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Sorption of atrazine, alachlor and trifluralin from water onto different geosorbents

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Abstract

The sorption behavior of the herbicides atrazine, alachlor and trifluralin on four sorbents (two modified organoclays, one model sediment, and one natural sediment) in three water matrices (synthetic water, natural groundwater and surface water) was investigated. The influence of the sorbent and water matrix characteristics was elucidated. All adsorption isotherms fitted well with the Freundlich model. Based on the K_d values, the organically modified bentonite and model sediment proved to be the most effective sorbents for the investigated herbicides. A linear correlation of K_d with the total organic carbon (TOC) concentration was found for trifluralin in synthetic water matrix (c_0= 0.01 mg/L). In the case of higher trifluralin concentration and for other tested herbicides at all concentrations the influence of both the sorbent organic matter quality and possible interactions with the mineral phase was indicated. Furthermore, the results showed different influence of the type and the content of dissolved organic carbon (DOC) in the water phase on the sorption of all the herbicides, depending on the herbicide concentration and the sorbent applied. It was confirmed that the comparison of sorbent efficiency should be done in native matrix since sorption coefficients vary depending on pollutant concentration DOC concentration and DOC fractions. This finding is considered to be important to pay attention for in remediation of contaminated sites.

Keywords: DOC; herbicides; organo-modified clays; sediment; sorption; water matrix

1. Introduction

Contamination of water bodies with agricultural pesticides poses a significant threat to aquatic ecosystems and water sources used for drinking water production.[1] Direct and indirect discharge of urban and industrial wastes and run off in the absence of an adequate wastewater treatment can cause water quality deterioration and result in the accumulation of toxic compounds such as pesticides, surfactants, halogenated aromatics and hydrocarbons on soils and sediments. Also, organic xenobiotics from non-treated or poorly treated wastes from agriculture pollution and from accidental situations may pass different technological and natural barriers.[2]

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Both abiotic and biotic processes in soils and sediments of a water body may contribute to natural attenuation of a chemical compound. Thus, sorption and desorption as well as degradation processes determine the mobility and persistence of organic pollutants in soils and sediments and their potential to contaminate surface water and groundwater through leaching and runoff. The sorption and retention of pesticides is strongly dependent on the structural and chemical composition of geosorbents. These are complex systems of inorganic minerals and natural organic matter that can be found in soils and sediments. Among the inorganic surfaces present in the sorbents, clay minerals and sesquioxides (oxides, hydroxides and oxyhydroxides of Al and Fe) have been reported to significantly contribute to the sorption of both hydrophobic and hydrophilic pesticides having wide range of solubilities.[3, 4] For pesticides with low polarity and low solubility in water, the organic matter deposited on the sorbent surface is one of the domains where sorption occurs. Adsorption of dissolved organic substances onto solid aquifer materials is very important for the attenuation of organic pollutants during bank filtration[5] or in the studies of remediation, since different sorbents can prevent leaching of herbicides into rivers, lakes and groundwater. Furthermore, the use of organo-clays as geosorbents has been found to be an efficient approach in removal or speciation of organic pollutants in water treatment.[6] In addition to the sediment organic matter, dissolved organic matter (DOM) in water has been a subject of considerable interest in recent years because it can interact with organic pollutants, and thus affect the fate of these pollutants in aquatic systems.[7,8] The extent and nature of the interactions of water DOM with organic pollutants depend on several factors such as the nature of pollutants, their molecular weight and polarity, as well as the size, polarity and molecular composition of DOM.[9]

The selection of herbicides in this study was based on the difference in their hydrophobicity (the range of log K_{ow} from 2.6 to 5.3). The triazine herbicide, atrazine, has been extensively used since the 1950s for selective weed control, mainly in corn production. Contamination of soil, groundwater and surface water by atrazine is thus a world-wide concern.[10] Due to its intensive use in crops such as soybeans and maize, alachlor has also been frequently detected in groundwater.[11] Trifluralin, a dinitroaniline herbicide, is a selective, pre-emergence herbicide, used to control annual grasses and broadleaf weeds in a variety of crops. This herbicide is strongly sorbed to soil particles and is not readily leached into the groundwater. Also, it can enter surface waters through the runoff of sediment. According to the databases from the US Department of Agriculture Natural Resources Conservation Service, persistence of these herbicides (characterized by the soil half-life) is 60 days for trifluralin and atrazine and 15 days for alachlor. The Water Framework Directive[12] has included these three herbicides in the list of priority pollutants that pose a significant risk to or via the aquatic environment, including such risks to waters used for the abstraction of drinking water. It is necessary to take measures for the progressive reduction of such substances.

The geosorbents selected for this study were one natural and one model sediment and two organically modified clays. The water matrices varied depending on the nature and content of their dissolved organic carbon (DOC), ranging from 0.5 to 7.2 mg C/L. The objectives of the investigation were: 1) to determine and compare the sorption coefficients of the mentioned herbicides using different geosorbents and 2) to elucidate how the sorbent and water matrix characteristics (different DOC type and content) influences adsorption with main goal to contribute to better understanding of sorption behavior of the herbicides with different solubilities and K_{ow} values. Model sediment was used as a representative of organic rich sediment or organically amended sand to prevent leaching of organic pollutants to surface- and groundwater, while for tetramethylammonium-bentonite and –kaolinite the lack of knowledge in behavior of these clays in this kind of sorption processes was detected in the literature. Comparison of natural sediment and organoclays could contribute to the possible use of these materials for in situ remediation of sediments. Granular materials such as quarry sand, natural sediments or soil materials should be considered as a physical barrier that isolates contaminated sediment from the surrounding environment and reduces contaminant migration into the water column. On the other hand, a newer approach involves the use of chemically active amendments such as organoclays that can reduce the mobility and/or bioavailability of contaminants by changing their chemical speciation.[13] Mostly, this technology was applied for remediation of inorganic pollutants while scarce information is known about in situ capping of organic pollutants.[14] In addition to, Ake et al.[15]developed a new organoclay fixed-bed system that could provide a less expensive and highly effective alternative to charcoal in decontaminating water that contains pentachlorophenol. According to literature review of Paria[16] a very promising technology developing which is based on the idea that clays present in subsoils and aquifers can potentially be converted to highly sorptive organoclays via subsurface injections of cationic surfactants.

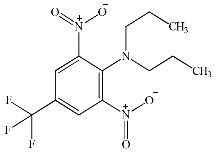
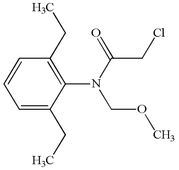
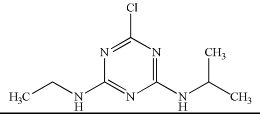
A literature survey showed that influence of DOC on pollutants sorption has been studied by many authors using mainly commercial humic acid and different extracts of various organic materials. [7, 17] This study have been focused on investigating sorption behavior of herbicides using natural water matrices that is more similar to real environmental conditions.

