FTIR photoacoustic spectroscopy for identification and assessment of soil components: Chernozems and their size fractions

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ABSTRACT

FTIR photoacoustic spectroscopy was used to approach inorganic matrix components and organic-matter constituents of chernozem size fractions (1–5000 μm, by dry sieving) with a different history of use (from intact steppe to permanent bare fallow, a continuous long-term field experiment). The conditions of FTIR photoacoustic measurements in continuous-scan modes were compared with attenuated total reflection measurements, the advantages of photoacoustic measurements resulting from a higher intensity of the incident radiation and signal-generating volume were discussed. Overtone peaks of quartz as a soil matrix component at 2000–1700 cm⁻¹ were selected as a possible internal-standard (guide) bands for the comparison of photoacoustic spectra. For different land-use samples, differences in the composition were found, which are differently manifested in normalized spectra of size fractions, with millimeter-size, 20–100 μm, and silt fraction bearing the maximum information.

1. Introduction

IR spectroscopy has been used in soil research for a long time, but over the last two decades its role has dramatically increased due to a new technological level, advances in instrumental capabilities, new modalities, and increased inherent sensitivity [1–5]. Interferometer-based FTIR photoacoustic spectroscopy (FTIR-PAS) proves to be a developed instrument for complex samples [6–10]. It can be used for mineral, polymer, and technological samples, and is capable for the measurements and modelling of the dependence of soil properties on its physical and elemental composition, moisture, porosity, and density [11–19].

Apart from bulk soil properties, studies on the roles of agrogenesis and anthropogenesis on the changes in physical and physicochemical properties of soils become more and more topical [20–22]. A new and demanding level is the assessment of composition of soil fractions and structures including changes at meso- and microaggregate levels [23–26]. Solving these problems requires highly informative methods and approaches because soils are complex ensembles of inorganic matrices and soil organic matter (SOM) [27]. The latter itself is an organic-nominal continuum of high- and low-molecular organic and inorganic substances in a finely dispersed state [28] and the largest solid carbon reservoir [29].

The most widespread applications of FTIR-PAS include the identification of some soil components (mainly mineral matrices like carbonate, silicate, and clay minerals; SOM; or fertilizers) and research focused on plants and other objects [18,30–33]. The possibilities of PAS for assessing the distribution of a substance over the depth of micro-particles were considered for model particles [34] and soils [6]. Quantitative FTIR-PAS measurements include the determination of soil organic/inorganic carbon ratio [35], soil water content [36,37], and carbonate contents in carbonate soils [17]. The distribution of the SOM on depth layers of soil samples in long-term experiments was shown [16]. Due to the complex nature of FTIR-PAS information, the mainstream in data interpretation includes multivariate calibrations, and generalized and self-adaptive models for integral soil parameters like total and exchangeable P, N, K and total carbon were proposed [13,15,18,38–40]. FTIR-PAS can be on demand for studies of changes of properties of entities of different hierarchical levels under the action of agrogenesis and anthropogenesis [33,41].

Thus, most of the applications of FTIR-PAS are focused on either qualitative analysis of bands in soil samples or building the prediction models for rather different soil type matrices or models for general soil indicators [33]. As far as we are concerned, there are no studies in which FTIR-PAS spectroscopy is used for a more detailed molecular (structural) or functional analysis of soils.

Chernozems were selected for this study as test soil samples because they belong to the most fertile soils and are a significant organic carbon...
source giving more than 400 tons of carbon per hectare [42,43]. They also have a unique aggregate structure due to the peculiarities in composition of organic matter. Due to heavy agricultural use, the changes in chernozem SOM (both composition and the distribution) is a topical problem [44]. In the same time, the matrix of chernozems may also change upon use, both in the fractional and aggregate properties. Thus, assessing and monitoring the physical, chemical, and the whole structural composition of chernozems is a relevant problem.

The samples of Kursk chernozems from a continuous long-term field experiment were selected from intact steppe to permanent bare fallow and represent different land uses. They have a silicate matrix and no significant amounts of carbonate (no self-effervescence after applying 10% HCl), sulfate, and phosphate species [45]. In the previous applications of FTIR-PAS, chernozems were not studied by this method in detail, though it was found that water-extractable organic carbon contents shows a definite positive correlation to the IR absorbance at 2920 cm\(^{-1}\) assigned to CH\(_2\) vibrations and this correlation increased with the probing depth at a micrometer scale [6]. However, no detailed information on FTIR-PAS measurements is presented so far.

Thus, the aim of this study is to work out the approaches for the identification and assessment of inorganic components and organic-matter components of bulk samples and size fractions (by dry sieving) of chernozems as SiO\(_2\)-based SOM-rich soils with different type of land use by FTIR-PAS.

2. Materials and methods

2.1. Instruments

2.1.1. FTIR measurements

IR spectra were recorded on a Vertex 70 and a Vertex 70 V single-beam IR Fourier spectrometers (Bruker Optik GmbH, Germany) equipped with a He-Ne laser as a calibration line, a standard KBr and a wide-range silicon beam splitters, and wide-range DTGS detectors. Bruker OPUS 7.5 software was used for signal acquisition and processing.

In attenuated total reflection (ATR) measurements, a GladiATR single-reflection attenuated total internal reflection accessory with a diamond crystal (incident angle 45°; Pike Technologies, USA) and a wide-range silicon beam splitters, and wide-range DTGS detectors. Bruker OPUS 7.5 software was used for signal acquisition and processing.

| Parameter | FTIR-PAS | ATR-FTIR |
|-----------|----------|----------|
| Spectral range, cm\(^{-1}\) | 6000-300 or 4000-400 | 8 |
| Wavenumber resolution, cm\(^{-1}\) | 2 | 64 |
| Number of background acquisition scans | 64-256 | 2 |
| Number of sample acquisition scans | 64-256 | 64 |
| Phase resolution | 10 | 16 |
| Phase correction mode | Mertz or manual (see the text) | Mertz |
| Apodization function | Blackman–Harris, three-term | — |
| Zero filling | 2 | — |
| Aperture, mm | 8 | — |
| Interferometer modulation frequency, Hz | 150, 250, 1600, 2500, 7500, 10000 | 60-100 |
| Background acquisition preamplifier gain | Automatic | — |
| Sample acquisition preamplifier gain | Automatic | — |
| Pre-amplification | Ref | — |
| Source | MIR | — |
| Beam splitter | KBr or wide MIR-FIR (Si) | — |

