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ASAC 1101 : FUNDAMENTALS OF SOIL SCIENCE (2+1)

Level : B.Sc (Ag), I semester

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Topic

Behaviour of pesticides and inorganic contaminants

CONCEPTS COVERED

Concepts Covered:

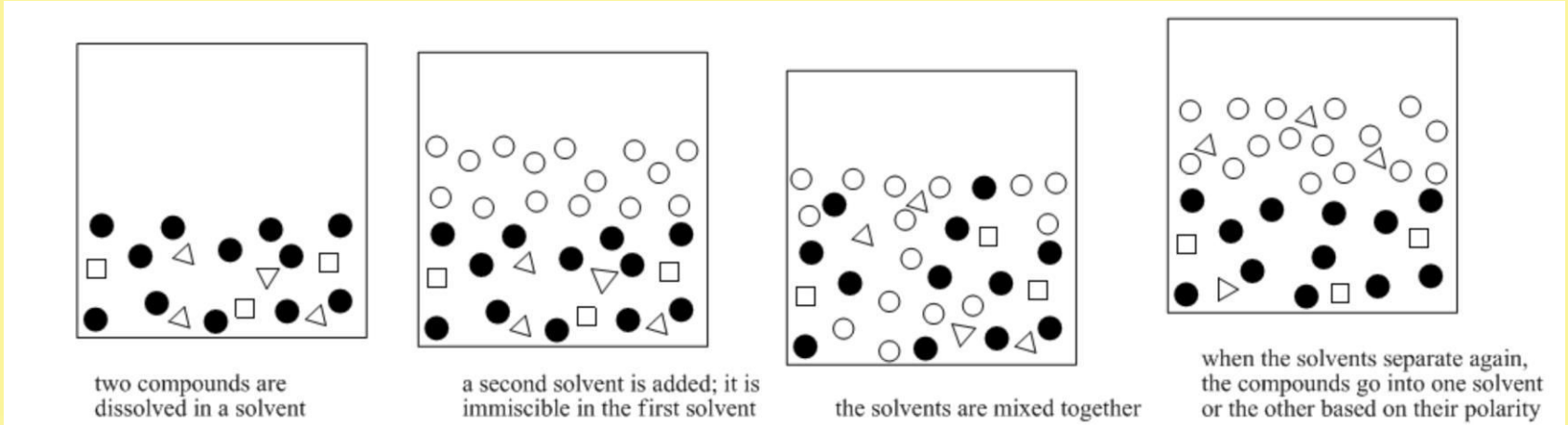
- Importance of pesticide sorption
- Distribution coefficient
- Binding of the biomolecules to clay and humus

Importance of the sorption of pesticides in soil

- Soil can adsorb charged organic ions by AEC or CEC.
- Sorption can reduces the movement into groundwater.
- It can allow time for soil micro-organism to break the chemicals down to less toxic byproducts.
- It can also produce inner-sphere complex.
- It is common for organic compounds to be absorbed within the soil organic colloids by a process termed partitioning.
- The hydrophobic part will not be adsorbed by moist clays.

What is partitioning?

This method is often called "extraction." Extraction means drawing a compound out of a mixture using a solvent. Solvent partitioning is more specific. It means compounds have a "choice" of two solvents that they can dissolve in. Some compounds dissolve in one solvent. Some compounds dissolve in the other solvent. That way the compounds in the mixture become separated into two groups.

