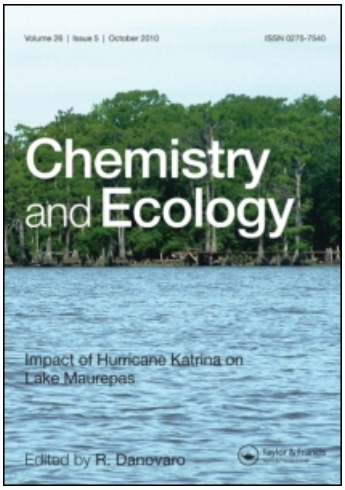

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The detection of nerve agent degradation products in different soil fractions using capillary electrophoresis with contactless conductivity detection

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The detection of nerve agent degradation products in different soil fractions using capillary electrophoresis with contactless conductivity detection

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The adsorption of various phosphonic acids in sand and loam was studied. Samples of both soil types were sieved into three different fractions according to particle size. The fractions used were in the range 0–100, 100–200 and 200–400 μm. The performance of the capillary electrophoresis equipped with contactless conductivity detection was investigated. The limit of detection for the phosphonic acids tested was in the range 0.11–1.4 ppm. Different isotherms were constructed for all adsorption curves. Adsorption was found to be higher in sand than in loam when the Langmuir adsorption isotherm was used. The adsorption of methylphosphonic acid was higher than that of other phosphonic acids due to the smaller molecular size of the former.

Keywords: adsorption; capillary electrophoresis; chemical warfare agents; contactless conductivity detection; soil fraction

1. Introduction

Organophosphorous nerve agents are one of the most toxic substances ever synthesised. Although having found limited use so far, determination of these substances or their degradation products is still an important field of research, especially in the last 10 years, which have seen terrorist activity increase. Therefore, there is a continuous need for rapid and reliable methods for the detection of nerve agents and their degradation products. Nerve agents are categorised according to structure into two groups: G- and V-type. Both types have several similar structural features, such as the existence of a double bond between the terminal oxygen and phosphorous or two lipophilic groups and one leaving group bound to the phosphorous. These features make nerve agents unique and distinct from the large group of organophosphates, such as the herbicides, pesticides, and insecticides widely found in soil due to their use in agriculture. In aqueous environments, these organophosphorous nerve agents hydrolyse more or less easily to produce non-toxic and more stable compounds. The most important degradation products of nerve agents are alkyl alkylphosphonic acids, which are suitable for verifying the presence or use of organophosphorous

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nerve agents. Moreover, being specific to particular nerve agents, these acids can be used to identify their parental nerve agents.

Various separation methods such as gas (GC) [1] and liquid chromatography [2] and capillary electrophoresis (CE) [3] can be used to analyse the degradation products of nerve agents. Nowadays, the chromatographic methods developed for this purpose are mostly coupled to mass spectrometry [4,5]. GC is a suitable tool for analysing easily volatile nerve agents whose degradation products, however, cannot be directly applied to GC analysis because of their high polarity and low water solubility. Therefore, a derivatisation procedure for conversion of the degradation products into more volatile compounds is needed. A detailed review of possible separation techniques for the analysis of nerve agents is given in Hooijschuur et al. [6]. In view of the fact that phosphonic acids need no derivatisation, the fast, simple and relatively inexpensive CE is often preferred. CE analysis requires simple sample preparation involving dilution and filtration, and easy equipment operations and maintenance. CE is less sensitive to sample matrix and, therefore, real samples such as aqueous soil extracts and river water can be subjected to CE analysis [3,7,8]. It is possible to use direct [3] and indirect UV [9] to detect nerve agents and their degradation products in CE. The indirect mode of UV detection is preferred as it is more sensitive because phosphonic acids do not contain any chromophoric groups. Lately, a contactless conductivity detection (CCD) has also been used to detect nerve agent degradation products [10–12].

Basic principles of CCD and a more detailed description of the current set-up are available as supplementary material S1 (available online only). In this work, a CCD–CE system was used to study the adsorption of phosphonic acids in different fractions of soil.

The adsorption curves can be fitted to different types of isotherms, the Langmuir and Freundlich types being the most common. Kothawala et al. fitted their experimental data for the adsorption of organic carbon onto mineral soils to four different types of adsorption isotherms [13]. The Langmuir isotherm was found to produce more robust results. Fitting the Freundlich and Langmuir isotherms to the same data has been compared in Vasanth Kumar and Sivanesan [14]. Again, the latter was more advantageous. In this study, a linear least squares method was used to estimate the performance of the Langmuir and Freundlich adsorption isotherms. In addition to the Langmuir and Freundlich adsorption isotherms, the Redlich–Peterson and BET-isotherms were also calculated. An introduction to the theoretical background of these adsorption isotherms is available as supplementary material S2 (available online only).