2.1.2. FTIR-PAS measurements

FTIR-PAS measurements were made using a PAC 300 photoacoustic detector accessory (MTEC Photoacoustics Inc., USA) for direct photoacoustic detection of optical absorption spectra of solids and semisolids with IR Fourier spectrometers. The working principle of the detector is based on a single-dimensional heat transfer model, Fig. 1 [46–48]. The incident IR beam from the interferometer is focused from above on a horizontally located sample placed in a closed environment filled with a working gas with a limited volume. The IR beam is absorbed by the upper layers of the solid sample depending on its absorption coefficient and converted into heat. The temperature modulations depend on the interferometer modulation frequency, absorption coefficient at given wavelengths, and thermal diffusivity of the sample. Produced interferometer-modulated thermal waves from the volume limited by the thermal diffusion depth (thermal-wave decay length, Fig. 1a) or radiation-absorption depth (Fig. 1b) are transferred into the working gas; the direction of this one-dimensional heat flow is considered opposite to the direction of the incident beam [46–48]. Thermal waves generate pressure (acoustic) waves in the working gas that are detected with a microphone located near the main axis of the FTIR-PAS instrument. The reflection losses of the incident beam on the sample surface are considered negligible. The lower (rear) sample surface is thermally grounded and optically non-reflective.

This accessory mounts in the standard baseplate of a Bruker spectrometer inside the spectrometer sample compartment for vibration isolation. The PAC 300 sample chamber is purged with helium gas in order to increase the heat transfer from the solid sample to the working gas and provide the maximum signal generation (over a factor of 3 compared to air) [46]. The IR beam from the interferometer is focused to a diameter of 5 mm onto the sample surface (http://www.mtecpas.com). PAS 300 microphone sensitivity id 50 mV/Pa.

Samples prepared according to the procedure described below (Section 2.2) were placed into a stainless-steel sample cup (diameter, 10 mm; depth, 3 mm) without significant pressing or compacting (Fig. 2a), the amount of sample was selected so that the flattened upper surface is approximately 1 mm below the brass cup holder rim to ensure the minimum working gas volume to increase the detection sensitivity. The test sample was put in the nest of the cup holder, which was put and sealed in the PAC 300 accessory (http://www.mtecpas.com). The cell compartment was purged with helium for 5–10 s; next, the helium flow was stopped, and the spectrum was measured. Before each FTIR-PAS measurement, the background (reference) spectrum (Fig. 3) was recorded using a highly pure compressed graphite (carbon black) standard reference sample from MTEC Photoacoustics Inc. (Fig. 2b). Except for slow-scan measurements (see below), where single sample measurements were made (due to significant time required for a single measurement), in all other cases, the data were obtained for three replicate measurements and averaged after the whole data post-processing described below (Sections 2.1.2–2.1.4).

The parameters for recording FTIR-PAS spectra are summed up in Table 1. FTIR-PAS spectra were obtained in continuous-scan modes, by varying the interferometer modulation frequency (rapid-scan modes of 10.0, 7.5, 2.5, and 1.6 kHz and slow-scan modes of 250 and 150 Hz at the reference He–Ne line of the FTIR spectrometer), which correspond to the optical path difference (OPD) velocities of 0.0095, 0.158, 0.101, 0.158, 0.475, and 0.633 cm/s, respectively. The number of scans for a sample and background are: at frequencies of 150 Hz −1.6 kHz, 64 and at 7.5–10.0 kHz, 256. The aperture of the FTIR spectrometer was set fully open. In each experiment, the preamplifier gain was set to provide the centerburst interferogram amplitude of several volts but without preamplifier clipping to provide the work of the AD converter of FTIR spectrometers [46]; the gain was set independently for the reference and sample measurements.

For all the samples, the whole information package—reference
interferogram and single-channel reference amplitude spectrum, sample interferogram, phase spectrum, and single-channel sample amplitude spectrum—were stored. The final reference-divided PAS spectrum was automatically calculated by point by point division of the single-channel sample spectrum to the single-channel reference spectrum by Bruker OPUS 7.5 software. Software correction of the peaks of environmental CO\textsubscript{2} and H\textsubscript{2}O was not used during acquisition and applied at this point. The insignificant effect of the water vapor contribution in the range 2000–1200 cm\textsuperscript{-1} was checked by the measurements of the reference material, poly(propylene), see Supplementary information, Fig. S1, and the acquisition of the reference-divided spectra of carbon black vs. carbon black by the software (Fig. 3, red line).

2.1.3. Data phase correction
For all FTIR-PAS measurements, the phase spectra for the reference and sample were checked (the phase spectrum for the reference was either calculated from the interferogram or used explicitly in carbon black vs. carbon black sample measurement). If the phase spectrum of the reference was below or in the crossing position with the sample spectrum, the reference interferogram was shifted by 1 or 2 points according to \cite{49} to obtain a reference phase spectrum completely above the sample phase spectrum. From this data, the new amplitude single-channel spectra and the resulting FTIR-PAS reference-divided spectrum were rebuilt manually with environmental correction by Bruker OPUS 7.5 software to account for water vapor contribution. In most cases, when relative positions of the phase spectra were correct, no manual reconstruction was done, and the spectra obtained by default Mertz phase correction provided by Bruker OPUS 7.5 software were used instead.

2.1.4. Post-measurement data processing
Spectra are always smoothed and wavenumber-corrected; in the case of quantitative estimations they were background-corrected and normalized by the range selected as an internal-standard band (quartz, quartz).
see below). Initially, all ATR-FTIR and FTIR-PAS spectra were processed using built-in functions of Bruker OPUS 7.5 software. FTIR-PAS spectra were smoothed out by 9–25 points; ATR-FTIR spectra, by 9–17 points. As carbon black was used as a reference, FTIR-PAS spectra were corrected by multiplication by $\sqrt{\nu}$, where $\nu$ is the wavenumber to balance the intensities in the shortwave range, according to [48].

For peak identification, the automatic peak picking function of Bruker OPUS 7.5 software was used; for shoulder and weak peaks, similar automatic peak picking was used on first and second-derivative spectra, respectively; derivative spectra were produced by Bruker OPUS 7.5 software.

To compare peak intensities for various size fractions and probing depths, peak areas were used. Peak integration was made by Method A (integration between peak boundaries without baseline subtraction [here, methods are named according to Bruker OPUS 7.5]) for soil matrix range 1300–300 cm$^{-1}$; by Method D (partial integration of overlapping peaks with double-side straight-line-regression baseline correction) in the overtone range 2500–1300 cm$^{-1}$, and by Method F (full integration of sharp peaks over broader peaks with double-side polynomial-regression baseline correction) for the shortwave range 6000–2500 cm$^{-1}$.

