VITAL SOIL VERSUS CONTAMINANTS

P. DOELMAN
Doelman Advice, August Faliseweg 10, 6703 AS Wageningen,
the Netherlands p.doelman@chello.nl

1. Introduction

The vital soil gradually evolved after the formation of earth. Beyond the illusion of the day there should be awareness that recycling of elements is a phenomenon existing over billions of years. Whereas the anoxic processes are far older than the oxic ones and consequently have a longer history of evolution. The principle of the infallibility of nature in recycling of elements is also applicable for the biodegradation of organic contaminants.

The history of environmental pollution, resulting in soil/sediment contamination, is relatively short. One of the first pollution affairs dates from the Roman period (Hong et al., 1996) and refers to heavy metals, the open smelting of ores. Since than non-optimal metal-processing industries resulted in heavy metal fallout, causing elimination of sensitive species in soils but also adaptation. Metal resistant grasses are Agrostis and Festuca (Ernst 1989), whereas *Arabidopsis halleri* became a hyper accumulator of Zn (Ernst, 2004). The soil microflora (Doelman et al., 1994) and the soil fauna (Hopkins, 1994) became affected in many ways. The soil contamination by organics is more recent and is mostly the result of mismanagement, such as overdoses of plant-protection chemicals as DDT. Since the early 1950s there is concern on those issues. The book Silent Spring (Carson, 1962) questioned the accumulation of DDT in food chains: birds of prey became well known victims. The relation between soil contamination and higher animals is qualitatively and quantitatively shown by Van den Brink (2004). Simultaneously those spillages became a source of inspiration to study their fate as microbial degradation. The anaerobic degradation pathways of oil compounds such as BTEX (Wilson et al., 1986) and of degreasing compounds, applied in the dry cleaning industry, were discovered and could be applied in in-situ remediation. Degradation rates and preferable degradation conditions became known. In table 1 some relevant historical events are mentioned.

M.D. Annable et al. (eds.), Methods and Techniques for Cleaning-up Contaminated Sites, 35–44.

TABLE 1. Some relevant landmarks in the history of bioremediation

Event	**Years ago**	**Reference**
Origin of the universe	13.500.000.000	Bryson, 2003
Formation of earth	4.500.000.000	De Duve, 1995
Anaerobic bacteria	3.500.000.000	,,
Aerobic bacteria	2.000.000.000	,,
Origin eukaryotes	1.500.000.000	,,
Cambrian explosion	570.000.000	,,
Cretaceous mass extinction	65.000.000	,,
Homo sapiens	?: 2.000.000	
Open ore smelters	> 2.000	Hong et al., 1996
Pollution by organics	> 200	
Anaerobic degradation of BTEX	20	Wilson et al., 1986
Halorespiration of VOCl's	15	Holliger, 1992
Dioxine mineralization	2	Bunge et al., 2003
Dehalococcoides, as proven technoloy	0	Bemmel & Klijn, 2006

There is sufficient knowledge available on the recycling of elements, on the biodegradation of organic contaminants and on the ecological recovery of mal-treated soils to come to practical application. There are many lessons to be learned without re-inventing wheels. Whether contamination can be fatal to soil depends on he time period and the degree of contamination, or combinations of contamination, or combined contamination with natural stress. Mostly with a bird's eye view and sometimes in detail, information will be provided on the interaction between contamination and soil with an attempt to reduce the complexity of both to rather simple applicable handles.

2. Contaminants and Biodegradation Principles, Pathways and Rates in Soil

In principle the number of contaminants that has reached soil systems all over the world the last decades is innumerably large. For reasons of simplicity and predicting their behaviour, those "contaminants" can be classified in seven structural groups: heavy metals (H.M), persistent organic pollutants as HCH, HCB, DDT, Dioxine, PCB's, Drins (POP's), crude hydrocarbons and poly aromatic hydrocarbons (PAH's), mono aromatic compounds as Benzene, Toluene, Ethylbenzene and Xylenes (BTEX), chlorinated aliphatics as PER, TRI and chlorinated benzenes, -phenols, etc (VOCl's), Cyanides (CN) and eutrophication elements as nitrogen and phosphorous (N,P). Their behaviour in the process of natural attenuation and the uptake by plants and the soil fauna is qualitatively given in table 2. Natural attenuation is, according to the United States Environmental Protection Agency (USEPA), the process of biodegradation, diffusion, dilution, sorption, volatilisation and chemical stabilization. The scientific literature is loaded with detail information.

