

ORGANIC COMPOUNDS IN THE VADOSE ZONE

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Summary

Groundwater contamination may arise from both point and non-point sources. Rainwater is responsible for the most serious infiltration of pollutants in soils. Methods for attenuating rainwater pollutant loads have been experimented with at the field scale. Agriculture, urban, and industrial activities release pollutants at soil surface, water table, and groundwater levels. Surface soil infiltration may be reduced by soil composting technology, which also may include the use of remediating trace amounts of toxics. However, on site bioremediation at the field scale is often impracticable due to the many unknown interactions between soil natural compounds and chemicals. These interactions may release intermediate metabolic compounds, which are highly active and can leach through the vadose zone.

1. Introduction

The area between the aquifer and the surface, the vadose zone, works like a giant sponge, soaking up water and contaminants. Groundwater contamination is common in highly developed industrialized areas, where urbanization, transportation, and industrial and agricultural activity affect surface and subsurface soil layers. However, in developing countries also, groundwater is suffering heavy pollution because of uncontrolled agricultural practices, improper management of paddy soils, mining, near-surface deposits of waste, domestic wastewaters and sewage sludge discharged into local channels, and overexploitation of forests. Different types of soils and landscapes, different rainfall retention and infiltration, and the recharge and discharge rates of the aquifers make movement and attenuation of pollutants in the vadose unpredictable. Contaminants in the groundwater may spread faster than predicted, or remain concentrated in slow-moving, localized plumes that may persist for many years. Scientists also predict that in the next few decades more contaminated aquifers will be discovered, new contaminants will be identified, and more contaminated groundwater will be discharged into wetlands, streams, and lakes.

Once an aquifer is contaminated, it may be unusable for decades. The residence time can be anywhere from two weeks to 10 000 years. Furthermore, the effects of groundwater contamination do not end with the loss of well-water supplies. Several studies have documented the migration of contaminants from disposal or spill sites to nearby lakes and rivers as this groundwater passes through the hydrologic cycle, but the processes are not as yet well understood. Contaminants may be present within the near-surface horizons, at lower depth within the vadose zone, or within the saturated zone. They may be adsorbed on the surface of mineral particles and organic matter, or be

associated predominantly within the aqueous phase, where they may occur in a truly dissolved, emulsified, or immiscible phase. Volatile contaminants will also infiltrate the gaseous phase within the interstitial space between soil particles.

2. Sources of Organic Pollutants

Human activity can significantly contribute to environmental pollution. Organic chemicals that spread in the environment and easily infiltrate into deep layers and groundwater are seriously affecting the possibility of using natural resources in the future.

Ground surface	
Infiltration of polluted surface water	Animal feedlots
Land disposal of organic wastes	Fertilizers & pesticides
Stockpiles	Accidental spills
Dumps	Airborne source particulates
Above water table	
Septic tanks	Underground pipeline leaks
Holding ponds & lagoons	Artificial recharge
Sanitary landfills	Sumps and dry wells
Waste disposal in excavations	Graveyards
Below water table	
Waste disposal in wells	Exploratory wells
Drainage wells and canals	Water-supply wells
Underground storage	Mines

Table 1. Activities that cause groundwater contamination

2.1. Rainwater and Stormwater Infiltration

Rain and storms can facilitate the infiltration into the vadose zone of pollutants that have accumulated onto ground surface. Emissions by urban and road traffic, industrial activity, oil refineries, incinerators, and smelters are significant sources of such pollutants. One of the most effective ways to mitigate rainwater pollution is to prevent potential pollutants from entering precipitation in the first place. This practice, known as source reduction, can also be the least expensive way to control a given pollutant. It is generally far more effective and cheaper to stop pollution at the source than it is to try to remove it after water has become contaminated.

2.2. Land Disposal of Organic Wastes

Although it is now a requirement that landfills be constructed with clay or synthetic liners and leachate collection systems, in the past thousands of landfills were built, operated, and abandoned without such safeguards. A number of these sites have caused serious groundwater contamination and are now being cleaned up by their owners, operators, or users. However, a lack of information about the location of many of these sites makes it difficult, if not impossible, to proceed to a remediation program. Improper

technologies of on-site soil remediation can often cause pollutants, including groundwater, to move off site.

