

Wastewater dissolved organic matter: characteristics and sorptive capabilities

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Abstract An evaluation of the mobility of organic pollutants with wastewater dissolved organic matter (DOM) is essential to better understanding their fate and toxicity to the environment. In this study, DOM from two wastewater treatment plants (in Lachish and Netanya, Israel) were fractionated to hydrophobic-acid (HoA) and hydrophobic-neutral (HoN) fractions. The fractions were characterised and their sorptive capabilities for *s*-triazine herbicides and polycyclic aromatic hydrocarbons (PAHs) were studied. For all sorbates, binding to the HoN fractions was much higher than to HoA fractions. The high binding coefficients obtained for the studied triazines by the HoN fractions suggested that their sorption is governed by hydrophobic-like interactions rather than H-bonding. The binding coefficients of PAHs measured for the HoN fractions were within the range reported for humic acids and much higher than for the HoA fraction, suggesting that the HoN fraction plays an important role in the overall sorption of these compounds by DOM. Higher sorption coefficients were measured for the Netanya DOM sample containing a higher level of hydrophobic fractions (HoA + HoN) than the Lachish DOM, suggesting that the sorption of hydrophobic organic compounds by DOM is governed by the relative content of these structural substances.

Keywords Dissolved organic matter; PAHs; sorption; triazine; wastewater

Introduction

Recycled wastewater is a potentially important source of irrigation water in semiarid and arid zones, such as the Middle East. Use of the treated effluent in agriculture improves the overall water budget and allows the fresh water to be shifted from agricultural users to domestic and industrial needs. Treated wastewater contains higher concentrations of suspended and dissolved organic and inorganic matter than fresh water. Influx of these components into soils can affect the latter's physical and chemical properties (Levy *et al.*, 1999; Tarchitzky *et al.*, 1999; Mamedov *et al.*, 2000). The influx of relatively high dissolved organic matter (DOM) concentrations into soils can significantly affect the fate of nonpolar and polar organic compounds in those soils.

Only a few studies have investigated the effect of DOM from wastewater on the sorption of pesticides and other organic contaminants (Graber *et al.*, 1995; Seol and Lee, 2000, 2001). The role of DOM in the sorption and transport of hydrophobic organic compounds is still not fully understood. Seol and Lee (2000) suggested that very high concentrations of dissolved organic carbon are needed to significantly suppress the sorption of triazine herbicides by soils. However, Spark and Swift (2002) concluded that the DOM in soil has little or no effect on the sorption and transport of some pesticides. In this study, we investigated the mechanism governing the binding of *s*-triazine herbicides (atrazine and ametryn) and polycyclic aromatic hydrocarbons (PAHs; fluoranthene, phenanthrene

and pyrene) to hydrophobic structural fractions of wastewater DOM in relation to their physico-chemical properties.

Methods

Wastewater sampling, extraction and purification of DOM

Treated wastewater was sampled from two municipal wastewater treatment plants in Israel, one based on activated-sludge treatment (Netanya) and the second on the operation of oxidation ponds (Lachish). The DOM samples were fractionated to hydrophobic acid (HoA) and hydrophobic neutral (HoN) fractions based on their sorption behaviour on DAX-8 resin as described in detail by Leenheer (1981) and Chefetz *et al.* (1998).

DOM characterisation

Freeze-dried samples were analysed for C, H and N contents, and total acidity was determined using a procedure described for humic substances (Swift, 1996). The Fourier transform infrared (FTIR) spectra of freeze-dried samples were collected for the wavenumber range of 4,000 to 400 cm^{-1} on a Nicolet 550 Magna-IR spectrometer (Nicolet Instruments, Madison, WI). The ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on a Bruker DSX-300 spectrometer. Freeze-dried samples were packed into a 7-mm rotor and spectra were acquired using the following acquisition parameters: spectral frequency of 75 MHz for ^{13}C and 300 MHz for ^1H , spinning rate of 3 kHz, contact time of 1 ms, 1 s recycle delay, and line broadening of 40 Hz.