TABLE 2. Overview of attenuation processes that affect the persistence of contaminants in soil

	H.M	**POP's**	**PAH's**	**BTEX**	**VOCl's**	**CN**
Sorption	++	+++	+++	+	+	+<>+++
Diffusion	+	+	+	++++	+++	+<>+++
Dilution	+	+	+	++++	+++	o<>+++
Evaporation	O	O	O	++++	++	O<>+++
Microbial transformation	+	+ <>++++	o<>++++	+++++	+++	O<>+++++
Chemical stabilization	+	+++	+++	+	+	+++
Uptake plants	++	O	O	O	O	O
Uptake soil fauna	++	++	++	O	O	+

++++: very general and strong
+++: general and strong
++: regularly
+: seldom/hardly
o: not

A Selection of the History of Biodegradation Research

Knowledge on the fate of contaminants in various soil types has also been obtained during decades. Here the attention will mainly be paid to biodegradation. General principles of biodegradation have been published by Alexander (1985) and many others. Atlas (1981) published the general aspects of biodegradation of hydrocarbons (Atlas, 1981). Wilson (1986) and co-workers were one of the first to discover the anaerobic degradation of BTEX and to implement it into in-situ bioremediation of groundwater. The anaerobic degradation of HCH was proven in the laboratory by Bachmann et al. (1988) and in the field by Doelman et al. (1990). For hexachlorocyclohexane (HCH) it took 12 years before the principle of biodegradation was partly unraveled. It should be emphasized that the limitation of biodegradation of organics is often due to non-optimal environmental conditions (Doelman and Breedveld (1999). For that reason in figure 1 the biodegradation of alpha-HCH under various conditions is given.

Already in 1973 Dennis Focht unravelled the degradation pathway of DDT, due to the successive different environmental conditions and consequently the contribution of different micro-organisms. So principally the mineralization of

DDT in soil may occur, however in some areas DDT is still a threat in food chains. The biodegradation of dioxine by halorespiration has been suggested in 2003 by Bunge and co-workers. However in 1995 Peter Adriaens already indicated in that direction by showing partly dechlorination of dioxins.

The halorespiring bacteria *Dehalococcoides* may play a crucial role in the bioremediation of soil and groundwater contaminated with VOCl's and POP's. *Dehalocococoides* has been discovered all over the world. Recently a Halococcoides-like bacterial strain has been isolated from HCB (hexa chloro benzene) contaminated sediment, enable to grow on HCB (Van Eekert, 2004, personal communication).