2.3. Abandoned Wells

Each year many wells are plugged and abandoned throughout the world. These include water wells, mineral exploration wells, and oil and gas production wells. Many wells penetrate one or more aquifers. The well borehole provides a channel for fluids and gases to pass between geological formations. When aquifers are involved, this poses a severe pollution threat. For example, if the borehole passes through both an aquifer with potable water and a brine-bearing formation, the aquifer may be contaminated with salt water.

2.4. Holding Ponds and Lagoons

Potentially the most significant sources of groundwater contamination are surface impoundments (for example, ponds, lagoons) used by municipalities, industries, and businesses to store, treat, and dispose of a variety of liquid wastes and wastewater. Although these impoundments are supposed to be sealed with compacted clay soils or plastic liners, leaks can and do develop.

2.5. Agricultural Activities

Agricultural activities also can directly introduce chemicals and nutrients into the vadose zone. The millions of tons of fertilizers and pesticides that are spread onto the surface, together with livestock wastes, contribute significantly to groundwater contamination. Nutrients leaching under root zones, may enhance the metabolic activity of resident microbes, thus increasing the degradation of organic compounds and the formation of secondary metabolites. The fate and migration of these secondary pollutants are of increasing interest to scientists and sanitary authorities because of their (not completely understood) behavior in natural environments and for their possible concentration in the food chain.

2.6. Underground Storage Tanks

Millions of underground tanks are used to store a variety of materials, including gasoline, fuel oil, and numerous chemicals. The average life span of these tanks is only from 10 to 20 years, and over time, they may be subject to corrosion and leaking of the stored material.

2.7. Accidents and Illegal Dumping

Accidents also can result in groundwater contamination. Large volumes of toxic materials are transported across countries by truck, train, and airplane. Accidental chemical or petroleum product spills occur daily, and if they are not handled properly the result can be groundwater contamination. The instinctive reaction of the first people at the scene of an accident involving a spill is often to flush the area with water to dilute

the chemical. This just washes the chemical into the soil around the accident site, allowing it to work its way down to the groundwater.

2.8. Septic Systems

Septic systems are designed so that some of the sewage is degraded in the tank and some is degraded and absorbed by the surrounding sand and subsoil. Contaminants that may enter groundwater from septic systems include bacteria, viruses, detergents, and household cleaners. These can create serious contamination problems. Despite the fact that septic tanks and cesspools are known sources of contaminants, they are poorly monitored and little study is made of them.

3. Major Categories of Organic Pollutants

Organic pollutants can be divided into two basic categories: substances that occur naturally, and substances introduced by human activities. Natural substances (usually soluble in flowing subsurface water in extremely low proportions) may include metal-organic chelates, dissolved organic carbon, organic nitrogenous compounds, and chlorinated compounds. Substances resulting from human activities include hazardous synthetic organic chemicals and oil-derived products (for instance, light and heavy oil-derived hydrocarbons, solvents, and pesticides), leachates from waste, and sewage sludge land disposal facilities. Both natural and artificial organic compounds are of special interest because they may function as metabolizable substrata supporting microbial growth. When partially transformed, the intermediate products can move from the polluted site and affect the biogeochemistry of soil, degrade groundwater quality, and also pose toxicity risks for aquatic and terrestrial organisms.

3.1. Pesticides

Pesticides or other chemicals introduced into any particular geological and hydrogeological environment can enter groundwater. The probability of this happening depends on many contributing factors, including:

- water solubility
- rate of hydrolysis
- rate of chemical oxidation
- microbial activity of both soil and water
- volatility
- adsorption to soil
- physical characteristics of geological formations
- natural groundwater recharge
- irrigation practices
- method of application

Many of these parameters tend to be examined individually or in combination in attempts to explain and predict the behavior of pollutants in the terrestrial and groundwater environments. However, most of these controlling parameters are themselves functions of numerous independent variables, such as those attempting to

describe and explain the pesticide's behavior under various field conditions. Thus, in order to gain a general understanding of the behavior of a single pesticide in saturated and unsaturated zones, it is necessary to develop and evaluate mathematical models that can take into account sets of geological and hydrogeological conditions (site), chemical and physical properties (molecular susceptibility), microbiological activity and soil physical component heterogeneity (soil spatial variability), and analytical approach (which includes speciation, that is, the analysis of the pollutant forms responsible for migration and accumulation in different environments). From the many studies in the literature, it is apparent that the investigation of those sites susceptible to groundwater contamination requires interdisciplinary teams composed of soil scientists, computer scientists, chemists, hydrogeologists, and others.