Sorption experiments

We have used the following sorbates: atrazine (2-chloro-4-ethylamine-6-isopropylamino-s-triazine), ametryn (2-(ethylamino)-4-isopropylamino-6methyl-thio-s-triazine), phenanthrene, fluoranthene and pyrene. The partitioning coefficients of the herbicides to the DOM fractions were measured using dialysis-bag sorption experiments and the binding coefficients of the PAHs were measured using solid-phase microextraction (SPME).

Results and discussion

Wastewater DOM characterisation

The DOM from the activated-sludge treatment plant in Netanya was composed of 33% hydrophilic and 67% hydrophobic fractions (on a C basis). The content of the hydrophobic fraction (HoA + HoN) was only 38% of the total carbon in the wastewater DOM isolated from the oxidation-pond treatment facility in Lachish. The two samples also differed in their relative contents of HoA fraction. This fraction made up 60% of the total DOC in the Netanya wastewater vs. only 30% in the Lachish sample. The level of the HoN fraction was similar in the two samples (8–9% of the total DOC). It is suggested that the advanced wastewater purification treatment (activated sludge as compared to oxidation ponds) results in a significant reduction in readily degradable compounds (i.e. the hydrophilic fraction), hence the relative enrichment of the hydrophobic fractions in the Netanya treated wastewater. Hydrophobic matter is assumed to be more resistant to microbial degradation.

The main absorbance peaks of the FTIR spectra of the various isolated DOM fractions ($> 1,000$ Da; Figure 1) were at the following wavelengths: 3300–3430 cm^{-1} (H-bonds, OH groups), 2,850–2,965 cm^{-1} (C–H stretch of $-\text{CH}_2$ and $-\text{CH}_3$), 1,710–1,720 cm^{-1} (C=O of COOH), 1,620–1,660 cm^{-1} (C=C in aromatic structure, COO^- , H-bonded C=O), 1,540–1,580 cm^{-1} (amide II bonds), 1,400–1,465 cm^{-1} (C–H deformation of CH_2 or CH_3 groups), 1,375–1,420 cm^{-1} (CH_3 , COO^-), 1,240–1,260 cm^{-1}

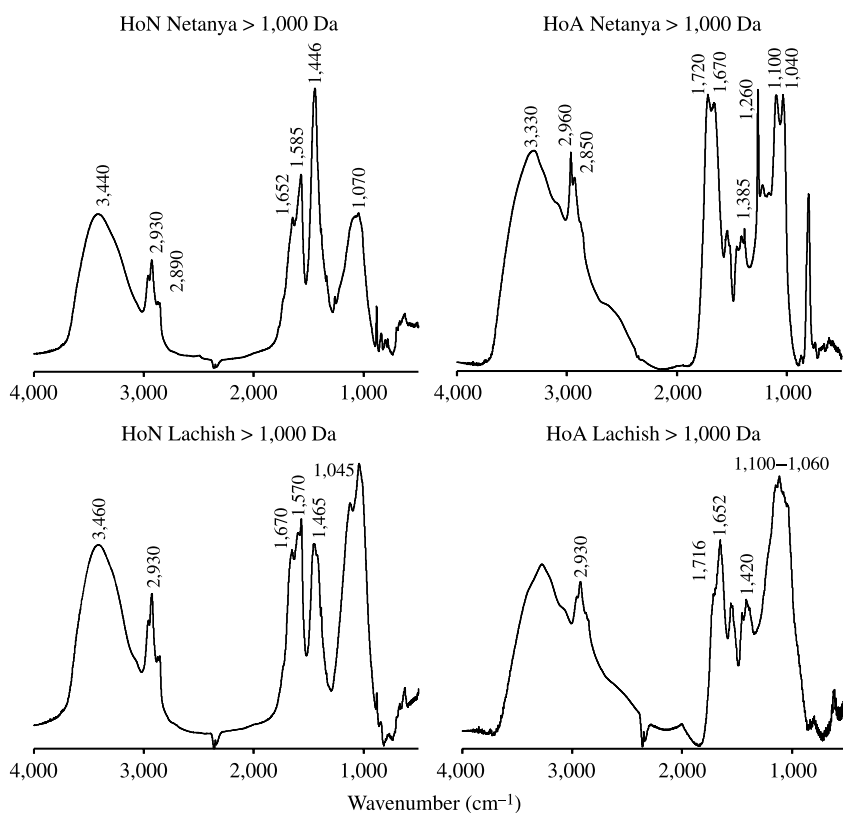


Figure 1 Absorbance FTIR spectra of the >1,000 Da fractions isolated from the wastewater samples

(aromatic C, C—O stretch), and 1,100–1,000 cm^{-1} (C—O stretch of polysaccharide) (Baes and Bloom, 1989; Niemeyer *et al.*, 1992).

