

*Sorption of Pesticides to Dissolved
Organic Matter Originated from
Treated Wastewater and its Effect
on Pesticides Mobility*

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Background

Wastewater dissolved organic matter (DOM) is highly heterogeneous in size and chemical composition : MW(< 500 to >5000 Da), and it is comprised of a mixture of compounds (humics, polysaccharides, proteins, lipids, and etc.)





Objectives

To study the mechanism governing the binding of *s*-triazine herbicides and polycyclic aromatic hydrocarbons (PAHs) to structural fractions of wastewater DOM.



Sampling sites

Activated sludge



Netanya

Oxidation ponds



Lachish





Selected properties of the studied treated wastewater

	Netanya	Lachish
BOD (mg/L)	3	22
COD (mg/L)	16	72
TSS (mg/L)	20	74
pH	7.3	7.7
EC (ds/m)	1.37	2.2
N total (mg/L)	2	74





Fractionation of treated wastewater DOM

bulk DOM
bulk DOM >1000

Acidify to
pH 2

NaOH 0.1N

Soxhlet extraction
with MeOH

HoN
HoN >1000

XAD-8


Hydrophilic fraction

Na⁺-HoA

H⁺-Cation exchange resin


H⁺-**HoA**
HoA >1000





Carbon mass balance of the DOM fractions (% of DOM)

Fraction	Netanya	Lachish
DOM	100 (12 mg/L)	100 (23 mg/L)
Hydrophilic	33	62
Hydrophobic:	67	38
HoA	59	29
HoN	8	9





C, N and H contents, atomic ratios and total acidity of the DOM fractions

sample	C	H	N	H/C	Total acidity
		%		Atomic ratio	meq/g
HoA Netanya	51.7	5.54	4.23	1.29	4.30
HoN Netanya	49.9	6.01	3.99	1.44	3.85
HoA Lachish	38.6	4.55	4.16	1.42	3.67
HoN Lachish	36.7	4.93	1.84	1.61	1.51



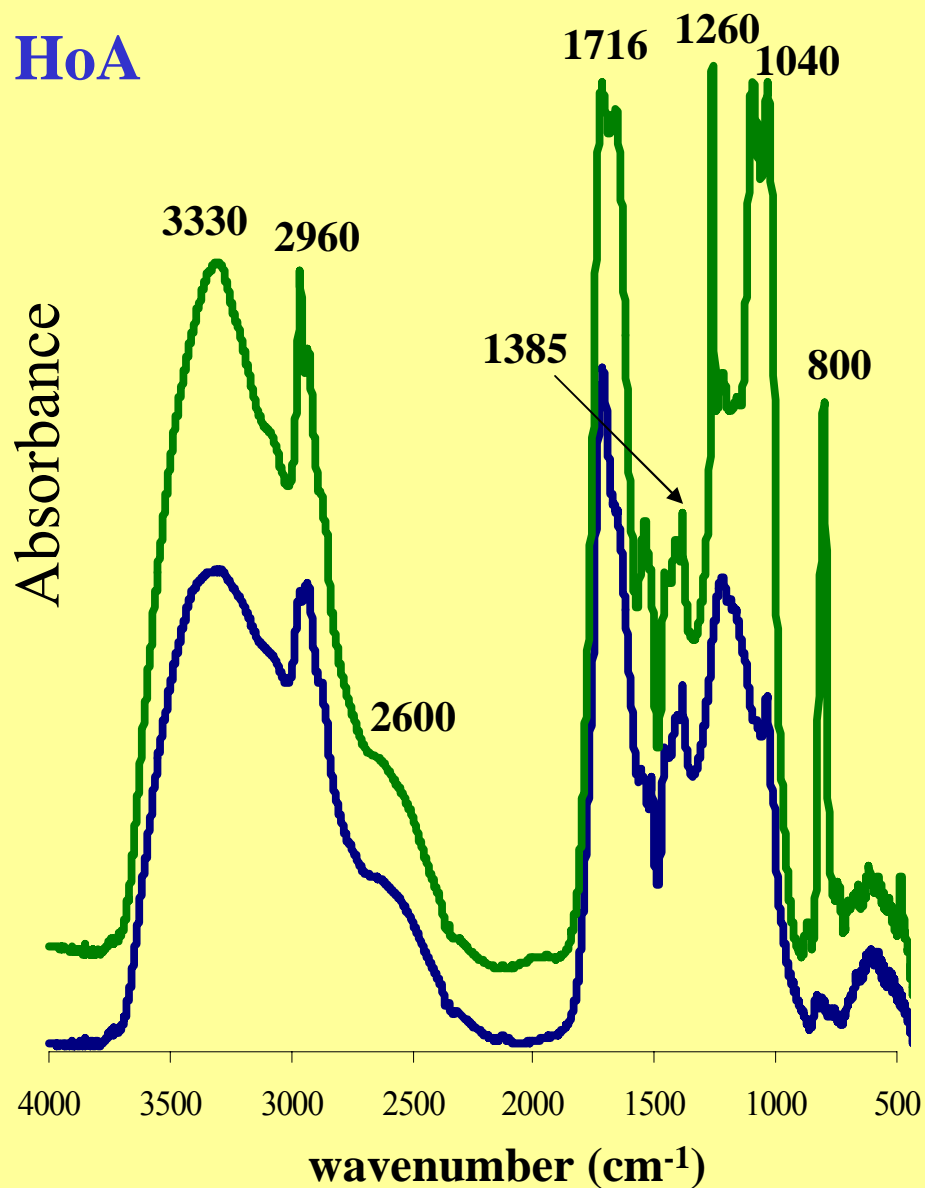


FTIR spectra of DOM fractions (Netanya)