2. Materials and methods

2.1. *Soil samples*

Environmental soil samples were collected from two different locations in Estonia. The sand sample was taken from a park in the city of Tallinn (latitude: 59°23′42.13″, longitude: 24°40′37.02″) and the loam sample from a forest in the Kõpu rural municipality, Viljandi county (latitude: 58°19′34.72″, longitude: 25°17′45.19″). Samples were collected from the surface layer of soil at a maximum depth of 5 cm. Sand and loam samples had not been exposed to nerve agents or their degradation products before. The sampling sites were chosen far away from agricultural areas to avoid possible contamination of samples with the other types of organophosphates used in agriculture, such as herbicides or insecticides.

Gravimetric analysis was used to determine the organic content of the soil samples. First, the crucibles used for the analysis were heated to 550 °C for 4 h in a muffle furnace to gain constant weight. Second, after cooling for 30 min, the crucibles were weighed and $\sim$ 1 g of a particular soil sample was added to the crucibles. The soil samples were treated for 4 h at a temperature of 550 °C. After a 30 min cooling period, the crucibles with temperature-treated samples were

Table 1. Organic matter in different soil fractions.

Size of fraction, μm	Amount of organic matter, %	
	Sand	Loam
<100	1.24	5.64
100–200	0.55	7.03
200–400	0.50	6.05

weighed again. The organic content of the soil samples was calculated using the difference between the two masses. Four hours was long enough for all the samples to lose their organic part.

The adsorption of phosphonic acids in soil may be considered as a sum of physicosorption and chemisorption. A simple explanation for this could be as follows. Phosphonic acids are adsorbed onto inorganic soil particles by undergoing physicosorption, whereas their adsorption onto the organic part of a soil sample takes place under the mechanism of chemisorption. This simplified theory may be applied to explaining the adsorptive behaviour of phosphonic acids in different types of soil. Therefore, the organic content of soil samples was determined using gravimetric analysis and muffle furnaces.

Data on the organic content of soil samples are presented in Table 1. The organic content of the loam samples (5.64–7.03%) was 10 times as high as that of the sand samples (0.50–1.24%). The organic content of the finest fraction of the sand sample was $\sim$ 2.5 times as high as that of the other two fractions. This means that the organic matter of the sample contained small fractions of clay, silt and very fine sand. However, in the case of loamy soil, the respective figures were slightly different. So, the organic content of its medium fraction was the highest and that of the finest fraction the lowest.

2.2. *Preparation of soil extracts*

Loam and sand samples were first dried at room temperature until the mass of both samples was constant. The procedure took three to four days. After that, the samples were fractionated by particle size using three sieves with different hole sizes. The sand and loam samples were sieved into three fractions: <100, 100–200 and 200–400 μm. Samples with a particle size >400 μm were disposed of. Basically, the fractions represented very fine, fine and medium-grained sand. Clay and silt were not thoroughly dealt with because Estonian soils are mainly sand-based. Silt and clay were the components of the finest fraction of samples.

For sample preparation, 0.5 g of the fractionated soil material was weighed into 2 mL plastic vials. The samples were spiked with a 2 mM stock solution of five phosphonic acids. The added amounts of phosphonic acids were 12.5, 25, 37.5, 50, 75 or 100 μL. After a 50 min exposure to phosphonic acids, MilliQ water was added to the soil samples to obtain a total volume of 1 mL. This means that the concentration of phosphonic acids in the samples was 25, 50, 75, 100, 150 or 200 μM, respectively. The samples were then shaken for 10 min and also centrifuged for 10 min. A 500 μL aliquot of an unfiltered supernatant was placed into 0.5 mL plastic vials and 2-aminoethyl dihydrogenphosphate (AEDHP) was added as an internal standard. The concentration of the internal standard was 500 μM. The unfiltered samples were subjected to CE analysis.

2.3. *CCD–CE experiments*

2.3.1. *Instrumentation*

All experiments were carried out using a commercially available Agilent Technologies CE instrument (Waldbronn, Germany) equipped with a diode array detector. For detection a CCD detector

was used instead of a UV detector. The CCD detector was made in-house. A detailed description of this detector is given in Seiman et al. [15] and supplementary material S1 (available online only). The combination of the in-house CCD detector and the conventional bench-top Agilent instrument enabled application of the detection schemes developed for CCD to a large number of samples because the Agilent instrument provides possibilities for programming long sequences of separate analyses.