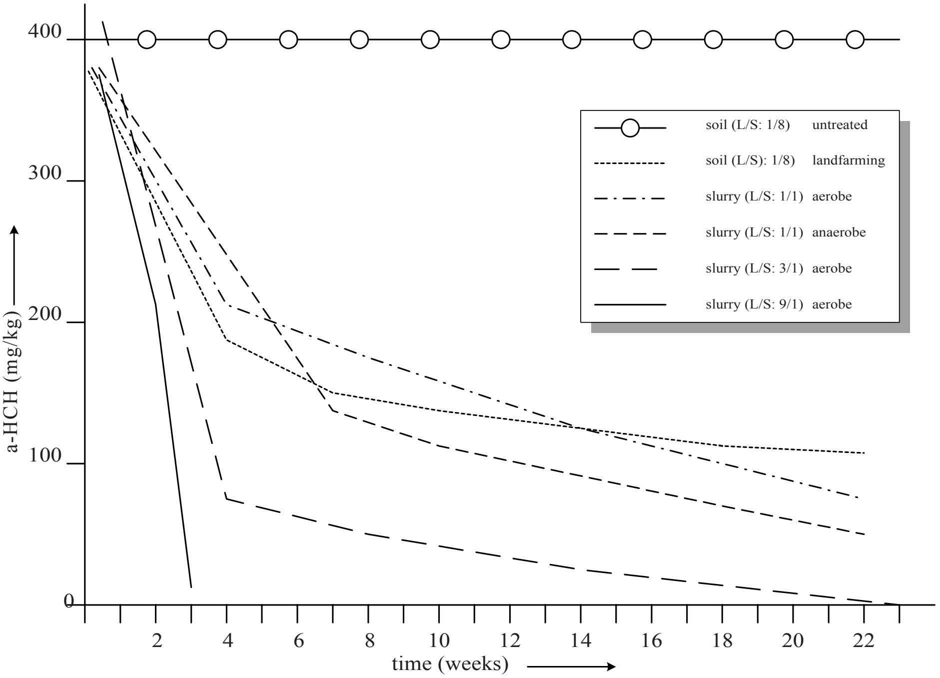


Figure 1. The biodegradation of alpha-HCH under various conditions

Since the biodegradation pathway of the various POP's can be very large and complex, it may be a suggestion to measure relevant intermediates, by checking the phase of degradation. Depending on environmental conditions chloro-phenoles and chloro-benzenes are considered to be key-intermediates. For several POP's the route to phenols has been given in figure 2.

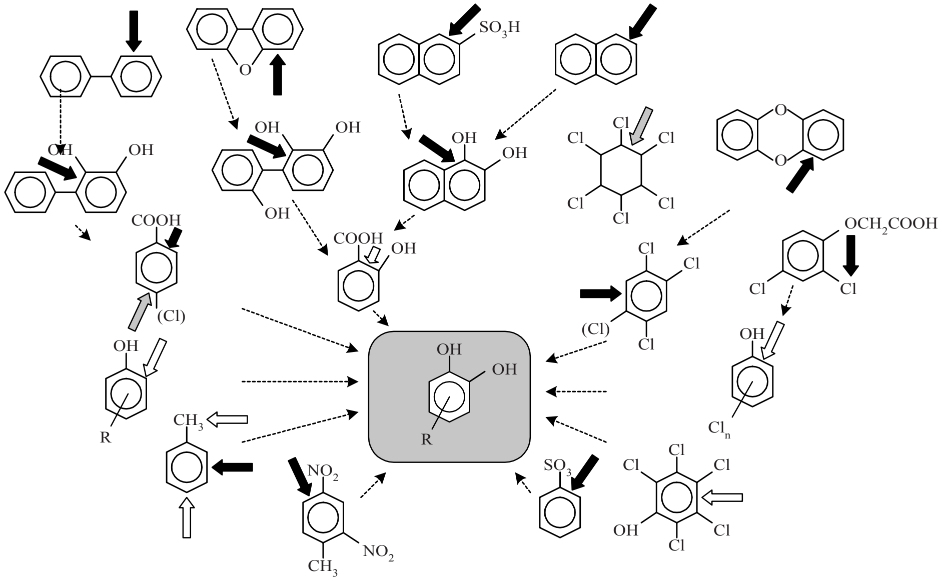
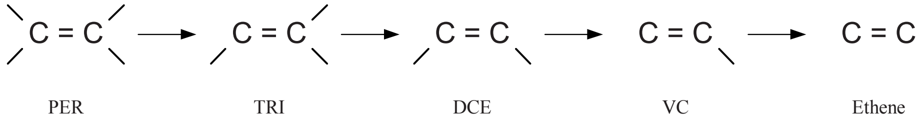


Figure 2. The degradation route of several POP's to phenoles (chlorinated)

Till the end of the 1970s the anaerobic microbial degradation of halogenated compounds such as PER (tetrachloroethene) and TRI (trichloroethene) was generally considered as "not occuring". In the eighties reductive dechlorination (Bouwer and McCarty, 1983) was discovered as a new phenomenon, leading to the formation of less harmful compounds. Then around 1992, also due to appearance of the PhD-theses of Holliger and others facts and principles on microbial degradation of chlorinated compounds became clearer.

