BIODEGRADATION IN THE VADOSE ZONE

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Contents

Summary

Biodegradation in the vadose zone involves the transformation of organic matter through biological reactions mediated by soil enzymes and microbial metabolism. Organic materials, the majority of which consist of the recalcitrant fraction of organic substances derived from surface plant material or introduced to soils by agronomic practices, may govern subsurface microbial metabolism. The key role played by microorganisms in nutrient cycling is the enzymatic conversion of complex, high molecular-weight carbon compounds (polysaccharides, lipids, proteins, lignin, or humic material) either to simple low molecular-weight components (sugar, fatty acids or aminoacids, or phenolic compounds) or to inorganic compounds (CO_2, NH_3, SO_4, PO_4) in the available nutrient pool. This catalysis is driven largely by the physiological need of heterotrophic microorganisms for carbon and energy. In soil habitats, the most obvious evidence for microbiological cycling of nutrient elements is a balanced steady state between pools of soil organic matter, crop residues, leaf litter, and living vegetation. The linkages in soil between microbiological decomposition of crop residues, humification processes, and the growth of crop plants are obvious; but the same types of linkage are far from obvious in subsurface systems. Subsurface habitats are inaccessible, opaque, spatially and temporarily complex, and pose problems to any rigorous study of the role played by microorganisms in catalyzing an even nutrient cycle.

1. Introduction

Groundwater systems, including subsurface aquifer sediments and vadose zone formations, are precious yet vulnerable resources worthy of both protection and scientific investigation. Agricultural practices may involve unforeseen negative consequences such as erosion, biomagnification of pesticides, and nitrate pollution of

groundwater. Physical manipulations of the Earth's surface by humans in order to produce food—agricultural practices—are likely to influence subsurface microbial communities as they carry on their normal ecosystem processes beneath the Earth's surface (subsurface microbial ecology). Furthermore, the relationship between agricultural practices and subsurface microbial ecology is itself one of the "impacts." Implicit in this latter term is the fact that microorganisms are responsive to changes in their surroundings and that the responses may take many forms. Subsurface microbial ecology and agricultural practices have their own independent characteristics.

The terrestrial subsurface habitat lies directly beneath all continental portions of the globe. To access the terrestrial subsurface, one must excavate or drill through surface materials composed of soil or rock (in upland areas) or freshwater and sediments (in aquatic regions). It is this vertical stratification of the Earth's surface, and the implicit gradation of its exposure to climatic and biological influences, that makes surface and subsurface habitats distinctive. In descending from the surface of the Earth through the soil, one typically encounters materials in the following vertical sequence:

- the *A and B soil horizons*
- the *C soil horizon*, from which the other soil horizons may have been derived
- an *unsaturated* (or *vadose*) *zone*, that begins with the C horizon and ends at the water table, and
- a *capillary fringe zone*, residing directly above a saturated zone which may extend through many different geologic strata

The groundwater habitat begins immediately below the B soil horizon, the level at which soil scientists have traditionally felt that significant biological activity ceases. The transition between soil and groundwater habitats is not delineated by soil horizons as such, because the demarcation is gradual. Regardless of the type of overlying material (be it soil, rock, or freshwater bodies and sediment), however, the top of the subsurface occurs where the influences of climate, animals, and plant roots diminish, and are replaced by predominantly hydrological, geochemical, and microbiological influences.

Although freshwater habitats represent a relatively small proportion of the total continental surface area, free passage of water from the subsurface to lakes and stream and *vice versa* may have significant hydrological and biological impacts. This may be especially true for agriculture land, because components of the terrestrial habitat are frequently adjacent to freshwater bodies. In a hydrogeological sense, the term "groundwater" refers to water that is easily extractable from saturated, highly permeable geological strata known as *aquifers*. Groundwater may exist in many forms: as part of the crystal matrix of minerals in rocks, in unconnected pores within solid rocks, in connected pores in solid rocks, in the saturated portions of aquifers, and in unsaturated strata in capillaries and pores in the liquid gaseous and solid phases. To microorganisms, which live (by definition) in microhabitats, all available forms of water, except those in chemical combination with minerals, may be important. As a habitat for microorganisms the subsurface includes the unsaturated zone, since this may contain significant amounts of biologically available water. In addition, unsaturated zones may

be transiently saturated during recharge events and may influence both the chemistry and microbiology of the saturated zone below.

