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The Soil Humic Acids Structural Changes upon Overphosphating

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Abstract—Phosphate anions play important part in the specific donor-acceptor interactions with humic acids, leading to the changes of structure and properties of the latter. Formation of the chelate nodes containing aluminum and iron atoms in the humic acids structure upon overphosphating has been observed. Behavior of P-modified humic acids in the polar media has been discussed.

Keywords: Phosphate anion, humic acid, P-containing organic ligand, metal chelate.

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The natural waters eutrophication has been generally considered the only outcome of the soil overphosphating. However, the decrease of soil humus quality is also of equal importance. Despite some data available [1–3] pointing at the possibility of soil humic compounds trans-formations under action of exogenic inorganic compounds, the corresponding intermolecular interactions have not been properly studied. It is commonly accepted that the non-specific van der Vaals interactions, not altering the humic acids structure, are of primary importance. The role of specific donor-acceptor interactions, being in some cases prevailing, has been underestimated so far. In the latter case, the properties (for instance, optical) of humic compounds can be significantly changed upon interaction.

The electron spectroscopy method allows study of the electronic shell of the molecules, determining their absorption spectra and efficiency of various interactions [4, 5]. This method has been widely used to compare the optical properties of humic compounds of various types of soils [6, 7]; however, it has not been applied widely to study the humic acids transformations in the soil of a certain type.

Humic acids are macromolecules, in this case the changes usually affect certain structural fragments. The electronic absorption spectra can be used to reveal the chromophores in organic molecules, for instance, conjugated C=C bonds and the multiple bonds formed by heteroatoms [4, 8]. The two typical absorption ranges in the case of organic multiple bonds are of 210–230 nm (C=C) and 250–280 nm (mainly C=O but also N=O, P=O, C=N, etc). In the presence of metals complexes with organic ligands, the chromophore groups are usually found in the ligands [9].

If a chemical bond is formed by a pair of elements with different electronegativity, the partial (effective) charges appear at them[1] [10, 11]. For example, in the case of C–OH bond, the more electronegative oxygen atom gains a certain negative charge, whereas the carbon atom bound to it becomes partially positively charged. The coordination of metal atom to the electronegative oxygen atom enhances the positive charge at carbon atom. The non-even distribution of the electron density leads to the bonds polarity. As compared to C–O bonds, the P–O ones are much more polar [10].

The presence of polar bonds in an organic molecule extends its ability to interact with other organic as well as inorganic species. Inorganic cations and anions can be coordinated to partially charged atoms of the organic molecule. The electron density is therefore redistributed, leading to structural changes of chromophores. If the redistribution of electron density

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[1] The partial (effective) charge appears due to the asymmetrical distribution of the electron density at the bond formed by atoms with different electronegativity [10, 11].

is slight, the chromophore can remain almost intact. However, in the case of significant electron density changes, the coordinated atoms can become the principle chromophore atoms [8], meaning its qualitative change, altering its spectrum and reactivity.

In the absorption spectra of the modified humic compounds, the relatively small structural changes can be masked by the absorption of practically unchanged macromolecule parts; therefore, the differential spectroscopy is more efficient in such cases [4, 12, 13], when the unmodified humic acid solution is used as a reference instead of pure solvent [14]. This allows precise estimation of the optical density changes related to the studied interaction.

This work aimed to study the spectral properties of phosphate-modified humic acids from alfisol in order to study the relationship between the spectral and chemical properties of the modified humic acids, and to investigate the phosphorus-induced transformation of humic macroligand in its iron complex.

EXPERIMENTAL

The study objects were: (1) samples of virgin (pH_{KCl} = 4.57) and arable (pH_{KCl} = 5.15) gray forest soils taken near Pushchino, Moskovskaya oblast, and (2) artificially prepared iron-humate complex. The arable soil was taken at the site where no fertilizer was applied during 10 years [15]. The basic chemical parameters of the soil samples are given in [16].

