PROCESSES CAUSING ATTENUATION IN THE UNSATURATED AND SATURATED ZONE

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Summary

Two zones are considered the most relevant physical media controlling the movement of water and pollutants: the unsaturated (vadose) zone and saturated depths. Contaminants arising from both point and non-point sources, such as municipal and hazardous waste landfills, suburban septic systems, mining and petroleum production, and agriculture, all filter through the vadose zone, where resident microbes, plant roots (rhizosphere), macrofauna (earthworms, ants, and termites), and organized colloids (humic matter, minerals) reduce their concentrations to levels acceptable by sanitary authorities. The principles of the vadose zone's functioning are not completely understood because of the presence of the many subsystems and their chemico-physical and biological interactions. The vadose zone (through the many microbiological and chemico-physical processes taking place) is potentially capable of blocking or/and

degrading any natural or artificially introduced contaminants flowing in deep waters. Soil overlying the water table provides the primary protection against groundwater pollution. Bacteria, sediment, and other insoluble forms of contamination become trapped within the soil pores. Some chemicals are absorbed or react chemically with various soil constituents, thereby preventing or slowing the migration of these pollutants into the groundwater. In addition, plants and soil microorganisms use some potential pollutants, such as nitrogen, as nutrients for growth, thereby depleting the amount that reaches the groundwater. In soils and sediments, the microbial mediated attenuation processes (natural or engineered) usually work through coupling electron acceptors such as nitrate, sulfate, and carbon dioxide with electron donors such as organic compounds.

1. Introduction

The aquifers are thought to behave as uniform, ideal porous media, but the heterogeneity of the many geological formations, preferential water flowing channels, natural biological barriers, physical interactions, geochemical reactions, and partition in the chemical phases, make pollutant transport, accumulation, and attenuation in saturated and unsaturated zones unpredictable. Technically grounded decision making for the vadose zone requires a full scientific understanding of the complex range of factors at work in this natural contaminant filter. A great variety of specific models are available to simulate movement, transport, and attenuation of an individual pollutant (pesticides below root zones, groundwater acidification, solvents, oil-derived compounds, viruses, biocolloids, sediments, nutrients, and so on), in saturated and unsaturated zones, have all been adopted for predicting groundwater contamination risks. However, studies based on laboratory simulative models have often failed in the assessment of pollutant geochemistry in real field conditions. Apart from the intrinsic heterogeneity and complexity of a particular site, the difficulty in predicting the fate of pollutants mostly arises from the lack of additional information such as frequency, time and point of infiltration, past history of the aquifer, and other forcing factors such as non-point contributions, climate, landscape, and land uses. Points of infiltration and land uses are the most important driving factors for pollutants' movement and attenuation. For example, ground surface intrusion may relates to sewage sludge disposal, dumps, animal feedlots, accidental spills, and infiltration of polluted water. Contamination of the zone above the water table may come from septic tanks, cesspools, holding ponds and lagoons, sanitary landfills, artificial recharge, underground pipeline leaks, graveyards, and waste disposal in excavation. Groundwater contamination is also possible through waste burial below the water table as well as bad maintenance of a variety of wells (exploratory, abandoned, water-supply, and waste disposal). Mine activity often constitutes a major cause of groundwater contamination because it seriously affects all aquifer layers and soil at the surface, above, and below the water table.

2. Principles of the Vadose Zone's Functioning

The principles of the vadose zone's functioning are not completely understood because of the presence of the many subsystems and their chemico-physical and biological interactions. Many disciplines have been introduced for the study and management of the vadose zone. This has dramatically implemented scientific knowledge of individual processes, but any attempt to drive these processes in such complex systems has resulted in difficulties, and the lessons learned from one site are not immediately transferable to others. In practice, this fragmented body of knowledge may be inadequate in terms of preventing groundwater contamination.

2.1. The Vadose Zone as a Natural Filter

The layer of soil and rock between the surface of the ground and an aquifer is called the vadose zone. This poorly studied "natural buffer" has been capable of protecting groundwater resources indefinitely through a natural abatement of pollutants entering the vadose system; however the advent of the modern industrialized era has brought with it serious risks of groundwater contamination from undesirable and harmful substances. That is to say, the vadose zone (through the many microbiological and chemico-physical processes taking place) was formerly potentially capable of blocking and/or degrading any natural or artificial-introduced contaminants flowing in deep waters. Today however, if we are to avoid pollutants overloading the vadose zone because of human activity, land-use planning is fundamental along with a multidisciplinary research to improve our understanding of such a complex system.

