THE PHYSICAL, CHEMICAL AND BIOLOGICAL BASIS FOR NATURAL ATTENUATION OF SOIL CONTAMINANTS

by

Winfried E. H. Blum

Institute of Soil Research, Department of Forest and Soil Sciences, University of Natural Resources and Applied Life Sciences (BOKU), Vienna, Austria
soil profile with horizons
THE SIX MAIN FUNCTIONS OF SOIL

3 ECOLOGICAL FUNCTIONS:

1. PRODUCTION OF BIOMASS, ensuring food, fodder, renewable energy and raw materials
2. FILTERING, BUFFERING, and TRANSFORMATION between atmosphere, groundwater and plant cover protecting the environment
3. BIOLOGICAL HABITAT AND GENE RESERVE

3 TECHNICAL, INDUSTRIAL AND SOCIO-ECONOMIC FUNCTIONS:

4. SPATIAL BASE FOR TECHNICAL, INDUSTRIAL AND SOCIO-ECONOMIC STRUCTURES AND THEIR DEVELOPMENT, e.g. industry, housing, transport, sports, recreation, dumping of refuse etc.
5. SOURCE OF GEOGENIC ENERGY, RAW MATERIALS AND WATER
6. GEOGENIC AND CULTURAL HERITAGE, forming an essential part of the landscape and concealing paleontological and archaeological treasures
Filtration of solid and liquid compounds (mechanical)

Buffering through adsorption and precipitation (physico-chemical)

Transformation through alteration and decomposition (microbiological/biochemical)

Input of solid, liquid and gaseous inorganic and organic compounds e.g. pollutants

Vegetation

Solution by soil water

Uptake by plant roots

Output into the groundwater

Soil

Groundwater
5 MAIN SOIL PARAMETERS FOR FILTERING BUFFERING AND TRANSFORMATION

- total inner surface of the soil (total surface of the pore system/pore walls)
- constituents of the inner soil surface (e.g. clay minerals, oxides, o.m.), their specific structures and electrical charges (positive/negative)
- soil organisms (flora, fauna) in the pore space
- pH and redox potential of the soil (soil solution)
- soil temperature (energy)
5 MAIN SOIL PARAMETERS FOR FILTERING BUFFERING AND TRANSFORMATION

- total inner surface of the soil (total surface of the pore system/pore walls)
- constituents of the inner soil surface (e.g. clay minerals, oxides, o.m.), their specific structures and electrical charges (positive/negative)
- soil organisms (flora, fauna) in the pore space
- pH and redox potential of the soil (soil solution)
- soil temperature (energy)
Calculation of the Inner Surface of a Soil Volume

Soil volume (cut out) = 1 ha (100m x 100m) and 20 cm depth with a bulk density of 1.5 t m\(^{-3}\)
= 3000 t soil material

Assumption: soil volume containing

- 20% clay minerals (200 m\(^2\) surface g\(^{-1}\))
  = 600 t clay minerals
  = 600 Mio. x 200 = 120 Bio. m\(^2\) = 120 000 km\(^2\)

- 3% organic matter (humic substances) 1000 m\(^2\) surface g\(^{-1}\)
  = 90 t humic substances
  = 90 Mio x 1000 = 90 Bio. m\(^2\) = 90 000 km\(^2\)

Total surface = 210 000 km\(^2\)

Example:

The total land surface of Germany (= 356.854 km\(^2\)) is contained in a soil volume of 130 m x 130 m (1.7 ha) and 20 cm depth.
Fig. 3. Model of aggregate organisation with major binding agents indicated.