The influence of $NH_4H_2PO_4$ on the structure and properties of the soil humic acids was studied. The virgin soil was incubated during 3 years without addition (control) or with addition of $NH_4H_2PO_4$ (100 mg P_2O_5/100 g) in the wet state (55% of the total water capacity) at room temperature. The arable soil was incubated similarly; the experiment included three treatments: (1) without any additives (control), (2) with addition of $NH_4H_2PO_4$, (3) with addition of NH_4NO_3. The amount of phosphorus introduced was the same as in the case of virgin soil, the amount of nitrogen introduced in the form of NH_4NO_3 corresponded to its content in $NH_4H_2PO_4$ (20 mg N/100 g of soil). The incubation period of 3 years was selected according to the previously reported results [17]: the structural changes of humic acids are generally being developed quite slowly.

The humic compounds were extracted (without priory decalcification) from the dried soils by 0.1 N NaOH (soil : solution = 1 : 50). The soil suspensions were shaken in the closed flasks during 2 h and then left overnight and filtered off. No chemicals were added in order to accelerate filtration. From the alkaline extracts after their acidification with 1 N HCl or 1 eq/L aqueous H_3PO_4 (the acid volume was 1/3 of the extract volume), the humic acids HA(HCl) and HA(H_3PO_4) were precipitated. The humic acids were not purified of the inorganic admixtures. To estimate the humic acids yield, their precipitation was performed from four equal volumes (aliquots) of the alkaline extract. After addition of the acid, the mixtures were incubated during 15 min at 50–55°C and left overnight. The humic acids precipitates were then filtered off through the weighed dense filters. The precipitates were washed with water and dried in air to constant mass. Humic acids were then dissolved in 0.1 N NaOH for further analysis.

Carbon content in humic acid solutions was determined by oxidation with dichromate [18]. Metals (Al and Fe) and phosphorus contents were determined after the aliquots combustion with 3 : 1 mixture of concentrated H_2SO_4 and 57 wt.% solution of $HClO_4$. Metals concentration was determined by plasma spectrometry. Phosphorus content was determined by standard photocolorimetry method with ascorbic acid [19]. The same method was used to determine phosphorus content after addition of ethanol to the neutralized after combustion solutions of humic acids.

Carbon content in humic acid solutions used for absorption spectra registration ranged within 6.6–7.6 mg/50 mL (virgin soil) and within 4.8–5.2 mg/50 mL (arable soil). The conventional and differential absorption spectra were recorded at 190–450 nm (Hitachi-557, Japan). The reference samples were 0.1 N NaOH (pure solvent) in the case of conventional spectroscopy and the alkaline solution of humic acid extracted from the untreated soil in the case of differential spectroscopy. Spectra were recorded in the cell with optical path of 0.5 mm [14].

The dry sample of HA(HCl) with ash content of 22% was isolated from the untreated arable soil as described in [20]. 50 mL of deionized water (control) or 50 mL of 1 mol/L solution of KH_2PO_4 was added to 50 mg of the humic acid, the pH of the systems was of 4.04 and 3.99, respectively. The systems were shaken during 1 h, and the liquid phases were then analyzed for Al, Fe, and C contents.

In another experiment, 50 mg of the humic acid was dissolved in 50 mL of 0.1 N NaOH, and the equal

Table 1. Carbon, metals, and phosphorus content in HA(HCl) of the untreated and phosphated virgin and arable soils (mg per 100 g of soil, mg per 1 g of humic acid)[a,b,c]

Soil	C	Al	Fe	P		C/(Al + Fe)
				without ethanol	with ethanol	
Virgin:						
Untreated	507 (230.5)	60.1 (27.3)	29.2 (13.3)	4.5 (2.1)	6.9 (3.1)	5.7
Phosphated	346 (227.6)	63.4 (41.7)	31.7 (20.9)	6.7 (4.4)	not determined	3.6
Arable:						
Untreated	320 (367.8)	27.6 (31.7)	25.4 (29.2)	2.9 (3.3)	18.2 (20.9)	6.0
Phosphated	320 (238.8)	54.2 (40.5)	42.1 (31.4)	5.7 (4.3)	not determined	3.3

[a] Phosphated soil refers to the soil treated with $NH_4H_2PO_4$ (100 mg of P_2O_5 per 100 g of soil).

[b] The content of the elements per 1 g of humic acid is given in parentheses (see also Table 2).

[c] The coefficient of variation of the elements content was not higher than 4% ($n=3$) (C), 5% ($n=3$) (metals), and 2% ($n=3$) (P).

volume of KH_2PO_4 solution was added so that P_2O_5 concentration in the system was of 0.25 mg per 1 mL of the humic acid solution. The absorption spectra of the control system and that containing P were recorded during 1 h (Specord UV VIS, Germany) with the 20 mm optical cell.