2.2. Soil Components

Soil is the thin upper part of the Earth's crust where rock (lithosphere), air (atmosphere), water (hydrosphere), and living organisms (biosphere) interpenetrate (pedosphere). Soils may indeed be the most complex systems known to science. Composed of inorganic and organic matter, and with solid, liquid, and gaseous components, they contain large numbers of living organisms—fungi, bacteria, micro-and macrofauna, rooting plants, and algae species—and are the medium that supports a wide biodiversity. Soil is commonly thought of as an inexhaustible resource that can be exploited for continually increasing production. On the contrary, since its formation takes place at the average rate of 100 to 400 years per cm of topsoil, soil must be considered as a non-renewable resource at human-life scale, and must be preserved. Unlike air, water, and biota, which are mobile systems, soil is site-specific, and although more stable than the other three systems, it shows great variability in space and time.

2.3. Main Functions of the Soil

Soils have at least six main functions relevant to human life and the environment:

- They are necessary for food and fiber production.
- They protect the food chain and drinking water reserves by filtering out both natural and chemical pollutants.
- They are a source of raw materials, such as clay, sand, and gravel for construction.
- Soils greatly contribute to the terrestrial cycling of the elements and to biochemical energy preservation as a stabilized (humified) carbon pool.
- They form biological habitats and gene material reserves.
- Finally, soils form an essential part of the landscape and biosphere in which human civilization has developed.

2.4. Structural Aspects of a Soil–Water–Plant System

Soil components are organized at various levels and in such a way that they continuously exchange energy and matter. The extent of exchanges depends on the water content and movement, and on soil porosity. Two zones are considered the most relevant physical media controlling water movement: the unsaturated (vadose) zone and saturated depths (Figure 1).