2. Materials and methods

2.1. Preparation of sorbates

The hydrophobicity of the herbicides, expressed as a logarithm of the octanol-water partition coefficients (log K_{ow}), increases in the following order: atrazine (log $K_{ow} = 2.61$) < alachlor (log $K_{ow} = 3.52$) < trifluralin (log $K_{ow} = 5.34$). All the herbicides (purity > 99 %) were purchased as crude substances from the Sigma-Aldrich Chemical Company. They were dissolved in methanol to prepare the corresponding stock solutions (~1000 µg/mL). All the other solvents and chemicals used were of gas chromatography (GC) and analytical grade. Selected properties and structures of the investigated compounds are listed in Table 1.

Table 1. Selected physical and chemical properties of the investigated herbicides

Compound	Structure	Chemical group	Molecular weight, g/mol[a] MW	Octanol/water partition coefficient[a] logK_{ow}	Solubility in water, mg/L[a] S_w
Trifluralin		Dinitroaniline	335.30	5.34	2.24
Alachlor		Chloroacetamide	269.77	3.52	240
Atrazine		Triazine	215.68	2.61	34.7

[a] Toxicology Data Network (2003).[18]

2.2 Preparation of sorbents

The sorbents used in this study were: 1) a natural sediment obtained from the River Danube (further denoted as D), 2) a model sediment (denoted as M), and 3) organo-modified clays, kaolinite and bentonite (denoted as TMA-K and TMA-B, respectively).

The Danube sediment was a typical sandy aquifer material with total organic carbon content of 1.2% (w/w). Several samples were taken from different sediment depths ranging from 0 to 30 cm, and a composite mixed sample was prepared in order to obtain a representative sample. Particle size distribution analysis of the natural sediment ranging from 63 to 2000 μm was performed by wet sieving method (Sieve Shaker mode. PR.09. CISA), while the analysis below 63 μm was performed according to the ISO method 13317-2:2001.22. The precision of the particle size determination expressed as RSD was ±5 %. The natural sediment consisted mainly of sand (96.2%), while the contents of silt (2-63 μm) and clay (< 2 μm) were 8.17% and 0.78%, respectively.[19]

The model sediment was prepared according to the OECD 219 standard procedure, [20] which represents a reproducible "standardized matrix" consisting of 74% of sand, 20% of clay (kaolinite) and 5% of sphagnum peat. The organo-modified kaolinite and organo-modified bentonite were prepared from kaolinite and bentonite with the aid of organic surfactant tetramethylammonium bromide according to Groisman et al.[21] Based on the cation exchange capacity (CEC) determined by ammonium acetate method [22] the coverage was about 78% and 83% for TMA-K and TMA-B, respectively.

The total C, H, N and S contents of all the sorbents were determined using a CHNS/O elemental analyzer (Vario EL III Elementar). The organic carbon (OC) content of sorbents was determined on a TOC analyzer (liquiTOCII, Elementar, Germany).

Microstructural properties of the TMA-B, TMA-K and model sediment were determined by the X-ray diffraction method on a Philips PW automated X-ray powder diffractometer. The specific surface area, pore volume, and pore size of the sorbents were determined based on the adsorption and desorption isotherms of N_2 at 77 K obtained on an Autosorb iQ Surface Area Analyzer (Quantochrome Instruments, USA). The samples were outgassed at 120°C for 5 h before running isotherms. Pore volumes were derived from the desorption isotherms using the BJH (Barrett-Joyner-Halenda) model. Size distribution was evaluated by Dollimore and Heal (DH) method. Micropore volumes of the sorbents were additionally calculated using the t-test method and Horwath-Kawazoe (HK) method.

2.3 Preparation of water matrices

Three water matrices were used for testing: synthetic water (prepared as 0.01 M $CaCl_2$ in deionised water with 100 mg/L NaN_3 as a biocide in accordance with the OECD 106 test[23] for testing chemicals) and two natural water matrices after filtration through 0.45μm membrane filter (deep groundwater and the River Danube surface water with DOC contents of 7.2 mg C/L and 3.5 mg C/L, respectively). The characteristics of the water matrices are given in Table 5.

The DOC content was determined on a TOC analyzer (liquiTOCII, Elementar, Germany). The analytical measurements of the method performance were obtained from six duplicate measurements in the concentration ranging from 0.5 to 25 mg C/l. The recovery and precision were within the range of 93.7% to 105%, and 2.0% to 9.5%, respectively.

The DOC fractionation by liquid size exclusion chromatography with organic carbon detection was performed using an 8th generation LC-OCD system (DOC-Labor Dr. Huber, Karlsruhe, Germany) at Technische Universität Dresden, Germany. This technique enables characterization and quantification of DOC, with the latter defined as the sum of hydrophobic organic carbon (HOC) and chromatographable dissolved organic carbon (CDOC). In the LC-OCD system, the CDOC is separated according to apparent molecular weight into five fractions: (1) biopolymers (BP) comprising polysaccharides, proteins and colloids; (2) humic substances (HS); (3) building blocks (BB), or hydrolysates of humics; (4) low-molecular weight humics and acids (LMWA); and (5) low-molecular weight neutrals (LMWN) such as alcohols, aldehydes, ketones and amino acids. A detailed description of the method has been published elsewhere.[24, 25] The interpretation of the results was performed using the version of ChromCALC software provided by the manufacturer of the instrument.

2.4 Sorption experiments

The sorption isotherms were obtained by batch equilibrium experiments at room temperature (20±2ºC). It involved the addition of 0.5 g of M, 5 g of D, and 1 g of TMA-B and TMA-K samples to 40 ml glass vials with a screw cap having a Teflon-lined septum covered with silver foil. The vials were filled up to the top with the investigated water (synthetic water, surface water and groundwater). The initial herbicide concentrations ranged from 100 to 2000 µg/L. The isotherms consisted of 8 concentration points, and each point was run in duplicate. The volume of stock solutions of the compounds used for solution spiking was < 0.1% (v/v), which has been shown to have no measurable influence on the sorption behavior of the organic compounds.[17] The amount of the sorbent corresponded to a sample/solution ratio that resulted in a 20-80% uptake of the solute (example given in Table 2). Based on the preliminary kinetic experiments, the equilibration periods were between 5 and 48 h, depending on the compound and the sorbent.

Table 2. Experimental design for the investigated herbicides at concentration of 100 µg/L

Sorbent (mass/volume)	Herbicide		
	Trifluralin	Alachlor	Atrazine
	Solute uptake (%)		
D (5 g/40 mL)	78.8	80.0	80.0
M (0.5 g/40 mL)	76.8	70.0	68.7
TMA-K (1 g/40 mL)	65.0	63.0	68.0
TMA-B (1 g/40 mL)	64.2	62.8	69.8

After shaking, the contents of the flasks were allowed to settle for 24 h, and the clear supernatants were sampled for the determination of the herbicides equilibrium concentration. To determine the initial concentration of herbicides for each isotherm point and to account for pesticide losses other than adsorption to the sorbents, two control flasks without sorbent were prepared and treated in exactly the same way. The recoveries of the initial concentrations of compounds were in the range of recoveries for the applied analytical methods (Table 3). No significant losses of the compounds were observed that would be due to the processes other than adsorption. The solid-phase solute concentrations were calculated from a mass balance of the solute between the solid and aqueous phases. The pH was not additionally adjusted during the experiments.

