

# **Part 2. The Hydrosphere**

## **Chapter 12. Organic Matters in Water**

# Chapter 12. Organic matter in Water

## 12.0 Generals

- Organic matter (OM) : determined by the  $C$  content, but can exist in inorganic forms like  $CaCO_3$  minerals in sedimentary rocks

NOM: natural organic matter

DOM: dissolved organic matter

POM: particulate organic matter

Table 12.1 Carbon pools in the global environment	
Carbon reservoir	Mass of carbon/Pg
Atmosphere	720
Terrestrial environment	
Plants	830
Soil surface detritus	60
Soil organic matter	1400
Peat	500
Fossil Fuels	5000
Aquatic environment (oceans)	
Living organisms	3
Dissolved organic matter	1000
Dissolved inorganic matter	37 000
Sedimentary carbonate material	20 000 000

Data from Bolin, B., Requirements for a satisfactory model of the global carbon cycle and current status of modeling efforts, in *The Changing Carbon Cycle: A Global Analysis*, eds Trabalka, J. R. and Reichle, D. E., Springer, New York; 1986.  
Pg = petagram =  $10^{15}$  g.

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## 12.1 Origins of organic matter in water

- NOM: from

- delivered from land to hydrosphere

- produced *in-situ* in a water body

DOM: produced by ab.10% of the  
microscopic animals

activity in water, and by

- Anthropogenic organic matter: includes domestic sewage or pulp-mill effluent, products or byproducts of industrial processes

- Two categories of organic species

- Discrete small molecules, i.e low molar mass OM

- Macromolecules

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## 12.2 Environmental issues related to aq. OM

- **Toxicity** to living organisms: e.g. PAHs, Polychlorinated biphenyls (PCBs), Dioxins, residues of pesticides
- **influence environmental processes**: e.g. alkylation of inorganic tin to form monomethyl tin ( $\text{CH}_3\text{Sn}^{3+}$ ) and dimethyl tin ( $(\text{CH}_3)_2\text{Sn}^{2+}$ ), occurring in the fish gut or via microorganisms in the water and the organotin species produced are more toxic to aquatic biota than are the original inorganic tin compounds. Toxicity increases with increasing number and increasing length of alkyl groups.
- **Oxidation of bulk OM in water** – makes the system oxygen-deprived state, leading to low pE environment and therefore change of the chemistry of the entire system

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## 12.3 Humic material: **Formation of humic material**

- **Humic material (HM):** NOM of plant or microbial origin
  - typically makes up ab. 50% of DOM in surface water
- **Three categories of HM:**
  - Fulvic acid (FA):
  
  - Humic acid (HA):
  
  - Humic (Hu):

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## 12.3 Humic material: **Formation of humic material**

- **Formation of HM:** two hypotheses

- hypothesis 1: plant biopolymers keep degrading to produce smaller and oxygen rich molecules, soluble in both acid and base. During this process, lignin, paraffinic macromolecules, melanins and cutin are selectively transformed to produce a high molar mass precursor of humin

- hypothesis 2: condensation polymerization, i.e. degraded small molecules are repolymerized to form humic substances. As a consequence, FA would be a precursor of humic acid and then of humin

- Elemental composition (%)

C: 45-60, O: 25-45, H: 4-7, N: 2-5, ash: 0.5-5

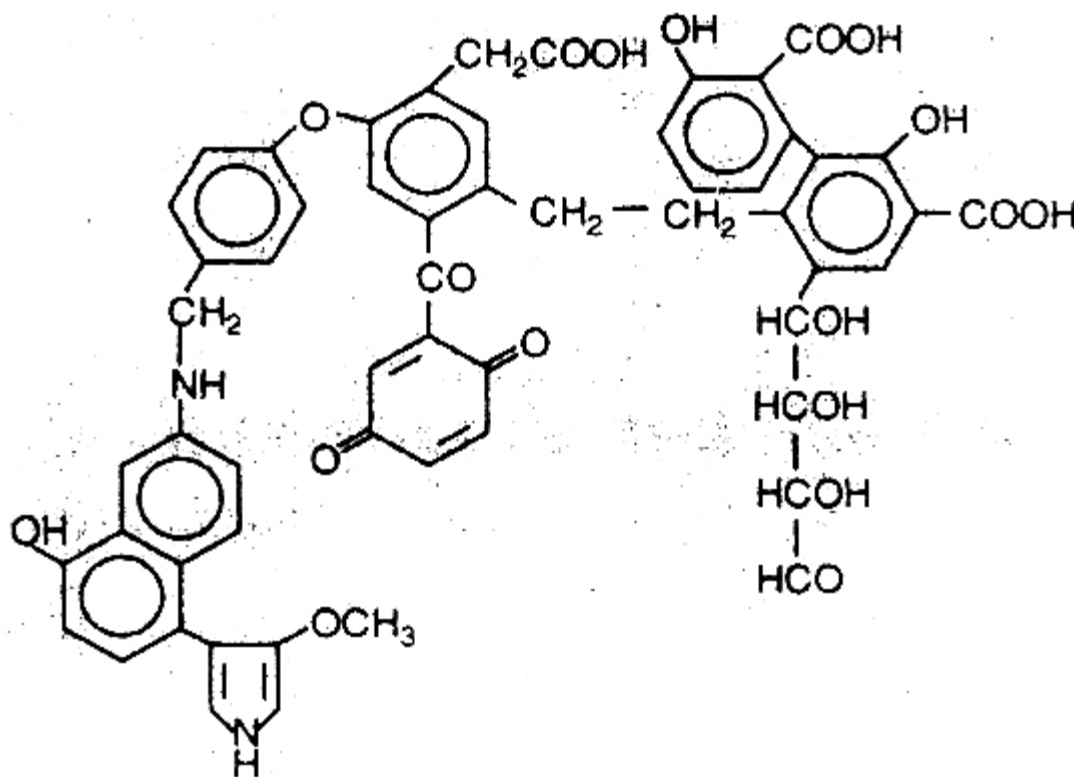
Carbon contents:

Oxygen contents:

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## 12.3 Humic material: Aqueous humic material as a proton acceptor

- Free forms of humic materials are acids: largely due to  $(pK_a=2.5-5)$  and  $(pK_a=9 \text{ or } 10)$  groups



**Fig. 12.3** Structure of a generic molecule of a humic substance.

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## 12.3 Humic material: Aqueous humic material as a proton acceptor

- E.g. ionic species in 8.0 mg L<sup>-1</sup> Canadian Shield

H <sup>+</sup>	pH = 5.88	Cl <sup>-</sup>	0.138 mg L <sup>-1</sup>
NH <sub>4</sub> <sup>+</sup>	3.6 μg L <sup>-1</sup> (as N)	NO <sub>3</sub> <sup>-</sup>	7.0 μg L <sup>-1</sup> (as N)
Na <sup>+</sup>	75.9 μg L <sup>-1</sup>	HCO <sub>3</sub> <sup>-</sup>	14.4 μg L <sup>-1</sup> (as C)
K <sup>+</sup>	50.8 μg L <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup>	59.4 μg L <sup>-1</sup> (as S)
Mg <sup>2+</sup>	0.124 mg L <sup>-1</sup>		
Ca <sup>2+</sup>	0.569 mg L <sup>-1</sup>		

	Conc/μmol L <sup>-1</sup>	Charge/μmol L <sup>-1</sup>
H <sup>+</sup>	1.3	1.3
NH <sub>4</sub> <sup>+</sup>	0.2	0.2
Na <sup>+</sup>	3.3	3.3
K <sup>+</sup>	1.3	1.3
Mg <sup>2+</sup>	5.1	10.2
Ca <sup>2+</sup>	14.2	28.4
Σ + ve charge		44.7
Cl <sup>-</sup>	3.9	3.9
NO <sub>3</sub> <sup>-</sup>	0.5	0.5
HCO <sub>3</sub> <sup>-</sup>	1.2	1.2
SO <sub>4</sub> <sup>2-</sup>	1.9	3.7
Σ -ve charge		9.3

Charge imbalance

$$=(44.7-9.3)=35.4 \mu\text{mol L}^{-1}$$

To balance this, contribution of DOM should be considered

$$8 \text{ mgL}^{-1} \times C_{\text{COO}^-} \cdot \text{mmol g}^{-1} = 35.4$$

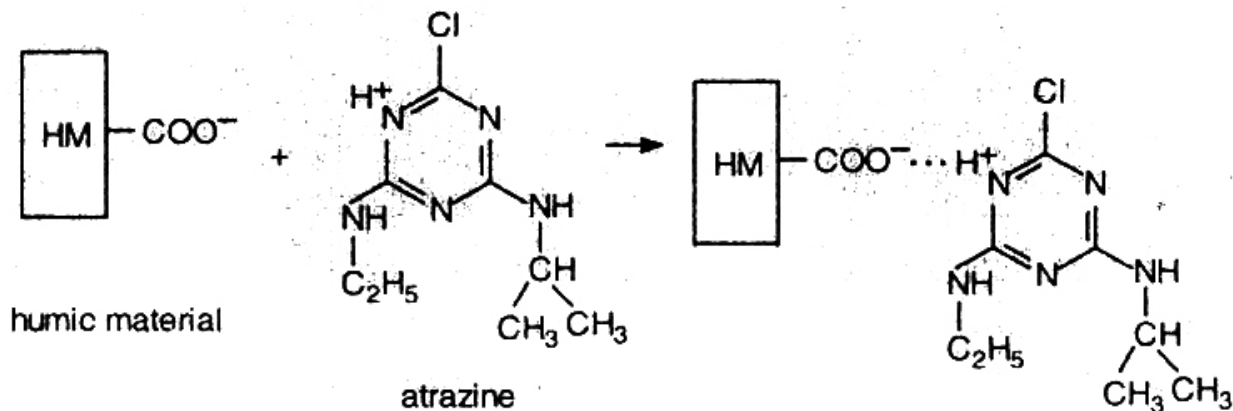
$$C_{\text{COO}^-} = 4.5 \text{ mmol g}^{-1}$$