2. Vadose Zone

2.1. Definitions

The *vadose zone* is the unsaturated zone lying between the Earth's surface and the top of groundwater. It is also called the *zone of aeration*. Soil pores contain both air and water. The vadose zone is of zero thickness in swamp land but several hundred meters thick in mountain regions. It transmits rainwater to aquifers, while capillary forces hold water in place for plant uptake: this latter water body is not available as a human water-supply source. Initial amounts of water from precipitation onto dry soil are held very tightly as a film on the surfaces and in the micropores of soil particles in a belt of soil moisture. At intermediate levels the soil particles are covered with films of water, but air is still present in larger voids in the soil. The region in which such water is held is called the *unsaturated zone*, or *zone of aeration*, and the water present in it is *vadose water*. At lower depths, in the presence of adequate amounts of water all voids are filled to produce a zone of saturation, the upper level of which is marked by the *water table*.
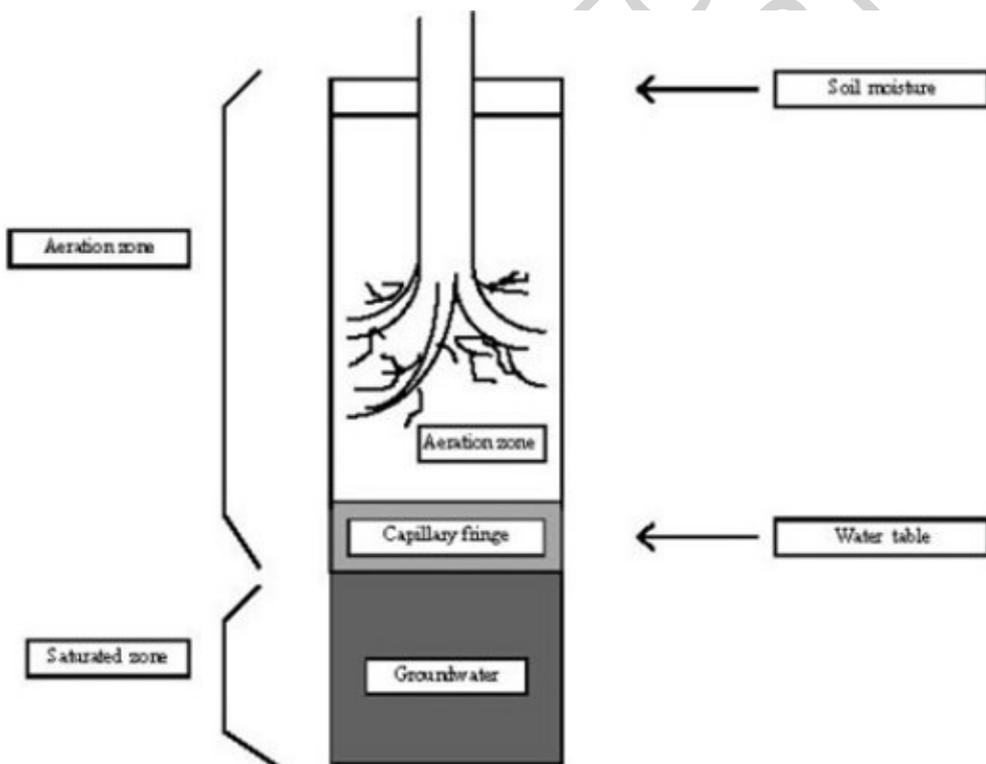
Figure 1. Some major features of the distribution of water underground

Water present in a zone of saturation is called *groundwater*. Because of its surface tension, water is drawn to a level somewhat above the water table itself by capillary-sized passages in a soil region called the *capillary fringe* (Figure 1). Groundwater flow is an important consideration in determining the accessibility of water for human use, and in assessing the risk of transport of pollutants from underground waste sites.

Groundwater flow is also strongly influenced by rock permeability. Porous or extensively fractured rock is relatively pervious, meaning that water can migrate through the holes, fissures, and pores. Because water can be extracted from such a formation, it is termed an *aquifer*. The amounts of water that can be extracted from such a formation are limited, and the water is vulnerable to contamination.