Baseline correction for the whole spectra was not applied due to the complex nature of the spectrum and no means to account for the band of water in 1000–500 cm$^{-1}$ [50]; for certain parts of the spectra, automatic concave rubber-band baseline correction was used separately in the ranges corresponding to ranges indicated in the previous paragraph.

FTIR-PAS spectra normalization was made by manually selecting the normalization range in Bruker OPUS 7.5 software, the range was no wider than 500 cm$^{-1}$. Built-in vector normalization protocol was used. For quantitative estimation, the data were normalized using appropriate band ranges: 3700–3600 cm$^{-1}$ (aluminosilicate peaks) for 6000–2500 cm$^{-1}$; 2000–1750 cm$^{-1}$ (quartz combination bands) for the overtone range 2500–1300 cm$^{-1}$, and 800–700 cm$^{-1}$ (quartz lattice bands) for the matrix range 1300–300 cm$^{-1}$. Overtone SiO$_2$ bands of 2052–1924, 1924–1836, and 1832–1751 cm$^{-1}$ were used as internal standards for comparing various land use types. The integral intensities of selected bands (3050–2800, 1712–1570, 1540–1515, 1480–1440, 1420–1365, 1350–1315, and 1310–1225 cm$^{-1}$) were divided by the peak area of one of the internal standards.

In SOM annealing experiments (Section 2.2), FTIR-PAS spectra of initial (unheated) and processed (heated) samples were exported to Excel spreadsheet software, corrected, and normalized as above, and the difference spectra were built. Due to different matrix absorptions, the spectra were processed by subranges and then manually reunited.

The profiling depths of specific absorption bands at a wavenumber $\nu$ under different modulation frequencies were estimated using the thermal-diffusion length $\mu(\nu) = D_T/\pi f(\nu)$, where $D_T$ is sample thermal diffusivity and $f(\nu)$ is the modulation frequency at the wavenumber $\nu$ [48]. The values of $f(\nu)$ were calculated from OPD velocities as $f(\nu) = \text{OPD} \cdot \sqrt{\nu}$. The values of thermal diffusivity of quartz were taken from [51]. The values for thermal diffusivities of chernozems were taken from the previous findings on chernozem by photo-thermal-beam deflection measurements [52].

To achieve comparable intensities in ATR-FTIR, all values of the ATR spectra were corrected $(I_a + a) \times b = I_{corr}$, where $I_a$ is the registered intensity, $a$ is the coefficient lying in the interval 0.02–0.005; $b$ is the coefficient in the interval 20–35; and $I_{corr}$ is the intensity after the correction.

### 2.2. Samples

Typical (Haplic) chernozems (Loamic, Pachic) from the Kursk region (Russia) with a significantly different history and intensity of land use: native (intact) steppe vegetation, shelterbelt since 1964, cropland under wheat cultivated without rotation since 1964, and permanent bare fallow since 1964 were selected for the study. The details on these samples are given elsewhere [53]. Samples were taken on the site of a long-term field experiment of Kursk Research Institute of Agricultural Production and the Streletska k STEP of the V.V. Alekhin Tsentralno-Chernozemny Nature Reserve [54]. Soil granulometric composition is a heavy silty clay loamy texture. Main components are quartz, 35–40%; illites, 12–15%; smectites, 12–15%; and total organic carbon, 4–6%. The humus horizon (A + AB1) is 105–130 cm. Soil effervescence after applying 10% HCl starts from a depth of 65–70 cm. The density of the arable layer (0–30 cm) varies from 1.20 to 1.25 g/cm$^3$ [45]. For comparison with soils, model samples of pure quartz sand (fraction 10–50 µm) and silica gel were used.

General soil samples (4–5 kg), in triplicate, were taken in 2017 at sites with a radius of 5 m using an envelope method according to GOST 17.4.4.02-2017 Russian State Standard, the sampling depth is 0–10 cm (topsoil). General samples were dried for two weeks in air, then stored at room temperature. An average sample of 0.5 kg was taken from the corresponding general sample, crushed, and sieved through a 1 mm sieve.

Fractionation of the average samples was carried out on an AS 200 sieving machine (Retsch GmbH) with a dry sieving holder and a set of precision sieves with a stainless steel mesh, 200 mm in diameter and square mesh sizes of 50, 63, 71, 80, 90, 100, 250, and 500 µm, and 1, 2, and 5 mm (Retsch GmbH). Ultramicro sieves with a diameter of 200 mm and square cells of 20, 30, and 40 µm (Precision Eforming LLC, USA) were used to obtain fine fractions. Dry sieving procedure consisted in sieving the whole sample (ca. 300 g) on a 5000, 2000, 1000, 500, 250, 100, and 50 µm sieve column. Then, a fraction of 50–100 µm (ca. 10–30 g) was processed on a column with 90, 80, 71, and 63 µm sieves. The obtained fraction below 50 µm (ca. 1–20 g) was sieved through a column of 40, 30, and 20 µm sieves. The sieving time on each of three stages was 15 min (paused for a short time each minute) at a sieving amplitude of 3 mm. Thus, soil fractions with particle sizes below 20, 20–30, 30–40, 40–50, 50–60, 60–71, 71–80, 80–90, 90–100, 100–250, 250–500, 500–1000, 1000–2000, 2000–5000, and above 5000 µm were obtained.

Silt soil fractions (below 1.0 µm) were isolated by Shaimukhametov modification of the elutriation method [55,56]; the sample is exposed to ultrasound (UltraSonic, power 75%, 22 min) and then the particles are separated to < 0.2 and 0.2–1.0 µm fractions on an Eppendorf 5910R centrifuge. The remainder of the soil after the sludge separation was divided into 1.0–2.0; 2.0–5.0; 5.0–10.0, 10.0–50.0, and > 50 µm fractions by sedimentation according to [56], the conditions were calculated by the Stokes equation.

To remove the organic constituents of the fractionated samples, annealing in air was performed for 3 h at a temperature of 525°C in a SNOL 10/900 shaft high-temperature electric laboratory furnace (AB Umega Group, Lithuania).

### 3. Results and discussion

#### 3.1. Band assignment and modality comparison

FTIR-PAS measurements of chernozems show rather distinct IR spectra with many features (Fig. 4 and 5) resembling previous data on chernozems obtained by other infrared modalities [57,58]. For all the studied samples, FTIR-PAS spectra show good precision of the measurements of the replicate portions of the same sample. The procedure of manual correction of the reference interferogram [49] (Section 2.1.3) provided extra account for PAS spectra difference due to reference interferogram changes. As a result, high reproducibility of spectra of replicate measurements of the same sample was achieved: the relative standard deviation was as low as 0.05–0.07 for the range of 4000–1000 cm$^{-1}$.