3.1.1. The Most Frequently Detected Herbicides

Although numerous studies have been conducted into the occurrence of herbicides in groundwater, few of them have considered degradates of these herbicides.

Atrazine was the most frequently detected parent compound in many groundwater analyses. This is probably because of the comparatively slow rate of atrazine degradation under environmental conditions and its high rate of application in soils for many years.

Surprisingly, *prometon* was the second most frequently detected parent compound. Prometon is used primarily for nonagricultural purposes such as domestic and commercial applications to driveways, fences, lawns, and gardens, and as an asphalt additive. This demonstrates that agricultural activities are not the only sources of herbicide contamination of groundwater; nonagricultural activities (such as urban and suburban use) also may contribute to it. The limited information available about prometon suggests that it is used far less than most of the other herbicides examined. The low level of use may be compensated for by prometon's persistence in the environment, as it has the longest half-life of the herbicides examined.

Figure 1 displays the 10 pesticide compounds with the highest frequencies of detection at or above $0.05 \mu\text{g L}^{-1}$. The frequency of detection of pesticides and other surface-derived contaminants in groundwater might be expected to increase after extensive flooding because of the substantially higher rates of groundwater recharge that occur while the land surface is inundated. Seasonal patterns of pesticide application and groundwater recharge from either precipitation or irrigation are also likely to be responsible for seasonal fluctuations in pesticide detection frequencies observed during other investigations. Results from other studies indicate that the frequency of pesticide detection in shallow groundwater beneath agricultural areas generally increases during late spring and early summer (after major agricultural applications and rainfall have occurred in many areas), diminishes during late summer and autumn, and is lowest during the winter and early spring. These seasonal fluctuations in pesticide detection frequencies usually become more muted with increasing depth.