The uncoated fused-silica capillary (i.d., 75 μm; o.d., 360 μm) with a total length of 55 cm was purchased from Agilent Technologies (Santa Clara, CA, US). The length of the capillary to the CCD cell was 45 cm and to the DAD cell, 49 cm.

2.3.2. *Standards*

For analysis of the degradation products of toxic organophosphates the following phosphonic acids were used: methylphosphonic acid (MPA), ethylphosphonic acid (EPA), 1-butylphosphonic acid (1-BPA), propylphosphonic acid (PPA) and pinacolyl metylphosphonic acid (PMPA). MPA, EPA and 1-BPA were purchased from Alfa Aesar, Lancaster Synthesis (Windham, NH, USA) and PPA and PMPA were from Sigma-Aldrich (Steinheim, Germany). AEDHP used as the internal standard, and BGE components, L-histidine (His) and 2-(*N*-morpholino)ethanesulphonic acid hydrate (MES hydrate), were also purchased from Sigma-Aldrich (Steinheim, Germany). Sodium hydroxide was purchased from Chemapol (Prague, Czech Republic).

Standard stock solutions were prepared by dissolving an exact amount of each phosphonic acid in MilliQ water to a concentration of 10 mM. This was followed by a further mixing of all five analytes into a standard solution of a total concentration of 2 mM.

BGE for capillary electrophoresis analysis was prepared by dissolving an exact amount of His and MES in MilliQ water.

2.3.3. *Procedures*

A new capillary was flushed with a 1 M NaOH for 10 min and then with water for 10 min and with BGE for 10 min. Before starting the experiments, the capillary was flushed with a 0.1 M NaOH for 3 min, with water for 10 min and with BGE for 10 min every day. Between each run it was rinsed with water for 2 min and with BGE for 3 min. The BGE was a 15 mM Mes/His buffer. The sample was injected hydrodynamically for 10 s (50 mBar). In all experiments, the cartridge with the separation capillary was thermostated at 25 °C. The separation voltage was 20 kV.

3. Results and discussion

3.1. *Performance of the CCD-CE system*

For the analysis of adsorption of phosphonic acids in soil, first, calibration curves had to be constructed. This was a suitable opportunity to evaluate the performance, including the reproducibility, sensitivity, etc., of the combined CCD–CE equipment. The calibration curve of seven points was constructed in the region 10–200 μM. An internal standard AEDHP was added to every sample at a concentration of 500 μM. The constructed calibration curve demonstrated good linearity in the measured range as the coefficient of determination between experimental data and the constructed calibration curve was close to one ($R^2 > 0.99$ for all phosphonic acids). Multiple repetitive analyses needed for the construction of the calibration curve were performed to calculate the reproducibility of the CCD–CE system. Detailed performance data are given in Table 2. The reproducibility of the system was acceptable as the relative standard deviations (RSD) of

Table 2. Performance data for phosphonic acids.

	LOD* (μM)	RSD† (%)	$b_0^{\ddagger}$	$b_1^{\ddagger}$	$(R^2)^{\S}$
PMPA	7.56	5.68	−0.0514	0.0068	0.9915
1-BPA	5.96	3.48	−0.0572	0.0096	0.9977
PPA	5.45	4.23	−0.0605	0.0111	0.9974
EPA	5.84	2.58	−0.0847	0.0145	0.9952
MPA	1.20	6.92	−0.0236	0.0196	0.9984

Notes: *Limit of detection. †Relative standard deviation of peak areas. ‡Calibration line equation $y = b_0 + b_1 c$ parameters: b_0, intercept; b_1, slope; y, detector response; c, concentration. §Square of correlation coeficient of calibration line.

peak areas were in the region 2.6–6.9%. To estimate the sensitivity of the CCD detector, LODs for all the phosphonic acids analysed were calculated by interpolating the calibration curves. The LODs were in the range of 1.2 (0.11) and 7.6 (1.4) μM (ppm).

3.2. *Analysis of blank soil extracts*

When developing procedures for the extraction of nerve agent degradation products from soil, all possible unknown substances that could have been extracted from soil had to be separated from phosphonic acids using CCD–CE analysis. Otherwise it would have been impossible to estimate the adsorption of nerve agent degradation products in soil. Blank extracts of loam and sand samples were examined first to discover all unknown peaks belonging to substances which extracted from soil under the current extraction procedures. A comparison of blank soil extracts and extracts containing phosphonic acids was necessary to find out if peaks of the latter were separated from each other and from all unknown peaks belonging to soil extracts.