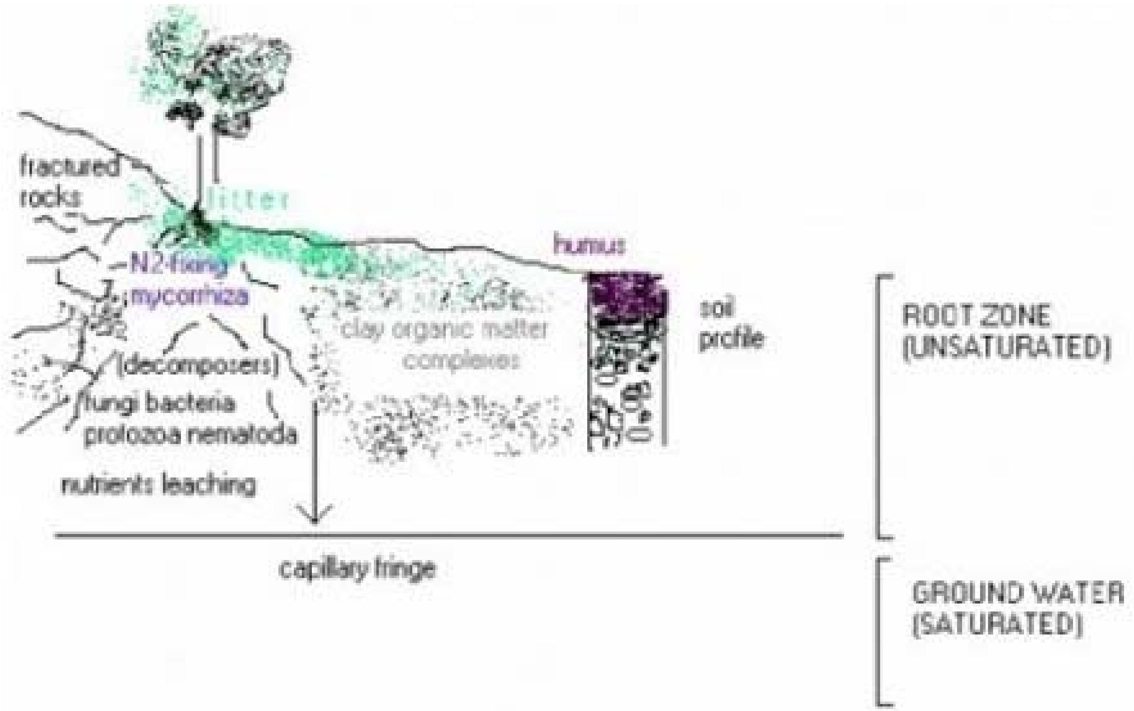

Figure 1. Schematized structure of a soil–water–plant system

2.5. Soil Water Characteristics

Soil water affects not only moisture available to living organisms but also soil aeration, nutrients' solubility and movement, osmotic pressure, pH of soil solution, and physical and chemical reactions. Soil water has currently been reported to exist in three forms: gravitational, capillary, and hygroscopic. The former is largely responsible for transport processes in soils following heavy rains, irrigation, flooding, and so on.

2.6. Matric and Osmotic Potentials

This currently accepted terminology refers respectively to bound and unbound water characteristics. Matrix-potential is expressed in Pascals (usually given in megapascals, MPa) and constitutes a negative value related to the free-energy reduction of water due to water attraction on soil surfaces. Solutes in the soils also reduce the free energy of water and create another negative potential, the osmotic potential. The combined matric and osmotic components of soil water determine the stress against which an organism must work to obtain water. Generally, microbial activity in soil is optimal at –0.01 Mpa; it decreases as the soil becomes waterlogged at near zero (saturated) water potential or more liable to drought (unsaturated) at large, negative water potential. Fungi are generally more tolerant of higher water potentials (greater water stress) than are bacteria.

3. The Unsaturated Zone

3.1. Physical Aspects

The unsaturated zone may contain air and water in the soil pores. Its thickness can range from zero meters, as when a lake or marsh is at the surface, to hundreds of meters, as is common in arid regions. Other names for the unsaturated zone are the "zone of aeration" and "vadose zone." The unsaturated zone holds only a tiny fraction of the Earth's fresh water and nutrients, which are vital for the biosphere. From the hydrologic point of view, the unsaturated zone is a zone that to a large degree controls the transmission of water and other substances to aquifers, land or surface water, and to the atmosphere. It controls the amount of water that replenishes an aquifer, and once the aquifer characteristics are known replenishment may be quantified and manipulated. Physical manipulation of the unsaturated zone should be based on determination of soil surface cracking, pore dimensional distribution and morphology, and pores dimensional classes.

Pores with a diameter of 0.5–50 μm, called "reservoir pores," contain water and mineral nutrients available for plants and microorganisms. Pores ranging from 50 to 500 μm are called "transmission pores" and are considered the most important in the soil–water–plant relationship. Pores greater than 500μm are called "cracks;" they are useful in root penetration and water permeability, and are indexes of low structural soil condition and low aggregates stability.

3.2. Biological Aspects

The unsaturated zone is continuously subjected to physical alteration by the cultivation of plants, construction of buildings, excavation of mineral ores, and disposal of waste. The heterogeneity in soil physical structure may lead to higher levels of microbial diversity, which is affected not only by cultivation regimes but also by the presence and activity of plants that create biopores and habitat for the mesofauna, which are directly responsible for much of the soil structure. Spatial heterogeneity in soil microbial communities occurs at a broad range of scales, from humic colloids (molecular interaction), microorganisms (cellular metabolism), macrobiota (earthworms, nematoda, roditors) soil mineral-organic particles (for example, soil macroaggregates), plant rhizospheres (complex microcosm), to field plots, and to the ecosystem and global levels.

4. The Saturated Zone

The zone below the unsaturated zone is characterized by pores saturated with water (saturated zone). Water in the saturated zone is referred to as groundwater and is the only subsurface water available to supply wells and springs. The term "water table" is often misused as a synonym for groundwater, but the water table is actually the boundary between the unsaturated and saturated zones (the capillary fringe). It represents the upper surface of the groundwater. Technically speaking, it is the level at which the hydraulic pressure is equal to atmospheric pressure.

The water table is the top of the saturated zone, or the area in which all interconnected spaces in rocks and soil are filled with water. In areas where the water table occurs at the ground's surface, the groundwater discharges into marshes, lakes, springs, or streams and evaporates into the atmosphere to form clouds, eventually falling back to earth again as rain or snow—thus beginning the cycle all over again. Groundwater is stored under many types of geologic conditions.

