SORPTION OF DISSOLVED ORGANIC C AND P TO AGRICULTURAL TOP- AND SUBSOIL

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ABSTRACT

In order to study the mobility of dissolved organic carbon (DOC) and dissolved organic P (DOP) in soil, the pH-dependent sorption of dissolved organic matter to an agricultural top- and subsoil was investigated. In general, sorption isotherms had convex shapes and DOC and DOP sorption increased with time of reaction. There was a very pronounced effect of pH resulting in much higher sorption of DOC at pH 5 than at pH 7; actually extensive desorption was observed at pH 7 especially for the topsoil. Similar sorption patterns were observed for DOP, but they were not as pronounced as for DOC.

INTRODUCTION

Dissolved organic matter (DOM) is supposed to represent the most active and mobile form of organic matter in soil [1, 2]. DOM is, by definition, the most mobile soil organic fraction and, therefore may be a substrate for organisms not proximal to a food source, e.g. in soil aggregates, deeper soil horizons, and aquifers. Metabolization of the DOM may cause a number of effects in soils, such as consumption of oxygen and nitrate, causing local variation in soil redox status [2]. In addition, DOM mobility is a major factor affecting the export of nutrients from soils to surface waters. E.g. nitrogen (N) and phosphorus (P) in DOM can make up a significant fraction of total dissolved concentrations of N and P in soil pore water. Thus, Qualls *et al.* [3] estimated that > 90 % and > 66 %, respectively, of total dissolved N and P leaching from a deciduous forest soil were in the form of dissolved organic N (DON) and DOP, respectively. Additionally, Grant *et al.* [4] estimated that DOP accounted for 16 - 23 % of the annual loss of total P from four arable catchments in Denmark.

DOC concentrations are repeatedly observed to decrease considerably with depth in forest soil profiles [5]. The change in quantity of DOC during passage through the mineral subsoil is presumed to be caused by sorption of DOC to the soil, and several batch sorption experiments verify that substantial DOC sorption takes place to soil samples [6, 7]. Almost all laboratory adsorption experiments demonstrate that sorption of DOC increases with decreasing pH [6, 8]; however, only limited data are available for agricultural soils.

It is often found that soil is able to release DOC when exposed to aqueous solution containing no or very low concentrations of DOC [9]. Thus, the soil solid phase may not only sorb DOM but may also release it depending on solution DOC concentrations. Nodvin *et al.* [10] developed the initial mass isotherm to take this into account. The initial mass isotherm have in several studies been able to describe the amount of DOC, removed or released to the solution by the soil, as a linear function of the initial amount added to the soil-water system [7, 11, 12]. The initial mass isotherm has also been able to describe the exchange of DOP [9].

The aim of the present study was to investigate the sorption of DOM to agricultural top- and subsoil material at two pH levels, and describing the sorption behavior with the approach of the initial mass isotherm.

MATERIAL AND METHODS

The soil characteristics

The soil used is located at the Burrehøjvej field at Research Center Foulum in the central part of Jutland, Denmark (9°34′E, 56°29′N). In the previous 9 years (1994-2002) the soil has been covered by grass-clover and grassed by dairy cattle approximately 150 days per year. The soil is classified as a Humic Hapludult /13/. Bulk soil material was sampled every 20 cm from the surface to 130 cm depth; samples from the genetic Ap, EB, and Bt horizons were collected from appropriate depths. For pedogenetic analyses air-dried soil passed through a 2 mm sieve was used. Selected data are listed in Table 1.

Table 1. Soil characteristics of Burrehøjvej field soil.