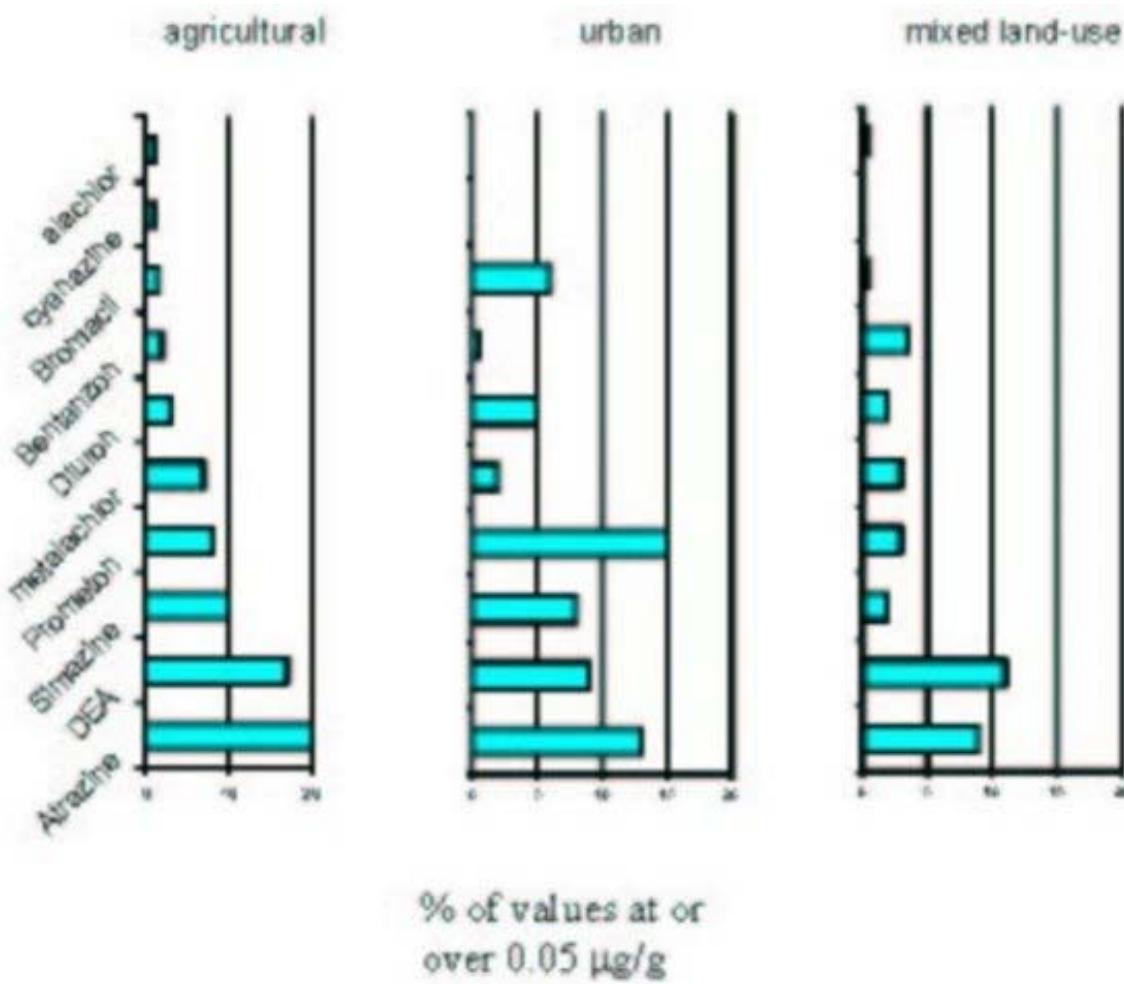


Figure 1. Frequency of occurrence (%) of the most frequently detected herbicides.

3.2. Nitro Aromatic Munitions

Various nitro aromatic compounds are released into the environment during manufacturing, load, assembly, and pack processes at ammunitions plants and other military facilities. They include 2,4,6-trinitrotoluene (TNT) hesahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5-tetrazocine (HMX), N-methyl-N-2,4,6-tetranitroanilina (tetryl), and associated by-products and degradation products. Many of the sites are located in marginal and relatively undisturbed lands that provide diverse habitats that support a variety of aquatic and terrestrial species. Nitro aromatics are potentially toxic to the indigenous species at these sites and present a significant concern for site bioremediation. A list of detected concentrations of the nitro aromatic compounds in groundwater, surface water, sediments, and soil at military and manufacturing sites shows that concentrations vary from undetectable to values higher than 20 000 to 36 000 µg L⁻¹ in groundwater, 200–3000 µg L⁻¹ in surface water, 40 000 to 711 000 mg kg⁻¹ in sediments, and 60 000 to 87000 mg kg⁻¹ soil for some chemicals. These may be critical concentrations for aquatic and soil organisms, mammals, and plants. The munitions chemicals are moderately or highly toxic to freshwater organisms, with chronic screening values < 1mg L⁻¹. The biodegradation process occurs in water,

soil, sediment, and sludge by bacterial and fungal species under both anaerobic and aerobic conditions. Primary transformation mechanisms involve photolysis, hydrolysis, and microbial degradation. Biodegradation proceeds more slowly than photolysis, with the estimated half-life ranging from one to six months in surface waters. Microbial degradation for both nitro and nitro amine aromatic compounds involves rapid reduction of nitro groups to amino groups, but further metabolism is slow. Transformation occurs faster under anaerobic conditions than under aerobic conditions. RDX was resistant to microbial degradation.

3.3. Polychlorinated *n*-Alkanes (PCAs)

Polychlorinated *n*-alkanes (PCAs) or chlorinated paraffins consist of C10 to C30 *n*-alkanes with chlorine content from 30% to 70%. The release of PCAs into the environment could occur during production, storage, transportation, industrial use, and carrying-off of manufactured products releasing from plastics, paints, flame retardants, and sealant in which they are incorporated, and leaching, runoff, or volatilization from landfill, sewage sludge-amended soils, or other waste disposal sites. Burning of waste containing PCAs may be another potential source of entry into the environment. There is limited information on the levels, fate, or biological effects of PCAs in the environment, resulting from the difficulty of quantifying PCAs (because of the complexity inherent to commercial formulation), and from the limited knowledge of their physicochemical properties and biodegradation rate. There are indications that PCAs are widespread environmental contaminants at ng L⁻¹ levels in surface waters and ng g⁻¹ levels in biota. Short chain PCAs with low chlorine content generally appear to have shorter half-lives in biodegradation experiments than persistent organochlorines such as PCBs, DDT, and chlordane. The hydrophobic nature of PCAs suggests that a large fraction is associated with suspended and bottom sediments. The rate of PCAs degradation was higher under anaerobic than aerobic conditions, and the higher chlorinated compounds (70% chlorine) was degraded to a greater extent than the lower chlorinated PCAs (42% chlorine).