HoA > 1000

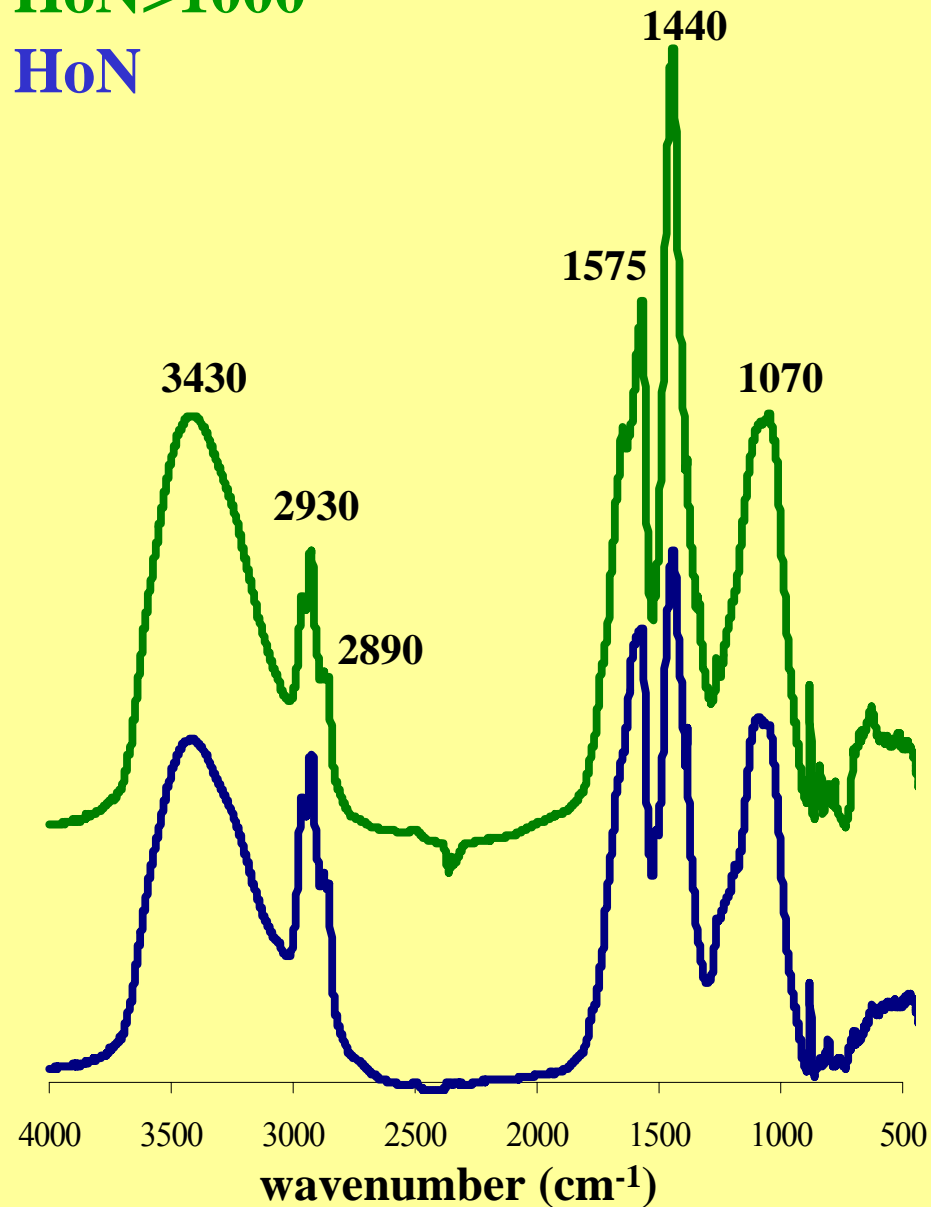
HoA

Absorbance




HoN > 1000

HoN



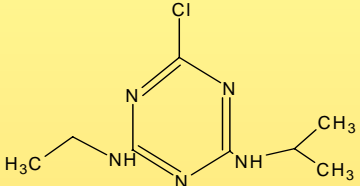
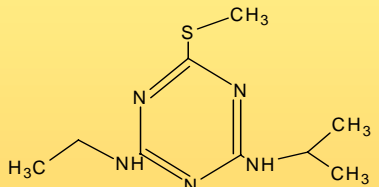
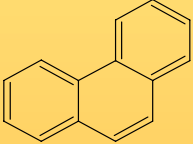
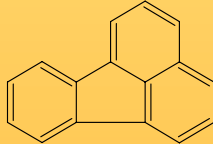



Characterization summary

- **The HoN fractions exhibited more aliphatic nature than the HoA fractions.**
 - **The >1000 Da fractions contained more polar groups than corresponding bulk fractions (HoA and HoN).**
 - **The fractions from Lachish WW exhibited higher aliphaticity character than the fractions from Netanya WW.**
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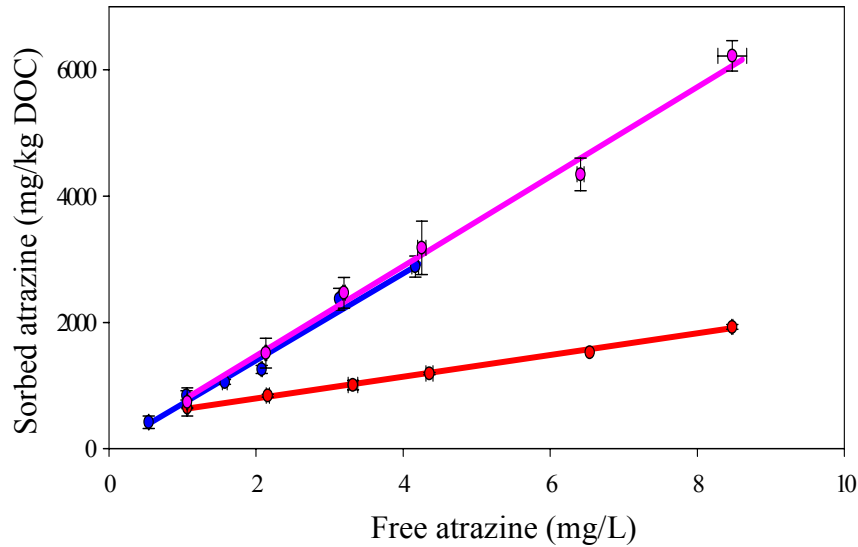
Selected properties of the sorbates

Compound	Structure	Formula	Log K_{OW}	Aqueous solubility (mg/L)	pKa
Atrazine		$C_8H_{14}ClN_5$	2.70	33	1.7
Ametryn		$C_9H_{17}N_5S$	2.82	185	4.1
Phenanthrene		$C_{14}H_{10}$	4.46	1.1	
Fluoranthene		$C_{16}H_{10}$	5.16	0.23	
Pyrene		$C_{16}H_{10}$	5.18	0.13	