2.5 Herbicide analysis

The aliquots of each aqueous phase (1.0 mL for trifluralin and 30 mL for alachlor and atrazine) were extracted with 1.0 ml of hexane (J. T. Baker, for organic residue analysis).[26, 27] After 15 min of liquid-liquid extraction, 0.5 mL of the extract was used for organic residue analysis by gas chromatography with electron capture detection (GC/µECD; Agilent Technologies 6890 with 63Ni ECD) on a DB-XLB column (J&W Scientific, 30 m x 0.25 mm x 0.25 µm), and the herbicides were quantified according to internal standard calibration procedure, using pentachloronitrobenzene as an internal standard. The GC/µECD analysis conditions were: split mode with the ratio of 50:1, inlet temperature 250ºC, column flow 2.0 ml/min. The initial oven temperature was 70ºC (held for 1.0 min), ramped up to 270ºC at a rate of 20ºC/min for atrazine and trifluralin, and 70ºC (held for 1.0 min), ramped up to 270ºC at a rate of 10ºC/min for alachlor.

The results of the extraction and analysis were obtained from three measurements at each of the four concentration levels: 1, 5, 10 and 20 µg/L for the range from 1 to 20 µg/L, and 0.5, 1, 50 and 100 µg/L for the range from 0.5 to 100 µg/L (Table 3).

Table 3. Evaluation of the extraction and analysis performance

Compound	Measurement range, µg/L	Recovery, %	Precision, %
Atrazine	1-20	98-106	1.5-2.1
Alachlor	1-20	101-115	3-10
Trifluralin	0.5-100	99-118	5-16

2.6 Data analysis

The adsorption data were fitted using the Freundlich isotherm:

$$q_e = K_F \cdot C_e^n \qquad (1)$$

where q_e and C_e are the solid phase and aqueous phase equilibrium concentrations (in µg/g and mg/L, respectively); K_F is the Freundlich sorption capacity coefficient (expressed as (µg/g)/(mg/L)^n), and the exponent n is the site energy heterogeneity factor indicating isotherm nonlinearity (dimensionless). K_F and n were obtained from direct nonlinear curve fitting of the adsorption data sets.

The single-point distribution coefficients (K_d) for the selected equilibrium concentrations (C_e) were determined by calculating the q_e values corresponding to the C_e value from the respective best fits of the Freundlich isotherms according to the following general equation:

$$K_d = K_F \cdot C_e^{n-1} \qquad (2)$$

where K_d is the adsorption distribution coefficient (in L/kg).

3. Results

3.1 Characterization of the sorbents

The results of the characterization of the sorbents are shown in Table 4.

Table 4. Chemical and physical properties of the sorbents

Sorbent	pH	CEC [a] (meq/100g)	TOC [b] (%)	Elemental composition (% w/w)				BET [c] (m^2/g)	Micropore t-test (cm^3/g)	Micropore volume HK method (cm^3/g)	BJH [d] pore volume (cm^3/g)	Average pore radius (Å)
				C	H	N	S					
D	8.50	0.85	1.20	2.88	0.32	<0.1	n.d.[e]	3.19	0.000	0.0013	0.018	113
M	7.30	0.96	2.20	2.60	0.41	<0.1	n.d.[e]	1.73	0.000	0.0006	0.017	204
TMA-B	8.89	11.7	3.92	4.87	2.28	0.35	n.d.[e]	84.1	0.007	0.0324	0.224	50.8
TMA-K	6.86	4.25	0.14	0.27	1.42	<0.1	n.d.[e]	17.7	0.000	0.0068	0.211	242

[a] CEC-cation exchange capacity, [b] TOC – total organic carbon, [c] BET - Brunauer–Emmett–Teller theory, [d] BJH - Barrett-Joyner-Halenda model, HK method- Horvath-Kawazoe method, [e] not detected.

The investigated sorbents contained different amounts of total organic carbon, with 0.14, 1.20, 2.20, and 3.92% of TOC in TMA-K, D, M and TMA-B samples, respectively.

The elemental analysis showed that total nitrogen was present in small amounts in all the sorbents (<0.1%), except for TMA-B, which contained 0.35% of N (Table 4b). The total carbon content decreased as follows: 4.87% (TMA-B) > 2.88% (D) > 2.60% (M) > 0.27% (TMA-K). The X-ray structural analysis gave information on the difference in structures of the investigated sorbents. The diffractogram of the model sediment showed that silicon was present as silicon dioxide (quartz), while iron, aluminum and nickel were present in the form of their hydrated oxides (Fig. 1). Iron was bound in the form of magnetite, hematite and ferrihydrite, calcium in the form of carbonate. Besides, the model sediment contained kaolinite. Organoclays contained SiO_2. In the TMA-K sample, iron and aluminum were present in the form of their oxides. TMA-K had Al and Si bound in the crystal lattice of hydrated Al-oxide, while TMA-B showed the presence of Mg, Na, Al and Ca, as well as of calcium silicate hydroxide (CSH). The diffractogram of the Danube sediment was published elsewhere. [28]