3.3.1. Chlorinated Solvents

Trichloroethylene (TCE) can sink to the bottom of an aquifer and be a source of contamination for many years. The total mass of contaminants in saturated soil and groundwater is the sum of that in free phase, adsorbed phase, vapor phase, and aqueous phase. Unlike aerobic biological processes, anaerobic biotransformations occur for all chlorinated aliphatics, while aerobic biotransformations occur only for some of them. The lack of specificity in this process of dechlorination, coupled with the fact that most contaminated aquifers are anaerobic, may make anaerobic bioremediation an alternative or supplement to aerobic processes. *In situ* bioremediation, combined with electron acceptor bioremediation technology, is a promising technology that may be operated under conditions similar to those observed in contaminated aquifers. All of these technologies are based on the use of anaerobic bacteria at field scale, particularly methanotrophs, which successfully reduce the concentrations of three chlorinated aliphatics that are not degraded by aerobic bacteria: perchloroethene, 1,1,1-trichloroethane, and carbon tetrachloride.

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Biographical Sketches

Grazia Masciandaro was born in 1967 in Matera, Italy, and holds a doctorate in Biology from the University of Pisa. She is a research biologist at the Institute of Ecosystems Studies (ISE) – Research Unit of Soil Chemistry, Italian National Research Council, Pisa, Italy (e-mail grazia.masciandaro@ise.cnr.it). Her areas of specialization are: 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 mulching, and soil ecosystem functionality biomonitoring.

Hers main research efforts are centered on: soil biochemistry; isolation and characterization of humus-enzyme complexes from soil and compost; the 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 following manuring practices including living mulch; wastewaters, municipal solid wastes treatment and recycling into the soil; water quality and irrigation, and plant biochemistry in stressed environments.

Her scientific activities include at national level: Doctoral thesis at ICT-CNR Laboratory “Studio di un processo di digestione anaerobica della paglia e liquame suini per la produzione di metano e di un compost vegetale”(1990), Specialization Course at ICT-CNR for the professional qualification (1992), Grant of ICT-CNR on the theme “Biological Soil Fertility”(1992–1995), and in 1997 membership of the CCD (Convention to Combat Desertification) of the United Nations Non-Governmental Organization (NGO). At international level her activities include: leading an International Project CNR-CSIC (Italy-Spain) (1997–2000), and a workshop on “Long-term perspectives for effects of rural land use changes on

"soil contaminants" at Arona, Italy 8–10 June, 1995; a stage of six months at Way College, University of London (Kent) carrying out field experiments with mulching material, CNR fellowship (1997), a stage of 21 days at Way College, University of London (Kent) carrying out studies about mulching effects on soil biochemistry, and an OECD fellowship (2000).

She is a member of the following national and international societies: (SICA) Italian Agricultural Chemical Society, (SISS) Italian Soil Science Society, (ISSS) International Soil Science Society, and (IHSS) International Humic Substances Society.

From 1995–2000 she was Assistant Professor of Soil Enzymology and Soil Biochemistry at the University of Pisa, and she has authored more than 70 publications.

Brunello Ceccanti was born in 1948 in Peccioli (Pisa) in Italy and graduated in Chemistry at the University of Pisa with the title doctor Ph.D., and the position of senior scientist. He works at the Institute of Ecosystems Studies (ISE) – Research Unit of Soil Chemistry, Italian National Research Council, Pisa, Italy (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, wastewater purification and recycling in soil, sludge composting and soil amendment, soil ecosystem biomonitoring, tannery waste, and wastewater reuse.

His main research efforts are centered on: 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, and 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, fertilization, earthworms, and vermicompost; and 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 research-line of the Institute "*Soil biochemical fertility*." At international level he was involved in 1981–1986 CNR/Academia Sinica, (P.R. of China) "*Phytotoxicity in flooded soils*," and 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 Agricultural Chemistry Society, (SISS) Italian Soil Science Society, (ISSS) International Soil Science Society, (SSSA) Soil Science Society of America, (IHSS) International Humic Substances Society, and from 1994–1997 he was President of the Commission III: *Soil Biology* (Italian Soil Science Society).

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.