In order to obtain the iron-humate complex, $FeCl_3$ was added to the alkaline solution of the humic acids isolated from arable soil, 300 mg of Fe per 50 mg of C (pH = 5.1). The precipitated complex was filtered off, washed with water, and dried at ambient. The C : Fe ratio in the so obtained complex was of 1 : 3.2. The complex was treated with KH_2PO_4 solution (pH = 4.01) during 3 or 5 weeks. The phosphorus content in the complex – phosphate solution system was such that C : P = 1 : 18 and Fe : P = 1 : 5. That way, the phosphate content corresponded to the conditions in the thick layer of soil surrounding the granule of water-soluble phosphate fertilizer [21, 22]. Immediately after the addition of phosphate solution, the liquid phase of the system turned brown. Simultaneously, white turbidity and dark-brown flakes formation was observed.

At the end of the experiment (3 or 5 weeks) the system became multiphase, consisting of light-brown liquid and two solid phases (crystalline and X-ray amorphous), being easily separable. All the phases were analyzed for C, Fe, and P content. The solid amorphous dark-brown phase with the highest C content was analyzed by means of IR spectroscopy (KBr). The spectra were assigned following [23, 24].

All the presented data were obtained in 3–4 replicates. The variation coefficients are given as notes to the corresponding tables.

RESULTS AND DISCUSSION

The conventional absorption spectra of the HA(HCl) alkaline solutions prepared from the untreated virgin and arable soils (Fig. 1a) revealed the absorption bands at 210–230 nm (more intense) and at 250–280 nm, assigned to conjugated C=C and multiple heteroatomic bonds (mainly C=O), respectively [4]. The optical density of solutions prepared from various types of soil was significantly different. In particular, in the case of virgin soil (Fig. 1a, curve *1*) the optical density was higher than that in the case of arable soil (curve *3*).

The optical density of humic acid solutions is generally ascribed to the presence of carbon [6, 7]. Indeed, the optical density of the studied solutions (Fig. 1a, curves *1* and *3*) was correlated with the carbon content (507 and 320 mg C/100 g of soil, respectively) (Table 1). However, the correlation was not observed in the case of the phosphate-treated samples of the same soils. Carbon content in the HA (HCl) of the phosphate-treated virgin soil was of 346 mg/100 g of soil, lower than in the case of untreated soil (507 mg of C/100 g of soil) (Table 1), however, the optical density of the solution increased upon phosphating (Fig. 1a, curve *2*). In the case of arable soil, the increase of the optical density upon phosphating was even more significant (Fig. 1a, curve *4*) at equal carbon content (Table 1).

From Table 1 it is to be seen that the solutions of HA(HCl) from the phosphate-treated soils contained