Blank samples (Figure 1(B)) had two peaks that were observed in case of all loam and sand samples. Only the height of the peaks in different fractions varied. All unknown peaks migrated slower

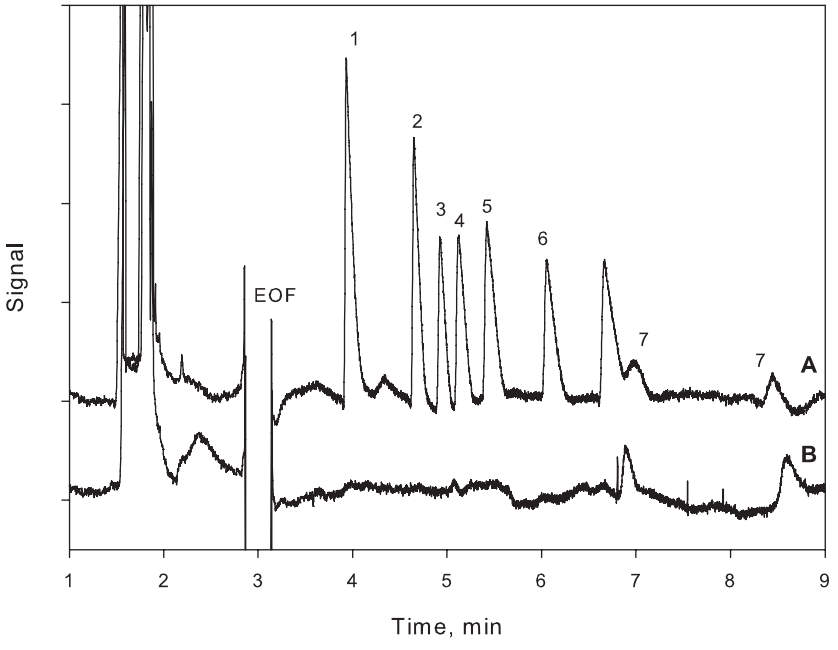

Figure 1. Separation of blank soil extract and phosphonic acids. (A) Blank extract from sand, fraction 100–200 μm; (B) extract of 100 μM phosphonic acids from sand, fraction 100–200 μm. EOF, electroosmotic flow; 1, AEDHP; 2, PMPA; 3, BPA; 4, MPA; 5, EPA; 6, MPA; 7, unknown peaks.

than phosphonic acids (Figure 1(A)). It may be assumed that these unknown peaks corresponded to some small anions, though they were not identified as it was not the goal of this article.

3.3. *Adsorption isotherms of different soil samples*

Sand and loam extracts were prepared using six different concentrations of phosphonic acids by spiking a particular sample with a certain amount of the standard mixture of phosphonic acids. Spiked samples were extracted with water after a certain time. With no adsorption at all the concentration of phosphonic acids in these extracts would have been 25, 50, 75, 100, 150 and 200 μM. In reality, all these concentrations were lower as some amount of phosphonic acids was adsorbed into the soil. The difference between these two concentrations was well suited for estimating the degree of adsorption of phosphonic acids in a particular soil sample. All together, adsorption curves were constructed for two types of soil and three fractions of each. Six concentrations of phosphonic acids were measured to construct one adsorption curve. With three parallel experiments for every sample, 108 soil extracts were analysed in total.

On the basis of the experimental data, four different types of adsorption isotherms were constructed. A comparison of the determination coefficients of experimental data and fitted isotherms enables an assumption to be made about which isotherm of the four is the closest to the performance of real soil. The parameters and determination coefficients for all calculated isotherms are given in Table 3. The parameters of the Langmuir and Freundlich isotherms were calculated using a least square method in a linearised form. The parameters of the Redlich–Peterson and BET-isotherms could not be found using a linear form of the method because they contain three unknown parameters. Instead, a nonlinear trial and error procedure was used to determine all three parameters. The coefficients of determination of calculated isotherms and experimental data were used to compare different adsorption models.

A comparison shows no significant difference to exist in determination coefficients between the Langmuir, Freundlich and Redlich–Peterson isotherms in the measured concentration region. The isotherms follow closely each other's path when plotted on the same graph. When extrapolated to higher concentrations, the Langmuir isotherm levels out at $q_{\max}$, while the other two isotherms continue to grow. The Redlich–Peterson isotherm would have been expected to have superior fitting because it is described with the aid of three adjustable parameters, instead of two as is the case with the Langmuir and Freundlich isotherms. Apparently, there is no significant difference in determination coefficients (R^2) between the above adsorption isotherms, and the type of the best fitting isotherm varies from sample to sample. Therefore, the Langmuir isotherm may be considered to be no worse in performance than the other two and its parameter, $q_{\max}$, which is a maximum adsorption on the monolayer coverage, could be used to compare the adsorptive capacity of various samples.

