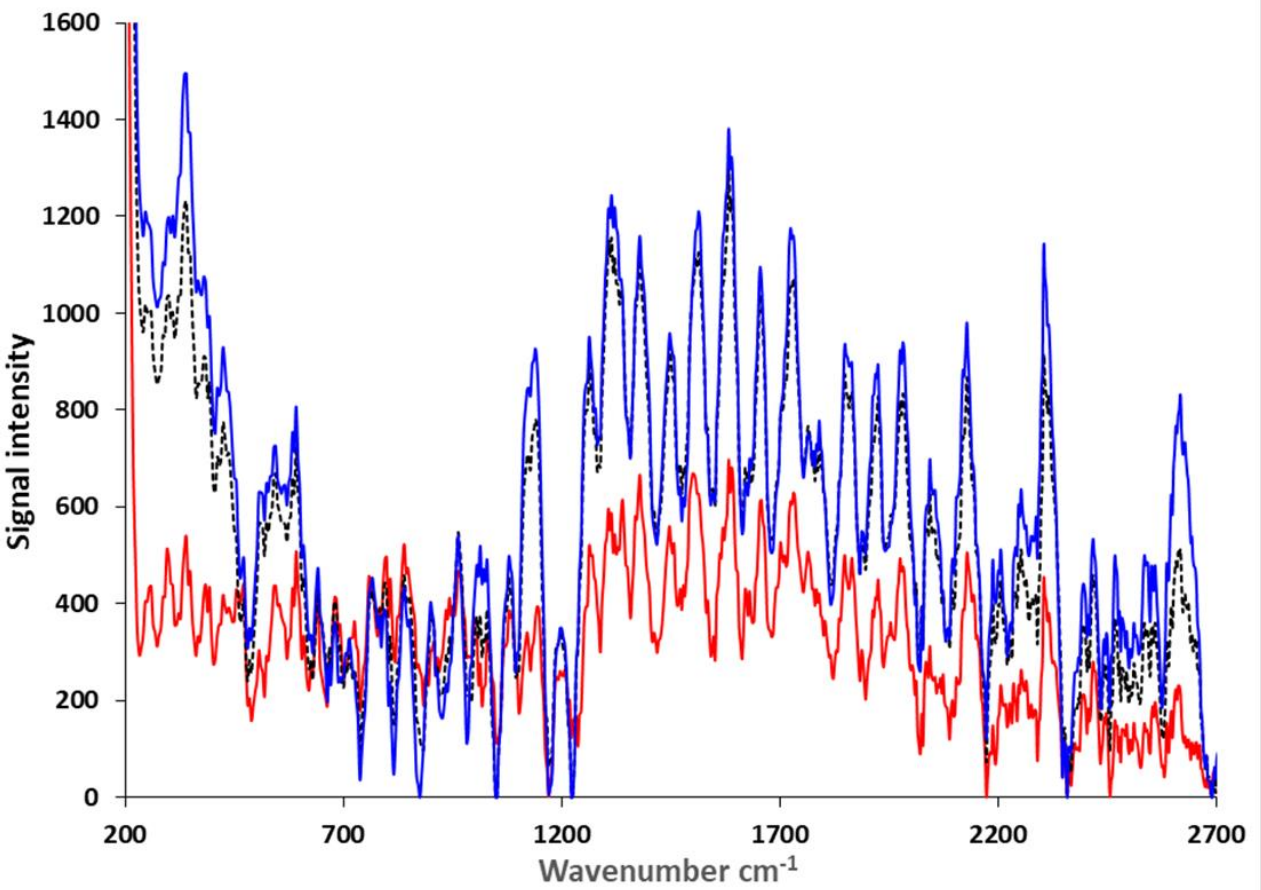


Figure 2. Raman spectra of bulk soils collected from site 1 (Blue), site 2 (Black dotted), and site 3 (Red).

3.2. Rhizosphere Soil

Overall, the rhizosphere and bulk soils contained the same mineral and organic compounds. However, some differences were found that indicated certain changes caused by plant growth in the soils. It is known that properties of soils can be modified by root exudates (Gregory, 2006). In particular, it can be assumed that organic compounds released by plant roots can cause not only changes in the composition of organic compounds in soil near the roots but can also lead to mineralogical transformations of the rhizosphere soil.