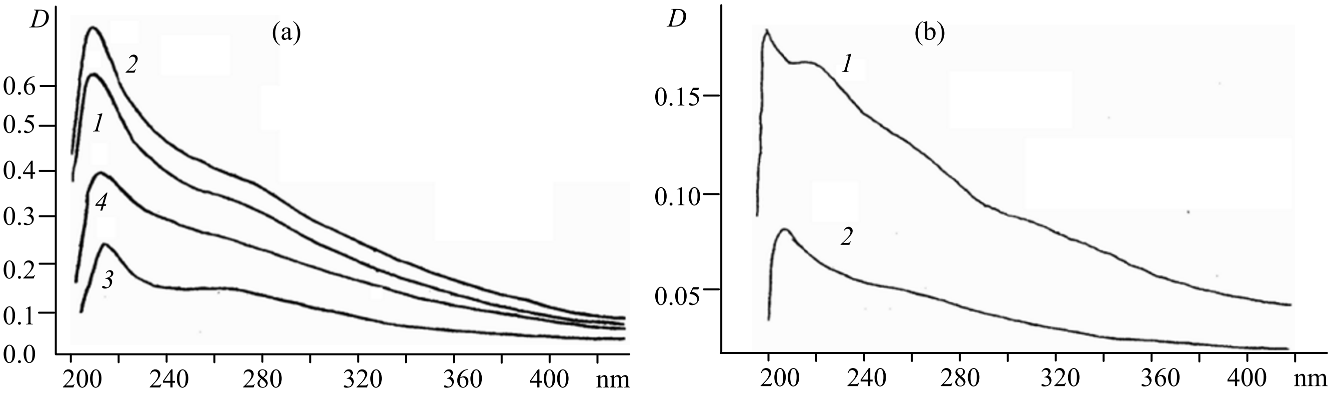


Fig. 1. Conventional and differential absorption spectra of HA(HCl) of the untreated and phosphated soils. (a) Conventional spectra: (*1*) untreated virgin soil, (*2*) phosphated virgin soil, (*3*) untreated arable soil, (*4*) phosphated arable soil. (b) Differential absorption spectra of HA(HCl) from phosphated soils: (*1*) arable soil, (*2*) virgin soil.

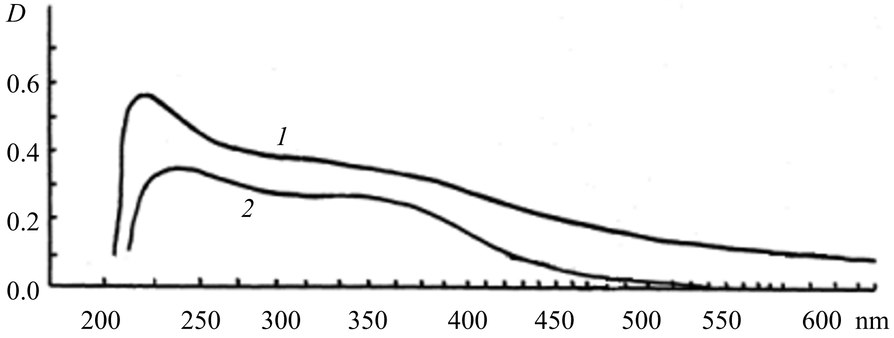


Fig. 2. Change of absorption spectrum of humic acids alkaline solution under treatment with phosphate solution: (*1*) initial humic acid, (*2*) after addition of the phosphate solution.

more of Al and Fe than the corresponding solutions prepared from the untreated soils. That was especially noticeable from the data on metals content with respect to the yield of humic acids (Table 1, 2). Therefore, the ratios of C/(Al + Fe) were decreasing upon phosphating, thus indicating the poorer quality of humic acids (Table 1).

According to data in Table 3, significant fraction of metals and carbon was eliminated from the humic acids and transferred into the liquid phase upon treatment with the phosphate solution. Simultaneously, the absorption spectra of phosphate-modified humic acids (Fig. 2, curve *2*) were changed: the absorption was weakened, especially in the visible wavelength range, the metal complexes being responsible for absorption at >350 nm. Possibly, the decrease of absorption intensity was due to elimination of the peripheral metal-containing groups, causing the significant part of the untreated humic acid absorption.

The data on the initial changes in the humic acid structure caused by phosphating (Table 3, Fig. 2) in combination with Table 1 data led to conclusion that the metal-phosphate complexes transferred into the solution could be incorporated into the structures of humic macroligands.

The metals contained in the peripheral fragments of the humic compounds could act as coordination centers for the exogenous phosphate anions bearing the electronodonor oxygen atoms; as a result, the oppositely charged metal-phosphate complexes could be formed [16, 25, 26]. The negatively charged complexes of the $[Me^{3+}(HPO_4)_2]^-$ type could pass into the liquid phase of the soil – phosphate solution systems, as was observed experimentally [16].

The formation of metal-phosphate fragments in the P-modified humic acid structure (Fig. 2, curve *2*), increasing the absorption of chromophores with heteroatomic bonds, was additionally evidenced by the red shift of absorption bands assigned to the multiple bonds, due to increase of their polarity.

The metal-phosphate anions, being more nucleophilic agents as compared to the ordinary phosphate

Table 2. Humic acids yield from the untreated and phosphated soils (g per 100 g of soil)[a, b]

Soil	Humic acids precipitation	
	with HCl (1 N)	with H_3PO_4 (1 N)
Virgin:		
untreated	2.20	3.98
phosphated	1.52	2.57
Arable:		
untreated	0.87	1.53
phosphated	1.34	1.95

[a] Phosphated soil refers to the soil treated with $NH_4H_2PO_4$ (100 mg of P_2O_5 per 100 g of soil).