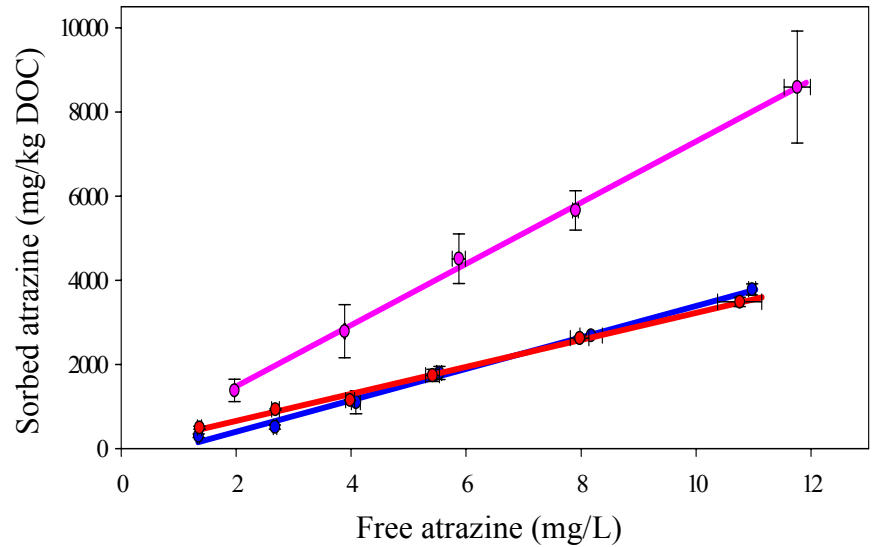


Atrazine binding isotherms by the DOM

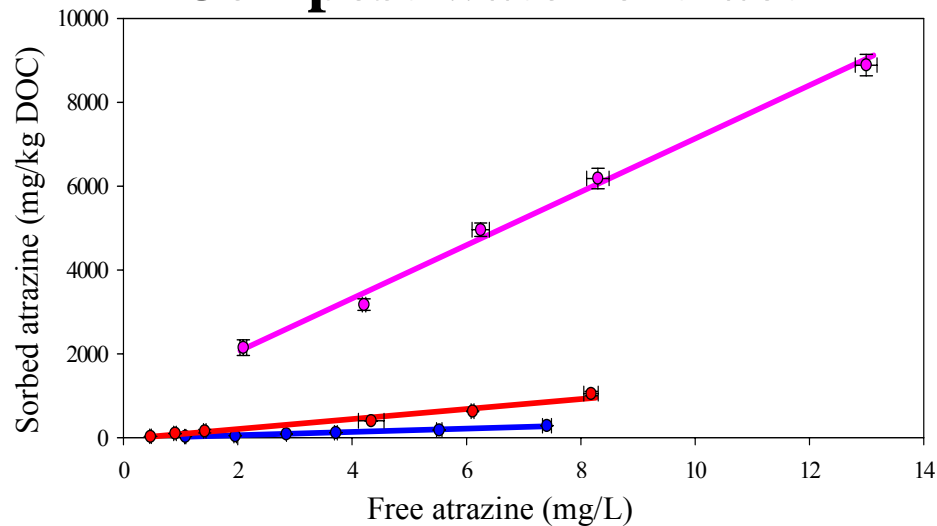
Netanya



Lachish



Compost water extract



bulk DOM


HoA

HoN



Sorption coefficients of atrazine


DOM fraction	K_{DOC} (L/kg DOC)
bulk DOM > 1000 Da Netanya	690±31
HoA >1000 Da Netanya	175±4
HoN >1000 Da Netanya	710±31
bulk DOM > 1000 Da Lachish	373±11
HoA >1000 Da Lachish	321±8
HoN >1000 Da Lachish	846±38
bulk DOM > 1000 Da compost	40±1
HoA >1000 Da compost	120±6
HoN >1000 Da compost	568±20