It is claimed that mid-IR absorbance bands of soil samples associated with characteristic soil attributes drop into three regions: 4000–2000, 2000–1400, and 1200–500 cm$^{-1}$ [11], corresponding to...
hydrogen-bond region, organic matter region, and inorganic soil matrix, respectively. The authors of [59] used individual databases for interpreting peaks in FTIR-PAS spectra, although this interpretation showed peak assignment as organic or inorganic only without possible overlapping of different compounds. In our opinion, this picture is too simplified, because the inorganic part of the soil is more sophisticated and manifests itself in the whole region. According to [60], the mid-IR range of such complex organomineral samples can be divided into three main parts (Fig. 4): matrix fingerprint region 1100–500 cm\(^{-1}\), overtone-combination band region 2500–1200 cm\(^{-1}\), and OH-region, 4000–2500 cm\(^{-1}\). We believe that this region division better suits the studied soil samples.

As the selected soil type, chernozems and their size fractions, are free from calcium carbonate, phosphates, and sulfates at the level they are seen that are usually attributed to SOM. However, this range is also known to have complex high-level vibrations of amorphous SiO\(_2\) and quartz species [60,62,63]. Still, the shape and relative positions of these peaks is rather from SOM, which was previously commented in various cases of soil FTIR analysis [35,38,57,58]. It is worth mentioning here that these peaks are clearly seen in slow-scan modes of FTIR-PAS (Fig. 6) and almost disappear in rapid-scan modes at 7.5 kHz or higher.

The region 2500–2000 cm\(^{-1}\) does not show any peaks except for the atmospheric CO\(_2\) doublet; the only exception are low-intensity peaks at 2230 and 2140 cm\(^{-1}\), which most probably should be assigned to the second overtone and combination of SiO\(_2\) vibrations of 1153 and 1070 cm\(^{-1}\) [60,63]. These bands start the range that is dominated by overtone and combination bands of SiO\(_2\) peaks.
The region 2050–1750 cm\(^{-1}\) has some distinct peaks, which are claimed to be the manifestation of C–O stretching vibrations of various oxidized moieties of chernozem SOM and are consistent with the data from isolated humic substances [64, 65]. However, this range is known to contain rather strong combination bands of lattice vibrations of SiO\(_2\) amorphous or SiO\(_2\) overtone–combination bands in negligible. These peaks manifested themselves only for fractions of large sizes, for silt fractions all these peaks are negligible (Fig. 5), which agrees with low contents of crystalline minerals in silt soil fractions.

A medium-to-weak and relatively broad peak can be found by deconvolution in 1710–1680 cm\(^{-1}\) of the shortwave shoulder of the intense broad peak centered at 1620 cm\(^{-1}\). This peak can be assigned as C=C stretching of aromatic components of SOM [57] and has no distinct counterparts in inorganic matrix components. Still, the intensity of this peak is very low, and it can be used for detecting some extra absorptions and, no quantitative approaches without sample preparation were able under the conditions of the experiments.

Bands at 1650–1580 cm\(^{-1}\) are primarily associated with soil water and silicon dioxide [35]. The intense rather wide peak at

| Band, cm\(^{-1}\) | Organic (matrix) constituent | Organic constituent | PAS | ATR |
|---|---|---|---|---|
| 5300 | Water, combination band v1 + v3 + v4 | n/a | Weak | Absent |
| 3730 | Si–OH stretching (kaolinite, clay) | n/a | Shoulder | Absent |
| 3700 | Si–OH stretching, tilted (kaolinite, clay) | n/a | Medium | Absent |
| 3620 | Al\((\text{Si},\text{Al})\)-OH stretching, straight | n/a | Intense | Medium |
| 3600–3580 | Water, stretching, comprised of: N–H stretching | Intense, broad | Medium |
| 3490 | asynchronous v3 | O–H, phenolic, alcohol, carboxylic | | |
| 3270 | synchronous, v3 | O–H, phenolic, alcohol, carboxylic | | |
| 2940–2860 | (7) SiO\(_2\) overtone, complex overtone–combination bands | C–H aliphatic chains, stretching | Medium to weak, broad | Weak |
| 2260–2220 | SiO\(_2\) overtone \(\approx 2 \times 1095\) | n/a | Weak | Negative, Artefact |
| 2140 | SiO\(_2\) overtone \(\approx 2 \times 1070\) | n/a | Weak | Negative, Artefact |
| 2030 | SiO\(_2\) combination band \(\approx 1000 + 1037\) | C–H aromatic bending overtone | Shoulder | Absent |
| 2000 | SiO\(_2\) overtone \(\approx 2 \times 1000\) | C=O stretching | Medium | Negative, Artefact |
| 1970 | SiO\(_2\) combination band \(\approx 920 + 970 + 1000\) [60] | C=O stretching | Shoulder | Negative, Artefact |
| 1950 | SiO\(_2\) combination band \(\approx 960 + 1000\) | C=O stretching | Shoulder | Weak |
| 1880–1866 | SiO\(_2\) combination band \(\approx 697 + 1163\) | C=O stretching | Intense | Weak |
| 1783 | SiO\(_2\) combination band \(\approx 697 + 1072\) | C=O stretching | Intense | Weak |
| 1710–1680 | SiO\(_2\) combination band \(\approx 760 + 920\) | N–H bending, amine; silene –C=C– stretching, amide I, aromatic –C=C– stretching [16] | Weak shoulder | Absent |
| 1650–1640 | water, bending v\(_3\), absorbed | Intense, sharp | Medium |
| 1620–1610 | SiO\(_2\) overtone \(\approx 2 \times 795\) | C=O stretching | Intense | Intense |
| 1540–1515 | SiO\(_2\) combination band 450 + 1070 [71] | amide II, aromatic rings, carboxyl C | Shoulder | Absent |
| 1460 | SiO\(_2\) amorphous, combination band \(\approx 350 + 1153\) | O–H, C–H bending | Shoulder | Absent |
| 1420 | Mg–OH stretching [60] | C–H stretching | Shoulder | Weak, shoulder |
| 1380 | SiO\(_2\) amorphous or SiO\(_2\) overtone \(\approx 2 \times 697\) or combination band \(\approx 350 + 1000\) [60] | O–H (coordinated bonded water) | Intense | Absent |
| 1260 | SiO\(_2\) combination band \(\approx 450 + 795\) | amide III, C–O stretch of aromatic rings and carboxylic acids [38], C–O stretching | Medium shoulder | Absent |
| 1230 | Combination band SiO\(_2\) \(\approx 470 + 760\); silicates | amide III, C–O stretch of aromatic rings and carboxylic acids | Shoulder | Absent |
| 1175 | Combination band SiO\(_2\) \(\approx 305 + 964\) or \(\approx 450 + 697\) [60], amorphous silica [86] | n/a | Medium, shoulder | Absent |
| 1153 | Lattice SiO\(_2\) | n/a | Medium | Medium |
| 1095 | SiO\(_2\), silicate Si–O stretching [86] | cellulose | Medium, shoulder | Medium |
| 1070 | Lattice SiO\(_2\), Si–O stretching (kaolinite, illite) | n/a | Intense | Intense |
| 1037 | Silicate Si–O stretching (kaolinite, illite) | carbohydrates | Intense, shoulder | Intense |
| 1000 | SiO\(_2\) Si–O stretching lattice | n/a | Intense, shoulder | Intense |
| 975 | SiO\(_2\) silicate Si–O stretching (kaolinite, illite) [86] | n/a | Intense, shoulder | Intense |
| 930–910 | Silicate, aluminosilicate overtone SiO\(_2\) \(\approx 2 \times 450\) | n/a | Shoulder | Absent |
| 860 | Al–OH (clay minerals) | n/a | Weak | Shoulder, Absent |
| 830 | Al–OH (clay minerals), smectite and illite [61] | cellulose | Weak | Weak |
| 796 | SiO\(_2\) lattice stretching SiO\(_2\) silicate [86] | C–H bending (non-aromatic) | Intense | Medium |
| 774 | Mg–OH, Al–OH (clay minerals) | n/a | Intense | Intense |
| 750 | Mg–OH, Al–OH (clay minerals) | n/a | Intense | Intense |
| 720–690 | Water, librations, C–H bending (aromatic) | n/a | Intense | Intense |
| 697 | SiO\(_2\) Si–O–Si bending, lattice | n/a | Intense | Intense |
| 665 | Silicate Si–O–Si bending, iron oxide | n/a | Intense | Intense |
| 513 | SiO\(_2\) silicate Si–O–Si bending | n/a | Shoulder | Intense |
| 490 | SiO\(_2\) Si–O–Si bending | n/a | Shoulder | Intense |
| 470 | SiO\(_2\) Si–O–Si bending [86] | n/a | Weak | Intense |
| 450 | SiO\(_2\) Si–O–Si bending lattice | n/a | Intense | Intense |
| 430–420 | Mg–OH, Al–OH (clay minerals) | n/a | Shoulder | Intense |
| 400–395 | SiO\(_2\) Si–O–Si bending lattice; water, librations | n/a | Intense | Intense |
| 370–365 | R(SiO\(_2\)) [60]; amorphous silica [86] | n/a | Medium | Intense |
| 350 | SiO\(_2\) | n/a | Medium | Intense |
| 330 | (7) Mg–O stretching [60] | n/a | Medium | Intense |
| 318 | Mg–O stretching | n/a | Medium | Intense |
1620–1615 cm\(^{-1}\) is composite and seems to be a combination of two peaks at 1640 and 1600 cm\(^{-1}\) corresponding to main bending vibrations of absorbed water [50] and one of the main overtone bands in quartz and silica (Table 2), respectively.