The anaerobic microbial degradation of chlorinated xenobiotics became general knowledge, and applicable to bio-remediation. It became clear that bacteria can use PER (tetra chloro ethane) and other chlorinated compounds as electron acceptor. The role of the various prevailing electron acceptors, such as O_2, NO_3^-, Fe_3^+, SO_4^{2-} and CO_2 and various electron donors became clear. For example the fact that in the presence of nitrate complete dehalogenation seems to be impossible. The principle of "halorespiration" was added to the phenomenon of recycling elements. Suitable electron-donors and suitable environmental conditions became aspects to study to apply dechlorination in in-situ bio-remediation processes. BioSoil R&D developed together with the laboratory of Microbiology of the Wageningen University a technique for the anaerobic dehalogenation of PER, TRI (tri chloro ethene) and a number of chlorinated hydrocarbons. This technique is now widely applied both in- and outside The Netherlands. The determination of the intermediates and their ratio show the degree of degradation. The degradation pathway is:



Biodegradation Rates

From ten VOCl in-situ bioremediation locations in the city of Rotterdam (the Netherlands) Den Haan (2003) calculated the average biodegradation rate as first order constant. These values are given in table 3. The groundwater conditions were sulphate-reducing and methanogenic, while the DOC (dissolved organic content) was rather high due to the soil type, which was predominantly peat and loam.

TABLE 3. First order degradation rates of VOCl's

	Calculated rates from literature; until 1997	**Degradation rate in Rotterdam groundwater; until 2003**	**Degradation rate after introduction of Dehalococcoides (Bemmel & Klijn, 2006)**
PER	0.0023	0.0088	0.09
TRI	0.0033	0.0076	–
DCE	0.0038	0.0094	–
VC	0.0015	0.0049	–

The rates in Rotterdam are about 3 times higher than average literature value (Table 4). Those field rates are far lower than rates determined under laboratory conditions. Rates from laboratory data can not be translated to field expectations on an one to one basis. Nowadays (2006) bioremediation of PER can be called in The Netherlands "proven technology". This due to changing environmental conditions towards extreme anoxic conditions by addition of organinc matter the bacterial strain Dehalococcoides, as published by Bemmel and Klijn (2006). In principle the biodegradation of complex organics in the field (in-situ) is slow, as shown by Van der Werff (1992) for vegetation types.

TABLE 4. Some typical examples of degradation rate constants (k) of organic matter of defined vegetations (modified after Van der Werff, 1992)

Type of predominant vegetation	***k***	**Type of predominant vegetation**	***K***
Phragmites australis	0,0035	*Scirpus americanus*	0,0021-0,0025
Phragmites karka	0,0045	*Scirpus mucronatus*	0,0044
Typha domingensis	0,0078	*Juncus squarrosus*	0,0013
Typha glauca	0,0014	*Juncus roemerianus*	0,0016-0,0017
Typha Latifolia	0,0043	*Paspalum repens*	0,00717
Typha angustata	0,006	*Carex rostrata*	0,0046
Typha elephantina	0,0038	*Carex riparia*	0,0029
Scirpus fluviatilis	0,0018	*Zizania aquatica*	0,077

3. Fundamental Knowledge and Practical Monitoring Options

When a soil adapts to changes by microbial degradation of the contaminant, binding or becoming resistant it shows its vitality. Fatal may be sudden changes leading to another functioning (Ernst, 2002) or even to no functioning at all. It is the author's view that the state of the art on soil functioning is sufficient to predict the consequences of soil contamination. There is practical experience, all over the world, to predict where sustainable soil functioning is under threat due to contamination. Judging the sustainability, the health, the value or the functioning should not only contain that chemical aspects but also soil physical, soil chemical and soil biological ones (Figure 3).