At a low concentration of phosphonic acids, the Langmuir adsorption isotherm is linear because no molecules were adsorbed on the surface. At higher acid concentrations, the adsorption curve decreases until it reaches a constant value, the maximum adsorption, when all adsorption sites are filled and the monolayer of phosphonic acids is formed on the surface of soil particles.

The results obtained demonstrate the adsorption capacity of sand to be higher than that of loam. The adsorption capacity of smaller fractions of sand samples is higher. However, the difference in adsorption capacity between the smallest fractions (below 100 μm) of sand and loam samples is not as significant as that between their larger fractions (200–400 μm).

Figure 2 illustrates the adsorption of EPA in different soil samples. EPA was chosen as an example to illustrate the adsorptive behaviour of all the phosphonic acids tested in this work, with the exception of PMPA. In case of the sand sample, adsorption was lowest in the medium-sized fraction and highest in the smallest fraction. In case of the loam sample, two smaller fractions

Table 3. Parameters of various adsorption isotherms for sand and loam samples.

		< 100 μm				100–200 μm				200–400 μm			
		BPA	PPA	EPA	MPA	BPA	PPA	EPA	MPA	BPA	PPA	EPA	MPA
Sand													
Langmuir	q_{max}	238.3	205.5	252.8	495.2	323.6	62.2	193.4	282.6	581.4	241.7	268.9	339.9
	K_a	0.0036	0.0042	0.0035	0.0022	0.0017	0.0162	0.0035	0.0038	0.001	0.0026	0.0027	0.0033
	r^2	0.9681	0.937	0.9808	0.9837	0.8856	0.9191	0.9376	0.9735	0.9971	0.9867	0.9804	0.9967
Freundlich	n_F	1.9377	2.1648	1.9888	2.0327	1.1653	3.983	1.5924	2.6812	0.8138	1.0074	1.3423	2.1561
	K_F	1.3332	1.4033	1.3302	1.2281	1.2679	2.071	1.3598	1.3877	1.0992	1.1915	1.235	1.2702
	r^2	0.9795	0.9494	0.9912	0.9902	0.8872	0.8938	0.9474	0.9842	0.997	0.9728	0.98	0.9914
Redlich–Peterson	K_R	0.3013	0.3362	0.2941	0.2398	0.2076	0.5458	0.3169	0.3306	0.1360	0.2126	0.2426	0.2657
	a_R	3.9656	4.4092	3.9590	4.2556	1.8591	8.1942	3.3096	5.5674	1.6945	2.0340	2.7244	4.3811
	b_R	1.3516	1.3996	1.3419	1.2711	1.2307	1.7260	1.3729	1.3917	1.1457	1.2369	1.2746	1.3043
	r^2	0.9790	0.9491	0.9912	0.9903	0.8921	0.8970	0.9474	0.9838	0.9970	0.9749	0.9805	0.9924
BET	q_{max}	64.9	58.9	67.2	72.6	35.7	58.8	43.4	66.4	159.9	229.7	153.7	n.a.*
	K_L	0.0024	0.0023	0.0023	0.0027	0.0032	0.0003	0.0026	0.0023	0.0010	0.0000	0.0007	n.a.
	K_S	0.0170	0.0191	0.0167	0.0203	0.0248	0.0165	0.0229	0.0232	0.0041	0.0027	0.0051	n.a.
	r^2	0.9862	0.9578	0.9939	0.9488	0.9545	0.9791	0.9634	0.9145	0.9959	0.9876	0.9814	n.a.
Loam													
Langmuir	q_{max}	167.7	331.8	108.7	435.3	125.2	199.1	90.0	368.7	61.6	86.6	59.9	229.4
	K_a	0.0028	0.0008	0.005	0.0014	0.0046	0.0013	0.0079	0.002	0.0085	0.0035	0.0096	0.0027
	r^2	0.9871	0.9673	0.8948	0.9805	0.8258	0.9584	0.9797	0.9886	0.9253	0.9643	0.8089	0.9244
Freundlich	n_F	1.0132	0.3921	1.834	1.1518	2.0919	0.3123	1.9376	0.9902	2.2886	0.7218	2.7946	1.7001
	K_F	1.2983	1.1093	1.5672	1.1988	1.6124	1.0709	1.5453	1.1162	1.8659	1.351	1.9951	1.3879
	r^2	0.991	0.9691	0.9171	0.9762	0.8534	0.9342	0.9544	0.9581	0.9583	0.9714	0.8584	0.919
Redlich–Peterson	K_R	0.2844	0.1899	0.4067	0.2224	0.4218	0.1001	0.3956	0.1502	0.4906	0.3117	0.5303	0.3165
	a_R	2.1268	0.9382	3.8715	2.4948	4.3833	0.6155	3.8379	1.9644	4.5442	1.4922	5.8916	3.5245
	b_R	1.3290	1.2091	1.5018	1.2491	1.5247	1.1052	1.4852	1.1621	1.6333	1.3658	1.6995	1.3723
	r^2	0.9911	0.9542	0.9181	0.9788	0.8545	0.9373	0.9582	0.9655	0.9590	0.9713	0.8571	0.9454
BET	q_{max}	40.6	79.4	21.8	45.7	23.4	n.a.	n.a.	n.a.	24.3	37.6	19.5	27.6
	K_L	0.0023	0.0009	0.0033	0.0029	0.0033	n.a.	n.a.	n.a.	0.0023	0.0013	0.0028	0.0034
	K_S	0.0163	0.0039	0.0631	0.0222	0.0586	n.a.	n.a.	n.a.	0.0377	0.0100	0.0762	0.0590
	r^2	0.9949	0.9931	0.9960	0.9740	0.9821	n.a.	n.a.	n.a.	0.9968	0.9965	0.9921	0.9359