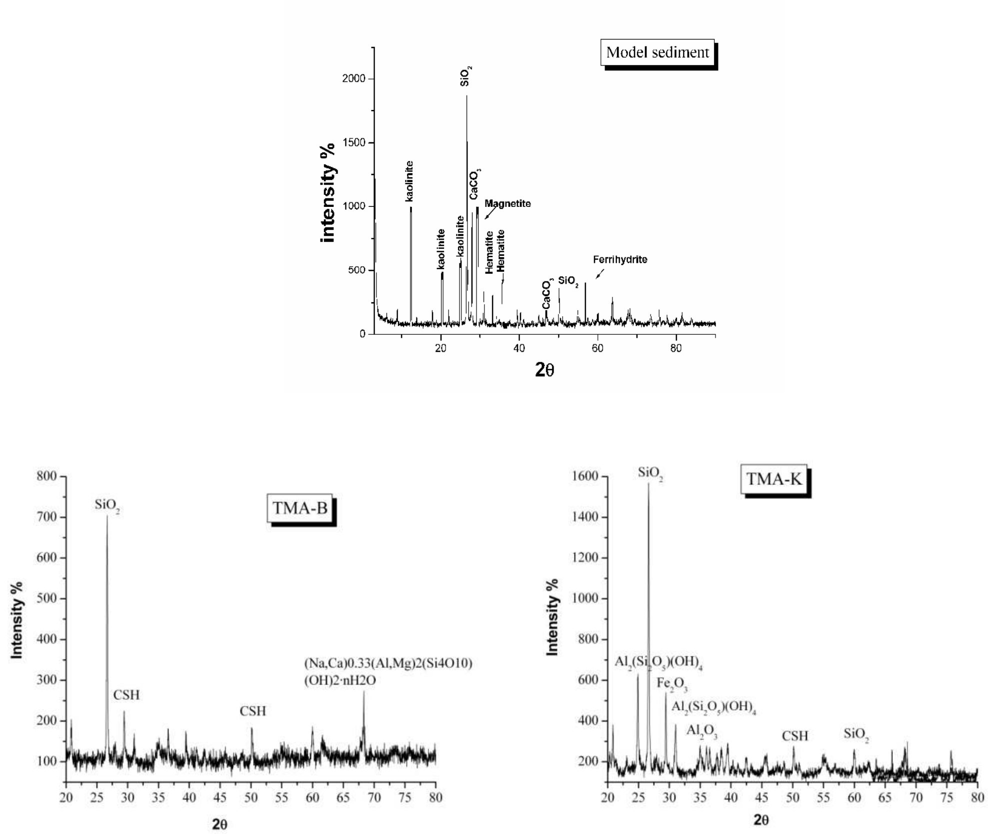


Figure 1. Diffratograms of the model sediment and organomodified clays

Adsorption and desorption isotherms of N_2 at 77 K, for all materials, are given in Fig. 2. The results of the specific surface area and pore analyses (Table 4a) show that the organoclays possess a higher specific surface area than the natural and model sediments (17.7 m^2/g and 84.1 m^2/g for TMA-K and TMA-B, respectively), as well as BJH pore volume (for M and D ~0.02 cm^3/g and for TMA-B and TMA-K ~0.2 cm^3/g). Similar distribution of pore sizes was obtained by Dolimore and Heal (DH) method for D and M sediment. 78% and 85% of total pores were assigned to pore sizes between 77 and 700 Å (Fig. 3). When it comes to organoclays, TMA-K has similar characteristics as examined sediments with 92% of pore volume related to pore sizes between 77 and 790 Å. In case of TMA-B, pore volumes are more equally distributed among different pore sizes. Pores in radius up to 23 Å occupy 46%, while pores between 77 and 770 Å occupy 27% of pore volume according to DH method (Fig. 3).

Regarding the micropore volume, different results obtained by two methods were compared (see Table 4a). Micropore t-test showed the presence of micropores only for TMA-B sorbent (0.007 cm^3/g). HK method showed the presence of micropores in all examined sorbents, but TMA-B had the highest and the most significant content of micropores.

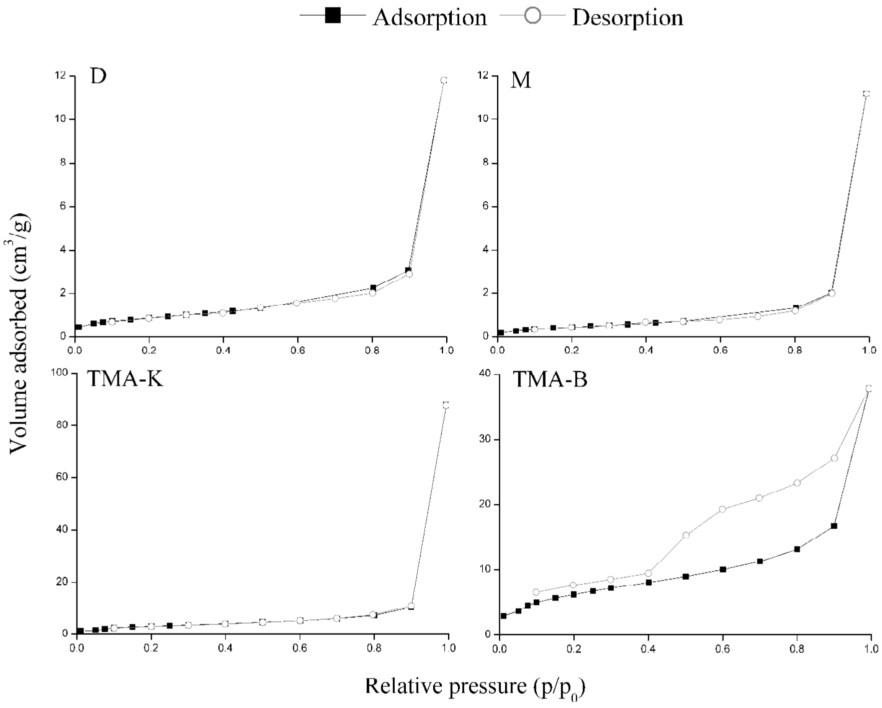


Figure 2. Nitrogen adsorption–desorption isotherms of the samples

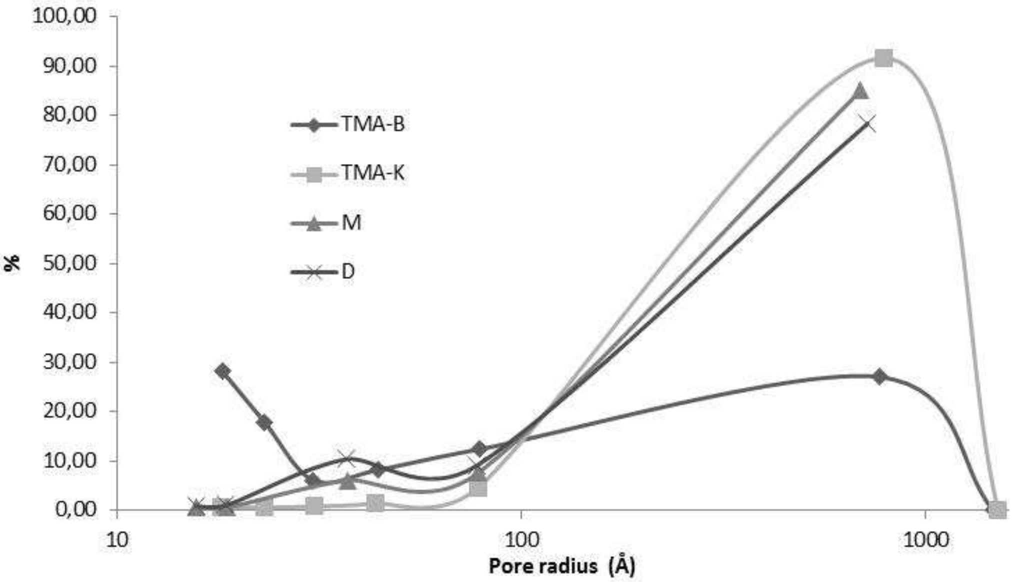


Figure 3. Pore size distribution according to DH method

3.2 Characterization of the water matrices

The concentration of dissolved organic carbon ranged from 0.5 mg DOC/L in synthetic water to 2.9 mg DOC/L as the annual average value in surface water and to 5.9 mg DOC/L as the annual average value in groundwater. Additionally, as the very first attempt to characterize organic matter in these waters, the distribution of DOC fractions was obtained by Liquid Chromatography with Organic Carbon Detection (LC-OCD) in the single sample of each matrix.