[b] The coefficient of variation of the humic acids yield was not higher than 4% ($n = 4$).

anions, could be added to the electrophilic atoms of organic molecules, in particular, to carbon atoms of the multiple bonds [10, 11, 27]. Therefore, the metal-phosphate (chelate) nodes could appear in the structure of humic macroligands.

The absorption band assigned to chelate nodes of organic polymers is typically found at 290–390 nm [28–30]. The conventional absorption spectra of HA (HCl) solutions from the untreated as well as phosphated soils (Fig. 1a) did not reveal the corresponding bands, as they were possibly overlapped by the other organic chromophores of humic acids. However, in the differential spectra (Fig. 1b) of the humic acids from phosphated soils (both virgin and arable), the P-modified fragments were detected. The absorption at 310–370 nm was detected in the spectra of P-modified HA(HCl) of the arable soil (Fig. 1b, curve *1*), it could be ascribed to the chelate nodes. The absorption was especially clearly seen after subtraction of the bands of ammonium component of phosphate salt (Fig. 3). The broad band at 230–430 nm (Fig. 3) could possibly evidence that the chelate nodes were formed with participation of heteroatomic multiple bonds.

The absorption at 310–370 nm was not clearly detected in the spectra of P-modified HA(HCl) of the virgin soil (Fig. 1b, curve *2*), however the absorption at 370–440 nm was somewhat enhanced, the effect being the most prominent in the spectrum of humic acids precipitated with 1 N H_3PO_4 solution (Fig. 4, curve *1*). The absorption band at 340–440 nm is generally assigned to the electron transitions in the inner sphere of the metal complexes, induced by addition of new (phosphate) ligands [9, 29]. Besides the above-mentioned absorption, the absorption band at 270–350 nm was observed in the spectrum of HA(H_3PO_4) from the P-modified virgin soil (Fig. 4, curve *1*), being assigned to the metal-phosphate groups incorporated into the humic acid structure. As phosphate treatment did not influence the organic chromophores (Fig. 4, curve *1*, 200–260 nm range), the interaction between virgin soil humic acids with phosphate ions was likely limited to the coordination of metal-phosphate complexes to the electrophilic atoms of humic macroligands.

Table 3. Metals and carbon elimination into the liquid phase, % of the initial content in humic acids

System	Al	Fe	C
Humic acid–H_2O	Traces	Traces	Traces
Humic acid–H_2O–P_2O_5	31	33	14

As far as HA(H_3PO_4) of arable phosphate-treated soil is concerned, the spectral changes (Fig. 4,curve *2*) revealed significant rearrangement of the chromophores, due to the influence of metal-containing fragments initially present in the humic macroligand. Thus, the additional phosphate treatment of the P-modified humic macroligands of the arable soil led to deeper rearrangement of HA(H_3PO_4) structure.

According to data shown in Figs. 1b and 4, the P-modified humic acids precipitated from the alkaline extracts of the two types of soil (virgin and arable) by the two inorganic acids (HCl and H_3PO_4) differed in their spectral properties and, thus, in structure. The observation was in line with the data on structure of humic acids precipitated by HCl and H_2SO_4 [14]. In the both cases, the influence of the acids anion was more pronounced in the case of arable soil as compared to virgin soil.

The anion nature of inorganic acid influenced much the yield of humic acids from the soil and on their composition (Tables 1, 2, and 4). The yield of humic acids from arable soil was lower than in the case of virgin soil; however, the phosphate treatment of arable soil enhanced the humic acids yield significantly, due to accumulation of aluminum, iron, and phosphorus. The stronger influence of the inorganic acid nature on the structure of humic acids from arable soil was likely due to the preceding agricultural use, in particular, phosphate fertilizers application. As seen from Table 1, the humic acid from arable soil was initially enriched in phosphorus as compared to that from virgin soil; however, the major part of phosphorus was not detected by the standard procedure, unless the phosphorus-containing bonds splitting in ethanol medium.