The long-wave shoulder of this peak at 1600–1580 cm\(^{-1}\) is another region with possible non-matrix contribution, and it was previously used for nitrate species in soils [38]. However, in our opinion, apart from large contributions from water and silicates, it corresponds to the strong absorption band of black carbon [67] used as a FTIR-PAS reference (Fig. 3), so distortions in possible contributions are unavoidable. Finally, the secondary peaks appear centered at 1530 cm\(^{-1}\), which is another overtone band of quartz [62]. Thus, the region 1600–1500 cm\(^{-1}\) is disadvantageous for quantification with FTIR-PAS unless another reference sample is used.

The region of 1450–1220 cm\(^{-1}\) also shows well defined medium-intensity peaks that are attributed to overtones and combination bands of bending vibrations in quartz and hydrosilicates, especially 1390, 1270, and 1240 cm\(^{-1}\) (Table 2). According to existing DRIFT measurements, main bands in typical soils are \(\text{CH}\)–bending vibrations including aliphatic and aromatic \(\text{CH}\)–(1300–1500 cm\(^{-1}\)) and \(\text{CO}\)–stretching vibrations from carbonates (1400–1500 cm\(^{-1}\)); however, no control over possible inorganic constituents was done [58,68]. The band at 1400 cm\(^{-1}\) varying in different soil types is attributed to \(\text{NO}\)–contributions [38]. Thus, in our opinion, this region cannot be used for SOM quantification.

A small series or peaks between main and overtone ranges of quartz at 1200 and 1190 cm\(^{-1}\) cannot be unambiguously attributed to quartz or hydrosilicate, although some discussion exists in the literature [60]. Still these peaks reside on a shoulder of intense peaks at 1170 and 1153 cm\(^{-1}\) corresponding to main absorption bands of quartz (Figs. 4 and 7), so that the assessment of these minor components using peaks at 1200 and 1190 cm\(^{-1}\) is hardly possible.

The region of 1190–900 cm\(^{-1}\) is not well-defined intensity-wise, as the intensities are distorted due to saturation effects [46,48]. As the absorption coefficient of crystalline components of the soil matrix is about 4000–10,000 cm\(^{-1}\) at wavenumbers of 900–1100 cm\(^{-1}\) [69], the signal generation shifts from a thermally governed (Fig. 1a) to a radiation-governed mode (Fig. 1b), and the peaks become distorted intensity-wise [46]. Well defined overtone and combination bands are also the manifestation of this. The same picture is observed for quartz and large to medium soil fractions. The same spectra were observed for rapid and slow-scan modes (Fig. 6) with significantly different penetration depths, which is also an evidence of radiation-based character of these saturation effects. In amorphous \(\text{SiO}_2\), the same saturation effect is observed, while overtone and combination regions are poor due to no significant contributions from the silicate lattice.

Despite the saturation effects, all major quartz and hydrosilicate bands are distinguishable. The band at 1020–950 cm\(^{-1}\) is attributed to \(\text{SiO}\)– stretching from both quartz and clay minerals, with the bands at 950–600 cm\(^{-1}\) dominated by the vibration of \((\text{Mg,Al})-\text{OH}\) in clay minerals at 915 cm\(^{-1}\), iron oxides at 700–600 cm\(^{-1}\) together with possible contributions from aromatic and amine vibrations [15] are clearly seen. A low-intensity, but very stable peak at 830 cm\(^{-1}\) may be attributed to illite and smectite minerals [61].