Note: *Not available, statistically best fitted isotherm does not correspond to real life expectations having negative q_{max}, etc.

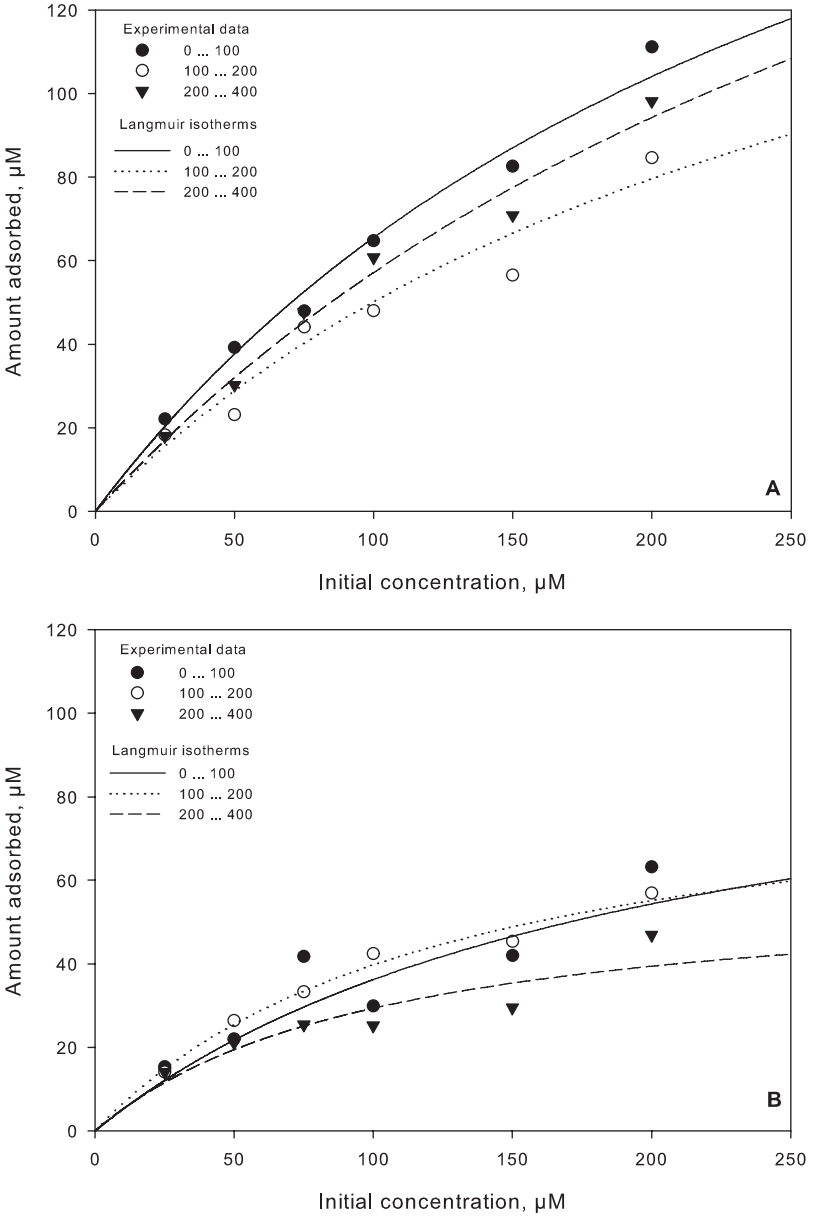

Figure 2. Adsorption data with fitted Langmuir isotherm of EPA in different soil fractions. (A) Sand samples, (B) loamy soil samples.

demonstrated a similar adsorption, while the largest fraction had an adsorption isotherm which was significantly higher than that of the other fractions.