Areas where groundwater exists in sufficient quantities to supply wells or springs are called aquifers, a term that literally means "water bearer." Aquifers store water in the spaces between particles of sand, gravel, soil, and rock as well as cracks, pores, and channels in relatively solid rocks.

An aquifer's storage capacity is controlled largely by its porosity, or the relative amount of open space present to hold water. Its ability to transmit water, or permeability, is based in part on the size of these spaces and the extent to which they are connected.

4.1. The Vulnerability of an Aquifer

Most of the contaminants that commonly cause concern originate above ground, often as the result of human activities. It used to be generally thought that groundwater was indefinitely protected from contamination by the layers of rock and soil that act as filters, but practical experience has demonstrated that contaminants can infiltrate into groundwater and affect its quality.

Once groundwater has been contaminated, it is usually very difficult and costly to clean. The vulnerability of an aquifer to contamination is in large part a function of the susceptibility of its recharge area to infiltration. Areas that are replenished at a high rate are generally more vulnerable to pollution than those replenished more slowly.

4.1.1. Soil Filter

Unconfined aquifers that do not have a cover of dense material are susceptible to contamination. Bedrock areas with large fractures are also susceptible as these provide pathways for the contaminants. Confined, deep aquifers tend to be better protected with a dense layer of clay material. Soil overlying the water table provides the primary protection against groundwater pollution (Figure 2).

Bacteria, sediment, and other insoluble forms of contamination become trapped within the soil pores. Some chemicals are absorbed or react chemically with various soil constituents, thereby preventing or slowing the migration of these pollutants into the groundwater.

In addition, plants and soil microorganisms use some potential pollutants, such as nitrogen, as nutrients for growth, thereby depleting the amount that reaches the groundwater.

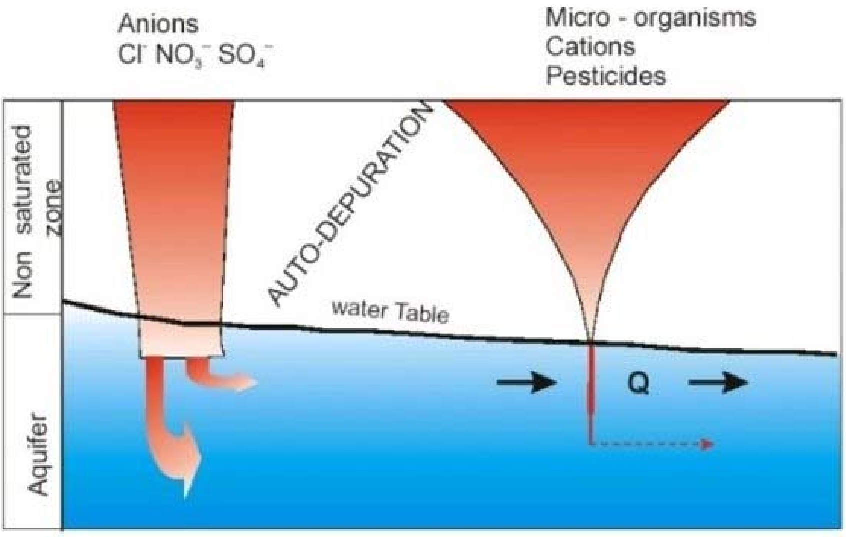

Figure 2. Different behavior of principal compounds in the vadose zone

5. Attenuation Processes

5.1. Natural Attenuation

During infiltration and transport in aquifers, many contaminants are naturally attenuated, depending on the characteristics and compound nature of specific sites (Figure 2). Progress has been made in recent years in understanding the underlying intrinsic physical, chemical, and biological processes of natural attenuation. However, much remains unclear, and especially the complexity of natural mechanisms and their efficiency in protecting groundwater. To date, quantitative information on the rates at which these processes occur has been limited. Often, it is wrongly thought that aggressive methods of remediation are more successful and quicker in protecting groundwater from pollutants than are gentle or natural methods. This approach has lead to an underestimation of studies on the naturally occurring mechanisms, which, in some cases, have been irremediably inhibited by aggressive interventions.