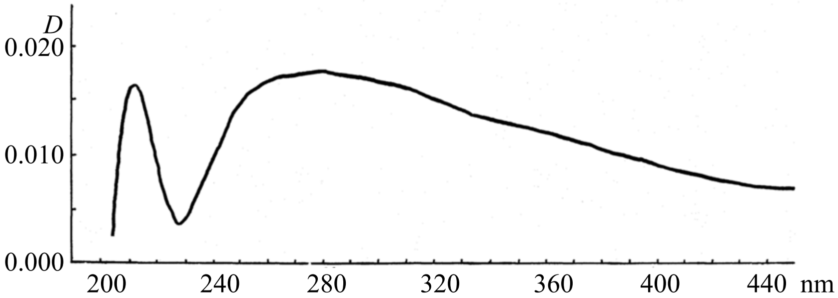


Fig. 3. Changes in the differential absorption spectrum of HA(HCl) of arable soil caused by the phosphate part of $NH_4H_2PO_4$.

As was discussed above, the initially P-modified humic macroligands from arable soil were subjected to further transformation upon additional phosphate treatment. As humic acids are products of the soil metal-humate complexes transformations in the alkaline medium, it was important to study the corresponding mechanism of transformation of humic macroligand incorporated into a metal complex.

The transformations of macroligand in the phosphate solution were studied using the iron-humate complex as a model. The initial stage of transformation was found to be the complex decomposition to form solid and soluble products. About 45% of C and 7% of Fe contained in the starting complex were found in the liquid phase of the system. Hence, coordination of phosphate anions at iron atoms was accompanied by the substitution-elimination of the initially coordinated ligand groups of the humic macroligand that passed into the solution along with the newly formed iron phosphate complexes. The compounds passed into the liquid phase could account for the subsequent transformations of the solid products of the initial complex decomposition (Fig. 5).

Table 4. Carbon and metals content in $HA(H_3PO_4)$ from untreated and phosphated soils (mg per 100 g of soil, mg per 1 g of humic acid)

Soil	C	Al	Fe	C/(Al + Fe)
Virgin:				
Untreated	600 (150.8)	19.4 (4.9)	7.4 (1.9)	22.4
Phosphated	560 (217.9)	36.1 (14.1)	13.2 (5.2)	11.4
Arable:				
Untreated	422 (275.8)	18.2 (11.9)	3.4 (8.8)	19.5
Phosphated	360 (184.6)	26.1 (13.4)	8.2 (4.2)	10.5

The two solid products of the iron-humate complex decomposition (Table 5) were iron complexes with the ligands containing phosphorus and carbon. The phosphorus content was about 2 and 7 times higher than that of carbon, confirming P atoms incorporation into the organic ligands. The IR spectra (Fig. 5) allowed elucidation of the transformation stages in the case of the macroligand with higher carbon content (Fig. 5a). The spectra (b) and (c) confirmed the significantly different structure of the macroligand after 3 anf 5 weeks of the interaction with the phosphate solution.

After 3 weeks of the interaction, the band at 1052 cm^{-1} appeared in the spectrum (Fig. 5b), confirming the addition of phosphate groups (O–P–O vibration was assigned to the band at 538 cm^{-1}) at the carbon atoms of C–O bonds (alcoholic, phenolic, polysaccharide or other groups of the macroligand) to form the C–O–P groups with P atom being partially positively charged [22, 23]. Noteworthily, after 3 weeks of interaction, the bands assigned to stretching of OH groups and of carbonyl groups coordinated to the metal [22] retained in spectrum.

After 5 weeks of incubation (Fig 5c), the IR spectrum was further changed. In particular, the bands at 1100–1000 cm^{-1} assigned to P–O–C groups [23] were due to addition of the free organic ligands at the positively charged P atoms (see details above). The phosphate groups were likely added at the P atoms as well, as confirmed by the band at 910 cm^{-1}, ascribed to pyrophosphate organic fragments [22]. Thus, the organic and phosphate free ligands contained in the liquid phase could be incorporated into the structure of humic macroligand contained in the solid complex via addition at the positively charged P atoms.