The HoA spectra were characterised by a dominant C=O carboxylic vibration peak (1,716–1,720 and 1,652 cm^{-1}), polysaccharide vibration peaks of variable intensities, and minor peaks of methyl and methylene vibrations. The intensity of the carboxyl vibration band made it the governing peak in the spectra of the HoA fraction isolated from Netanya wastewater, but it was shifted to lower frequency (1,652 cm^{-1}) in the spectrum of the Lachish HoA fraction. This latter sample was also characterised by a lower acidity value than those isolated from Netanya (Table 1). Moreover, the Netanya HoA sample exhibited an H/C atomic ratio that was lower than recorded for the HoA fraction from Lachish. The higher H/C ratio of the fraction from Lachish suggests its higher

Table 1 Selected chemical characterisation of the isolated samples: dissolved organic matter (DOM), hydrophobic acid (HoA) and hydrophobic neutral (HoN)

	C	N	H	C/N	H/C	Total acidity
		(%)		(atomic ratio)		(meq/g)
Netanya treated wastewater						
DOM-bulk	4.92	1.24	1.11	4.65	2.71	
HoA-bulk	51.67	4.23	5.54	14.26	1.29	4.30
HoN-bulk	49.93	3.99	6.01	14.60	1.44	3.85
Lachish treated wastewater						
DOM-bulk	4.85	0.32	0.78	17.84	1.93	
HoA-bulk	38.59	4.16	4.55	10.82	1.42	3.67
HoN-bulk	36.39	1.84	4.93	23.26	1.61	1.51

aliphaticity. The FTIR spectra and the chemical properties of the HoA fraction from Netanya were similar to data recorded for other isolated HoA fractions and fulvic acids (Qualls and Haines, 1991). It has been suggested that the HoA fraction resembles a light fraction of fulvic acid. The spectrum of the Lachish HoA fraction suggests that it has a lower carboxylic content and is richer in polysaccharide and paraffinic structures than the Netanya HoA fraction. The different wastewater treatments resulted not only in DOM containing different contents of HoA (60 vs. 30%), but also HoA fractions exhibiting different chemical properties. Therefore, it is suggested that advanced wastewater treatment increases the level of hydrophobic fractions in the DOM and increases the oxidation stage of these fractions. This hypothesis is supported by the high carboxyl content exhibited by the HoA isolated from the final stages of composting.

In contrast to the FTIR spectra of the HoA fractions, the carboxylic C=O vibration peak is absent in spectra of the HoN fractions, suggesting a less polar character. As a result, the relative intensities of the paraffinic and aromatic functionalities (peaks at 2,960–2,850, 1,660 and 1,440 cm^{-1}) were significantly pronounced. The HoN fractions from the wastewater exhibited lower acidity values than the corresponding HoA samples. The H/C level and the FTIR spectra suggest that the HoN fraction is composed of aliphatic (paraffinic) structures with a low level of polar functionalities.

The main differences between the spectra of the unfractionated (bulk; not shown) and the $>1,000$ Da samples were a relative increase in peak intensities of the polysaccharides (1,000–1,100 cm^{-1}) and aromatic C=C (1,620 cm^{-1}) vibration bands as compared to the intensities of the carboxyl C=O and saturated C–H stretch vibration peaks. The same trend was observed for all HoA $>1,000$ Da and HoN $>1,000$ Da samples, but it was more pronounced for the fractions isolated from the Lachish DOM. These data suggest that the higher-molecular-weight fraction of both HoA and HoN samples is composed of a polymeric structure of covalently linked carbohydrates. The relative enrichment of the $>1,000$ Da fractions with polysaccharides and aromatic structures will be further discussed in relation to the sorptive properties of this fraction.