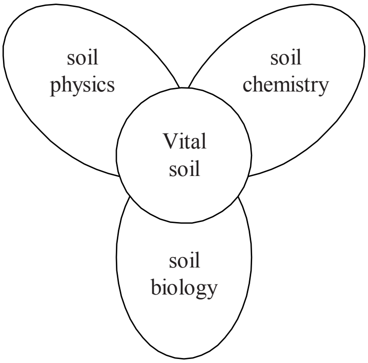


Figure 3. The golden triangle to monitor soil vitality

Implementation of bioremediation techniques demands those controlling monitoring options. Only in combination they are the basic elements of soil vitality. In relation to remediation the presence and action of the relevant microflora can be determined by molecular techniques. The basic soil chemical properties are soil type with carbon-content and -turn over, nitrogen and phosphorous content, and electron acceptors. Soil structure relates to physical properties. The bulk density of a soil is extremely important, but too often neglected in soil ecological contemplation and monitoring options. Waters and Oades (1991) show very nicely that the pore size of soils determines the presence possibilities of soil biota. This adds to the earlier emphasized saying that environmental conditions are the keys to specific aimed functioning of the soil system. The biological aspects contain microbial biomass, species diversity and functional diversity of earthworms and nematodes and many others. Specific monitoring sets can be attuned to various contamination groups (Table 5) (Doelman, 2004). For detailed information beyond this table 5, the various chapters Vital Soil (Doelman and Eijsackers, 2004) are recommended, since this table more or less combines in a synthesized way all chapters.

TABLE 5. Specific monitoring sets attuned to various contamination compound groups

<table>
<tr><td colspan="2">Carbon content
N content
Soil type
Soil compaction (structure)
Soil pH, redox
Landscape structure</td></tr>
<tr><td>Heavy metals</td><td>POPs (+ PAHs)</td></tr>
<tr><td>Chemical litter composition
Bacterial biomass
Bacteria: ratio sensitive/resistance
Nematodes: MI and functional diversity
Earthworms: species diversity and bio-accumulation
Soil fauna
Food web accumulation
Extractable level heavy metals</td><td>Bacteria: catabolic genes
Biodegradation rate
Earthworms: species diversity and bio-accumulation
Food web accumulation
Extractable level POP and PAH</td></tr>
</table>

Besides nematodes and earthworms the bio-accumulation of heavy metals and POP's and PAH's in food chains are illustrative mirrors of the quality of soil. The state of the art of nematodes overlaps the state of the practice, and has been applied all over the world (Bongers, 1990; Bongers and Ferris, 1999; Yeates and Bongers, 1999) Its application is based on species diversity and the functional meaning of the species composition (Figure 4).

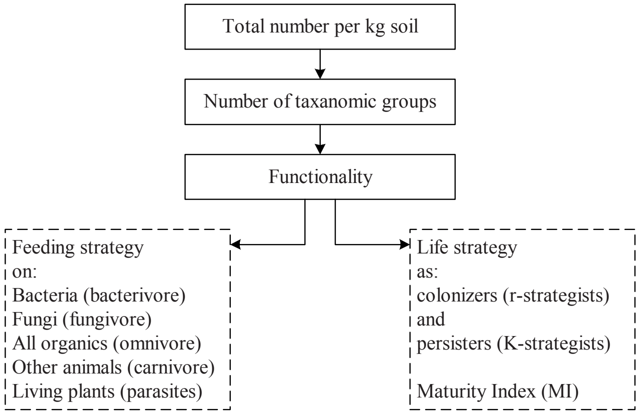


Figure 4. Nematode characterization on two aspects of functional diversity

The ambition for the soils system (what to plan, what to want, what to anticipate) determines the relevant monitoring schedule. The ambition to have or to maintain agriculture, is quite different from obtaining city green or obtaining an ecological system with an extensive biodiversity. Ecological recovery in general is a long lasting process of many years.

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