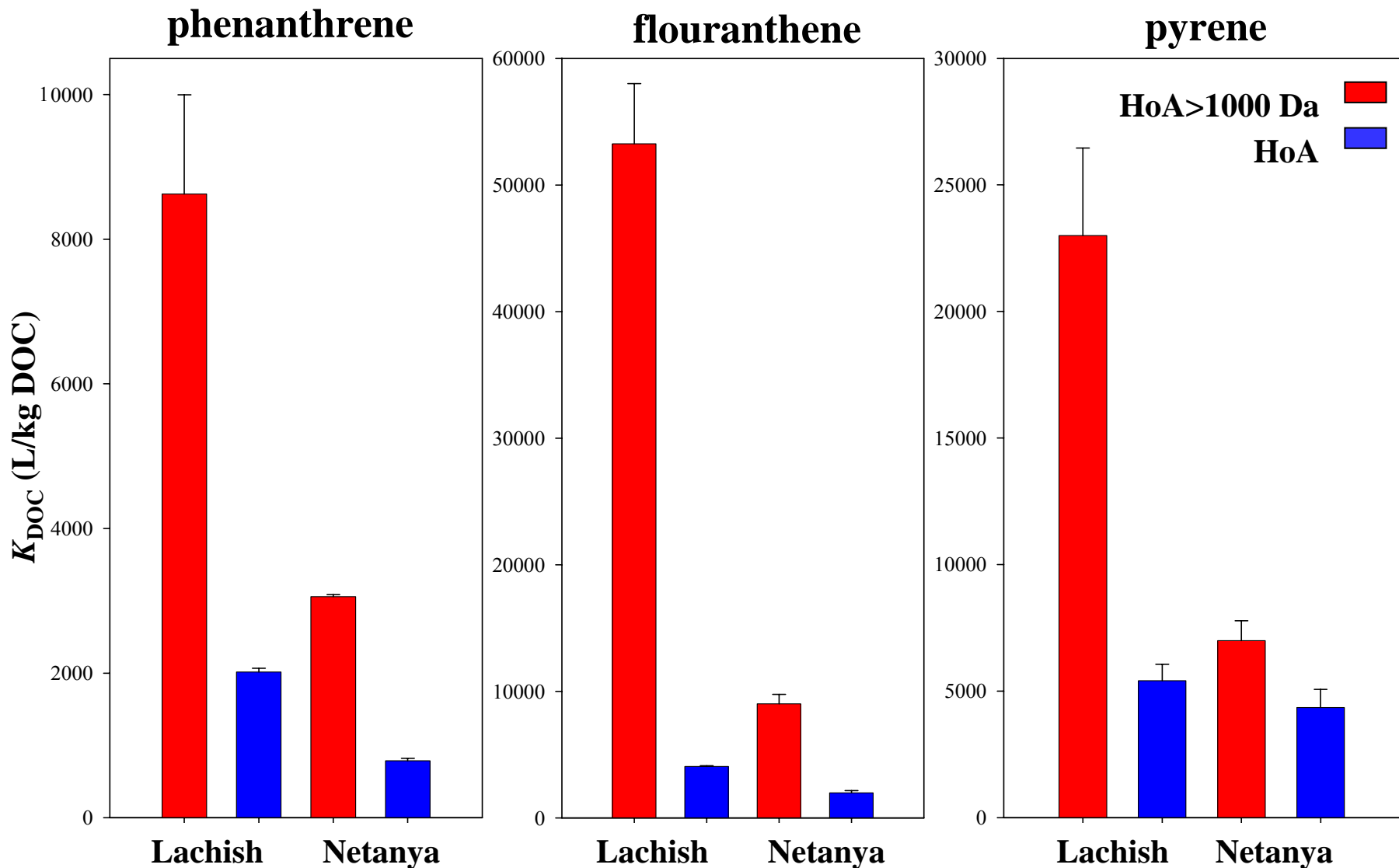
Sorption coefficients of PAHs

	K_{DOC} (L/kg DOC)		
	Phenanthrene	Fluoranthene	Pyrene
HoA Netanya	790±35	1,980±190	4,360±170
HoN Netanya	9,375±430	23,425±2,150	22,800±1,290
HoA Lachish	2,020±50	4,070 ±65	5,415 ±650
HoN Lachish	8,020 ±200	18,870 ±2,660	37,120 ±2,510
HoA compost	880 ±130	1,770 ±360	2,820 ±310
HoN compost	2,790 ±535	25,710 ±1,560	44,635 ±7,325





Sorption coefficients of PAHs (HoA and HoA>1000 Da fractions)





Summary

- K_{DOC} values : HoN > HoA

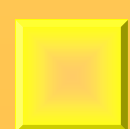
K_{DOC} values of the HoA fractions:

Lachish > Netanya > compost water extract

- K_{DOC} values of the HoN fractions:

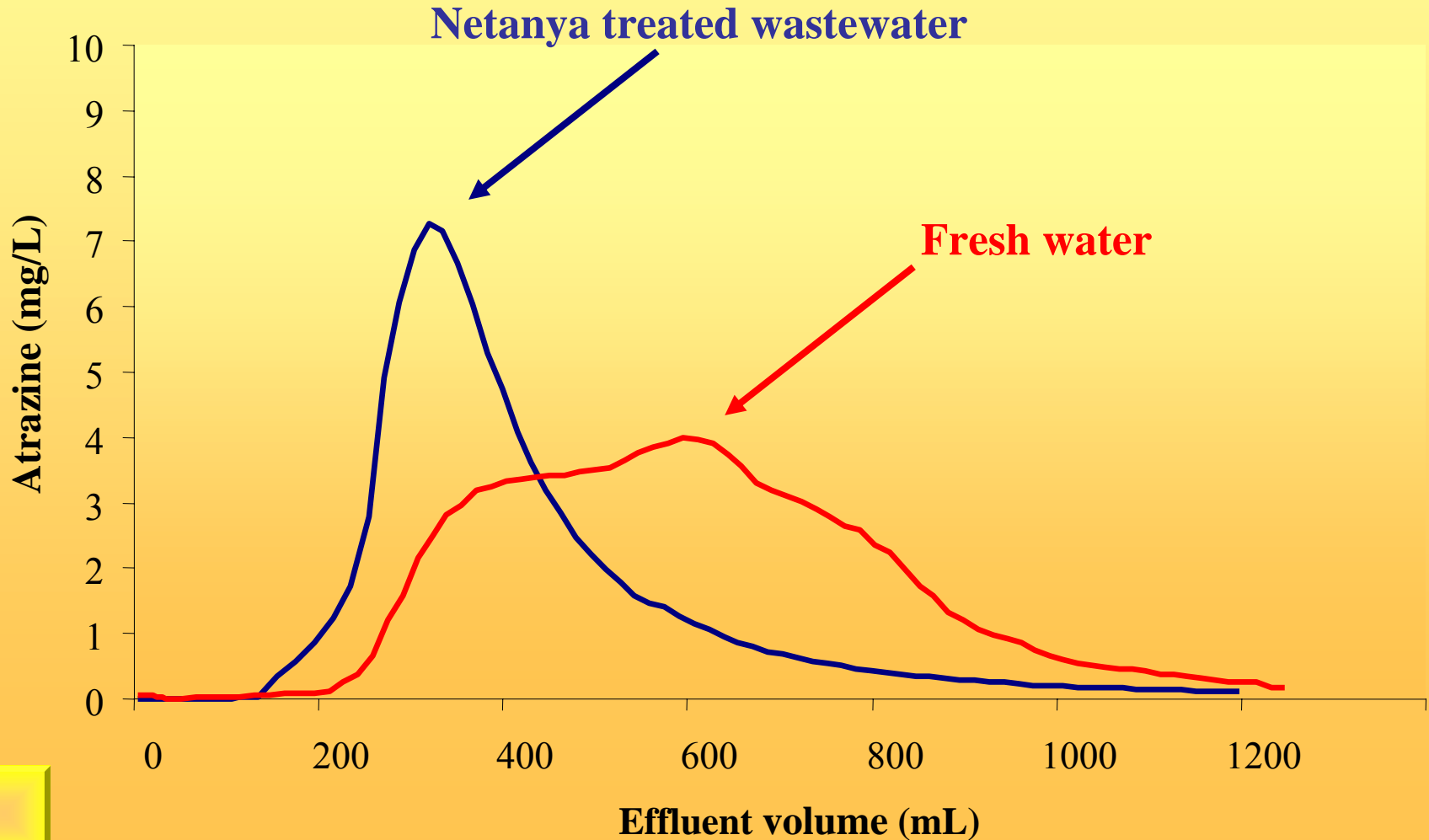
Lachish \approx Netanya > compost water extract.


The fractions from the compost water extract have a more polar character than the fractions from wastewater.