The method allows the measurement of low concentrations of organic carbon in water down to the ppb level. Furthermore, the dissolved organic substances can be fractionated according to their molecular weight which is based on their interaction with the material located in the column and, thus, the retention time during LC–OCD analysis. This technique has been used in the characterization of both, aquatic and pedogenic humic matter as well as non-humic matter.[29] The results are presented in Table 5.

Table 5. Characterization of the water matrices

	Water matrix		
Parameter	Synthetic water	Surface water	Groundwater
pH	7,0	7,1	8,10
Conductivity (µS/cm)	2470	387	345
Average TOC value (mg/L)[a]	0.60	3.23	7.16
RSD of TOC measurements, %	-	16	3.8
Interval of DOC values	n.m.[d]	2.7-3.5	5.0-7.2
Average annual DOC value (mg/L)[b]	0.50	2.9	5.9
RSD of DOC measurements, %	-	8.9	16
Results of DOC fractionation by LC-OCD analysis			
Hydrophobic DOC, %	n.m.[d]	4.10	18.9
Chromatographable DOC, %	n.m.[d]	95.9	81.1
Biopolymers, %	n.m.[d]	4.70	1.40
Humic substances, %	n.m.[d]	65.1	48.3
Building blocks, %	n.m.[d]	12.6	15.6
LMW[c] neutrals' %	n.m.[d]	13.5	15.9
LMW[c] acids, %	n.m.[d]	n.d.[e]	n.d.[e]

[a]n=2, [b] n= 4 in case of groundwater and n=5 in case of surface water , [c]low molecular weight, [d]not measured, [e]not detectable.

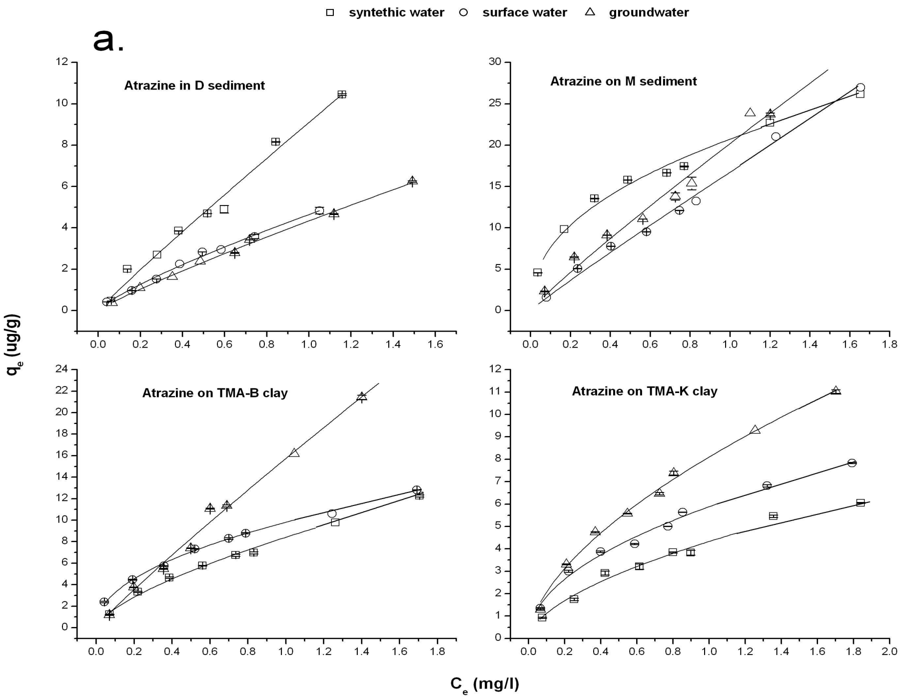
Five DOC fractions were obtained after the characterization using LC-OCD. The non-chromatographable fraction of the DOC (hydrophobic) accounted for 4.10% and 18.9% of the total DOC for the surface water and groundwater, respectively. Chromatographable DOC consisted of biopolymers (4.70% and 1.40%, respectively), humic substances (65.1% and 48.3%, respectively), building blocks (12.6% and 15.6%) and LMW neutrals (13.5% and 15.9%), whereas humic substances represented the largest DOC fraction in both water samples. The molecular weight of humic substances in the surface water (751 g/mol) was found to be slightly higher than that of the groundwater (707 g/mol). They were assigned to the group of pedogenic fulvic acids.

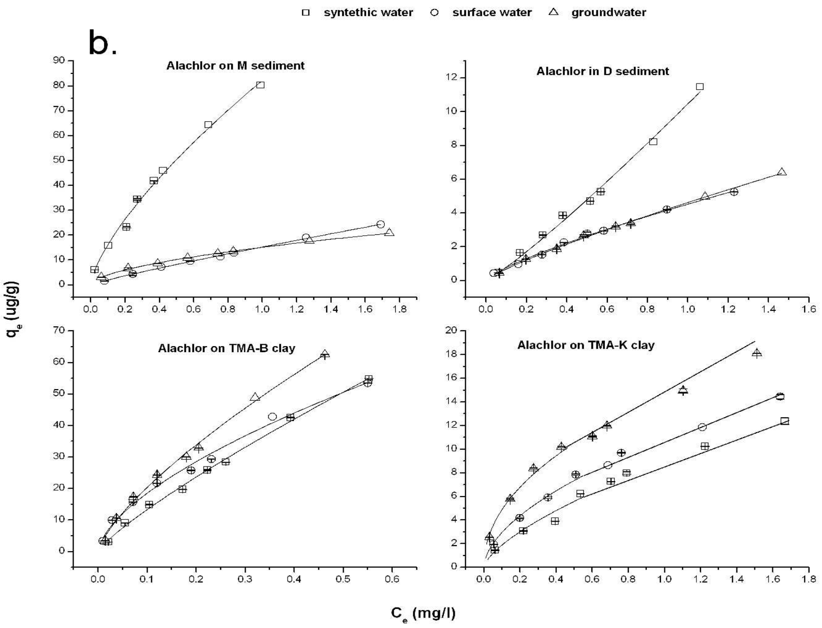
3.3 Sorption of the herbicides

Figure 4 shows the isotherms for the sorption (average values of duplicate measurements with error bars representing standard deviations for each point) of three herbicides by four sorbents in three investigated water matrices.

It can be observed that the most of the isotherms are of the L-type (n<1) (Fig. 4, Table 6). The values of the Freundlich model constants K_F and determination coefficient ($R^2 > 0.95$) for the sorbents are given in Table 6.

The differences in the sorption behavior between two natural waters could be seen in most of the cases (see Figure 4, showing the surface water and groundwater isotherms for each pair of herbicide and sorbent separately, where q_e and C_e are the solid phase and the aqueous phase equilibrium concentrations). Apparently, they were most pronounced for trifluralin, the compound with the highest hydrophobicity (for both sediments and one modified clay, TMA-K), while the differences for atrazine and alachlor in the sorption from the groundwater and surface water were observed mostly for the modified clays. In most cases there was no significant difference between these two compounds in the sorption behavour on the sediments.