The ^{13}C NMR spectra presented in Figure 2 support the FTIR data. The HoA samples exhibited a pronounced carboxylic peak at 172 ppm and were richer in aromatic moieties (peaks at 128 and 145 ppm) than the HoN sample. The fractions from Lachish (both HoA

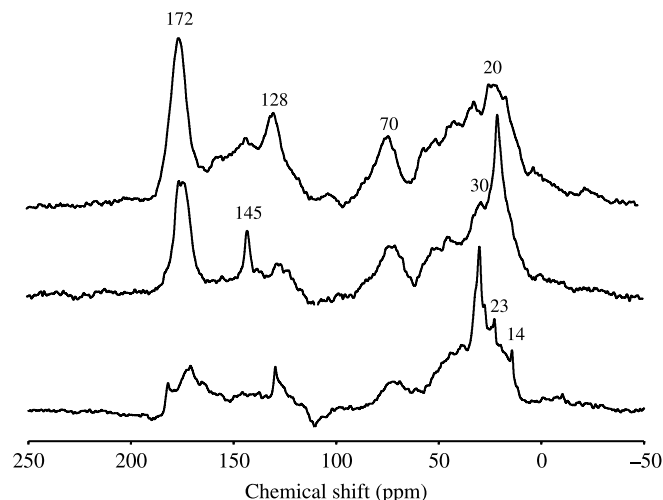


Figure 2 ^{13}C NMR spectra of the $>1,000$ Da fractions isolated from the wastewater samples (HoA Netanya, top; HoA Lachish, middle; HoN Lachish, bottom)

and HoN) exhibited a higher aliphaticity content (pronounced paraffinic peaks at 14, 23 and 30 ppm). In contrast to the spectra of the HoA samples, the HoN spectrum was dominated by an alkyl carbon peak and exhibited relatively low level of aromatic carbon functionalities. In this sample, the alkyl carbons made up more than 62% of all carbon in the sample.

Sorption of triazine herbicides

Atrazine and ametryn are widely applied herbicides (Barbash *et al.*, 2001) which have different physico-chemical properties due to their different substituents (Cl and SCH₃, respectively). The sorption coefficient data are summarized in Table 2. In all cases, sorption of atrazine to the HoN fraction was greater than to the HoA and unfractionated DOM samples. These data contradict the hypothesis that a high content of carboxylic functionalities and high acidity values, as exhibited by the HoA fractions, lead to increased sorption due to H-bonding. At the pH of the solutions (7.8), the carboxylic groups of the HoA can interact with atrazine by forming H-bonds with the hydrogen atom of the side-chain amino group of the triazine molecule. However, it appears that specific atrazine–DOM interactions are dominated by non-specific (hydrophobic-like) sorbent–sorbate interactions since the sorbents containing higher carboxylic functionalities (i.e. HoA) exhibited lower sorption potential than the HoN fractions.

Another interesting observation is that the measured K_{DOC} values for the fractions isolated from the two wastewater samples can be arranged in the following order: HoN > DOM > HoA. The relatively similar K_{DOC} values calculated for the HoN and HoA samples indicate similar sorptive properties within each group of sorbents. We suggested that the lower polarity of the HoN (i.e. the absence of a carboxyl band in the FTIR spectrum) isolated from Lachish DOM resulted in higher K_{DOC} values. The presence of polar functional groups in the HoA fractions probably decreases the overall hydrophobicity of this sorbent, thus reducing its affinity to nonpolar organic chemicals. These findings support the hypothesis that nonspecific hydrophobic binding is the key interaction of atrazine with DOM. Similar conclusions were drawn by Kulikova and Perminova (2002), who investigated atrazine sorption by dissolved humic substances. They demonstrated the importance of aromatic structures for atrazine sorption to DOM. Our experiments show very high sorption coefficients for the samples rich in paraffinic moieties. Therefore, we speculate that the nonspecific binding of atrazine to DOM can be governed by both aromatic and aliphatic domains of the sorbent.

Atrazine showed higher complexation than ametryn to both the HoA and HoN fractions (Table 2). It is important to note that the partition coefficient values for ametryn to HoA were close to the values obtained for atrazine (except for HoA from Lachish).