3.2.1. pH of the Rhizosphere Soil of Experimental Sites

Soil pH is one of the most routine parameters that can be measured using standard soil analysis (Miller & Kissel, 2010). There are many factors, both abiotic and biotic, that can influence soil pH. In particular, root exudates are capable of actively changing the pH of the rhizosphere by releasing various organic compounds into the surrounding soil, thereby altering their immediate environment (Badri & Vivanco, 2009). It was reported that the soil pH at the root surface can differ from the pH of the bulk soil by 1-2 units (Nye, 1981). However, usually the differences between pH on the root surface and in the bulk soil do not exceed 0.5–1 units (Kuzyakov & Razavi, 2019). In our case, the pH of the rhizosphere soil of plants growing in the three sites was statistically significantly lower than the pH of the bulk soil in the sites; however, these differences did not exceed 0.5 units.

Plants are able to balance the pH in soil near their roots. The lower pH of the rhizosphere soil, compared to the pH of bulk soil, was also reported by other authors (Bai, Wei, Ming, Shu, & Shen, 2023; Blossfeld, Gansert, Thiele, Kuhn, & Lösch, 2011; Chiu, Wang, Hwong, & King, 2002). However, it should be noted that this effect was observed when the soil pH was around 7; when it was lower (e.g., less than 6), the effect may have been the opposite (Youssef & Chino, 1989).

3.2.2. RS of the Rhizosphere Soil of Experimental Sites

In addition to pH, plants actively influence the distribution of various organic compounds in the rhizosphere soil, which is usually rich in carbon (Gianfreda, 2015). It has been shown that the closer the soil mass is to the plant roots, the greater the increase in the concentration of organic matter in the soil (Blossfeld et al., 2011). It is quite expected that the metabolic processes occurring in the rhizosphere can lead to the creation of a specific environment that will differ from that of the bulk soil (Hinsinger, Bengough, Vetterlein, & Young, 2009).

The effect of root exudates on soil properties depends on the physicochemical characteristics of the soil (Czarnes, Dexter, & Bartoli, 2000). It can be assumed that for the same plant species growing in soils of different composition, the relationship between root exudates and rhizosphere soil may differ, and the release of the same organic compounds by plant roots can change the chemical and physical properties of the soils in different ways. As an example, Figure 3 illustrates the Raman spectra of the soils taken from roots of nettle at 15:00 in the three sites. Except for quartz, the signal intensities of many bands were generally arranged as follows: site 1 ≥ site 2 >> site 3.