2.2. Environmental Interest

Technical study of the vadose zone focuses on the processes that control contaminant movement through the vadose zone soil to the groundwater. The physical and chemical interface between the vadose zone and the groundwater, and the movement of contaminants between the groundwater and rivers, are both of great interest. Characterization of the vadose zone is important because it serves as a repository for wastes, and as a potential pathway for the migration of wastes to the regional aquifer. Preventing this occurring requires cleansing operations in the vadose zone before the pollution reaches the groundwater; in fact, the vadose zone contains water in the pores of the soil that is used by plants.

In subsurface water systems, cationic contaminants (such as plutonium) are often adsorbed to soil particles because most soil particles are negatively charged. Those contaminants are mobilized only through the transport of colloids. In the vadose zone, soil interstitial water moves normally in fine pores rather than in coarse pores due to the capillary force. Colloids, moving in fine pores, are easily coagulated and filtered and then are less mobile. However, preferential flow through continuous macropores, such as earthworm holes, has been observed and investigated over decades. Such preferential flow, if it occurs, will transport colloids relatively easily and rapidly into the deep soil horizons and the groundwater system.

3. Soil

Soil is a variable mixture of minerals, organic matter, air, and water, capable of supporting plant life on the Earth's surface. It is the final product of the weathering action of physical, chemical, and biological processes on rocks, which largely produces clay minerals. The organic fraction of soil consists of plant biomass in various stages of decay. High populations of bacteria, fungi, and animals such as earthworms may be found in soil. Soil moves continually in a natural cycle aided by oxygen, water, minerals, and decomposing animal and plant matter. These elements create life in the soil, in a process that is ongoing if it is not disturbed. Good soil consists of 93% mineral and 7% bio-organic substances. The bio-organic parts are 85% humus, 10% roots, and 5% edaphon. Edaphon is itself a "world" of life consisting of microbes, fungi, bacteria, earthworms, microfauna, and macrofauna (Table 1).

Fungi/algae	40%
Bacteria/actinomycetes	40%
Earthworms	12%
Macrofauna	5%

Micro/mesofauna	3%

Table 1. Edaphon composition

Typical soils exhibit distinctive layers, or horizons, with increasing depth (Figure 2). The top layer of soil is known as the *A horizon*, or *topsoil*. This is the layer of maximum biological activity in the soil and contains most of the soil organic matter. The next layer is the *B horizon*, or *subsoil*. This receives materials, such as organic matter, salts, and clay particles, leached from the topsoil. The *C horizon* is composed of weathered parent rock from which the soil originated. The parent rocks from which soils are formed obviously play a major role in determining their composition.
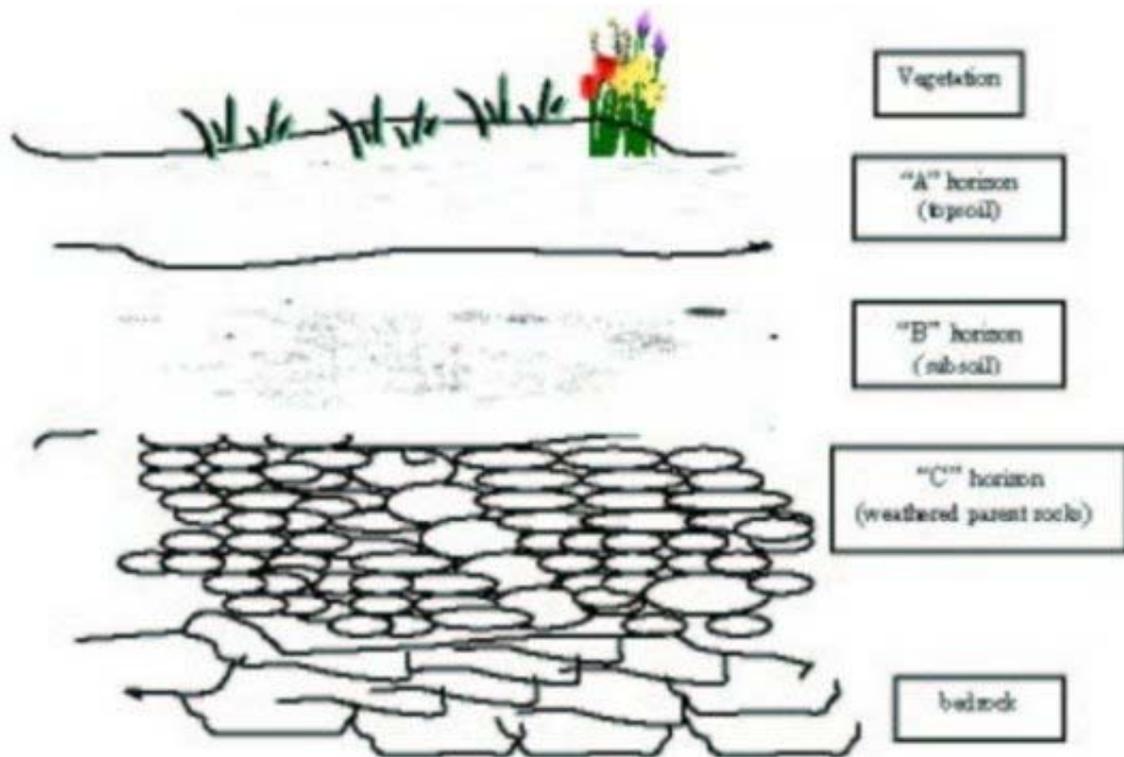