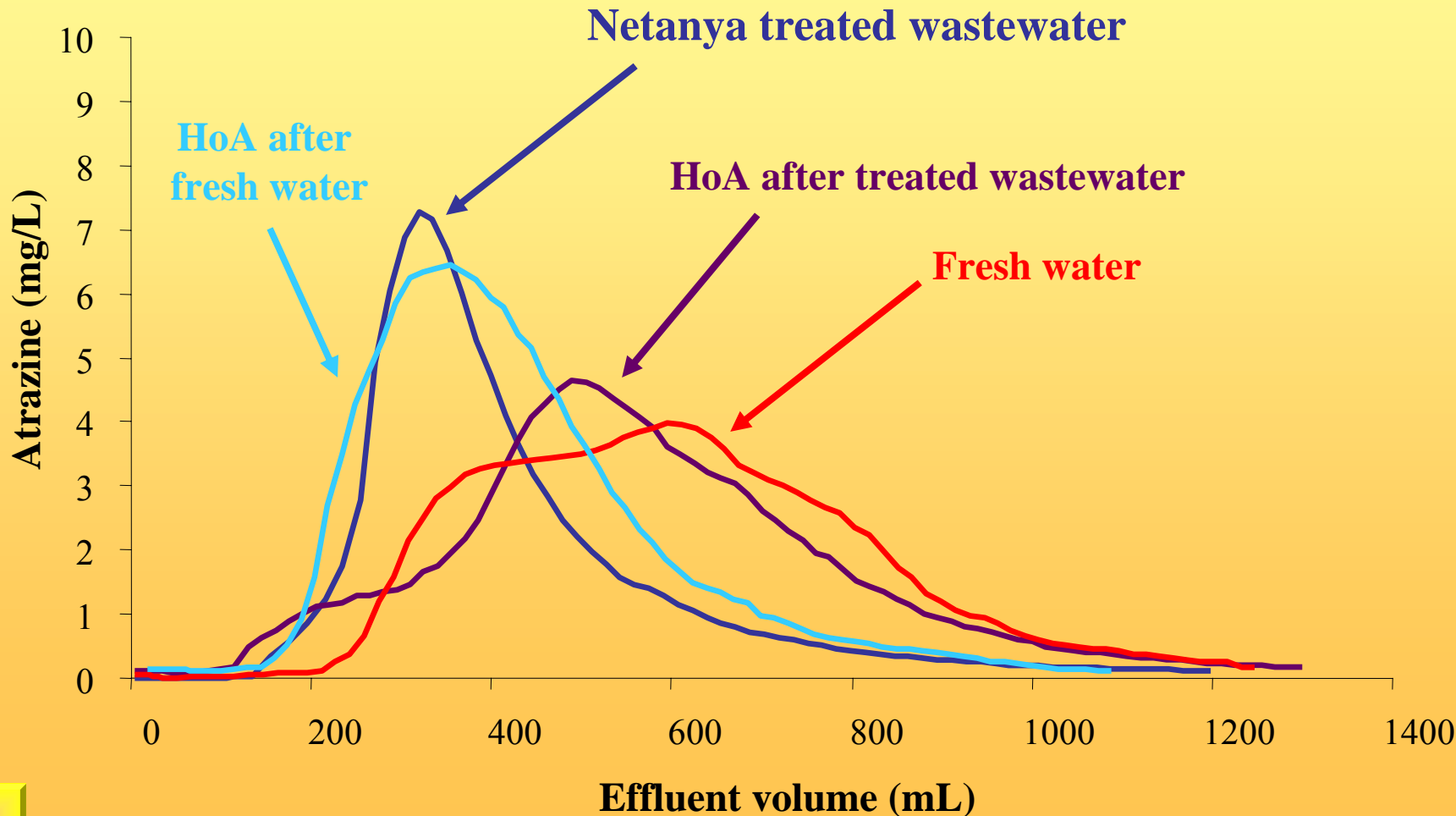


Transport of atrazine in soil (Bazra sandy soil, 3 mg/kg atrazin)





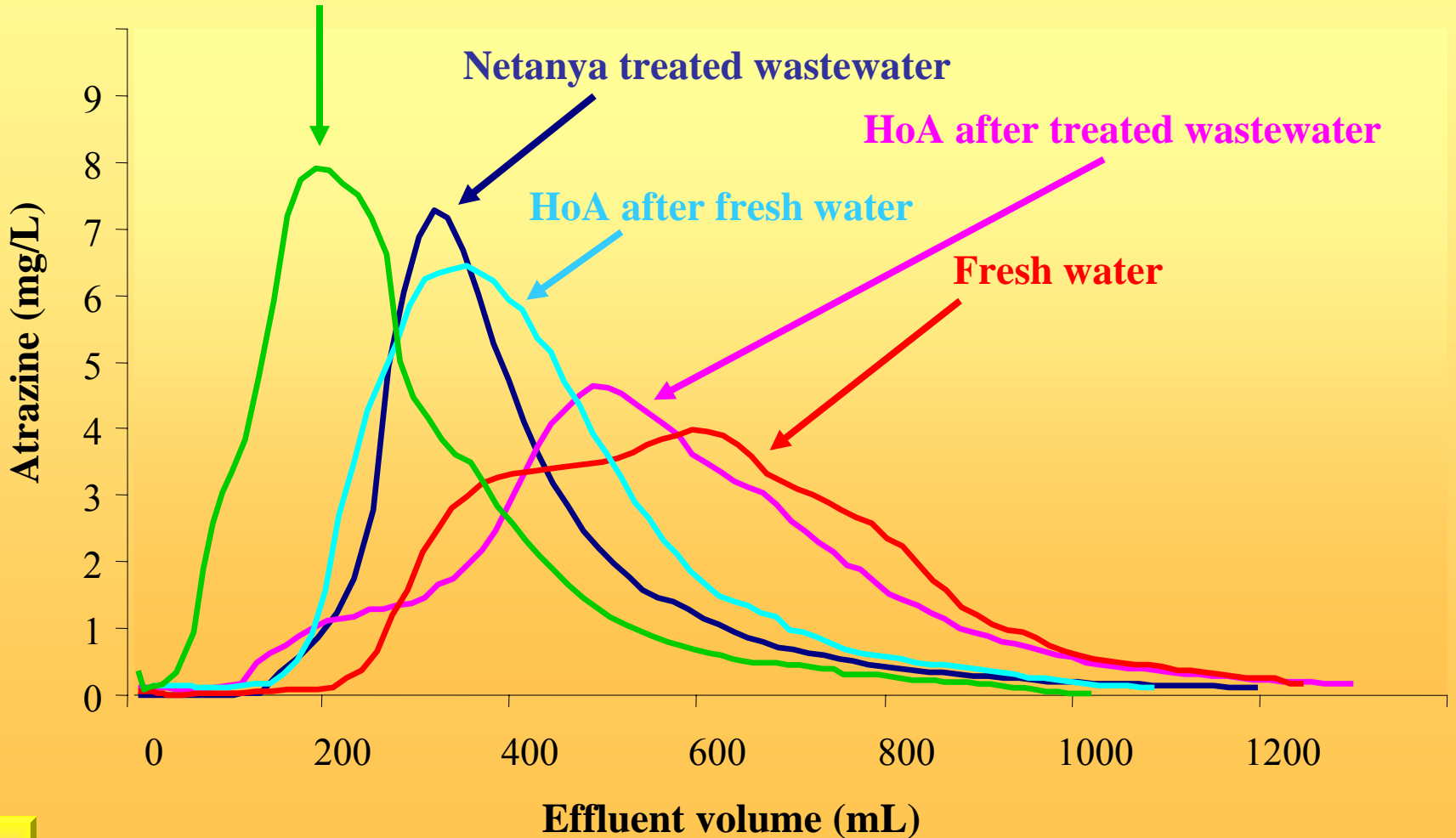
Transport of atrazine in soil (Bazra sandy soil, 3 mg/kg atrazin)