	Ap horizon	*EB horizon*	*Bt horizon*
pH	5.68	5.75	4.27
	----------------- *cm* ------------------		
Depth	0-30	30-70	70-130
Particle sizes:	-----------------$g\ kg^{-1}$ ----------------		
< 2 μm	68	126	148
2-20 μm	127	114	97
20-200 μm	805	760	755
Nutrients:	-----------------$g\ kg^{-1}$ ----------------		
Total C	30.10	1.41	0.76
Total N	2.01	0.09	0.05
Total P	0.80	0.41	0.23
Aluminium and iron fractions	---------------- $mmole\ kg^{-1}$ ---------------		
Al_{cbd}†	133	115	71
Al_{ox}‡	111	81	62
Fe_{cbd}	80	77	83
Fe_{ox}	62	22	32

† : *cbd* acronym for citrate-bicarbonate-dithionite. ‡ : *ox* acronym for oxalate.

For the sorption experiments moist soil stored in the refrigerator were used. The water content of the soil material was measured by drying at 105 °C every time a sorption experiment was performed. A stock solution of DOM to be used in the sorption experiments was prepared by extraction of the A-horizon material using a chelating, sodium saturated resin, Chelex® 100 Resin (from Bio-Rad), see Gjettermann *et al.* /14/ for further details on the extraction procedure.

Sorption experiments

Six series of sorption experiments were conducted with two pH levels (pH 5 and 7) for each of the Ap, EB, and Bt horizons. A sorption series comprised six bottles (250 ml Blue Cap) with a soil:solution ratio of 1:10, and with initial concentrations of DOM of 0, 0.4, 0.8, 1.7, 3.4 and 4.7 mmol C L^{-1}, respectively. A 10 mM NaCl solution was used as background electrolyte throughout, and all sorption experiments were carried out in duplicate. For each bottle 20 g of moist soil and 150 ml of triple-deionized (TI) water plus 1.8 - 2.0 ml of 1 M NaCl was pre-equilibrated at pH 5 or 7. The pH was adjusted twice using 0.01 M HCl / NaOH in the following hours and once again the following day, right before addition of TI water to reach a total of 200 ml solution, including the addition of 0 - 15 ml DOM stock solution. The bottles were shaken horizontally on a shaking table (60 rev min^{-1}). The amount of DOC, dissolved inorganic phosphorus (DIP), and total dissolved phosphorus (TDP) in solution was measured after 1, 120, 1440 and 4320 minutes of reaction by withdrawing 10 ml of suspension, centrifugation (4000 g) and filtering through 0.45 μm Millipore filters (regenerated cellulose, from Frisenette). It was tested that the filter did not sorb DOM.

Quantification of DOC, TDP, and DIP in the supernatant was carried out as follows. DOC concentration in the samples was determined using a total organic carbon analyzer (Shimadzu TOC-500). DIP was measured directly in the sample as molybdate reactive P (MRP) (see below). TDP was measured by a modification of the method of Bedrock et al. /15/: After drying of 1 mL sample at 70 $^{\circ}$C and ignition at 550 $^{\circ}$C, the residue was dissolved in 0.25 ml 6 M H_2SO_4 and diluted by 0.5 mL of TI-water. After complete dissolution the extract was transferred to 10 mL volumetric flask and filled with TI-water for phosphate measurement. All phosphate measurements were carried out by Flow Injection Analysis as MRP by the molybdenum blue/stannous chloride method at 690 nm /16/.

Sorption isotherms for each soil and pH level were plotted as sorbed amounts of DOC and DOP versus the respective equilibrium solute concentrations of DOC and DOP, respectively. Sorbed DOC is calculated as the difference between added and measured DOC in solution at time of sampling. The DOP solute concentration is calculated as the difference between measured TDP and measured DIP in solution. Sorbed DOP is calculated as the difference between initial DOP concentration and DOP concentration in solution at time of sampling.