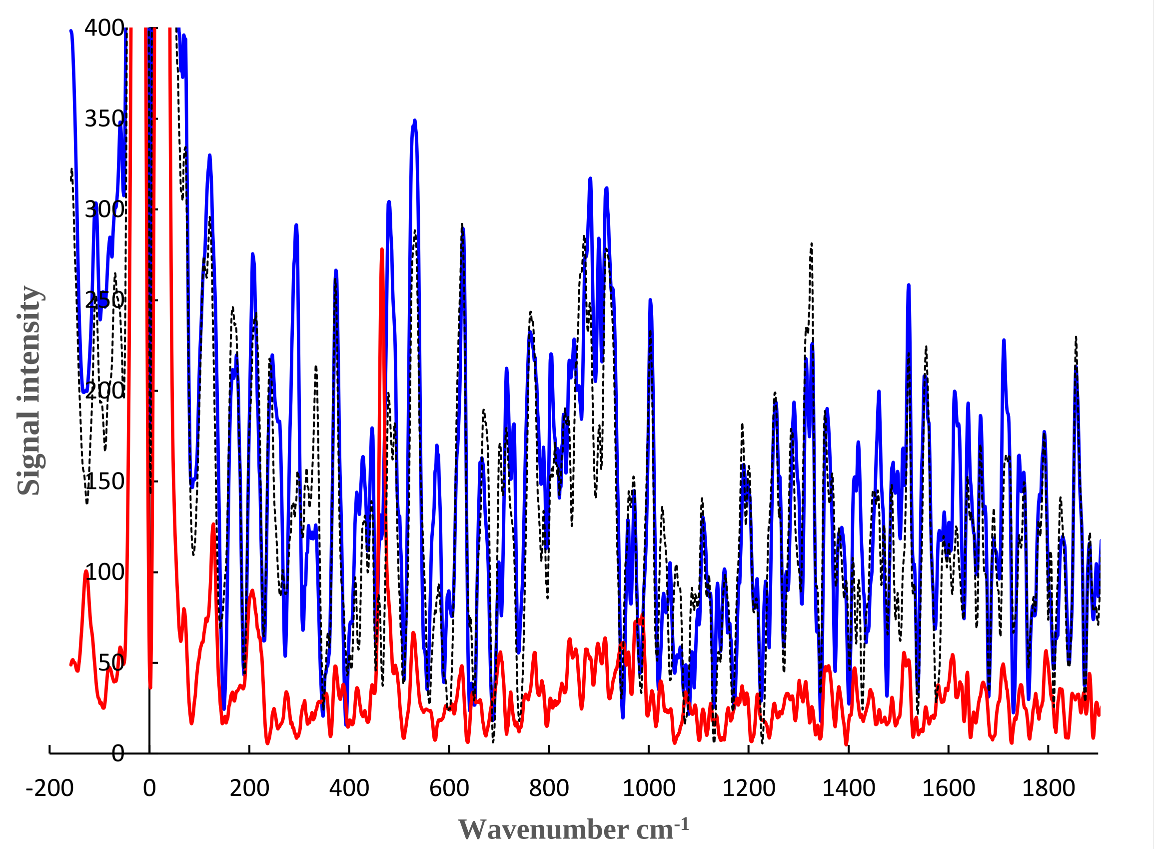


Figure 3. Raman spectra of soils taken from roots of nettle at 15:00 in site 1 (Blue), site 2 (Black dotted), and site 3 (Red).

Interestingly, the differences in the signal intensities in the spectra of the soils taken from roots of the plants growing in sites 1 and 2 and in site 3 increased compared to the differences between bulk soils in the sites. For many compounds, the differences between sites have reached 5-6 times. This was probably due to varying degrees of increase in organic matter concentration in the rhizosphere zone as a result of the release of various organic compounds by the roots of plants growing in these sites.