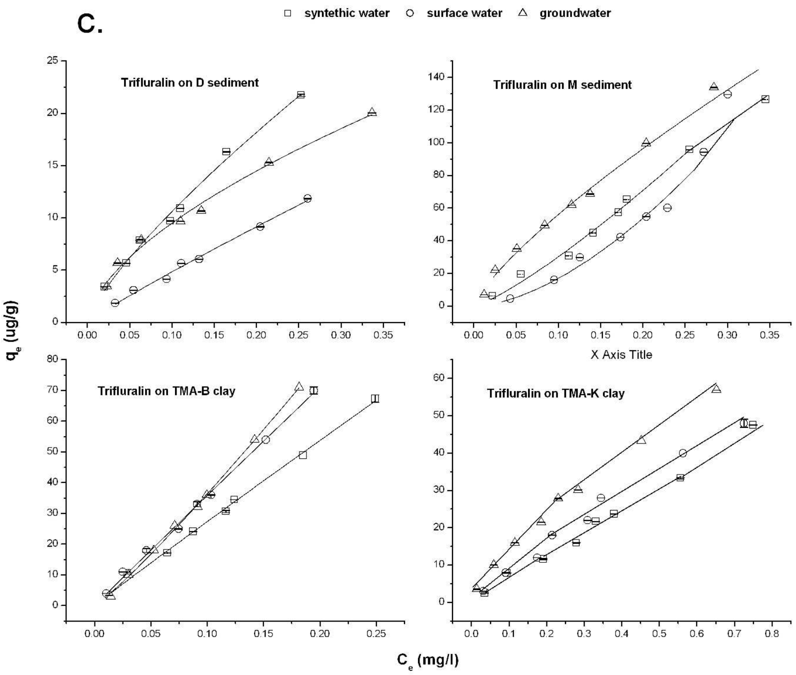


Figure 4. Sorption isotherms of: a) atrazine; b) alachlor and c) trifluralin in the concentration ranging from 100 to 2000 µg/l on the selected sorbents in three water matrices

Single-point distribution coefficients (K_d) based on equation (2) were calculated at three selected equilibrium concentrations, i. e. C_e = 0.01, 0.05 and 0.5 mg/L (Table 6) in order to compare their affinities for sorption. The equilibrium concentrations obtained to cover a wide range of concentration, were less than 10% of the solubility of atrazine and alachlor, and 0.4%, 2.2% and 22% of the solubility for 0.01, 0.05 and 0.5 mg/L of trifluralin, respectively.

The obtained K_d values of the herbicides were in accordance with those reported by the authors[30-32] who investigated sorption of herbicides in a variety of soils and clays.

Table 6. Parameters of the Freundlich adsorption model for the investigated sorbents

Water matrices	Compound	Sorbent	Freundlich adsorption model parameters			K_d (L/kg)		
			R^2	n	K_F (μg/g)/(mg/L)^n	0.01	0.05	0.5
Synthetic Water	Trifluralin	D	0.991	0.736	58.09	195.9	128.1	69.8
		M	0.991	1.085	396.4	268.0	307.3	373.7
		TMA-B	0.989	0.957	251	306.0	285.5	258.6
		TMA-K	0.991	0.919	58.02	84.3	74.0	61.4
	Alachlor	D	0.996	1.089	10.35	6.9	7.9	9.7
		M	0.988	0.704	80.97	316.5	196.5	99.4
		TMA-B	0.992	0.852	93.26	184.4	145.3	103.3
		TMA-K	0.985	0.67	8.83	40.4	23.7	11.1
	Atrazine	D	0.93	0.972	9.2	10.5	10.0	9.4
		M	0.987	0.442	20.78	271.4	110.6	30.6
		TMA-B	0.991	0.694	8.49	34.7	21.2	10.5
		TMA-K	0.989	0.601	4.34	27.3	14.3	5.7
Surface water	Trifluralin	D	0.991	0.875	36.91	65.6	53.7	40.3
		M	0.99	1.639	790.5	41.7	116.6	507.6
		TMA-B	0.992	0.973	337	381.6	365.4	343.4
		TMA-K	0.993	0.938	69.51	92.5	83.7	72.6
	Alachlor	D	0.991	0.759	4.43	13.4	9.1	5.2
		M	0.998	0.898	15.24	24.4	20.7	16.4
		TMA-B	0.982	0.656	82.4	401.7	230.9	104.6
		TMA-K	0.997	0.591	10.97	72.1	37.4	14.6
	Atrazine	D	0.986	0.754	4.4	13.7	9.2	5.2
		M	0.99	0.885	16.19	27.5	22.8	17.5
		TMA-B	0.996	0.455	9.72	119.6	49.7	14.2
		TMA-K	0.989	0.516	5.92	55.0	25.2	8.3
Groundwater	Trifluralin	D	0.979	0.61	38.77	233.6	124.7	50.8
		M	0.974	0.866	410.6	761.1	613.4	450.6
		TMA-B	0.995	1.17	544	248.7	326.9	483.5
		TMA-K	0.999	0.722	76.48	275.1	175.9	92.7
	Alachlor	D	0.997	0.855	4.65	9.1	7.2	5.1
		M	0.998	0.555	14.88	115.5	56.4	20.3
		TMA-B	0.983	0.795	122.6	315.1	226.6	141.3
		TMA-K	0.955	0.497	14.78	149.9	66.7	20.9
	Atrazine	D	0.995	0.904	4.43	6.9	5.9	4.7
		M	0.99	0.739	17.63	58.6	38.5	21.1
		TMA-B	0.992	0.951	15.85	19.9	18.4	16.4
		TMA-K	0.989	0.646	8.25	42.1	23.8	10.5

4. Discussion

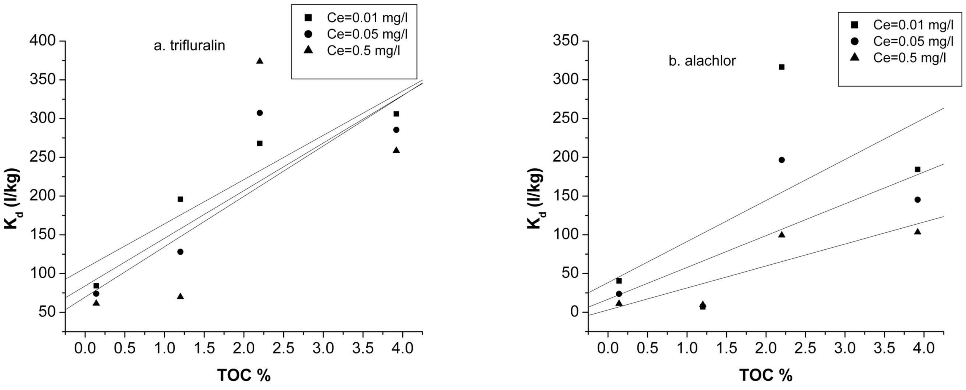
4.1 The effect of the solute characteristics on the herbicide sorption behavior

In most cases (16 out of 18 comparisons), irrespective of the C_e levels, organoclays were the sorbents for which the K_d of the investigated herbicides increased in the following order: atrazine < alachlor < trifluralin, in line with their log K_{ow} values. In two cases, the sorption on TMA-B showed deviation at the lowest concentration: a slightly higher K_d for alachlor than for trifluralin in both surface water and groundwater.