Additionally, the initial mass (IM) isotherm approach /10/ was used to analyze sorption data. In this approach the amount of substance sorbed or released, RE (normalised to soil mass), is plotted as a function of the initial amount of that substance X_i (normalised to soil mass). The release or removal of DOC or DOP is then given by $RE = m\,X_i - b$. The slope of the linear function, m, is related to the partition coefficient and is a measure of the affinity of the substance to the sorbent. The intercept of the linear regression, b, indicates the amount of substances released from the soil when a solution with no sorbate (DOM) is added /10,17/. The reactive soil pool, RSP, is defined as the amount of DOC or DOP present in the soil that can readily be exchanged with DOC or DOP in solution under the conditions of the experiment /10/. Hence, the size of RSP is a measure of the potential amount of DOC and DOP initially sorbed to the soil. The size of RSP is related to the intercept and slope of IM: $RSP = b/(1-m)$. The amount of substances removed from solution has been represented as a linear function of the equilibrium solute concentration where the slope has been termed the distribution

coefficient, K_d, which is directly related to the slope of the IM isotherm: $K_d = m/(1-m) *$ (volume of solution/mass of soil).

RESULTS AND DISCUSSION

Figure 1 and 2 show DOC and DOP sorption isotherms, respectively, for the Ap and Bt horizons, at pH 5 and 7, at different times of reaction. Similar results were obtained for the EB and Bt horizons. At both pH values, the Bt horizon has higher affinity for DOC than the Ap horizon, reflected by the steepness of the curves. After three days of reaction no sorption maximum is observed at pH 5 within the applied DOC concentrations. At pH 7 the very flat curves observed for the Bt horizon material reached a sorption maximum of approximately 15 mmol C kg^{-1} by extrapolating the curves to high solute concentrations (Fig.1). The solution concentration of Ca^{2+} in the sorption experiments with 10 mM NaCl electrolyte was at the same level as the Ca^{2+} concentrations measured in soil solution (0.9 mM) sampled from the Ap horizon with suction cells in the field (data not shown). Hence, the low sorption of DOC observed at pH 7 with NaCl seems not to be an artifact due to the experimental conditions.
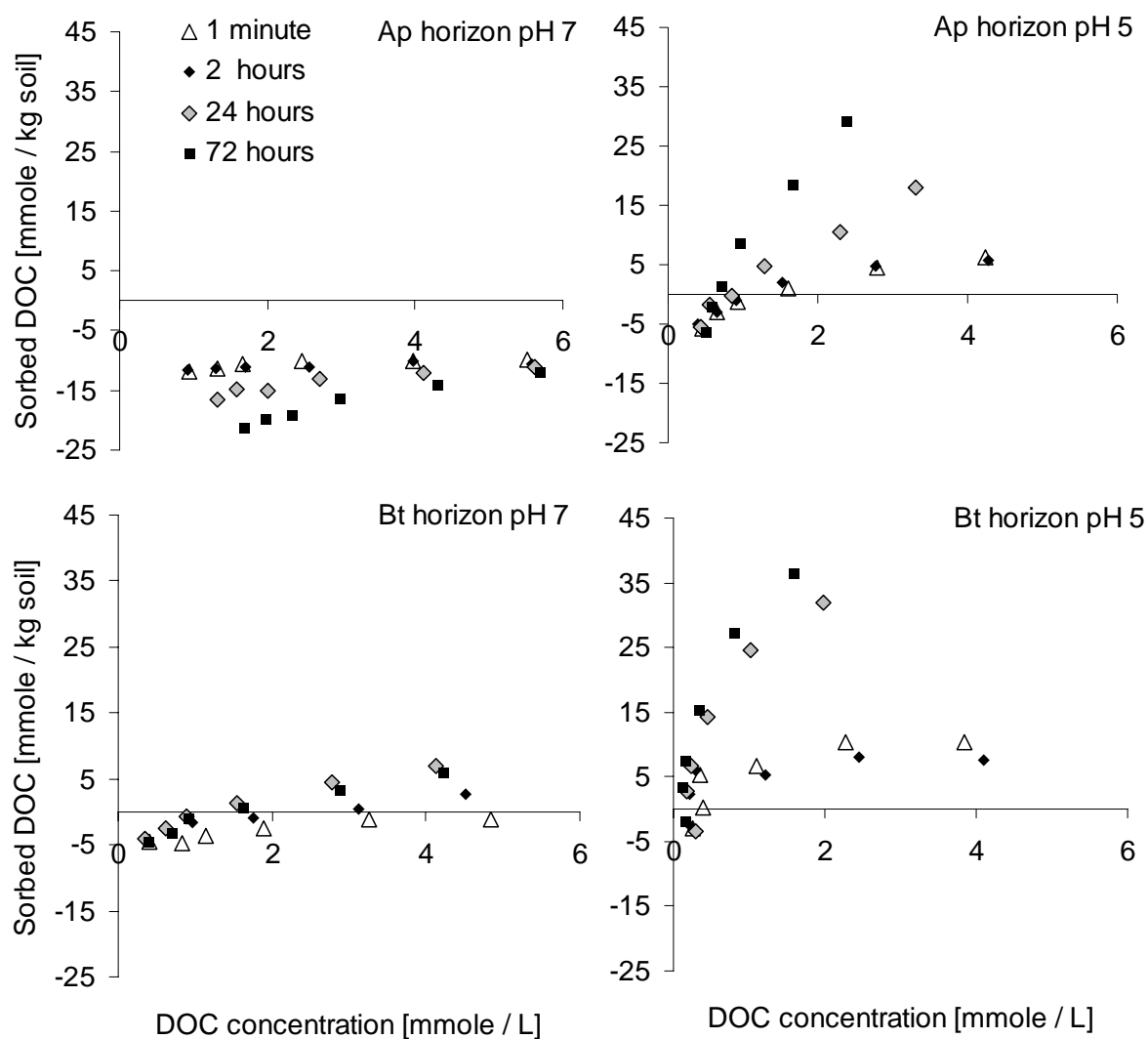