Reactions of the electrophilic phosphorus generally lead to formation of P=O bond [31, 32]. Its presence in the product of the studied transformation was

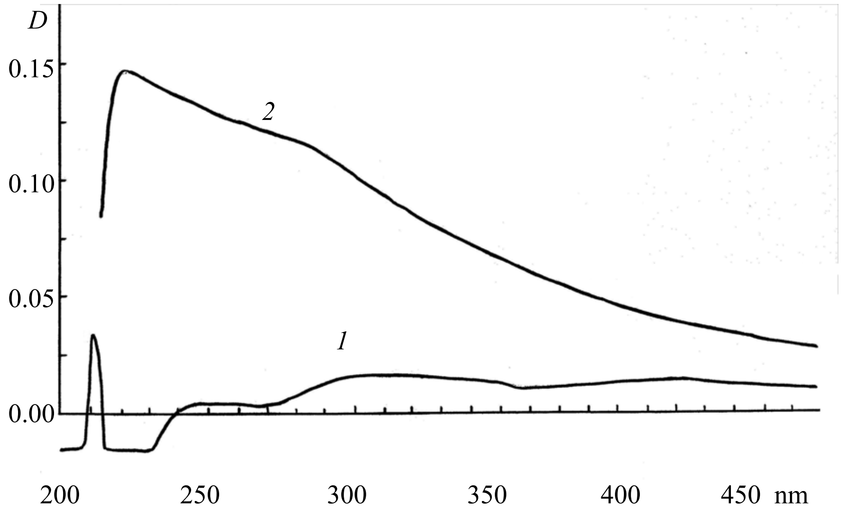
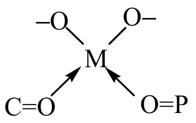


Fig. 4. Differential absorption spectra of HA(H_3PO_4) from the phosphated soil: (*1*) virgin soil, (*2*) arable soil.

confirmed by the presence of corresponding stretching bands of free (1250 cm^{-1}) and bound (1170 cm^{-1}) P=O groups. The presence of broad band at 2392 cm^{-1} evidenced that the P=O group was involved in the formation of strong intramolecular hydrogen bond with OH [23]. The disappearance of the absorption bands at 1630 and 1396 cm^{-1} (present in the spectrum after 3 weeks of incubation) and the appearance of a broad band at 1664 cm^{-1} was assigned to formation of the intramolecular chelate rings involving iron complexes with P=O-containing as well as with C=O-containing ligands [22].

Therefore, IR data (Fig. 5) along with the data shown in Tables 1 and 4 suggested the formation of the following metal-phosphate chelate fragments in the structure of P-modified humic acids of the arable soil:



Such fragments could be cyclic due to hydrogen bonding, therefore enhancing the conjugation chain in the molecules [9, 22]. That was reflected in the spectral features of P-modified humic acids (Fig. 1b, curve *1*; Fig. 4, curve *2*). In particular, the broad band overlapping absorption of all the chromophores was observed in the HA(H_3PO_4) spectrum (Fig. 4, curve *2*). The presence of such band could point at the formation of donor-acceptor complex with charge transfer, in particular, the intramolecular hydrogen bonds [4, 9]. Thus, it could be suggested that the intensity increase of C=O absorption and its expansion was due to the neighboring HO–P=O groups capable of hydrogen bonds formation [23, 32].

Due to capability of phosphate groups to form hydrogen bonds, the corresponding metal chelates could be additionally stabilized in the polar media [23, 32, 33]. That was clearly revealed in the case of

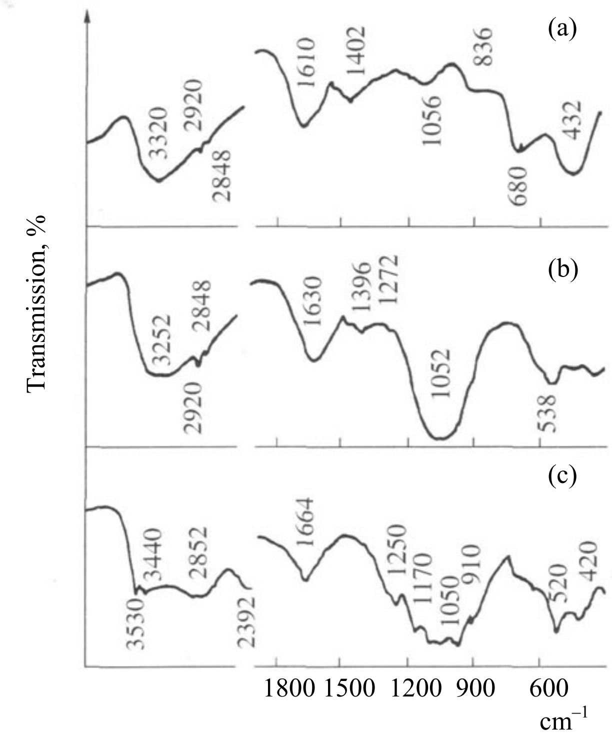


Fig. 5. IR spectra of initial iron-humate complex (a), after 3 weeks treatment with phosphate solution (b), and after 5 weeks treatment with phosphate solution (c).