The analysis of the data for M and D sediments (Table 6) showed that the values of K_d are in line with the log K_{ow} in the case of the model sediment at lower concentrations (0.01 and 0.05 mg/L) in the case of the groundwater matrix, and at 0.05 mg/L and 0.5 mg/L levels in synthetic water matrix. The same observations were made in the case of the Danube sediment at all C_e levels and at 0.5 mg/L level in the case of groundwater and surface water matrix, respectively. In all the other comparisons, K_d values for atrazine and alachlor were either very similar or even higher for atrazine. K_d values of the same order of magnitude are found in the literature.[11, 32] Thus, in the case of sediments in 7 out of 18 comparisons K_d values increased in order which is in line with their log K_{ow} values. This reflects the complexity of possible interaction in the system solute-DOC-sediment where not only partitioning between two phases is relevant but also other molecular characteristics.

4.2 The effect of the sorbent characteristics on the sorption behavior

It is well known that sediment organic matter has the crucial influence on organic pollutants sorption.[30] Therefore, sorption coefficients were correlated with the TOC content in sorbents. K_d values were used for comparison. Figure 5 shows the correlation of K_d values obtained for synthetic water matrix and TOC % in sorbents. The correlation between K_d and TOC (R^2= 0.886) is acceptable only in the case of trifluralin at the lowest concentration of 0.01 mg/L. Coefficients of determination for all the investigated cases are given in Table 7. The absence of clear linear correlations may be the consequence of different TOC nature of different sorbents (only organo-modified clays have the TOC of the same structure) and the contribution of the sorption on the mineral phase.



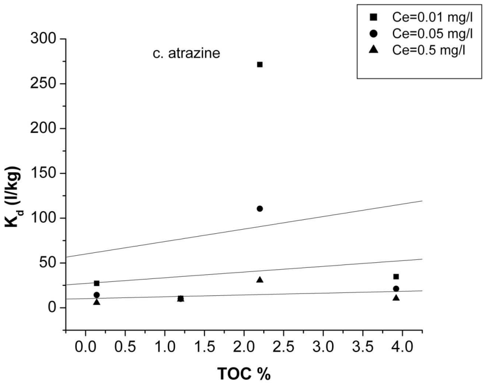


Figure 5. Correlations between the K$_d$ and TOC for the investigated herbicides in synthetic water matrix

Table 7. Coefficients of determination for linear regression between K_d values and TOC content in sorbents

Compound	Concentration level mg/L	Water matrix	R^2 value for linear correlation
Trifluralin	0.01	Synthetic water	0.8869
	0.05		0.7356
	0.5		0.4724
	0.01	Surface water	0.6031
	0.05		0.7852
	0.5		0.4497
	0.01	Groundwater	0.0122
	0.05		0.2149
	0.5		0.7396
Alachlor	0.01	Synthetic water	0.3583
	0.05		0.5126
	0.5		0.7538
	0.01	Surface water	0.6208
	0.05		0.6598
	0.5		0.7307
	0.01	Groundwater	0.4751
	0.05		0.6312
	0.5		0.711
Atrazine	0.01	Synthetic water	0.0327
	0.05		0.0455
	0.5		0.0846
	0.01	Surface water	0.4435
	0.05		0.5476
	0.5		0.4122
	0.01	Groundwater	0.0228
	0.05		0.0074
	0.5		0.3211

Literature findings show that all three herbicides could be involved in forming H-bonding with the sorbents. The presence of hydrophilic groups in alachlor structure may have an affinity for H-bonding with electropositive functional groups on the clay surface.[1] Alachlor could form hydrogen bonds with the O- and N-containing sites available on humic substances' macromolecules.[34] In the case of atrazine there is a possibility of H-bonding between the polar groups (C=O, OH) present on the sorbent surface and N atoms of the atrazine ring .[35] Trifluralin reportedly displays formation of H-bondings with the electropositive hydrogen nucleus of the functional groups such as -OH, -NH, Si-OH or Al-OH, present on the mineral surfaces.[36]

When the two sediments were compared with each other and the two organomodified clays as well, one could draw the conclusion that the increase in TOC content increased K_d for both types of sorbents.

Judging from the K_d results obtained for the investigated equilibrium concentrations (Table 6), the model sediment and organo-modified bentonite (2.20% and 3.92% of OC) showed the highest K_d values and the highest affinity for herbicides. TMA-B has the largest surface area (84.1 cm^2/g), the highest organic carbon content, micropores content and nitrogen in its structure. Model sediment has a small surface area (1.73 cm^2/g) and negligible content of micropores, but still high organic carbon content (less than TMA-B and higher than other sorbents). The presence of kaolinite (20%) in its structure could be beneficial for herbicide sorption. According to literature review of Moyo et al.[37] hydroxyl functional groups are the most reactive and often take part in various chemical reactions. The crystal lattice of kaolinite is neutral compared to other clays, and its two well-defined layers, alumina surface and silica surface, provide two different potential surfaces of adsorption because of the hydroxyl groups and the silica-oxygen bridged surfaces. Kaolinite has a high affinity for organic compounds compared to other clay surfaces. Literature findings show that only 25% of the kaolinite surface is hydrophilic and the rest is either neutral or hydrophobic. Furthermore, the presence of sphagnum peat in M sediment may contribute to sorption through charge-transfer and hydrophobic interactions between the benzene ring of the herbicides and the aromatic nuclei of sphagnum organic matter. However, based on the obtained results presented here it is not possible to determine separate contributions of the mineral and organic phase.

4.3 The effect of the water matrix characteristics on the herbicide sorption behavior

The complexity of possible interactions of pollutants in DOC containing water-sorbent systems is well known.[5, 38] In general, DOC can either enhance sorption of organic pollutants by association with sorbents (forming coats that increase the adsorption of pollutants) or decrease the amounts of pollutants sorbed by different mechanisms: competition or solubilization in excess of DOC (e.g. mobilizing of hydrophobic compounds). The behavior of polar compounds is even more complex depending on the amount and the type of NOM present.