Figure 1. Effect of pH and time of reaction on DOC isotherms for the Ap and Bt horizons. Left: pH 7, right: pH 5. Each data point represents the average of two replicates.

DOC sorption is much lower at pH 7 than at pH 5. In fact, at pH 7 DOC is desorbed from the Ap horizon DOC no matter how much DOC is applied to the solution. Also the Bt horizon desorbs DOC at pH 7 up to solution DOC concentrations of 2-3 mM. At pH 5 desorption of DOC occurred only when zero or very small amounts of DOC is applied (Fig. 1). The results indicate that pH exerts a strong control on the mobility of DOC.

Similar sorption patterns were observed for DOP sorption, but not as pronounced as for DOM sorption (Fig. 2). Again, the results obtained with the EB and Bt horizons were similar. A notable pH effect was observed with increasing DOP sorption at decreasing pH, particularly for the Bt horizon. For the Ap horizon the pH effect was limited. The Bt horizon did not sorb DOP at pH 7, but rather desorbed DOP within the tested DOP concentration range (0–0.03 mM DOP). Also the Ap horizon desorbed DOP at pH 7 up to solution DOP concentrations of 0.01 mM. At pH 5, the affinity for sorption of DOP is somewhat higher for the B-horizon than for the A-horizon as for DOC. No sorption maxima are observed within the applied DOP concentrations (Fig. 2).
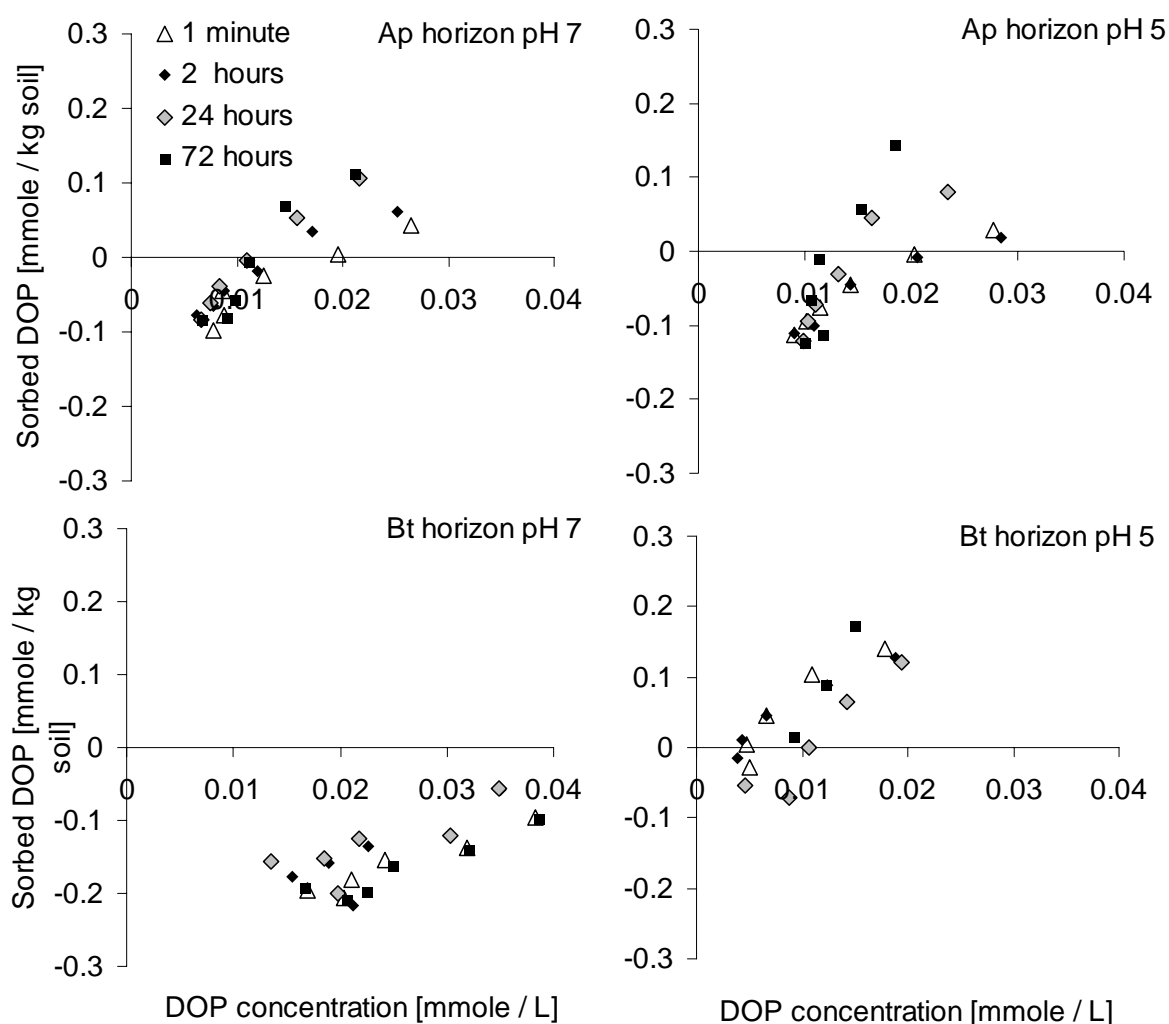

Figure 2. Effect of pH and time of reaction on DOP isotherms for the Ap and Bt horizons. Left: pH 7, right: pH 5. Each data point represents the average of two replicates.

Figure 3 show the fitted initial mass isotherms of DOP sorption to the Ap and Bt horizons. Linear correlation analysis of the IM isotherms of DOC showed that after 24 hours of reactions, all isotherms for the three horizons could be described accurately with correlations coefficients in the range of 0.92-0.99 as shown in Table 2. For DOP the correlation coefficients were in the range of 0.81-0.99.