Figure 2. Soil profile showing soil horizons

3.1. Inorganic Components of Soil

The weathering of parent rocks and minerals to form inorganic soil components results ultimately in the formation of inorganic colloids. These colloids are repositories of water and plant nutrients, which may be made available to plants as required. Inorganic soil colloids often absorb toxic substances in soil, thus playing a role in the detoxification of substances that would otherwise harm plants. The uptake of plant nutrients by roots often involves complex interactions with water and inorganic materials. For example, a nutrient held by inorganic colloidal material has to traverse first the mineral/water interface and then the water/root interface. This process is often strongly influenced by the ionic structure of inorganic matter. The most common elements in the Earth's surface are oxygen, silicon, aluminum, iron, calcium, sodium,

potassium, and magnesium. Therefore, minerals composed of these elements constitute most of the mineral content of the soil. Common soil mineral constituents are quartz (SiO_2), orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), magnetite (Fe_3O_4), calcium and magnesium carbonate ($CaCO_3$, $CaCO_3.MgCO_3$), and oxides of manganese and titanium.

3.2. Organic Matter in Soil

Soil organic matter, comprising 5–7% of a productive soil, largely determines soil productivity. It serves as a source of food for microorganisms, undergoes chemical reactions such as ion exchange, and influences the physical properties of soil. Biologically active components of the organic soil fraction include polysaccharides, amino sugars, nucleotides, and organic sulfur and phosphorus compounds. Humus, a water-insoluble material that biodegrades very slowly, makes up the bulk of soil organic matter. The accumulation of organic matter in soil is strongly influenced by temperature and by the availability of oxygen. Since the rate of biodegradation decreases with decreasing temperature, organic matter does not degrade rapidly in colder climates and tends to accumulate in soil.

The presence of polycyclic aromatic (PAH) compounds, fluoranthene, pyrene, and chrysene, which in soil results partly from combustion from both natural sources (grass fires) or pollutant sources, is an interesting feature of soil organic matter.

3.2.1. Role of Organic Matter

Soil organic matter (SOM) is a key component affecting the natural physical–chemical and biological properties of soil.

- *Physical–chemical aspects:* SOM is responsible for structure (i.e. aggregate formation), which in turn affects bulk density, aeration, and water-retention characteristics.
- *Biological aspects:* SOM is the largest pool of nutrients for heterotrophic microbes, containing the bulk of the organic soil carbon and most (50–90%) of the total nitrogen, phosphorus, and sulfur.

The large nutrient pool is distributed (ideally) across three SOM phases: *active* (degraded in days or weeks), *slowly available* (months or years), and *inactive* (tens or hundreds of years). The majority of the organic nutrient pool appears to reside in the latter two categories, and SOM thus acts as a type of slow-release nutrient source.