PORE VOLUME AND PORE SIZE DISTRIBUTION OF SOILS WITH DIFFERENT TEXTURE

The pore volume of soils is about 30 % - 65 % of the total soil volume, depending on soil texture, soil water content, soil biological activity etc.,

p.ex.: sandy soils ~ 36 - 56 % pore volume
loamy soils ~ 30 - 55 % pore volume
clay soils ~ 35 - 65 % pore volume

Pore Size Distribution:
- large macropores > 50 µm Ø
- small macropores 50 - 10 µm Ø
- media pores 10 - 0,2 µm Ø
- small pores < 0,2 µm Ø
Different pore sizes and constituents of a pore wall:

- Macro-pore: > 10μm
- Medium pore: 0.2-10 μm
- Small pore: < 0.2 μm
- Humic substances
- Clay minerals
- Oxides
# Importance of Pore Sizes for Physico-Chemical and Biological Soil Processes

<table>
<thead>
<tr>
<th>Pore Sizes</th>
<th>Hydraulic conductivity water retention capacity (in pF)</th>
<th>Biological conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>large macropores</td>
<td>excellent</td>
<td>large plant roots</td>
</tr>
<tr>
<td>&gt;50 µm Ø</td>
<td>0 – 1,8 pF</td>
<td></td>
</tr>
<tr>
<td>small macropores</td>
<td>good</td>
<td>small plant roots</td>
</tr>
<tr>
<td>50 – 10 µm Ø</td>
<td>1,8 – 2,5 pF</td>
<td>&gt; 10 µm Ø</td>
</tr>
<tr>
<td>medium pores</td>
<td>very limited</td>
<td>bacteria</td>
</tr>
<tr>
<td>10 – 0,2 µm Ø</td>
<td>2,5 – 4,2 pF</td>
<td>0,5 – 3 µm Ø</td>
</tr>
<tr>
<td>small pores</td>
<td>none</td>
<td>no space for plant roots or soil organisms</td>
</tr>
<tr>
<td>&lt;0,2 µm Ø</td>
<td>&gt;4,2 pF</td>
<td></td>
</tr>
</tbody>
</table>

*Note: Pore sizes are measured in micrometers (µm).*
5 MAIN SOIL PARAMETERS FOR FILTERING BUFFERING AND TRANSFORMATION

- total inner surface of the soil (total surface of the pore system/pore walls)
- constituents of the inner soil surface (e.g. clay minerals, oxides, o.m.), their specific structures and electrical charges (positive/negative)
- soil organisms (flora, fauna) in the pore space
- pH and redox potential of the soil (soil solution)
- soil temperature (energy)
Different pore sizes and constituents of a pore wall:

- Macro-pore > 10 µm
- Medium pore 0.2-10 µm
- Small pore < 0.2 µm
- Humic substances
- Clay minerals
- Oxides
Scheme of the Structure of a humus molecule bound to the surface of a clay mineral.

M = metal cation (Stevenson, 1982, mod.)
## SOLID PORE CONSTITUENTS: SURFACE STRUCTURES AND ELECTRIC CHARGES

<table>
<thead>
<tr>
<th>Solid Pore Constituent:</th>
<th>Specific Surface Structure:</th>
<th>Electric Charges:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary minerals</td>
<td>+</td>
<td>permanent, variable</td>
</tr>
<tr>
<td>Clay minerals</td>
<td>+++</td>
<td>permanent, variable</td>
</tr>
<tr>
<td>Oxides, Hydroxides</td>
<td>++</td>
<td>variable</td>
</tr>
<tr>
<td>Organic Matter</td>
<td>++</td>
<td>variable</td>
</tr>
</tbody>
</table>
5 MAIN SOIL PARAMETERS FOR FILTERING BUFFERING AND TRANSFORMATION

- total inner surface of the soil (total surface of the pore system/pore walls)
- constituents of the inner soil surface (e.g. clay minerals, oxides, o.m.), their specific structures and electrical charges (positive/negative)
- soil organisms (flora, fauna) in the pore space
- pH and redox potential of the soil (soil solution)
- soil temperature (energy)
Distribution of Biomass in a Pasture System
(per ha and 30 cm depth)

1.0 - 1.5 t (2 - 3 LSU)

25 t Biomass in the soil

10 t bacteria and actinomycetes
10 t fungi
4 t earth worms
1 t other soil animals
Ameba Flagellate Ameboid Protozoan Ciliate

Microfauna (0.002 - 0.2 mm)