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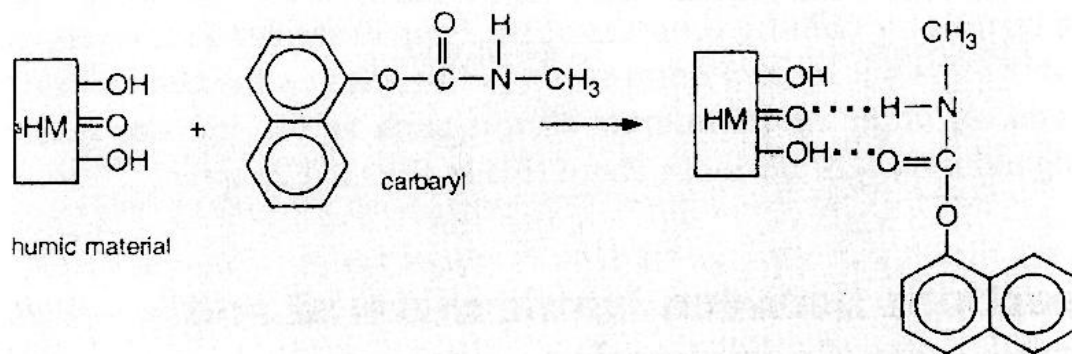
## 12.3 Humic material: Reactions b/w humic material and small OM

- Rxns b/w positively charged species and negatively charged humate sites



**Fig. 12.4** Atrazine bonded to HM by electrostatic forces.

- Hydrogen bonding

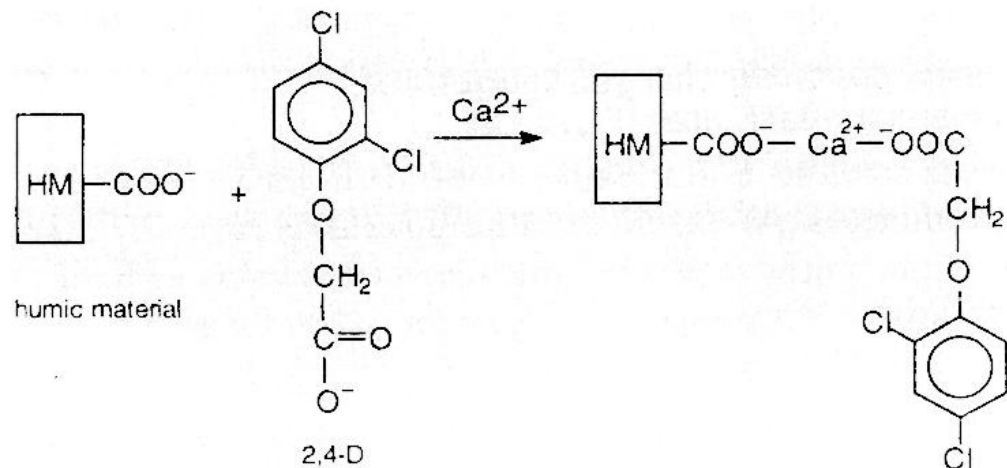


**Fig. 12.5** Binding of the pesticide carbaryl to HM through hydrogen bonding.

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## 12.3 Humic material: Reactions b/w humic material and small OM

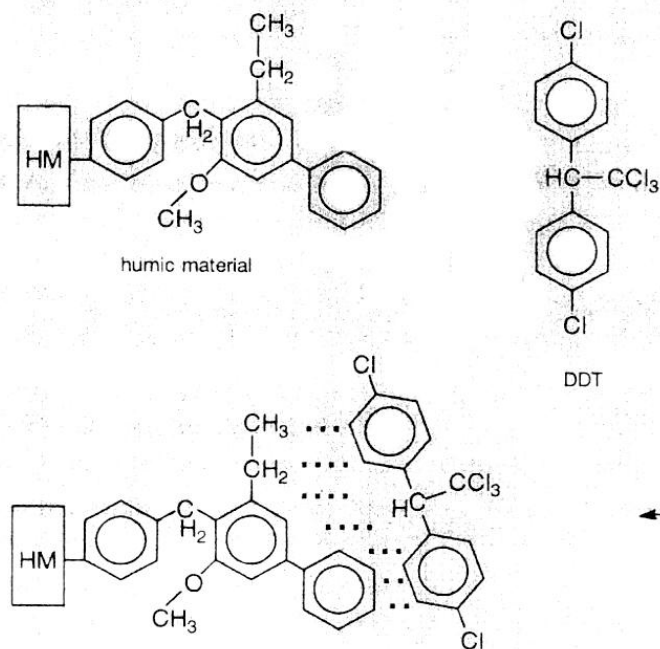
- Salt linkage or ligand exchange



**Fig. 12.6** Binding of the pesticide 2,4-dichlorophenoxyacetic acid to HM through a metal ion bridge.

- Hydrophobic interactions (fig 12.7)

DDT: dichlorodiphenyltrichloroethane



**Fig. 12.7** Binding of the insecticide DDT to HM through hydrophobic interactions. An essentially hydrophobic portion of the hypothetical humate molecule is specifically shown in this figure.