3.3. Humus

Humus is the most significant component of soil organic matter. Composed of a base-soluble fraction (humic and fulvic acids) and an insoluble fraction (humin), it is the residue left when bacteria and fungi biodegrade plant material. The process by which humus is formed is called *humification*. Soil humus is similar to its lignin precursors, but has more carboxylic acid groups. Part of each molecule of humic substances is nonpolar and hydrophobic, and part is polar and hydrophilic. Humic materials, because of their heterogeneous chemical composition (and "lignin-like" composition), are

intrinsically resistant to microbial degradation. However, sorption to clays contributes to some extent at least to "protecting" SOM from degradation.

During humification, microorganisms convert organic carbon to CO_2 to obtain energy. Simultaneously, bacterial action incorporates bound nitrogen with the compounds produced by the decay processes. Despite their very low proportion (0.01–1%) by volume, SHSs are involved in fundamental physical, chemical, and biochemical activities in soil. *Physical activity* is expressed by the cohesion forces binding humic molecules towards clay minerals, thus reducing risks of soil erosion, stabilizing aggregates of soil particles, and increasing the sorption of organic compounds by soil.

In particular, humic materials in soil strongly sorb many solutes in soil water, have a particular affinity for heavy polyvalent cations, and also have a strong affinity for organic compounds with low-water solubility such as DDT or Atrazine (a herbicide widely used to kill weeds in cornfields).

Chemical activity is related mostly to the high levels of exchange with mineral elements that are released regularly in the root zone, thus contributing to balanced plant nutrition and to decreasing the availability of toxic heavy metals in soil. *Biochemical activity* is related to the content of enzymatically-active humic complexes called "extracellular enzymes," which cooperate with microbial activity in carrying out biochemical reactions even when soil conditions prohibit microbial life.

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Biographical Sketch

Dr. Grazia Masciandaro was born on 19 July 1967 at Matera, Italy. She graduated in Biology at the University of Pisa, where she works as a researcher at Institute for Soil Ecosystem Studies, Research Unit of Soil Chemistry ex Istituto per la Chimica del Terreno-Consiglio Nazionale delle Ricerche (ICT–CNR: Institute of Soil Chemistry–National Council of Researches). Her areas of specialization include soil chemistry and biochemistry, soil fertility and pollution, soil enzymology, soil organic matter, humic substances, wastewater purification and recycling in soil, sludge composting and soil amendment, soil mulching, and biomonitoring of soil ecosystem functionality. Her main research efforts lie in several areas, including: soil biochemistry; isolation and characterization of humus enzyme complexes from soil and compost; study of composting processes of green manures, straw, sludges and municipal organic wastes; anaerobic digestion and biomethanization of animal excreta and straw; soil amendment with organic and mineral wastes; plant nutrition and toxicity levels following manuring practices, including use of living mulches; wastewaters, municipal solid wastes treatment and recycling into the soil; water quality and irrigation, and plant biochemistry in stressed environments.

In 1990, Dr. Masciandaro completed her Doctoral thesis at the ICT–CNR Laboratory. In 1992 she undertook a Specialization Course at ICT–CNR to gain professional qualification; in 1993–5 she received a grant from ICT–CNR for research on the theme *Biological Soil Fertility*. In 1997 she was a member of the CCD (Convention to Combat Desertification) of the United Nations. In 1997–2000 she led an Italian–Spanish collaborative project involving CNR and Consejo Superior de Investigacion Cientifica (CSIC), Spain. In 1995 she ran a workshop on *Long-term perspectives for effects of rural land use changes on soil contaminants* at Arona, Italy. During stays at Way College, University of London (Kent), in 1997 and 2000 she carried out field experiments with mulch materials and studied the effects of mulching on soil biochemistry.

In 1995–2000 Dr Masciandaro was Assistant Professor of Soil Enzymology and Soil Biochemistry at the University of Pisa. She is a member of the Italian Agricultural Chemistry Society (SICA), the Italian Soil Science Society (SISS), the International Soil Science Society (ISSS), and the International Humic Substances Society (IHSS). She has over seventy publications to her credit.