In Figure 4 are shown results of PCA of soil samples taken from roots of nettle growing in the three sites. The samples were well divided into different groups: nettle rhizosphere soil collected from sites 1, 2, and 3. The first principal component was responsible for the separation, and cellulose, quartz, carbohydrates, and carotenoids were highly correlated with PC1, suggesting that they were the main contributors to this separation.

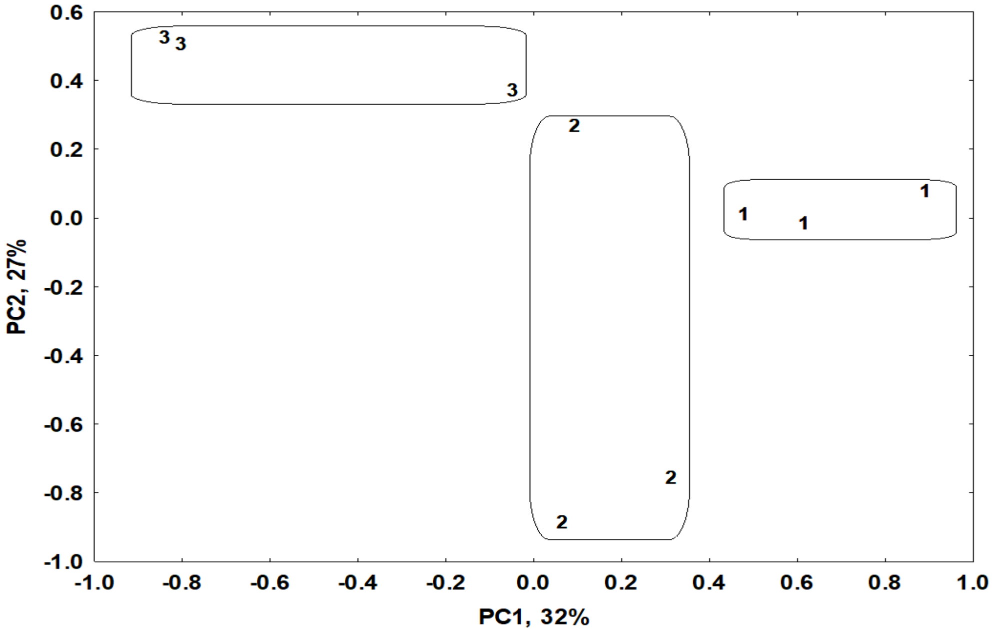
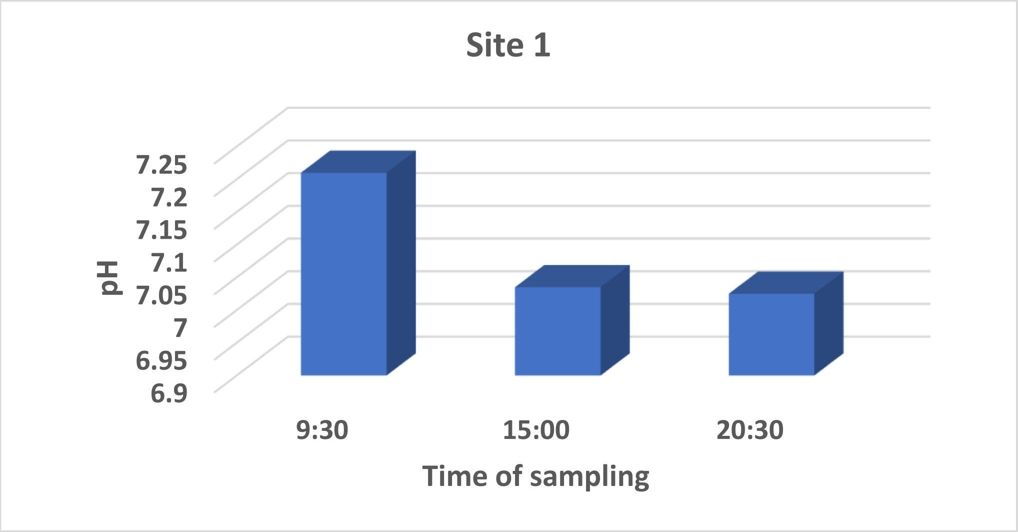