To sum up, the analysis of the spectra and band assignment shows that in the whole region the spectra of chernozem soils are dominated with the quartz/hydrosilicate matrix and soil water, so these should be main targets for assessment from IR spectra. Contrary to some previous findings, SOM components cannot be assessed directly without some chemical or thermal sampling or without further spectra processing.

As far as we are concerned, a full comparison of PAS, DRIFT and ATR features for soils was not done, although some advantages characteristic to PAS like depth profiling are shown [10,48,70]. Within the frames of this study, we intended to compare the spectral information provided by PAS and ATR modalities for the same samples. These modalities are somewhat complementary (Fig. 4). From the viewpoint of CH vibrations at 2900–2800 cm\(^{-1}\) region, the sensitivity of ATR and PAS modalities are the same, and the advantage of PAS is the depth probing only. For inorganic components, ATR provides more resolved structural modes of the main lattice vibrations of the matrix in 1150–900 cm\(^{-1}\) region due to no absorption saturation at the ATR penetration depth, while FTIR-PAS measurements of the soil in this region experience a serious change in relative peak heights for 1170, 1130, and 950 cm\(^{-1}\) due to the saturation effects as discussed in the previous section. However, the lower radiation intensity and shallower optical penetration depth in ATR does not provide enough absorption to reveal the overtone and combination bands of matrix minerals (Fig. 4) and they can be revealed only for a long accumulation time with low signal-to-noise ratios (Fig. 8). To the contrary, these overtone vibrations are induced in FTIR-PAS even for high rapid-scan frequencies (and, thus, shallow penetration depths), and crystalline matrix forms can be assessed in FTIR-PAS, even rather low-intensity combination modes at 2000 cm\(^{-1}\) can be found. It is noteworthy that other FTIR modalities usually require a rather significant absorption to reveal overtone bands, and in the case of minerals and optical quartz samples, a preparation of thin films of various thicknesses are required to reveal either main or overtone regions by transmission modes [60,71]. Still, several samples are required for the whole range of 6000–300 cm\(^{-1}\), while FTIR-PAS
provide the full band spectra (apart from the saturated region) from a single run. Thus, from the viewpoint of inorganic soil constituents, PAS more readily provides more detailed information, which under the same conditions is produced under transmission measurements in thin films [60,71]. From the viewpoint of SOM, its contribution is detectable, although the sensitivity is not high (see Section 3.3 below) and sample preparation techniques like SOM isolation or annealing should be used [57,58]. From this viewpoint, FTIR-PAS have the same advantages and disadvantages as DRIFT, which is discussed in the literature [66]. Also, it is noteworthy that ATR spectra of soil fractions in the main mineral part at 1200–300 cm\(^{-1}\) are well resolved, and it seems expedient to use PAS and ATR modalities together for a more detailed information on soil structure and composition, which was out of frames of this study.

### 3.2. Selection of internal standards for sample comparison

Contrary to many existing studies on soil properties by FTIR-PAS, when data processing consisted in normalizing the amplitudes in the whole studied range before applying partial least square (PLS) models, so that the spectrum area integral was equal to one [31,35], we worked with the spectra from initially different samples (size fractions or different land uses, Sections 3.4 and 3.5 below). Thus, we normalized the spectra according to internal-standard (guide) concept, when some part of each sample is considered the same despite the sample differences.

Candidates for such an internal standard in soil spectra may be peaks of major inorganic components. Among three main components of Chernozem soils, illite and smectite cannot be selected as they may have a different composition in the soil matrix and thus show some changes in the characteristic peaks. To the contrary, quartz and hydrosilicate band positions are much more stable [60,62,63] and characteristic. Still, the region of 1150–900 cm\(^{-1}\) cannot be used in FTIR-PAS due to the peak intensity distortion in this area due to saturation and also should be avoided due to possible specular reflections, especially for large particles, similarly to previously discussed DRIFT modalities [66]. The region below 900 cm\(^{-1}\) is much more promising as it holds the major lattice peaks of SiO\(_2\) at 797, 695, 450, and 394 cm\(^{-1}\).

In the shortwave region, characteristic peaks of clay minerals at 3700–3600 cm\(^{-1}\) are narrow and used for calculating some soil indices [72], see next section. However, they are overlapped with a OH\(^-\) bands at 3600–2600 cm\(^{-1}\) that is difficult to compensate and also can change its intensity after annealing [67]. In the overtone region, as discussed in the previous section, the peak at 1615 cm\(^{-1}\) cannot be used due to huge
overlap with the absorbed-water peak, also it is in the range of water vapors in both the reference and sample spectra and is close to the intense peak of black carbon (Fig. 3), which may distort the shape and intensity of this peak.

Thus, most promising as an internal standard is the triplet of SiO$_2$ combination bands at 2050–1750 cm$^{-1}$ (Fig. 4). The comparison of samples of various types, fractions, and before and after the annealing procedure (Section 2.1.4) showed that the relative intensities and shapes of these peaks change insignificantly. From the viewpoint of SOM analysis, in several research papers, the region of 2000–1200 cm$^{-1}$ was claimed to be used for SOC/SIC related soil analysis due to little interference in the peaks of inorganic species and not an individual peak can be used without spectral processing.

This triplet was checked for the possible distortion of these peaks during the acquisition of the reference-divided spectrum because of different contributions from water vapors in the reference (Fig. 3) and sample spectra. It was found that these peaks have the same area for replicate measurements of the same soil sample (subsequent measurements of portions of the sample, repeatability conditions) and measurements of the same sample in different days (reproducibility conditions). Also, the areas of these peaks are coincident for quartz and soil samples with the similar grain size (Fig. 7).

It should be noted that such selection of an internal standard should be accompanied with signal preprocessing like that mentioned by K. Michaelian [49]. As FTIR-PAS operates with sample-to-reference division spectra, and without a manual data phase correction (Section 2.1.3), the resulting peak intensity may change considerably, which makes the use of an internal standard incorrect.

### 3.3. Quantitative estimations of mineral indices

IR spectroscopy can provide the quantitative data from peak positions as corresponding vibrations depend on the participating atoms, the structure of characteristic fragments, and the clusters. In the spectra obtained, each of characteristic regions can be used for this purpose. In the lattice region, 1200–300 cm$^{-1}$, the peak positions correspond to quartz as a main component, and the shifts in the peak positions are within the error of measurements for crystalline SiO$_2$ and hydrosilicate minerals. The only exception is a weak peak at 830 cm$^{-1}$, which is present in the FTIR-PAS spectra of all fractions including silt fractions. It is attributed to illite and smectite and its position is known to depend on the ratio of smectite and illite [61]. We found that its position does not change from sample to sample by more than ±3 cm$^{-1}$, and it corresponds to the ratio of illite : smectite of 1 : 1 according to previous findings [61], which agrees with this ratio found by independent methods. No other peaks involving aluminum- and magnesium-containing minerals show a chemical shift depending on the concentration of mineral components, so they probably cannot be used for assessment of mineral components.