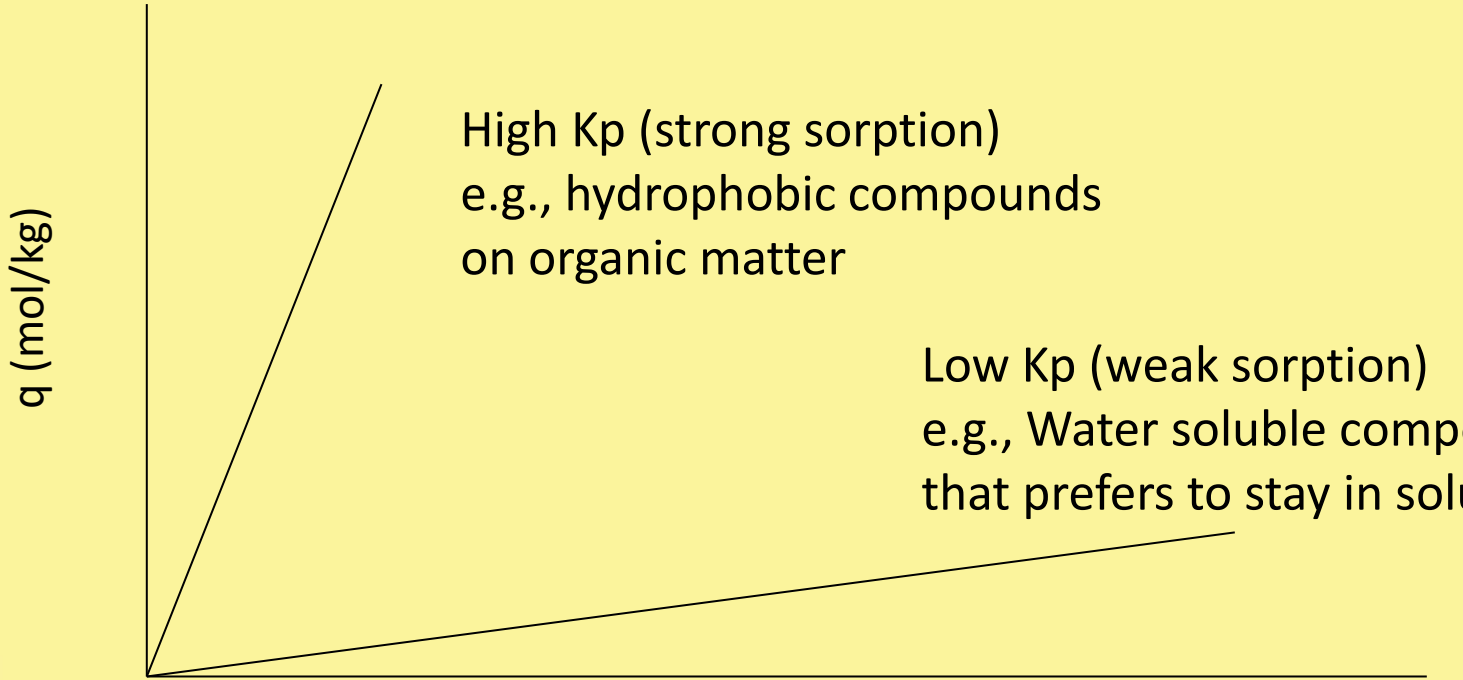


Kp, partitioning coefficient

$$Kp = \frac{\text{concentration on solid} \quad (q)}{\text{concentration in solution (Ceq)}}$$

Slope = rise/run

K = [sorbed]/[solution]



High Kp (strong sorption)
e.g., hydrophobic compounds
on organic matter

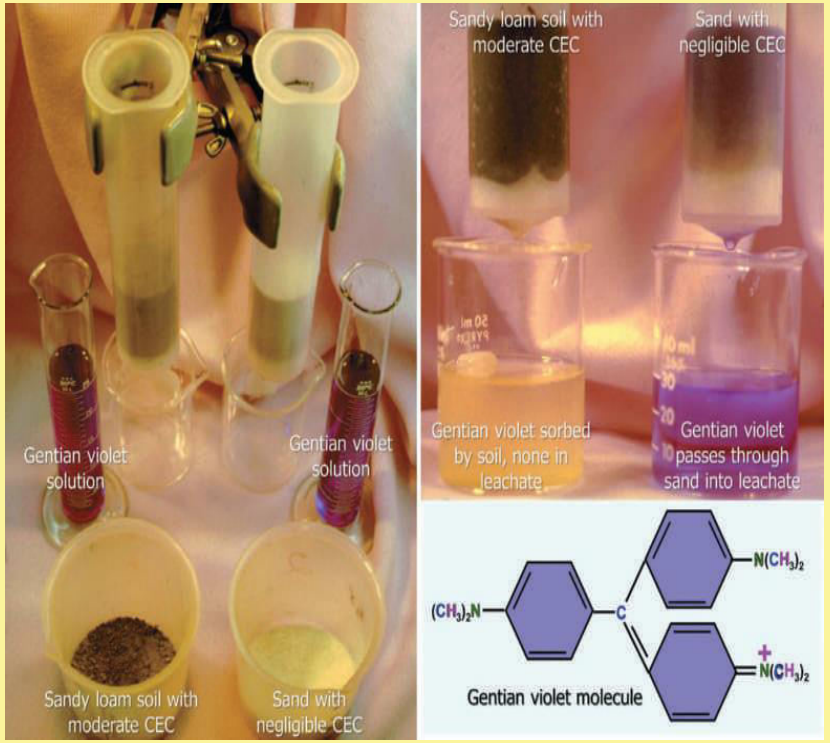
Low Kp (weak sorption)
e.g., Water soluble compound (hydrophilic)
that prefers to stay in solution

Organoclays:

- The hydrated metal cations (e.g., Ca^{2+}) that are adsorbed on the surface of smectites can be replaced with large organic cations, giving rise to what are termed organoclays (Smectites organoclay).
- Such clay surfaces are more friendly toward applied organic compounds, making it possible for the clay to participate in partitioning.