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Biographical Sketches

Brunello Ceccanti was born in 1948 in Peccioli (Pisa) in Italy and was awarded his Ph.D. in Chemistry at the University of Pisa. He is senior scientist at the Institute of Ecosystem Studies (ISE), Research Unit of Soil Chemistry, Consiglio Nazionale delle Ricerche (CNR), e-mail brunello.ceccanti@ise.cnr.it.

His areas of specialization include: soil chemistry and biochemistry, soil fertility and pollution, soil enzymology, soil organic matter, humic substances, wastewaters purification and recycling in soil, sludge composting and soil amendment, soil ecosystems biomonitoring, tannery waste, and wastewater reuse.

His main research efforts are centered on: the extraction and fractionation of soil humic substances; isolation and characterization of humus-enzyme complexes from soil and compost; study of composting processes of manures, straw, sludges and municipal organic wastes through earthworms; anaerobic digestion and biomethanization of animal excreta and straw; tannery wastewaters; soil amendment with organic and mineral wastes; chemical and biochemical processes in flooded soils; plant nutrition and toxicity following manuring practices; effects of S and N transformation in soils upon soil microbial activity; benefits and impacts of tannery sludges, wastewaters, municipal solid wastes recycling in soil; heavy metals in soil and plant pollution; water quality and irrigation.

His scientific activities at national level include: 1970–1978 laboratory, instrumental, and field experience in the study of soil biochemistry, soil humus, sludge processes and soil fertility, fertigation, earthworms, and vermicompost. 1979–1987 cooperation in the National Finalized Projects: "Amelioration of the Environmental Quality" and "Implementation of the Productivity and Agricultural Resources -IPRA." In 1986 Dr. Ceccanti was responsible for the "*Soil biochemical fertility*" research-line of the Institute. At international level: 1981–1986 CNR/Academia Sinica, (P.R. of China)- "*Phytotoxicity in flooded soils,*" and from 1985–1995 CNR/CSIC (Italy/Spain projects CNR-CSIC)

From 1989–2000 Dr Ceccanti was Assistant Professor of Soil Enzymology and Soil Biochemistry at the University of Pisa. He is a member of the following national and international societies: (SICA) Italian

Agric. Chem. Soc., (SISS) Italian Soil Science Soc., (ISSS) International Soil Science Soc., (SSSA) Soil Science Society of America, (IHSS) Int. Humic Substances Soc., and from 1994–1997 he was President of the Commission III: *Soil Biology* (Italian Soli Sci Soc.)

His consulting activity includes: member-consultant of the Special Commission for the Environment, Tuscany Region (1986); expert-witness appointed by the court on tannery wastes recycling in soil (1986); member-consultant of National Technical Commission for Wastewaters depuration (1988); and Expert of ICCD United Nations (1997).

Dr. Ceccanti has written more than 100 publications.

Roberto Spandre was born in 1950 and received a PhD in Geology from the University of Pisa, Italy and an M.Sc. in Hydrogeology from Complutense University, Madrid, in 1977.

Dr. Spandre has held the following posts: Invited Professor of Hydrology at UNAM, Universidad Nacional Autonoma de Mexico. Mexico City (1979); Senior Geologist, Libya, Geological Research Center, Florence, Italy (1980); Research Hydro geologist, Universidad Autonoma of Madrid; Foreign Office Ministry of Italy (1981–1991). Since 1991 he has been Research Hydro geologist and Titular Professor at the Earth Sciences Department, University of Pisa, Italy

His research projects and programs include work for: The European Community, Italian Ministry of University and Scientific and Technologic Research, National Research Council of Italy, Italian Foreign Office, and UNEP.

He is a member of the following professional bodies: AGID (Association of Geoscientists for International Development), IAH (International Association of Hydro geologists), IAEH (International Association of Environmental Hydrology), UNCCD (Convention to Combat Desertificacion), and CST (Committee on Science and Technology) of theUnited Nations.

Dr. Spandre has experience in the following countries: Spain (countrywide), Cuba, El Salvador, Ecuador, Colombia (Dep. Quindio), Mexico (DF, Aguascalientes, San Luis Potosi, Michoacan), Angola (Luanda, Benguela), Libya (Jabal Al Akdhar), India (Uttar Pradesh), Checa Republic, USA. (North Carolina), and Argentina (Province of Salta).

He is the author of 70 publications.