Transport of atrazine in soil (Bazra sandy soil, 3 mg/kg atrazin)

HoN after treated wastewater





Conclusions

- The **HoN fraction** has major effect on the overall sorption capability of the DOM; although it comprises less than 10% of the total WW DOC.
 - The **HoN fraction** can enhance the transport of weakly polar and apolar organic compounds in soils irrigated with wastewater.
 - The overall sorption capability of the DOM is governed by the level of hydrophobic fractions (HoA + HoN) → **Netanya > Lachish**
- 

The End

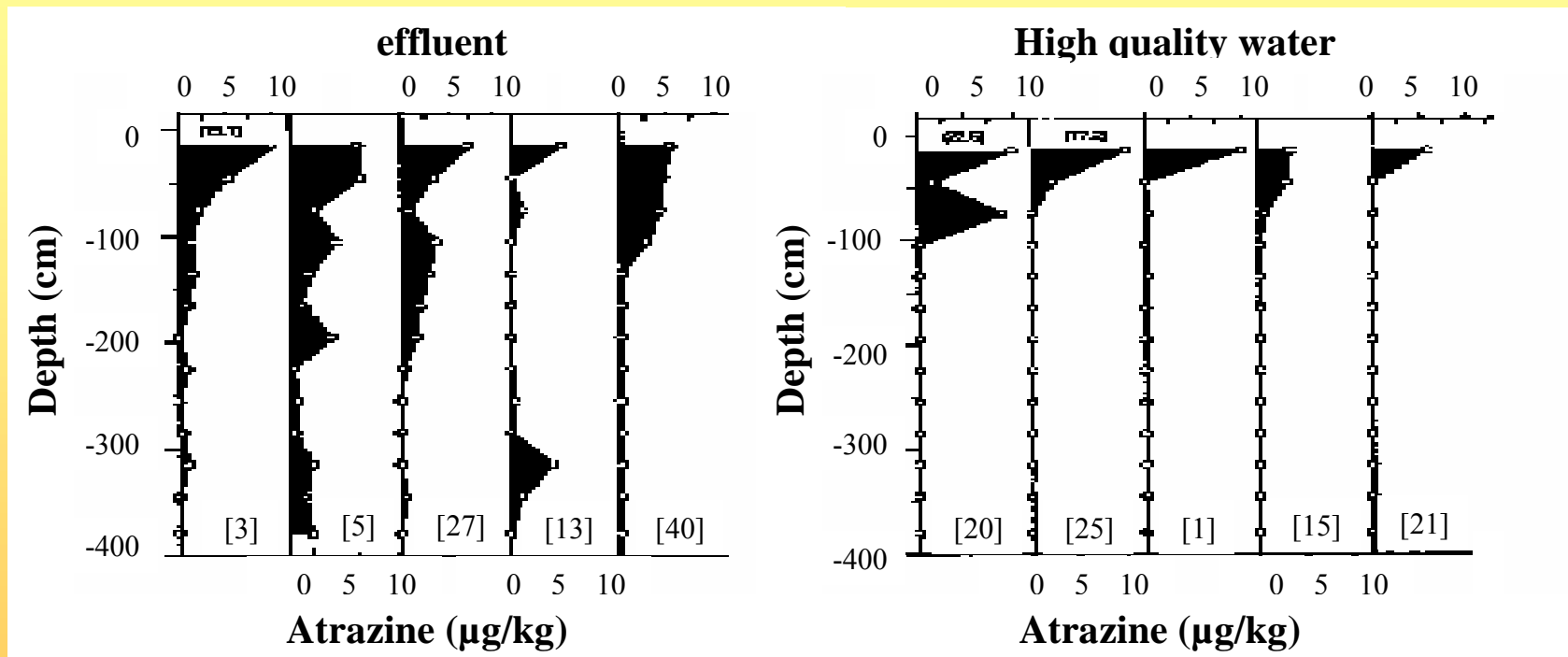


Pro
Frac.
mass
CHN
FTIR
sum1
sorb
atra
atra
PAH
big
sum2
move
Poll.
NMR
amet
SPME
Relt

Ilani, T., E. Schulz and B. Chefetz. 2005. Interactions of Organic Compounds with Wastewater Dissolved Organic Matter: Role of the Hydrophobic Fractions. *Journal of Environmental Quality*. 34:552-562.



Background



After Graber et al., 1995





PAHs and pesticides concentrations in the treated wastewater (ng/L; ppt)

	Netanya	Lachish
Napthalene	n.d.	n.d.
Acenaphthylene	n.d.	n.d.
Acenaphthene	16.60	45.33
Fluorene	43.25	n.d.
Phenanthrene	42.90	32.27
Antracene	n.d.	n.d.
Fluoranthene	29.87	n.d.
Pyrene	30.85	30.71
Beno[a]anthracen	n.d.	n.d.
Chrysene	n.d.	n.d.
Atrazine	n.d.	n.d.
Terbutylazine	n.d.	n.d.
Alachlor	n.d.	n.d.
Diazinon	550.45	325.40