In general, the distribution coefficients and the parameter *m* were higher at pH 5 than at pH 7 for both DOC and DOP, except for the EB horizon (Table 2). For DOC the distribution coefficients and *m* are higher for the Bt horizon than for the Ap horizon, confirming the above observation of higher affinity in the subsoil horizons for DOC.
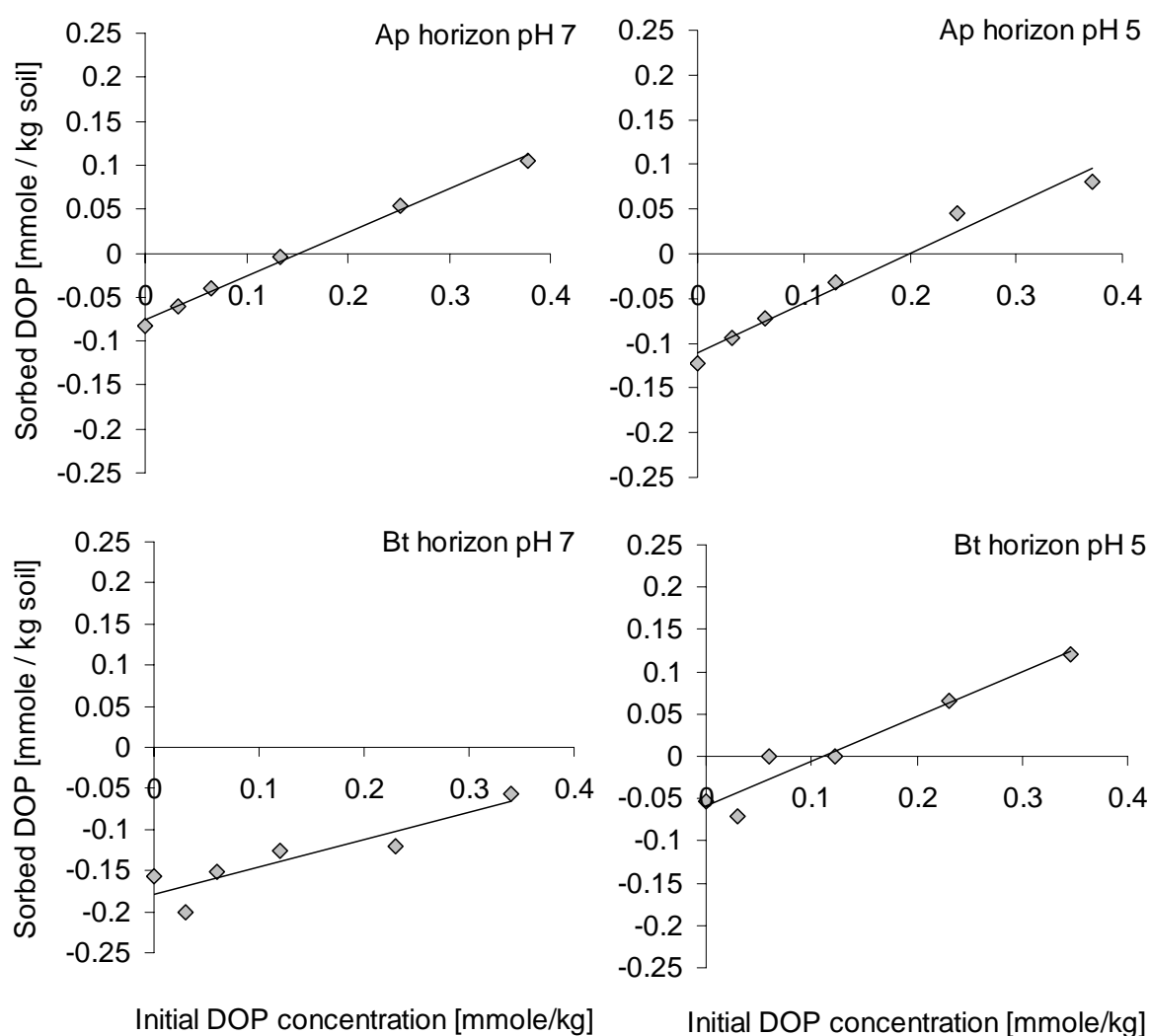

Figure 3. Initial mass DOP isotherm for the Ap and Bt horizons after 24 h of reaction. Left: pH 7, right: pH 5. Each data point represents the average of two replicates.