Ameba Flagellate Ameboid Protozoan Ciliate

Mesofauna (0.2 - 2.0 mm)

Tardigrade Nematode Woodmite Springtail

Macrofauna (1- 20 mm)

Larva of a Beetle Isopod

Megafauna (> 20 mm)

Earthworm

Important Soil Fauna
Bacteria, Actinomycetes and Fungi

Blum (1995)
5 MAIN SOIL PARAMETERS FOR FILTERING BUFFERING AND TRANSFORMATION

- total inner surface of the soil (total surface of the pore system/pore walls)
- constituents of the inner soil surface (e.g. clay minerals, oxides, o.m.), their specific structures and electrical charges (positive/negative)
- soil organisms (flora, fauna) in the pore space
- pH and redox potential of the soil (soil solution)
- soil temperature (energy)
5 MAIN SOIL PARAMETERS FOR FILTERING BUFFERING AND TRANSFORMATION

- total inner surface of the soil (total surface of the pore system/pore walls)
- constituents of the inner soil surface (e.g. clay minerals, oxides, o.m.), their specific structures and electrical charges (positive/negative)
- soil organisms (flora, fauna) in the pore space
- pH and redox potential of the soil (soil solution)
- soil temperature (energy)
EXAMPLES FOR DIFFERENT REACTIONS
SOIL AS A PHYSICAL FILTER AND BUFFER SUBSTRATE
Soil as a physico-chemical Filter and Buffer Substrate (e.g. through hydrolyses, precipitation, adsorption, desorption, complexation, oxidation and reduction processes)
Fig. 6: Content of Cu, Zn, Cd and Pb in the equilibrium soil solutions of different soil types in relation to pH (HERMS and BRÜMMER, 1980)

- Zn
- Cd
- Cu
- Pb

Key:
- calcareous marsh soil
- brown earth
- sol lessivé
- acid brown earth
- podsol
Influence of organic matter (o.m.) on the pH-dependent solubility of Cu, Zn, Cd and Pb in soils (HERMS and BRÜMMER 1980)

---

Without o.m.

With addition of 5% fermented o.m. under sterile conditions
Influence of pH and redox conditions on the concentration of Zn, Cd, Pb and Cu in the equilibrium soil solution of the A horizon of an acid brown earth (HERMS and BRÜMMER, 1979)

+-----+ oxidizing conditions
|     | reductive conditions
HEAVY METAL ADSORPTION AT INNER SOIL SURFACES

Mineral surfaces (clay minerals, oxides):
Cd < Ni < Co < Zn << Cu < Pb << Hg
Reactions dominated by metal (M) ion hydrolyses
\[ M^{2+} + H_2O = MOH^+ + H^+ \]

Organic surfaces (humic acids)
Zn < Cd < Co < Ni < Cu < Sn < Hg
Reactions dominated by complexation
SPECIFIC HEAVY METAL REACTIONS BETWEEN SOLID AND LIQUID SOIL PHASES

1. Mechanical filtration of liquid and solid heavy metal compounds in the pore space
2. Uptake of heavy metals by soil organisms (biological binding)
3. Physico-chemical reactions:
   - adsorption and desorption by ion-exchange at the surface of solid soil constituents (e.g. o.m., clay minerals, oxides)
   - complexation by humic substances
   - occlusion in oxides through co-precipitation
   - structural binding in clay minerals and oxides through diffusion into the crystal structure
   - precipitation and dissolution of defined compounds, such as carbonates, phosphates, sulfides etc.
Soil as a biochemical/biological transformation medium (e.g. mineralization, metabolization)
Schematic presentation of common types of reactions by microbial populations after soil contamination through organic compounds, e.g. pesticides.