Figure 4. PCA of soil samples. Score plot of the first and second principal components. 1 – site 1, 2 – site 2, 3 – site 3.

3.2.3. Diurnal Changes in the pH of the Rhizosphere Soil

Figure 5 shows the daily fluctuations in the pH of the soil taken from roots of nettle. In sites 1 and 2, the highest pH value was found at the beginning of the day, whereas in site 3, the pH value of nettle rhizosphere soil varied with changes in soil temperature and was highest in the middle of the day. The daily variations in the pH of the rhizosphere soil might be expectable because this soil is in closest contact with plant roots. The composition of root exudates can vary during the day. These changes are quite regular; they result from circadian variations typical for all living organisms (Shtangeeva et al., 2020). On the one hand, it might be expected that temporal variations would be similar across sites if sampling was carried out at all the sites simultaneously. However, as can be seen from Figure 5, the daily variations in the pH of the rhizosphere soil depended on soil characteristics. As a result, in sites 1 and 2, these changes in soil pH differed from those observed in site 3.



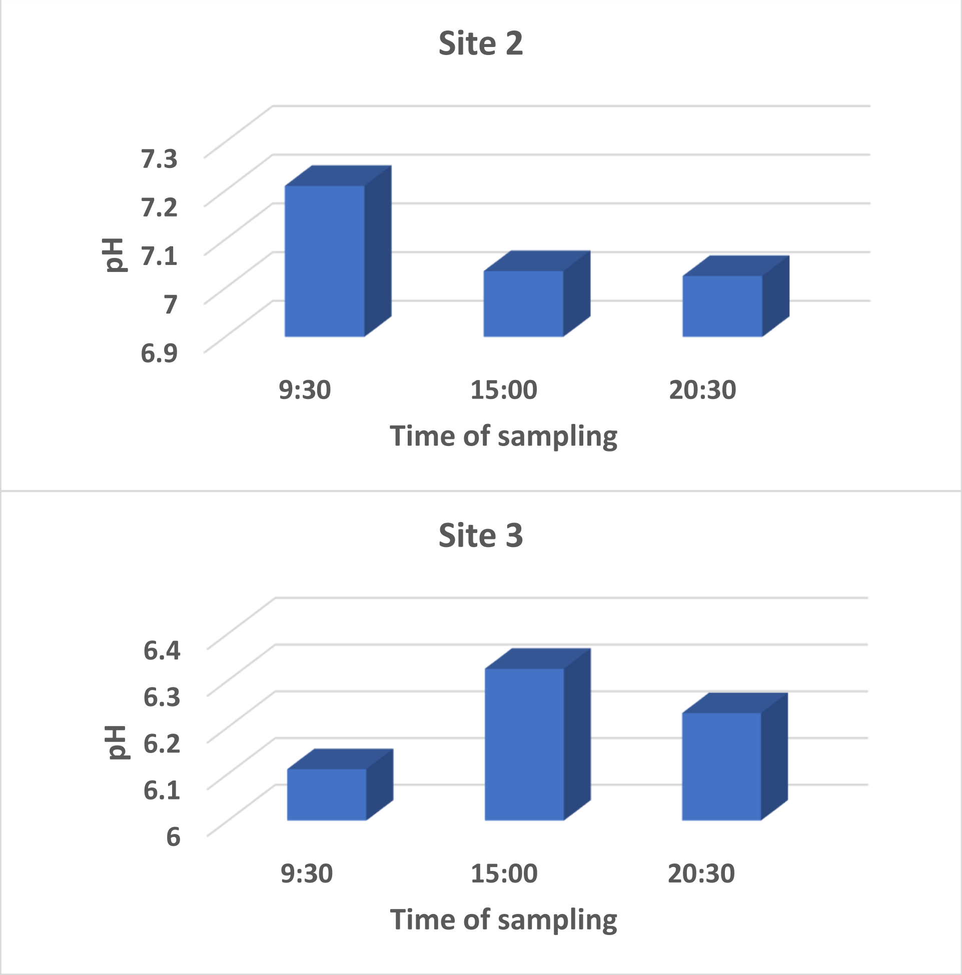
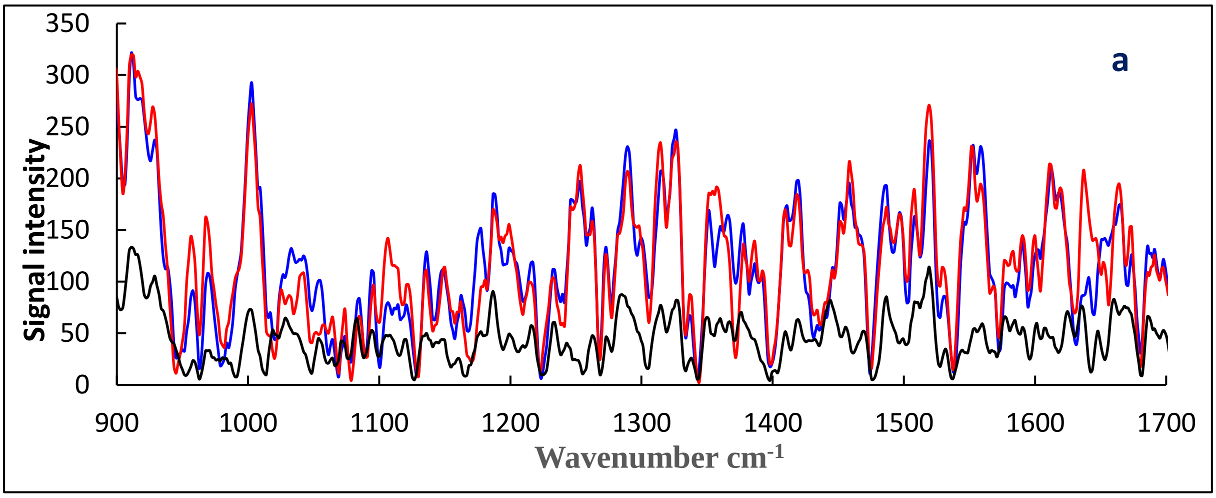