Examples of Sorption

- The experiment was done by a gentian violet colour solution, sandy loam soil with moderate CEC and sandy soil with negligible CEC.
- After leaching, a clear solution was found in case of sandy loam soil.
- In contrast, the water drained from the sandy soil was still purple in colour.



- The picture shows a field in Africa.
- After applying the herbicides, the field was still full of weeds.
- The soil has a upper (A) horizon with low CEC and a clayey subsoil with high CEC (argillic).
- All the pesticides was adsorbed by subsoil clay so they were no longer available to be taken up by the roots of the weeds.

Distribution coefficients

- **The tendency of a pesticide or other organic compound to leach into the groundwater is determined by the solubility of the compound and by the ratio of the amount of chemical sorbed by the soil to that remaining in solution. This ratio is known as the soil distribution coefficient *Kd*.**

$$K_d = \frac{\text{mg chemical sorbed/kg soil}}{\text{mg chemical/L solution}}$$

- **The unit of Kd is L/kg.**
- **It depends upon the nature of the soil.**
- **The variation is related mainly to the amount of organic matter (organic carbon) in the soils.**
- **So, it can also be represented by using a similar ratio that focuses on the sorption by soil organic carbon.**
- **This ratio is termed the organic carbon distribution coefficient *Koc.***

$$K_{oc} = \frac{\text{mg chemical sorbed/kg organic carbon}}{\text{mg chemical/L solution}} = \frac{K_d}{\text{g org. C/}g\text{ soil}}$$

- **Kd and Koc are used for herbicides and metabolites.**
- **Higher Kd and Koc values indicate that the chemical is strongly adsorbed by the soil and less susceptible to leaching.**

Kd and *Koc* for several widely used herbicides

Three of the listed compounds are metabolites that form when microorganisms decompose Atrazine. Higher K_d or K_{oc} values indicate stronger attraction to the soil solids and lower susceptibility to leaching loss. The values were measured for a particular soil (an Ultisol in Virginia, USA). Using the relationship between K_d and K_{oc}, it can be ascertained that this soil contained 0.013 g C/g soil (1.3%).

Herbicide	K_d	K_{oc}
Atrazine	1.82	140
Diethyl atrazine	0.99	80
Diisopropyl atrazine	1.66	128
Hydroxy atrazine	7.92	609
Metolachlor	2.47	190

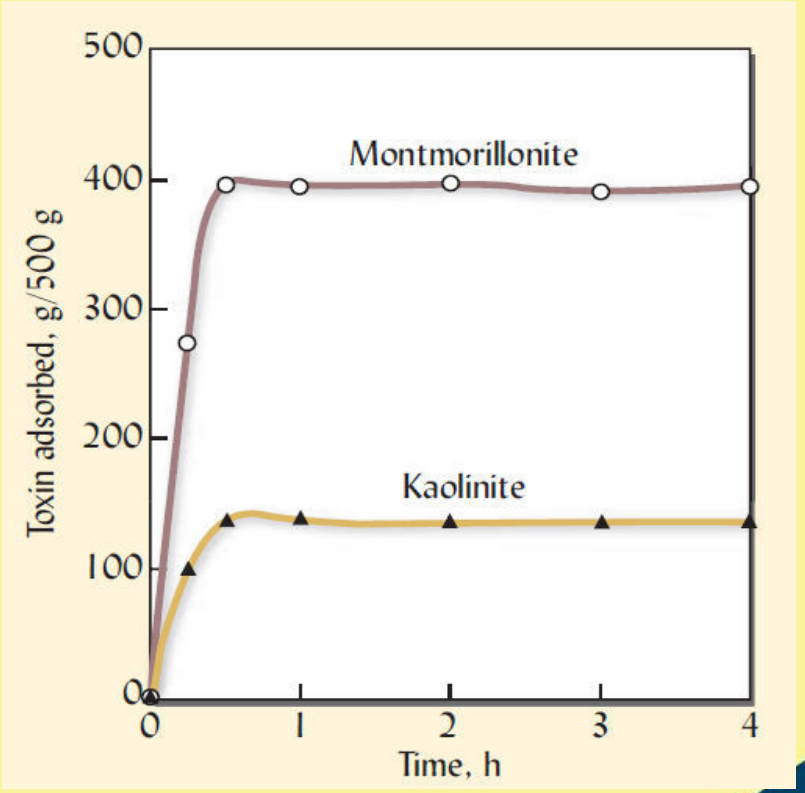
Data from Seybold and Mersie (1996).