**TYPE A**

- Stress
- Max. depression
- Compensation of depression

**TYPE B**

- Stimulation
- Stress
- Max. depression
- Compensation

Reaction (% of control) vs. Time
Microbial metabolization and mineralization of 2,4,5-T under laboratory conditions

- aerob
- 25°C +/- 0.1°C
- 2.8 % w/w OM
- 15 % WC
- application rate: 1.7 kg ha⁻¹

- $t_{1/2} = 13 +/- 3d$
- $t_{90} = 40 +/- 3d$
<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Soil type</th>
<th>7 days</th>
<th>14 days</th>
<th>21 days</th>
<th>35 days</th>
<th>Half-life (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-D</td>
<td>Heavy clay</td>
<td>60</td>
<td>15 (100)+</td>
<td>-</td>
<td>-</td>
<td>&lt;7</td>
</tr>
<tr>
<td></td>
<td>Clay loam</td>
<td>40</td>
<td>&lt;5 (85)</td>
<td>-</td>
<td>-</td>
<td>&lt;7</td>
</tr>
<tr>
<td></td>
<td>Sandy loam</td>
<td>37</td>
<td>&lt;5 (92)</td>
<td>-</td>
<td>-</td>
<td>&lt;7</td>
</tr>
<tr>
<td>2,4-DB</td>
<td>Heavy clay</td>
<td>12(104)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;7</td>
</tr>
<tr>
<td></td>
<td>Clay loam</td>
<td>25 (81)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;7</td>
</tr>
<tr>
<td></td>
<td>Sandy loam</td>
<td>0 (102)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;7</td>
</tr>
<tr>
<td>2,4,5-T</td>
<td>Heavy clay</td>
<td>68</td>
<td>54</td>
<td>33</td>
<td>13 (85)</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Clay loam</td>
<td>76</td>
<td>44</td>
<td>30 (86)</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Sandy loam</td>
<td>58</td>
<td>36</td>
<td>25 (88)</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

**Breakdown of phenoxyalkanoic acid herbicides in soils**

Smith (1978)
Effect of Chemical Structure on Decomposition of Halogenated Phenols by Soil Microorganisms

Alexander (1971)
### Bacteria and actinomycetes which degrade phenoxyacetic acids

<table>
<thead>
<tr>
<th></th>
<th>2,4-Dichlorophenoxyacetic acid</th>
<th>2-Methyl-4-chlorophenoxyacetic acid</th>
<th>2,4,6-Trichlorophenoxyacetic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudomonas sp.</strong></td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Mycoplasma sp.</strong></td>
<td>+</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td><strong>Achromobacter sp.</strong></td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Achromobacter sp.</strong></td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Flavobacterium</strong></td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Actinomycetes</strong></td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Nocardia sp.</strong></td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Streptomyces</strong></td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Iridochromogenes</strong></td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Substrate in enrichment and isolation media.
TIME SCALE OF PHYSICO-CHEMICAL AND BIOLOGICAL/BIOCHEMICAL REACTIONS

- velocity of physico-chemical adsorption, desorption, complexation, hydrolyses, precipitation, oxidation, reduction etc. is rather high (seconds, minutes, hours);

- velocity of biological/biochemical mineralization and metabolisation is rather low (hours, days, weeks, years), also depending on aerobic or anaerobic conditions.
IMPORTANT PARAMETERS FOR MODELLING

- hydraulic properties of the soil, determining the quantity and velocity of solute movement
- type of constituents of the pore walls
- soil organisms (type and quantity) in the pore space
- pH and redox potential of the soil (soil solution)
- soil temperature
Filtration of solid and liquid compounds (mechanical)

Buffering through adsorption and precipitation (physico-chemical)

Transformation through alteration and decomposition (microbiological/biochemical)

Input of solid, liquid and gaseous inorganic and organic compounds e.g. pollutants

Uptake by plant roots

Solution by soil water

Output into the groundwater
CONCLUSIONS

For the natural attenuation of soil contaminants the following soil characteristics are important:

1. The total inner surface of the soil, specially the pore space (total volume, size distribution and stability);
2. The constituents of the pore walls: clay minerals, oxides, organic substances and their electrical charges (permanent, pH-dependent);
3. The organisms living in the pore space (macro and micro organisms);
4. The pH- and redox conditions;
5. The soil temperature.