Figure 5. Daily variations in the pH of the rhizosphere soil of nettle in three experimental sites.

3.2.4. Short-Term Variability of Different Compounds in the Rhizosphere Soil of Nettle

The rhizosphere is a dynamic system. In our study, one of the most interesting observations was that the signal intensities of various compounds in the rhizosphere soil were not constant but changed during the day, and these changes were not uniform across the experimental sites.



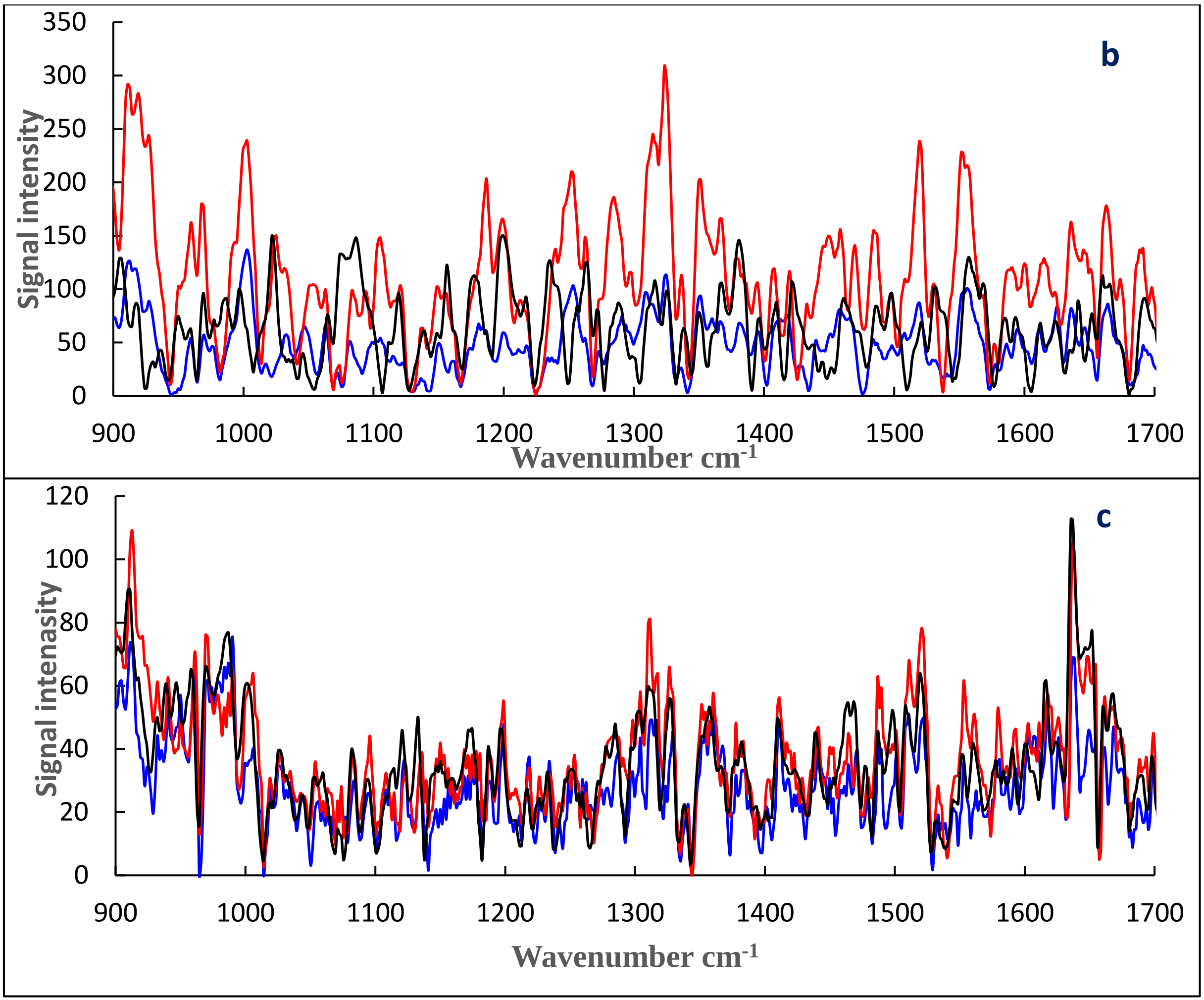


Figure 6. Raman spectra of the rhizosphere soil of nettle collected in the experimental sites at 9:30 (blue), 15:00 (red) and 20:30 (black). a – site 1, b - site 2, c – site 3.

Figure 6 shows the Raman spectra of the rhizosphere soil of nettle collected in the three sites at 9:30, 15:00, and 20:30. In site 1, signal intensities of many bands were often similar in the morning and midday, or slightly increased from 9:30 to 15:00 and then decreased significantly in the evening (Figure 6a). In site 2, the signal intensities of most bands were highest at 15:00 and much lower at 9:30 and 20:30 (Figure 6b). It is particularly noteworthy that although the soil characteristics of sites 1 and 2 were similar, there were some differences in the diurnal variations of many compounds in the rhizosphere soil of nettle growing at the sites. Compared with sites 1 and 2, the signal intensities of all bands (except quartz) in the soil taken from the roots of nettle collected at site 3 were significantly lower (Figure 6c). This was a result of the lower concentration of these compounds in the bulk soil at site 3. Additionally, daily fluctuations in the rhizosphere soil of nettle growing at site 3 were not as pronounced as in the other two sites.

Short-term changes in the signal intensities of different compounds in the soil taken from nettle roots in site 3 were in many cases similar to changes in the rhizosphere soil pH and soil temperature. In site 2, diurnal variations in the signal intensities were often correlated with changes in soil temperature, while in site 1, some correlation with rhizosphere soil pH was observed.