$HA(H_3PO_4)$ (Table 4). Even though phosphate promoted the accumulation of Al and Fe in the humic acids (Tables 1 and 4), the metals content in $HA(H_3PO_4)$ (Table 4) was lower than that in HA(HCl) (Table 1). Seemingly, in the presence of H_3PO_4 the humic acid fragments containing metal-phosphate groups were stabilized. The reactions involving positively charged P atoms in metal-phosphate groups could increase number of P=O bonds in the macroligand, thus increasing the extent of the charge separation.

The stabilization in polar media is connected with the charge separation in P-containing molecules, the latter being enhanced with increasing P content [5, 33]. This could account for the ability of humic acid from arable soil to participate in the donor-acceptor interactions with inorganic molecules (Table 1).

As was noted previously [17, 34], the structural changes of humic compounds could be evidenced by the alternation of acid-base properties of the P-containing fragments. As seen from Table 6, phosphorus extraction with 0.1 N NaOH was lower in the case of the untreated arable soil (total phosphorus content was of 0.14%) than that in the case of the untreated virgin soil (total phosphorus content was of 0.11%). On the contrary, phosphorus was better extracted from the arable soil by 0.2 N HCl. From that data, P-containing fragments of humic compounds of arable soil were more basic than those of the virgin soil. That was seemingly due to the differences in the metal atoms ligand surrounding.

The changes in ligand properties could in turn lead to the changes of the complex properties [35]. According to data from [36], at certain phosphating level of the arable soil, the extraction of both P and Fe by 0.1 N NaOH was decreased with respect to the untreated soil, whereas the extraction of the same elements by 0.2 N HCl was increased. In general, the extraction of Fe and P was suppressed upon the soil phosphating, thus pointing at the stabilization of P-containing components of arable soil in polar media.

Thus, the changes in spectral and chemical properties of humic acids from virgin and arable soils were due to varied reactivity towards inorganic anions. The more pronounced ability of humic acids from arable soil towards specific interactions was due to the higher polarization by the accumulated P-, Al-, and Fe-containing fragments.

Noteworthily, the humic compounds transformations in the soil are commonly related to the microbiotic activity, whereas the importance of abiotic reactions has been significantly underestimated. This work showed the importance of abiotic process in the case of phosphates under conditions close to that at the vicinity of the phosphorus-containing fertilizer granule.

To conclude, the data reported in this work demonstrated that the differential absorption spectroscopy was efficient in detection of the slight structural changes in the humic acids chromophores upon interaction with inorganic anions. The influence of intermolecular interactions on the humic acids structure was more prominent in the case of arable soil as compared to the virgin one, being depended as well on the phosphorus content in the soil. The nature of the inorganic anion strongly influenced the change of spectral properties, yield, and the chemical composition of the humic acids. In particular, specific donor-acceptor interactions involving phosphate anions were found to be important. The structure of humic acids from phosphated soils included the chelate nodes containing the atoms of Al, Fe, and P; their formation was likely due to incorporation of the metal-phosphate complexes into the humic acids structure. The P-modified humic acids were subjected to further transformations upon subsequent interaction with phosphate anion. The formation of P=O group strongly enhanced the macroligands ability to form metal chelates and their stabilization in the polar media. That

Table 5. Composition of the iron-humate complex and products of its transformation in phosphate solution, % (mean±SD)

Complex	C	Fe	P
Initial	21.1± 1.1	66.7± 2.3	0.25±0.02
P-transformed:			
dark-brown	5.1± 0.3	15.8± 0.9	11.8±0.27
light-grey	2.2± 0.2	30.1± 1.6	13.9±0.31

Table 6. Solubility of the soil phosphorus compounds, mg P per 100 g of soil

Untreated soil	0.2 N HCl	0.1 N NaOH	
		Total P (sum of inorganic and organic)	including organic P
Virgin	0.8	34.7	31.4
Arable	2.2	15.0	10.3

should be taken into account during the metals and phosphorus determination in the phosphated soils by the standard analytical techniques.

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