FTIR bands of dissolved organic matter

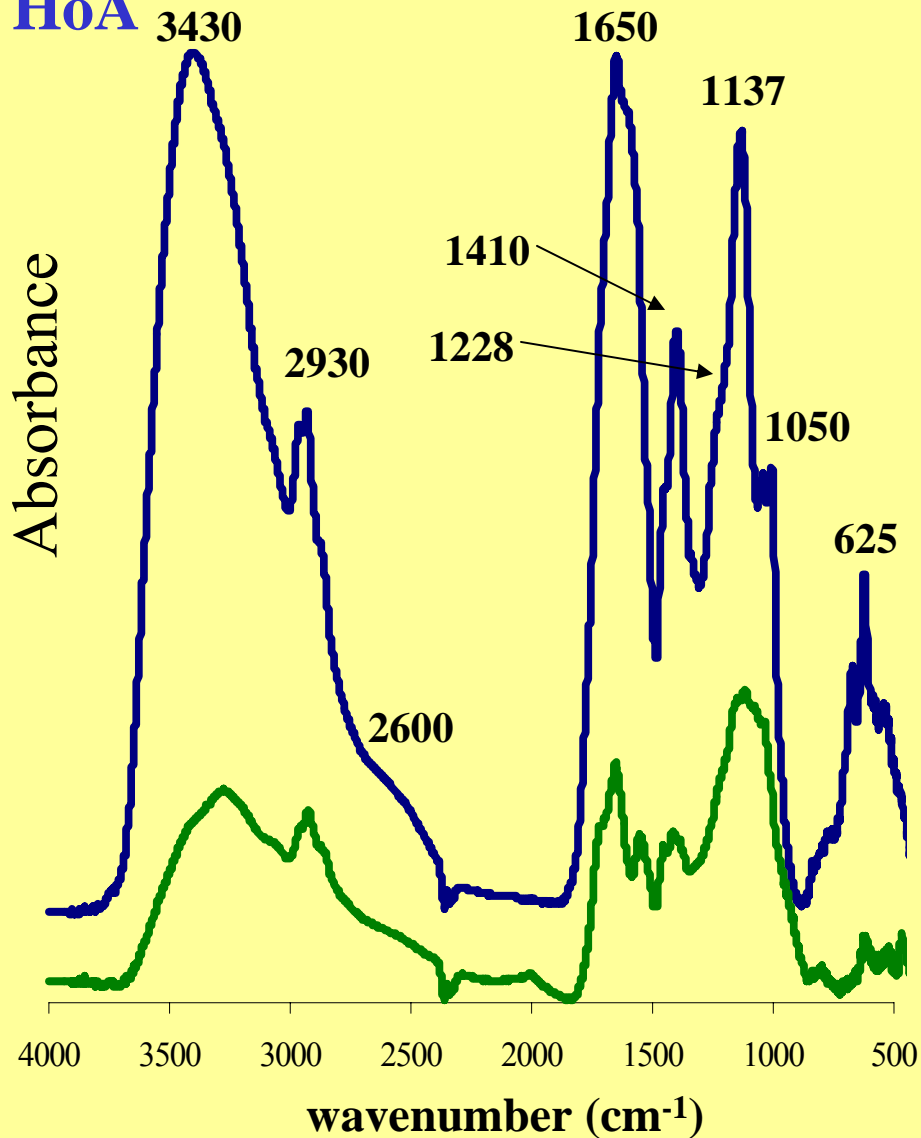
Wavenumber (cm ⁻¹)	Peak assignment
3250-3500	H-bonds, OH groups
3000-3150	Aromatic C-H stretch
2830-2970	Symmetric and asymmetric aliphatic C-H stretch (CH ₂ , CH ₃)
2600	OH stretch of H-bonds in COOH
1715-1730	C=O stretch of COOH
1615-1695	C=O stretch of aromatic COOH
1580-1650	C=C-C of aromatic rings
1517-1590	Symmetric stretch in COO ⁻ , N-H or C=N stretch in amide II
1400-1485	-CH deformation of -CH ₃ and -CH bending of CH ₂
1375-1385	-C-H deformation of C-CH ₃ groups
1200-1280	-C-O stretch and OH deformation of carboxyl and phenols
950-1225	C-H of aromatic ring
1060-1150	C-O-C stretch of ethers bonds
1000-1100	-C-O stretch of polysaccharides



FTIR spectra of DOM fractions (Lachish)