Table 2. IM isotherm parameters for DOC and DOP after 24 hours of reaction at pH 5 and pH 7.

| | DOC | | | | | | DOP | | | | | |
| | Ap horizon | | EB horizon | | Bt horizon | | Ap horizon | | EB horizon | | Bt horizon | |
	pH 5	pH 7	pH 5	pH 7	pH 5	pH 7	pH 5	pH 7	pH 5	pH 7	pH 5	pH 7
m	0.38	0.09	0.66	0.14	0.63	0.20	0.56	0.50	0.44	0.57	0.53	0.33
$-b^§$	4.23	15.76	0.21	6.35	0.34	3.13	0.11	0.08	0.02	0.09	0.06	0.18
R^2	0.992	0.922	0.987	0.960	0.972	0.974	0.974	0.994	0.924	0.991	0.939	0.817
$RSP^†$	6.85	17.26	0.61	7.39	0.94	3.91	0.25	0.15	0.03	0.20	0.13	0.27
$K_d^‡$	6.21	0.95	19.67	1.64	17.17	2.48	12.47	9.84	7.89	13.20	11.19	4.90

§ Given in mmole kg^{-1}, † mg kg^{-1}, ‡ L kg^{-1}.

Sorption strongly increases with time in particular at pH 5 and at higher DOC and DOP concentrations (Figs. 1 and 2). Hence, in our study about 60 % of the sorption observed at 72 hours toke place within the first 1 minute of reaction. After 24 hours an average of 90 % of the sorption had occurred. A preliminary study by Moore *et al.* [7] using soil samples initially containing 40 mg DOC L^{-1}, showed that > 90 % occurred during the first 24 hours of reaction (total sorption time was 48 h) , and most occurred in the first 2 hours. McDowell & Wood [18] also noted that equilibrium was essentially completed after 2 hours of reaction. DOP sorption also increases with time in particular at higher DOP concentrations (Figure 2). Thus, the sorption process is relative fast, achieving equilibrium within a couple of days.

DOP is sorbed as anions in soil, however, whether the negatively charged P ester group or the carboxylic acids determine this behavior has not been determined [19]. Analysis of relationship between dissolved molar DOC:DOP ratios as functions of dissolved DOC concentration for the two pH values (not shown), showed that increasing solute DOC (or DOP) concentration increased the DOC:DOP ratios. This indicates that at high concentration levels DOP is sorbed preferentially in relation to DOC, which could indicate that the negatively charged P ester group is the reactive site.

CONCLUSION AND PERSPECTIVE

In general, the sorption isotherms of DOC and DOP had convex shapes and sorption increased with time of reaction. However, DOC and DOP sorption were characterized as relatively fast sorption processes achieving equilibrium within a couple of days.

There was a very pronounced effect of pH resulting in much higher sorption of DOC at pH 5 than at pH 7. Extensive desorption was observed at pH 7 especially for the topsoil. Thus, pH exerts a strong control on the mobility of DOC. Similar sorption patterns were observed for

DOP, but they were not as pronounced as for DOC and pH exerted a minor control of the mobility of DOP in subsoil horizons.

Initial mass isotherm could describe DOC and DOP sorption to agricultural soil. Thus, in order to estimate the mobility of DOC and DOP in agricultural soil, the initial mass isotherm could be a future tool in modeling sorption of DOC and DOP. However, factors as pH are important factors concerning mobility of DOC and DOP that should be taken into account.

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