Binding of biomolecules to clay and humus

- The bond between the biomolecule and the colloid is often quite strong so that the biomolecule cannot be easily removed by washing or by exchange reactions.
- The initial attraction may be between charged colloidal surfaces and positively or negatively charged functional groups on the biomolecule.
- These type of reaction has two environmental impacts:
- Firstly, the bound chemical remains for a longer period in the soil as the microorganisms can not recognize and react with their target sites.
- Secondly, some chemicals remain active after adsorption so toxins remain toxic to susceptible organisms, enzymes continue to catalyze reactions.

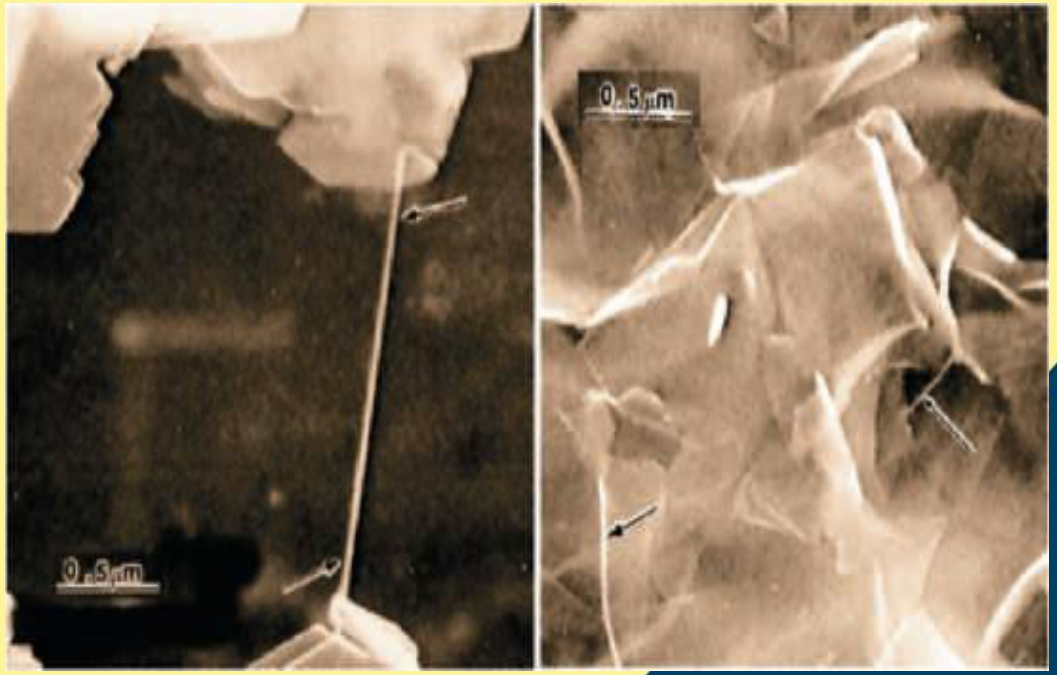
Bt toxin

- The adsorption Bt, a toxin, produced by a soil m.o. Bacillus thuringiensis.
- It is used in the organic farming for protecting crops from insect damage.
- It is adsorbed by the soil. The 2:1 clays like Montmorillonite can adsorb this toxin up to 30-80% of the its mass.
- 1:1 type of clay is not that efficient.
- The adsorption reaction completed within a minute.



DNA

- Scanning electron micrographs (SEMs) of DNA from Bacillus subtilis bound on kaolinite clay (left) and on mont-morillonite clay (right).
- The arrow point to stands of bound DNA.
- DNA bound to clay or humus is protected from decomposition but retains the capability of transferring genetic information to living cells.



Antibiotics

- The antibiotics also adsorbed by soil colloids via the process CEC.
- It also has a very high Kd values.
- After sorption, it develops positively charged sites in the soil.
- Increasingly research shows that even though sorption to soil colloids may reduce their efficacy somewhat, the soil-bound antibiotics still work against bacteria.
- There is evidence that at least some antibiotics can be taken up from soil by food crops and so enter the human food supply.
- It will increase the resistant against the life saving drugs in the body.

Chlortetracycline

- Adsorption isotherms illustrating the retention of chlortetracycline (CTC) by montmorillonite (pH 4.3–4.7) and kaolinite (pH 5.1–5.6) as a function of ionic background cation.
- CTC retention decreased in the presence of $Ca(NO_3)_2$ than $NaNO_3$.
- Ca^{2+} is more competitive with CTC than Na^{+}.
- So, CTC is adsorbed by the soil via CEC.