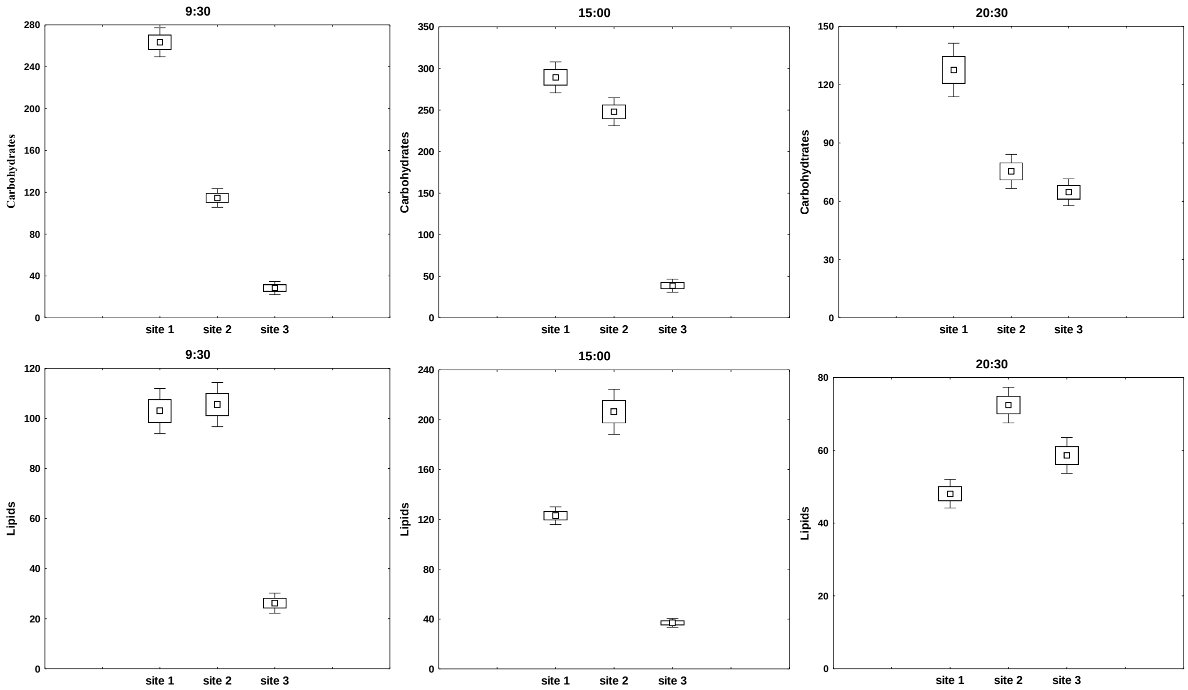
A comparison of the changes in the signal intensity of some typical organic compounds and quartz in the rhizosphere soil of nettle growing in three sites and collected simultaneously during the day showed the following (Figure 7):

- At 9:30, the signal intensities of carbohydrates, carotenoids, and chlorophyll in the rhizosphere soil of nettle were the highest in site 1, lower in site 2, and the lowest in site 3. The signal intensities of lipids in the soil taken from roots of nettle growing in sites 1 and 2 were similar and the lowest in site 3. The signal intensities of quartz in the nettle rhizosphere soil collected in sites 1 and 2 were similar and much lower than the quartz signal intensity in the soil taken from roots of nettle growing in site 3.

- After a short time, at 15:00, signal intensities of these organic compounds and also quartz increased, sometimes significantly. The only exception was quartz in the rhizosphere soil of nettle taken from site 2, where the intensity of its signal remained almost the same as in the morning.
- In the evening, at 20:30, the signal intensities of organic compounds in sites 1 and 2 decreased again. In the rhizosphere soil of nettle taken from site 3, these changes were often not so significant.

The circadian variations of organic compounds in the rhizosphere soil were expected. However, it was found that the signal intensities of bands of some minerals, including quartz, also changed quite regularly during the day. It is known that the release of organic acids by plant roots can affect the dissolution of mineral compounds (Lazo, Dyer, & Alorro, 2017). The review of published experimental data showed that the presence of organic acids in the rhizosphere soil increases the degree and rate of dissolution of different minerals (Lawrence, Harden, & Maher, 2014; Manimaran et al., 2025). It was also reported that the organic compounds exuded by roots can form organo-mineral associations through physicochemical interactions with soil minerals (Shabtai et al., 2024). Recent studies on the adsorption of organic molecules on the quartz surface have shown that amines in various forms are functional groups capable of strongly binding to quartz (Andersson & Stipp, 2025). It can be assumed that as a result of this process, new organo-mineral complexes may appear on the surface of soil particles in the rhizosphere soil. These new compounds can also presumably change in a relatively short time, just like organic compounds.

Serious differences between the distribution of various organic compounds and quartz in the rhizosphere soil of nettle growing in sites 1, 2, and 3 were expected. More interesting is the different behavior of these compounds and quartz in the soil taken from roots of nettle that grew in the sites with similar soil characteristics. The results of our experiments showed that even small differences in soil characteristics can influence the distribution of both organic and mineral compounds in the rhizosphere soil of plants growing in these sites.