Also, we attempted to used FTIR-PAS spectra for assessing the crystallinity of illite components by calculating so-called Fiehlm index ($I_{50}/I_{60}$) [72]. The results showed that for most fractions, its value is 0.2–0.3, which corresponds to a metamorphic illite. However, this calculation was hindered by the not very advantageous shape of the band at 750 cm$^{-1}$ (a rather weak shoulder that produced a high error of measurements). Still, the application of a mineralogical index to soil sample seems rather promising for the applications of FTIR-PAS for soil analysis due to the possibilities to get many intense and reproducible peaks from a single sample run without sample preparation.

### 3.4. Soil size fractions

The quality of FTIR-PAS spectra does not significantly differ for various size fractions (Fig. 5). All fractions, except the silt fraction of 1 µm show the characteristic peaks of quartz and hydrosilicate, see Section 3.1. As discussed above, the region 2050–1750 cm$^{-1}$ does not change due to dominating SiO$_2$ vibrations, so any of the peaks at 1980, 1880, and 1780 cm$^{-1}$ can be used as internal-standard bands. In the NIR region, aluminosilicate peaks can be used, however with caution.

Previously, FTIR-PAS measurements revealed an absorption region in the wavenumber range of 1500–1350 cm$^{-1}$ in samples near the surface (0–10 mm) of paddy soils that was claimed to be dominated by C–O (carbonate) and CH bending vibrations (organic materials); and these vibrations were assumed as representing soil inorganic carbon and SOM, respectively [35]. The range 1450–1380 cm$^{-1}$ was used as the soil total organic/inorganic ratio using a PLS model [35] and also for assessing carbonate contents in carbonate soils [17]. However, as discussed above, this is not true for silicate soils, as silicate and quartz matrix exhibit multiple intense peaks in this region.

The necessity for multivariate calibrations is mentioned and the generalized and self-adaptive models for total and exchangeable P, N, K and SOM were proposed [13,15,18,38–40]. The complex nature of soils both in inorganic and organic components requires a very large collection of calibration samples, and the same type of soil is highly demanded [18]. However, in our case, as most peaks were identified as inorganic matter, special treatment should be used for estimating SOM. We selected annealing at 525 °C (Section 2.1.4), a widespread approach for removing SOM from soils [3]. The comparison of spectra showed almost no changes in the matrix region, while OH and overtone regions changed significantly (Fig. 9). To sum up, water peaks at 3600 and

![Fig. 9. Photoacoustic spectra (Bruker Vertex 70, 2.5 kHz) of a cropland sample of Kursk chernozem, fraction 80–90 µm: (a) before (black) and after annealing at 525 °C for 3 h (red). Photoacoustic measurement parameters: resolution, 8 cm$^{-1}$; 128 scans; preamplifier gain, ×200 (position 7) for the reference and ×2000 (position 10) for the sample. Spectra were smoothed, normalized in the range 2080–1820 cm$^{-1}$, and not background-corrected.](image-url)
1640 cm$^{-1}$ decrease, and the latter changes the silicate peak at 1600 cm$^{-1}$. As expected, peaks of CH at 2900–2860 cm$^{-1}$ disappear completely, as do rather significant wide absorption bands at 1550–1450 and 1300–1150 cm$^{-1}$. Most changes are in 1550–1470 cm$^{-1}$ (the long-wave shoulder of 1640 cm$^{-1}$ peak), which may be due to a loss of both SOM and coordinated water. Another changing range is 1300–1200 cm$^{-1}$, which can be attributed to CO– stretching. Bands at 2260 and 2140 in the annealed spectra become more pronounced proving that they are SiO$_2$ overtone bands. These changes manifested themselves in all the fractions starting with 100–250 μm and below. In the cases of the lowest unseparated fraction (below 20 μm) and silt fractions, quantitative comparison is not possible as the most convenient triplet of quartz is absent, which hinders the normalization.

The whole set of used interferometer modulation frequencies of 10, 7.5, 2.5, and 1.6 kHz and 250 and 150 Hz (slow-scan modes) showed that all the studied samples experience a relative decrease in the intensities of peaks attributed to inorganic matrix components: 3700–3600, OH area 3600–2800, overtone triplet 2100–1900, silicate peaks at 1700–1500, and the whole matrix area 1150–300 cm$^{-1}$. Weaker overtone bands at 2230 and 1530 do not manifest themselves starting with frequencies above 1.6 kHz. However, peaks attributed to SOM (2900 and 2860 cm$^{-1}$) also become statistically insignificant in rapid-scan modes. In fact, no new statistically significant features that can be attributed to SOM appear for low modulation frequencies. However, for silt fractions, due to lower contents of crystalline quartz, the matrix effects are smaller, and the number of matrix peaks is also lower, so varying the modulation frequency does provide a change in spectra.

Penetration depths for the selected modes correspond to estimated thermal diffusion lengths of 30–40 μm for slow-scan modes, 10–30 μm for 1.6–2.5 kHz and 4–10 μm for 7.5–10 kHz. Thus, for most fractions, the penetration depth is shallower but comparable with the fraction sizes. The silt fraction is a different situation as the signal grain size ca. 1 μm is smaller than the thermal-diffusion length, so in this case we have the average signal from many grains. It manifests itself in the in the independence of the silt fraction spectra from the modulation frequency.

Apart from this, the interpretation of the results should consider the soil particle structure. In existing papers, the comparison of modulation frequencies is based on the model of layered soil particles [73]. However, in our opinion, this model for soil particles is not very realistic as usually soil particles have a very thin layer of SOM with SOM aggregates attached to the surface of larger matrix particles [74]. This was further proven by the comparison of samples of different soil use.

### 3.5. Samples of different soil use

Soil use type defines the SOM content [75], and the structure affects the stabilization processes of the SOM in general [76–78]. Nowadays, much attention is paid to the degradation processes of soils under their active use, as well as to the means to control or restore chernozem structure and hydrophysical properties [79–81]. Thus, we tested soils of the same type but with significantly different history and intensity of use. These samples belong to a 55-year-long field experiment of the V.V. Alekhin Tsentralno-Chernozemny Nature Reserve [54]. They can be sorted depending on the organic contents. The intact steppe is an example of chernozem with undisturbed properties and probably maximum SOM content, while forest shelterbelt is the previously used soil with restoration with fresh organic matter entering from the forest. Permanent fallow is the soil annually cultivated without sowing and preventing the weeds; hence, no fresh organic matter has entered the soil, contrary to the shelterbelt. Finally, cropland is the soil under constant agricultural use with depleting SOM without any restoration. Thus, these samples may be a good basis for a comparison of soils with similar SOM and inorganic constituents.