For the selected herbicides and different concentrations Figure 6 shows the K_d values for adsorption from surface water over the K_d value for adsorption from groundwater. Note that the synthetic matrix was not compared here due to a significant difference in electrical conductivity with the two natural samples. The figure reflects that the sorption coefficients do depend on the water matrix. The characterization of the natural water matrices is given in paragraph 3.2. Chromatographable fraction of DOC was 95.9% for the surface water and 81.1% for the groundwater. Despite the fact that the relative content of humics in groundwater (48.3%) was lower than in surface water (65.1%), an estimation based on the LC-OCD fractionation demonstrated that a higher absolute concentration of humics was present in groundwater (2.8 mg/L vs. 1.9 mg/L in ground and surface water, respectively).

As for trifluralin, the compound with the highest K_{ow} value and the lowest solubility, the ratio $K_{d\ \text{surface water}}/K_{d\ \text{groundwater}} < 1$ was observed in most cases, that is to say, the sorption coefficient was higher in groundwater than in surface water in 9 out of 12 cases .

However, at the concentration level of 0.5 mg/L model sediment had a higher K_d value for surface water matrix. At 10-50 times lower herbicide concentration levels (i.e. 0.01 and 0.05 mg/L), sorption enhancement, due to change of matrix to surface water, was observed only with TMA-B.

In the case of alachlor at the concentration level of 0.5 mg/L the ratio of $K_{d\,\text{surface water}}/K_{d\,\text{groundwater}}$ was near 1 only for the Danube sediment. At 10-50 times lower concentration levels, the ratio increased for D and additionally for TMA-B. The sorption coefficients were higher for groundwater in 7 out of 12 cases (the ratio $K_{d\,\text{surface water}}/K_{d\,\text{groundwater}} < 1$).

The compound with the lowest K_{ow} value, atrazine, showed the same behavior as alachlor at the highest concentration level (the Danube sediment was the only one that had higher K_d value in surface water matrix). At 10-50 times lower concentration levels, besides the Danube sediment, both organoclays had higher K_d values in surface water matrix. The model sediment was the only one with higher K_d values in groundwater matrix. On the whole, the sorption coefficient was higher in groundwater in 5 out of 12 cases (the ratio $K_{d\,\text{surface water}}/K_{d\,\text{groundwater}} < 1$).

One can assume that for substances with lower K_{ow} values sorption is enhanced for a larger number of sorbents tested in surface water matrix most probably due to the lower content of humic-like substances as potential competitors for sorption sites and/or solubilization effect that might be present in the groundwater matrix. For example, using flow-through experiments, Amiri et al.[39] found that aquatic humic substances reduced the nitrophenol sorption onto sandy aquifer material caused by complex formation with DOM. Similar effects were found related to pyrethroide sorption in sediments.[40]

A closer look into the most efficient sorbents showed that TMA-B sorbent efficiency (Table 6) for all three herbicides was higher in surface water matrix for the concentration of 0.01mg/L and 0.05 mg/L, while at the concentration of 0.5 mg/L higher K_d was observed in groundwater. One can conclude that solubilization and/or competition effects of DOC from groundwater are important at a concentration of 0.05 mg/L and below (higher K_d in surface water matrix) for this low cost sorbent. In the case of model sediment, higher K_d values for alachlor and atrazine were always found in groundwater regardless of concentration. However, in this particular sorbent, hydrophobic trifluralin had higher K_d in surface water only with the highest concentration indicating solubilization and/or competition with DOC from groundwater (Table 6).

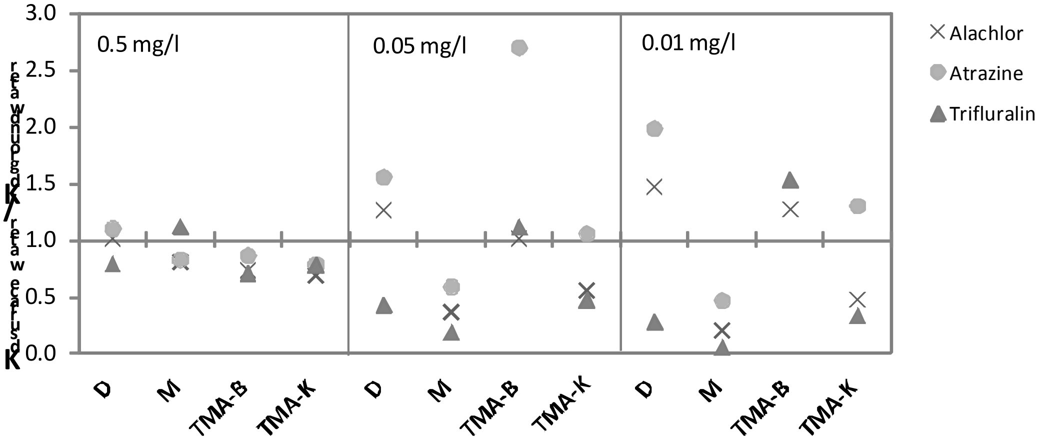


Figure 6. The ratio $K_{d\,\text{surface water}}/K_{d\,\text{groundwater}}$ for the sorption of the herbicides from the natural water matrices at different concentrations

5. Conclusions

The objective of this study was to determine the sorption behavior of the herbicides atrazine, alachlor and trifluralin on four selected sorbents (two organoclays, one model sediment and one natural sediment), and to elucidate the influence of the sorbent and water matrix characteristics on it.

In most cases of sorption on the organoclays, the K_d values followed the order of the log K_{ow} values. The K_d values for sediments exhibited a different behavior which was not always in accordance with herbicides' hydrophobicity.

Based on the K_d values, the organically modified bentonite and model sediment proved to be the most effective sorbents for the investigated herbicides. The two sorbents had the highest TOC content, while TMA-B had the highest surface area, pore volume and micropore content. The model sediment had small surface area and ten times smaller pore volume than TMA-K, but still exhibited better sorption characteristics than two other sorbents, most probably due to a high carbon content and possible contribution of interactions with the mineral phase.

The correlation of K_d and sorbent TOC content (R^2= 0.886) was acceptable only in the case of trifluralin and synthetic water matrix at the lowest sorbent concentration of 0.01 mg/L. The absence of clear linear correlations between K_d and TOC indicated the importance of sorbent TOC nature and possible interactions of TOC, the mineral phase and the herbicides. Furthermore, the results showed different influences of the type and concentration of dissolved organic carbon in the water phase on the sorption of all herbicides, depending on the sorbent applied and the concentration level of a herbicide. The highest K_d values were obtained for trifluralin in the groundwater matrix with the highest DOC and humic-like substances content. However, it was shown that surface water matrix with lower DOC and humic-like substances content can enhance sorption of alachlor and atrazine for some of the sorbents applied, especially for the Danube sediment and TMA-B. This confirmed that the comparison of sorbent efficiency should be done in the native matrix since sorption coefficients vary depending on the pollutant concentration, DOC type and the content. This finding might be useful for the purpose of *in-situ* remediation of polluted sites, for creation of subsurface sorptive zones for capturing organic contaminants since sorption enhancement in surface water could favor the reduction of herbicide environmental impact and may attenuate the leaching of these herbicides from polluted sites.

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