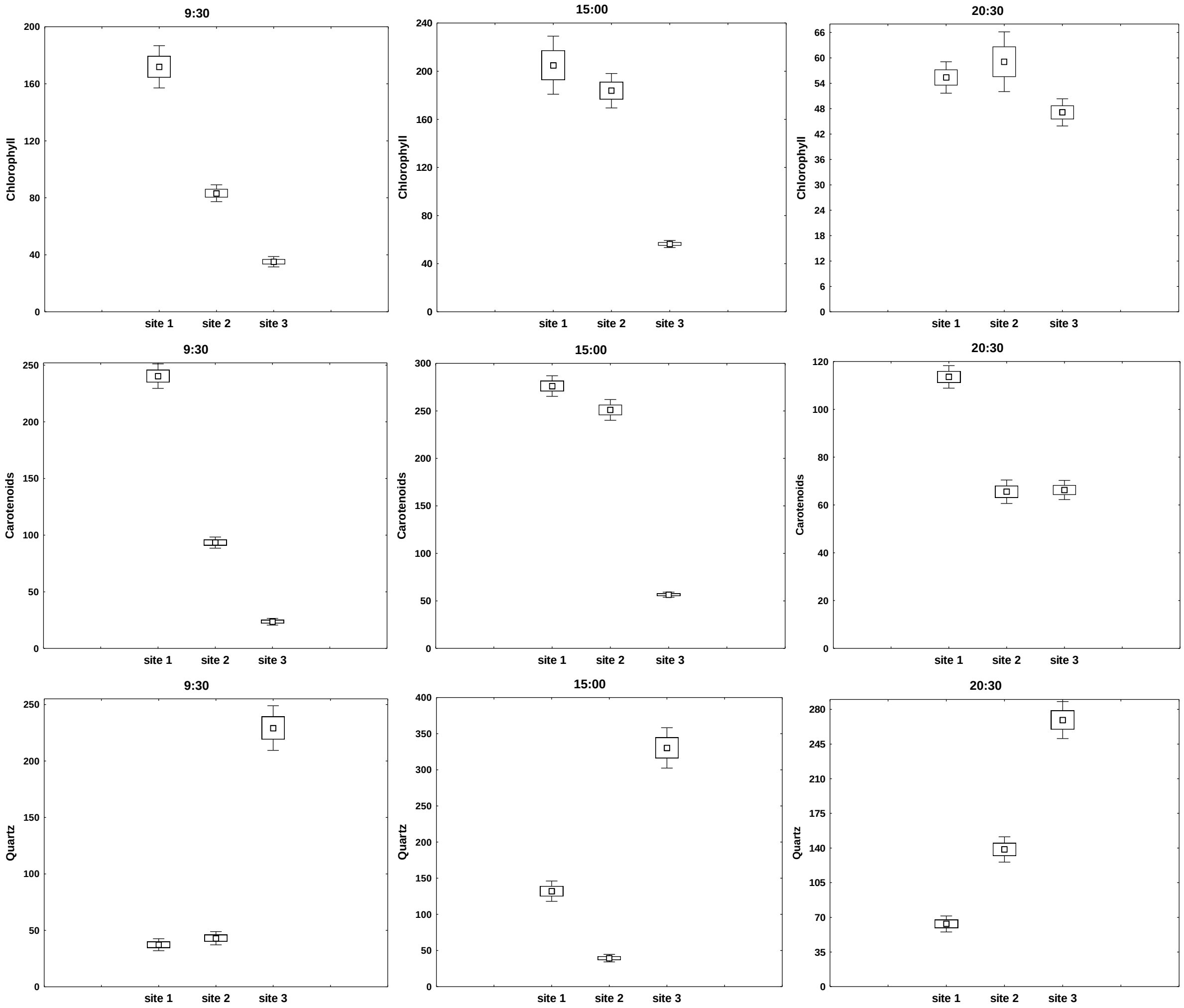


Figure 7. Signal intensities of carbohydrates, lipids, chlorophyll, carotenoids, and quartz in the rhizosphere soil of nettle collected simultaneously from three sites at 9:30, 15:00, and 20:30.

4. CONCLUSION

Our findings demonstrated that Raman spectroscopy is a promising analytical method for the analysis of environmental samples. This technique allows the identification of various mineral and organic compounds in complex materials such as soil and can be successfully used in biogeochemical studies. Data processing has enabled the reduction of fluorescence interference effects in Raman spectra of soil samples. The signal intensities of bands of organic and mineral compounds in the soils depend on the characteristics of the soils and can differ significantly between soils collected from different sites. The composition of rhizosphere soil is more variable compared to bulk soils. The concentration of various biomolecules in soil near plant roots can change over a short period (several hours). It has been suggested that these variations are primarily driven by circadian changes in root exudates released into the surrounding soil and may often differ between soils with different parameters. Such short-term variations should be considered during sampling.

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Competing Interests: The authors declare that they have no competing interests.
Authors' Contributions: All authors contributed equally to the conception and design of the study. All authors have read and agreed to the published version of the manuscript.

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