The FTIR-PAS spectra of whole soil samples for steppe, shelterbelt, fallow, and cropland do not differ significantly in all the most informative regions. Thus, the analysis of separate fractions seems expedient, as soil fractions are different from the contribution of soil fertility [82–85]. The obtained fraction spectra differ from each other (Supplementary information, Fig. S2). To compare the spectra, we normalized them to a band of SiO$_2$ internal standards (Section 3.2) as its content in various land use sample differ significantly, so changes in other components, both depending on the SOM, amorphous, and meso-structural components may be revealed after such an intensity normalization. According to the band identification (Section 3.1), changes in inorganic components, possible contributions from SOM, and the selection of internal standards (Section 3.2), we selected the following subranges. Overtone SiO$_2$ bands 2052–1924, 1924–1836, and 1832–1751 cm$^{-1}$ were selected as they may reflect changes mainly due to inorganic matrices; and bands at 3050–2800, 1712–1570, 1540–1515, 1480–1440, 1420–1365, 1350–1315, and 1310–1225 cm$^{-1}$ were selected as possibly containing SOM components and mostly quartz contributions that may be corrected by normalizing with a SiO$_2$ internal standard. As expected, for all three selected internal-standard bands, all the ratios between integral intensities 2052–1924, 1924–1836, and 1832–1751 cm$^{-1}$ do not change for all the studied soil types, size fractions, and modulation frequencies.

Comparing size fractions, it was found that coarse fractions

**Fig. 10.** Spectra of Kursk chernozem, fraction 2–5 mm (Bruker Vertex 70, 10 kHz), with different type of land use: intact steppe (light green), shelterbelt (dark green), permanent fallow (black), and cropland (red). Photoacoustic measurement parameters: resolution, 8 cm$^{-1}$; 128 scans; preamplifier gain. ×200 (position 7) for the reference and ×5000 (position 11) for the samples. Spectra are smoothed, wavenumber-corrected, and background-corrected and normalized by the range of 1924–1836 cm$^{-1}$.
experience more notable changes compared to fine fractions (see the example in Fig. 10). Ratios for bands at 1540–1515, 1480–1440, 1420–1365, 1350–1315, 1311–1225 cm⁻¹ to internal standards (2052–1924, 1924–1836, or 1832–1751 cm⁻¹) provide similar results (Fig. 11). The maximum ratios were found for the modulation frequency of 10.0 kHz, and the ratio drops down in a similar matter with a decrease in the modulation frequency. This can be accounted for a larger contribution from surface groups at high modulation frequencies. At this stage, we ran preliminary tests for a limited collection of samples, so it is difficult to attribute these changes to silicate, water, or SOM groups, but most changes were observed in the ranges showing difference peaks in annealing experiments.

For the band at 3050–2800 cm⁻¹, the signals for all the fractions increase with a decrease in the modulation frequency. The baseline correction in this area does not change the situation, so this behavior can be attributed to higher signals from SOM at this CH region at lower modulation frequencies as the thermal penetration depth under interferometer-modulation frequencies of 1.6 and 2.5 kHz correspond to probing the whole soil particles of fine fractions and a significant part of coarser fractions with more contribution from SOM.

From the viewpoint of different land uses, the bands at 1540–1515, 1480–1440, 1420–1365, 1350–1315, and 1310–1225 cm⁻¹ provide a similar picture (see Fig. 11 as an example): for coarse fractions shelterbelt samples provide the highest signal followed by intact steppe; cropland usually shows lower signals, and permanent fallow shows signals comparable or lower than the cropland samples. For finer fractions, the differences are smaller, but the division of samples into steppe/shelterbelt and fallow/cropland pairs remain. The same picture is for ranges 845–720 and 717–670 cm⁻¹, here both coarse and fine fractions are divided into unused and used land type pairs. For 3050–2800 cm⁻¹ range, shelterbelt still has the maximum signal, but close to them is fallow. A detailed discussion of the changes in chernozem soil on the land use was beyond the frames of this paper, but the difference in land types is in agreement with the behavior of the same soils in thermogravimetric experiments [53].

4. Conclusions

Thus, extended mid-IR photoacoustic spectra of chernozem soils of various agrogenesis conditions show differences depending of the land use that can be used as a basis for advanced soil studies. It seems important that apart from well-known features of depth analysis by FTIR photoacoustic modalities, FTIR-PAS provides rather reproducible conditions for various size fractions, and these fractions hold more differences compared to entire soils. FTIR photoacoustic modality shows a much higher sensitivity in the middle-wave range of the mid-IR range (SiO₂ overtone range) compared to an attenuated total reflection modality and provides the information similar to a diffuse-reflectance modality but without sample dilution. FTIR photoacoustic measurements are possible for soil aggregates up to 5 mm without sample decomposition or milling, which a unique property of this modality.

In our opinion, it seems important that no characteristic peaks in photoacoustic spectra of chernozem soils are free from overlapping of soil matrix components, by default. Thus, for studied silicate-based chernozem soils, despite a high level of soil organic matter, matrix minerals are dominant in the whole spectrum, and the organic-matter analysis is hardly possible without destructive sample preparation or organic-matter extraction or on some not-so-obvious assumptions. Inorganic-component analysis appears to be a more promising area for nondestructive photoacoustic FTIR as it can be based on large mineral databases and approaches to quantitative assessment based on mineral bands of different origin.

An important feature is that quartz overtone peaks at 2000–1700 cm⁻¹ can be used as internal standards of soil samples of the same type for a more balanced spectra comparison. A drawback of photoacoustic FTIR of soil components is rather sophisticated data processing, which is a huge asset in basic research of selected samples, or the necessity for some correlation or factor analysis [16,18,19,31,38,63]. However, they are rather inappropriate for serial or more or less rapid analysis of multiple samples (and which is not cured by PLS models due to possible bias introduced at the initial spectrum acquisition). Thus, some modelling and strict but simple data-handling algorithms are required for gaining more reliable and reproducible data in FTIR PAS. Still, the methodological approaches developed in this study together with previous findings seem reliable enough for using in soil analysis including both meso- and micro-aggregate levels.

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Transparency document

The Transparency document associated with this article can be found in the online version.
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Appendix A. Supplementary data

Supplementary material related to this article can be found in the online version, at doi:https://doi.org/10.1016/j.pacs.2020.100162.

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