The adsorption of different phosphonic acids in different fractions of sand and loamy soil samples was rather similar. On the basis of the adsorption isotherms of 200–400 µm fractions (Figure 3), some general conclusions can be drawn. First of all, adsorption was highest in the case of MPA. This could be explained by the different sizes of the various phosphonic acid molecules. Of the four phosphonic acids, the molar mass of MPA was by far the lowest. The other three acids had a similar adsorption rate in both sand (Figure 3(A)) and loamy soil (Figure 3(B)). From the two figures it can be seen that the Langmuir adsorption isotherm in the case of the loam sample

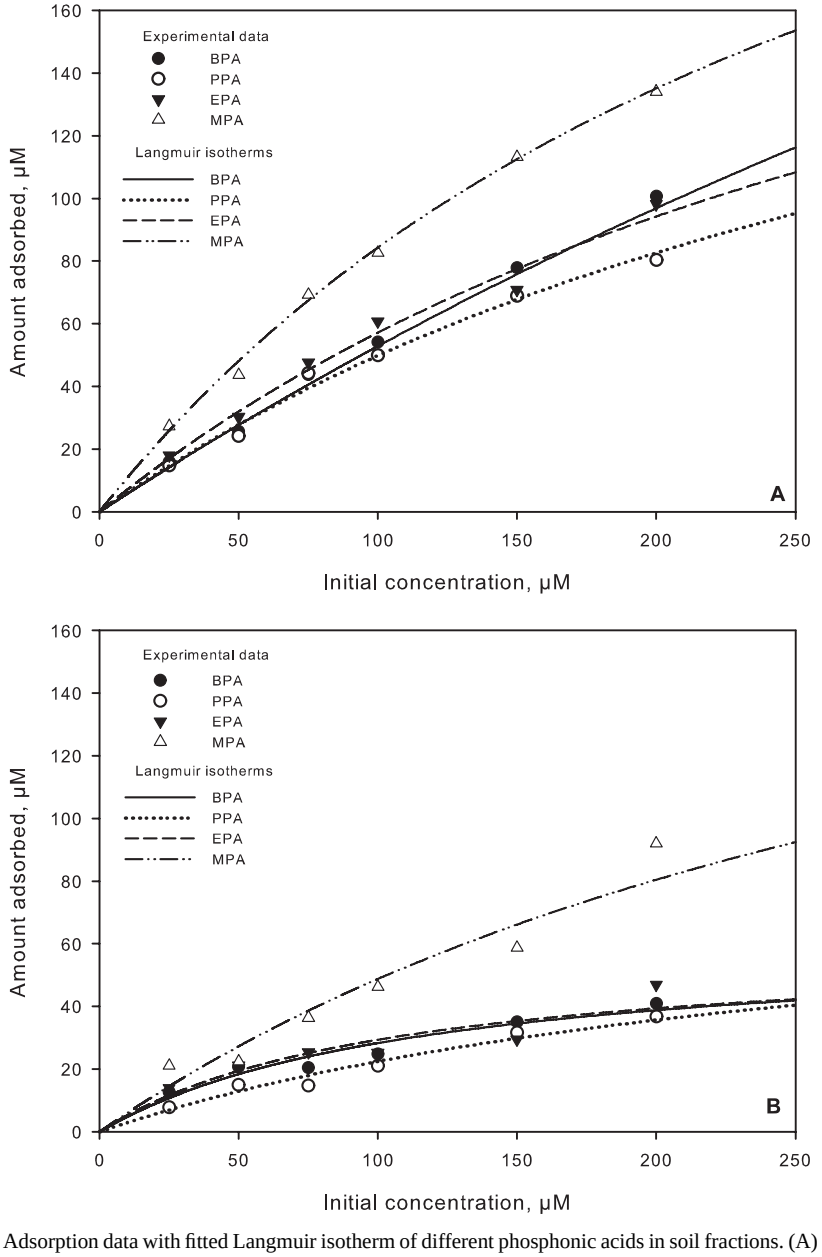

Figure 3. Adsorption data with fitted Langmuir isotherm of different phosphonic acids in soil fractions. (A) Phosphonic acids in sand, fraction 200–400 μm; (B) phosphonic acids in loamy soil, fraction 200– 400 μm.

achieved its constant value at an acid concentration of 200 mM, whereas in the case of the sand sample, the adsorption isotherm at this concentration, except for MPA, was still in the linear region. Therefore, one could expect that the adsorption of phosphonic acids in the sand sample would be higher, which was also confirmed by q_{max} values.