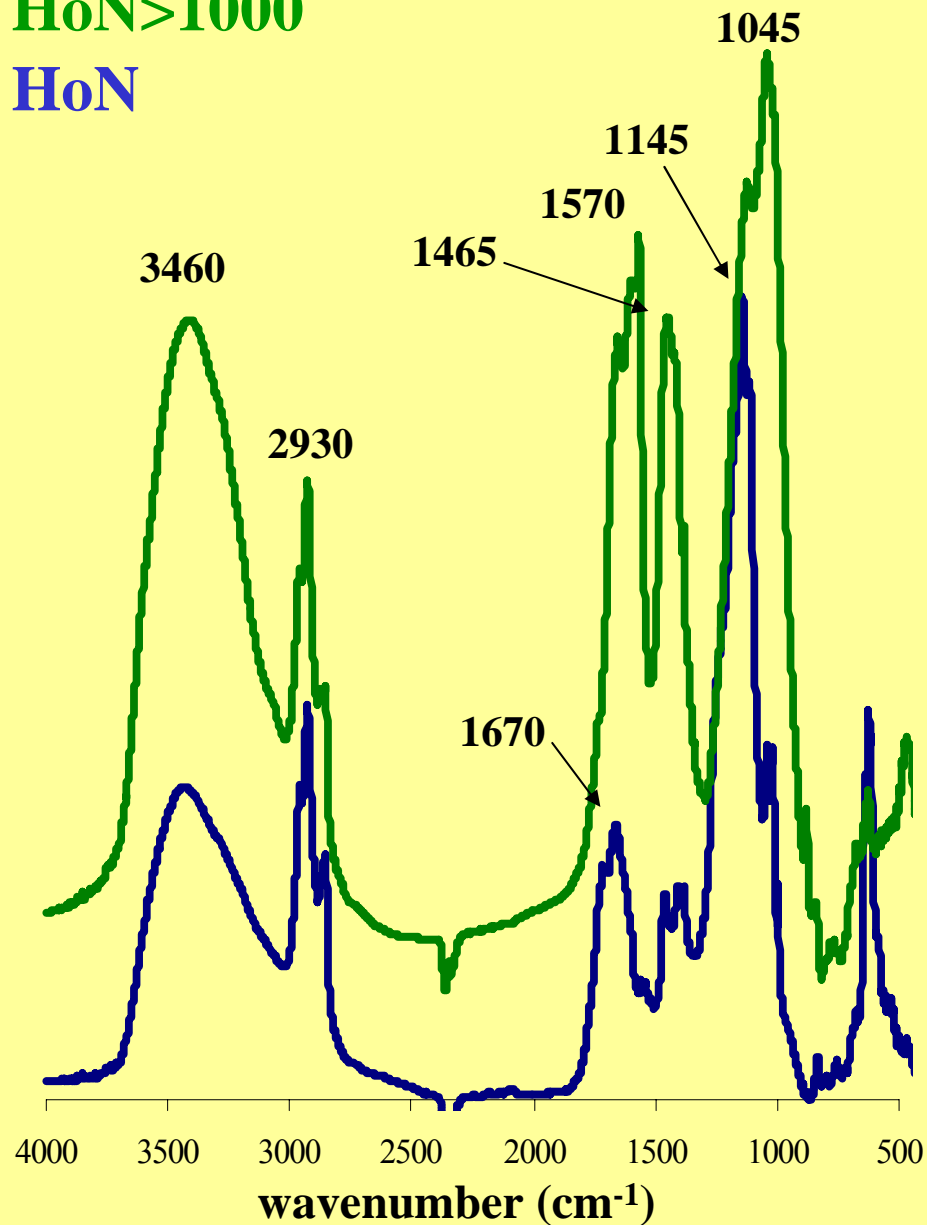
HoA > 1000

HoA



HoN > 1000

HoN



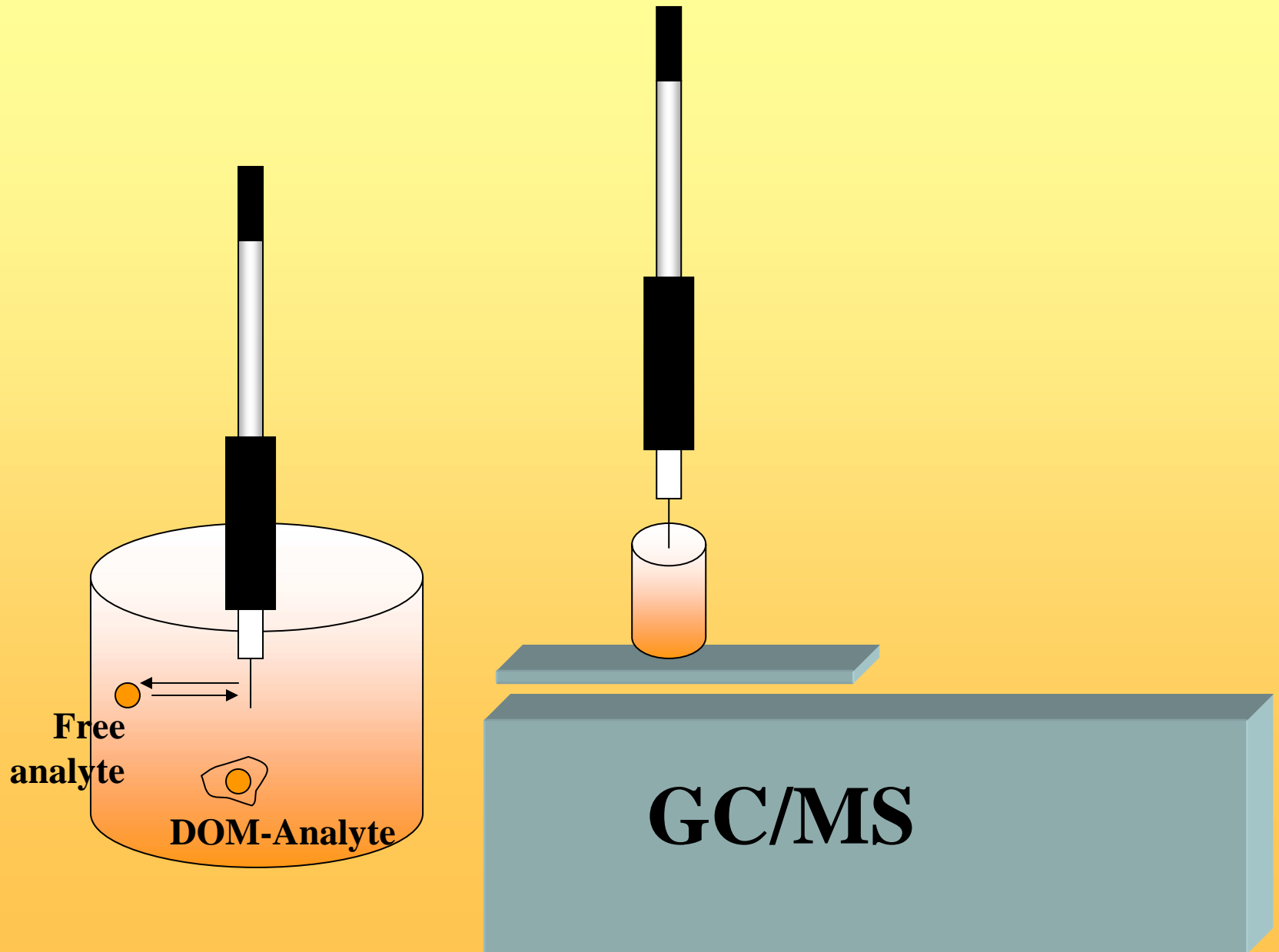



^{13}C NMR characterization of the DOM fractions (>1000 Da)

Chemical shift (ppm)	C-containing groups	HoN Lachish	HoA Lachish	HoA Netanya
		<u>% of total C in the sample</u>		
0-50	paraffinic	62	54	41
50-60	methoxyl	5	5	4
60-112	C-O, C-N	9	10	10
112-145	aromatic	8	9	18
145-163	phenolic	4	3	8
163-190	carboxyl	12	19	19



Sorption exp. using SPME





Sorption exp. using SPME

K_{DOC} calculations:

$$K_{DOC} = \left(\frac{n_2}{n_1} - 1 \right) \frac{1}{C_{DOC}}$$

K_{DOC} = experimental sorption coefficient, determined by using SPME.

n_1, n_2 = Extracted amount of analyte (fiber uptakes) from a DOM containing sample and from DOM-free solution sample, respectively.

C_{DOC} = Concentration of dissolved organic carbon (kg/L).





Relative K_{DOC}

		K_{DOC}	% from DOM	Relative K_{DOC}
Phenanthrene	HoA Netanya	789	59	465
	HoN Netanya	9,374	8	750
	HoA Lachish	2,017	29	585
	HoN Lachish	8,018	9	722

$$\text{Relative } K_{\text{DOC}} = K_{\text{DOC}} \cdot f_{\text{C(DOC)}}$$