Table 2 Partition coefficients of atrazine and ametryn to the isolated > 1,000 Da sorbents

	Atrazine		Ametryn	
	K_{DOC} (L/kg DOC)	r^2	K_{DOC} (L/kg DOC)	r^2
Netanya treated wastewater				
DOM > 1,000 Da	690 ± 31	0.97		
HoA > 1,000 Da	175 ± 4	0.99	151 ± 5	0.98
HoN > 1,000 Da	710 ± 31	0.97	189 ± 9	0.98
Lachish treated wastewater				
DOM > 1,000 Da	373 ± 11	0.98		
HoA > 1,000 Da	321 ± 8	0.99	196 ± 4	0.99
HoN > 1,000 Da	846 ± 38	0.97	202 ± 8	0.99

Dissolved organic matter, DOM; hydrophobic acid, HoA; hydrophobic neutral, HoN

Table 3 Partition coefficients of phenanthrene, fluoranthene and pyrene to the isolated bulk hydrophobic acid (HoA) and hydrophobic neutral (HoN) fractions

	Phenanthrene K_{DOC} (L/kg DOC)	Fluoranthene K_{DOC} (L/kg DOC)	Pyrene K_{DOC} (L/kg DOC)
Netanya treated wastewater			
HoA - bulk	790 ± 35	1,980 ± 190	4,360 ± 710
HoN - bulk	9,375 ± 430	23,425 ± 2,150	22,800 ± 1,290
Lachish treated wastewater			
HoA - bulk	2,020 ± 50	4,070 ± 65	5,415 ± 650
HoN - bulk	8,020 ± 200	18,870 ± 2,660	37,120 ± 2,510

In contrast, the K_{DOC} values calculated for ametryn by the HoN samples were significantly lower than the values recorded for the atrazine by the same sorbent. Moreover, a higher ratio (atrazine K_{DOC} /ametryn K_{DOC}) was exhibited by the Lachish HoN sample than the Netanya HoN sample (4.2 vs. 3.7, respectively). The lower sorption obtained for the HoA samples as compared to the HoN samples and the higher sorption recorded for HoN samples which exhibited the less polar functionalities suggest that the main sorption mechanism of ametryn is hydrophobic interaction.

Sorption of PAHs

The calculated sorption coefficients for the tested PAHs with the bulk DOM samples are summarized in Table 3. As observed for the triazine herbicides, all tested PAHs exhibited higher sorption affinity toward the HoN fractions than toward the more polar sorbent HoA. The K_{DOC} values for phenanthrene and fluoranthene with the HoN sample from Netanya were higher than the values calculated for the HoN sample isolated from the Lachish wastewater. The HoA sample from the Lachish wastewater exhibited the higher K_{DOC} values for all PAHs than Netanya HoA sample. This sample exhibited the lowest level of total acidity. Moreover, the HoA sample from Lachish is characterized by a higher H/C ratio (1.42), as compared to a ratio of 1.29 calculated for the fraction isolated from Netanya wastewater. These findings support the data obtained for the atrazines; it seems that the presence of polar functional groups in the HoA fractions reduces their affinity for interactions with nonionic organic chemicals. It is also suggested that the aliphatic/paraffinic-like domains within the HoA or HoN sorbents provide a hydrophobic environment, assisting in the sorption of very hydrophobic sorbates (Piccolo *et al.*, 1998).

Conclusions

The reported partition coefficients are of major importance for estimating the sorption of hydrophobic organic compounds by wastewater DOM. As indicated by the obtained K_{DOC} values, the HoN fraction showed significant sorptive capacity toward organic pollutants. Although this fraction made up a relatively small portion of the DOM (< 10%) and is mainly composed of aliphatic moieties, it is a dominant sorbent, especially in DOM which is characterised by low hydrophobicity. Another interesting observation was the higher atrazine binding coefficient obtained for the Netanya DOM as compared to the Lachish sample. This resulted from the higher content of hydrophobic fractions (HoN + HoA) in this sample. Although the Netanya wastewater showed lower DOC content than Lachish (12 and 23 mg/L, respectively), higher K_{DOC} values of the Netanya sample suggest that the chemical composition and properties of DOM have an important effect on the total DOM's sorptive potential. Hence, an evaluation of the mobility of organic pollutants by wastewater irrigation requires not only an assessment of the total DOC concentration, but also and more importantly, of the content of the hydrophobic fractions.

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