An alternative explanation for the adsorptive behaviour of nerve agent degradation products in soil could be given using the BET-isotherm. While the Langmuir isotherm treats adsorption in one monolayer, the BET-isotherm, on the contrary, assumes that the adsorption of phosphonic acids on the surface of soil particles takes place in several layers. Statistically it is not possible to tell which

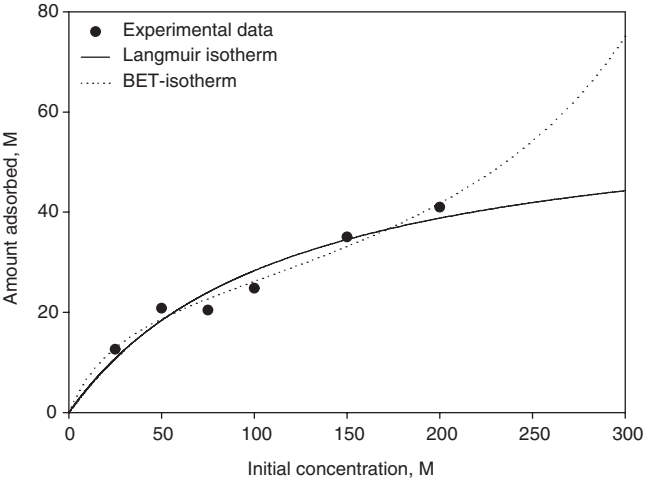

Figure 4. Comparison of fitting Langmuir and BET-isotherm to the same experimental data. Experimental conditions: MPA in soil fraction sized 200–400 μm.

model is more likely as there is no significant difference in determination coefficients between the Langmuir and BET-isotherms, i.e. the quality of fitting both isotherms to experimental data is almost similar. A comparison of two isotherms is given in Figure 4. Both isotherms follow the same path until the point where the second layer of the adsorbent starts to form in the BET-isotherm or the Langmuir isotherm starts to level as the monolayer around the soil particle is filling up. One of the three parameters describing the BET-isotherm is q_{max}, which is the concentration corresponding to a complete monolayer adsorption. The definition of this parameter is exactly the same as in the case of the Langmuir isotherm equation. Apparently, the values of q_{max} of the Langmuir isotherm are 3–10 times higher than those of the BET-isotherm.

For all the phosphonic acids tested, the adsorption mechanism is the same because their molecular structures are very similar. Therefore, it is unlikely that the adsorption concentration corresponding to a complete monolayer of one particular phosphonic acid could vary in such a wide range. Hence, the adsorption mechanism of nerve agent degradation products must be either Langmuir's or BET's. The concentration range under study is apparently too narrow to tell us which of the two mechanisms is more likely, because the measured points are in the range where only the first monolayer is filling up. Unfortunately, in a particular BGE system, much higher concentrations cannot be measured with CE because separation between high concentration phosphonic acid peaks is not sufficient. It is possible to use CE to measure the adsorption of every phosphonic acid separately at higher concentrations, but this may lead to different results compared with the situation when they are detected together because it is very likely that phosphonic acids with highly similar molecular structures compete for the same adsorption sites around a soil particle.

4. Conclusions

Phosphonic acids as degradation products of their parental nerve agents may serve as excellent fingerprint markers for the verification of the use of nerve agents. The adsorption of different phosphonic acids in different fractions of loam and sand samples was studied. The results demonstrated that the difference in adsorption between loam and sand samples was more significant than that between individual fractions. A comparison showed the adsorption of MPA in different soil samples to be relatively higher than that of other phosphonic acids.

CE has proven to be a suitable tool for separating phosphonic acids and could therefore easily be used for the analysis of adsorption. Moreover, it enables analysis of the adsorption of several components on the same adsorbent simultaneously. This offers a great opportunity to study a competitive adsorption of similar molecules on the same adsorption sites. In CE, the use of minimum concentrations of substances is restricted by the sensitivity of CCD–CE, while application of maximum concentrations is restricted by the separation system because separation is insufficient above certain concentrations.

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