

Intrinsic and stimulated in situ biodegradation of Hexachlorocyclohexane (HCH)

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Introduction

The pollution of soil and groundwater with hexachlorocyclohexane (HCH) has caused serious environmental problems. Lindane (gamma-HCH) is the best known and effective insecticide component of HCH, and only 17% of HCH consists of this gamma-isomer. The remaining part consists of alpha-, beta- and delta-HCH, which do not have insecticide activity. These isomers were separated from gamma-HCH, and dumped at waste sites resulting in polluted soils and groundwater. In contrast to alpha-, gamma- and delta-HCH, beta-HCH was for a long time known as recalcitrant towards biodegradation under anaerobic and aerobic conditions (1). However, recent research has shown that beta-HCH can be microbologically degraded to the intermediates monochlorobenzene and benzene under anaerobic conditions (3, 5). Complete mineralisation of all HCH-isomers can thus be expected, as these intermediates can be biodegraded aerobically and some anaerobically. HCH-biodegradation is summarised in Figure 1.

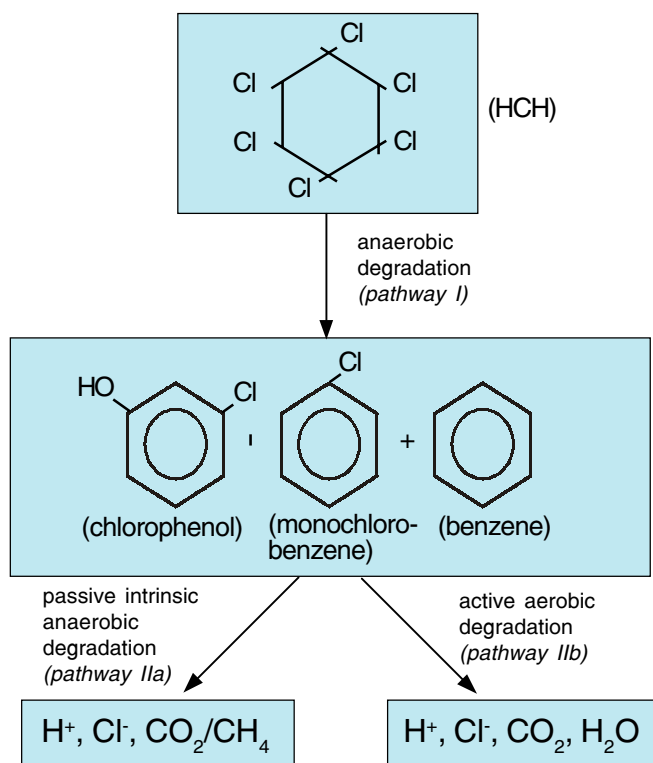


Figure 1. HCH-biodegradation pathways

In this paper the feasibility of anaerobic and aerobic biodegradation of HCH and its intermediates will be discussed, and the concept of a combined intrinsic and stimulated *in situ* bioremediation will be evaluated for HCH contaminated sites, using data obtained at an industrial and a non-industrial site.

Materials and methods

Field characterisation

The geohydrological situation of the industrial and non-industrial site has been characterised. Ten sampling wells have been installed at various depths in selected areas at the two sites to analyse the soil and groundwater on the following parameters:

- 1) organic compounds; hexachlorocyclohexane isomers (HCH), monochlorobenzene (MCB), benzene (B) and chlorophenols (CP)
- 2) redox parameters; O_2 , Mn(IV)/Mn(II), NO_3^-/NO_2^- , Fe(III)/Fe(II), SO_4^{2-}/S^{2-} and HCO_3^-/CH_4
- 3) electron donor capacity; DOC, TOC and N-Kjehldal

A selected area of the industrial site forms a small part of the total contaminated industrial site and will serve as the pilot plant.

Batch experiments

Batch experiments are performed with sediment and groundwater from the two sites. With material from the industrial site, the stimulation of the anaerobic degradation of HCH is tested by the addition of lactate, landfill percolate, and compost percolate. For the non-industrial site, the natural anaerobic degradation is tested only. In addition, the natural anaerobic degradation capacity of the sites is tested for monochlorobenzene and benzene as well as the aerobic degradation via the addition of oxygen.

Results and discussion

Non-industrial site

Site description

Lindane has been produced in the eastern part of the Netherlands from 1948 until 1954. Nowadays it is imported to manufacture lindane-containing products (4). HCH waste isomers were at that time amended with lime and stored at the industrial production site. A portion of this material was spread over the region (province) because it was used as backfilling material in roads and farmyards. The topsoil layer of most of these sites contained high concentrations of HCH and was removed a few years ago. However, the combination of rainfall and varying groundwater levels has caused heterogeneous groundwater contamination in the years before the removal of the topsoil layer. The non-industrial site is such a location with a removed top layer.

Field characterisation

Three defined sandy aquifers can be defined to a depth of 25 meter, and are separated by a peat-clay layer. The groundwater velocities are maximum 25 m.yr^{-1} in the three aquifers.

The concentration of HCH decreases over time and space, and the two breakdown products (monochlorobenzene and benzene) are found in the core of the HCH-plume. The monochlorobenzene and benzene concentrations are decreasing in the first aquifer, indicating intrinsic biodegradation of these compounds, see Figure 2. In the second and third aquifer, HCH, MCB, and B are hardly present.

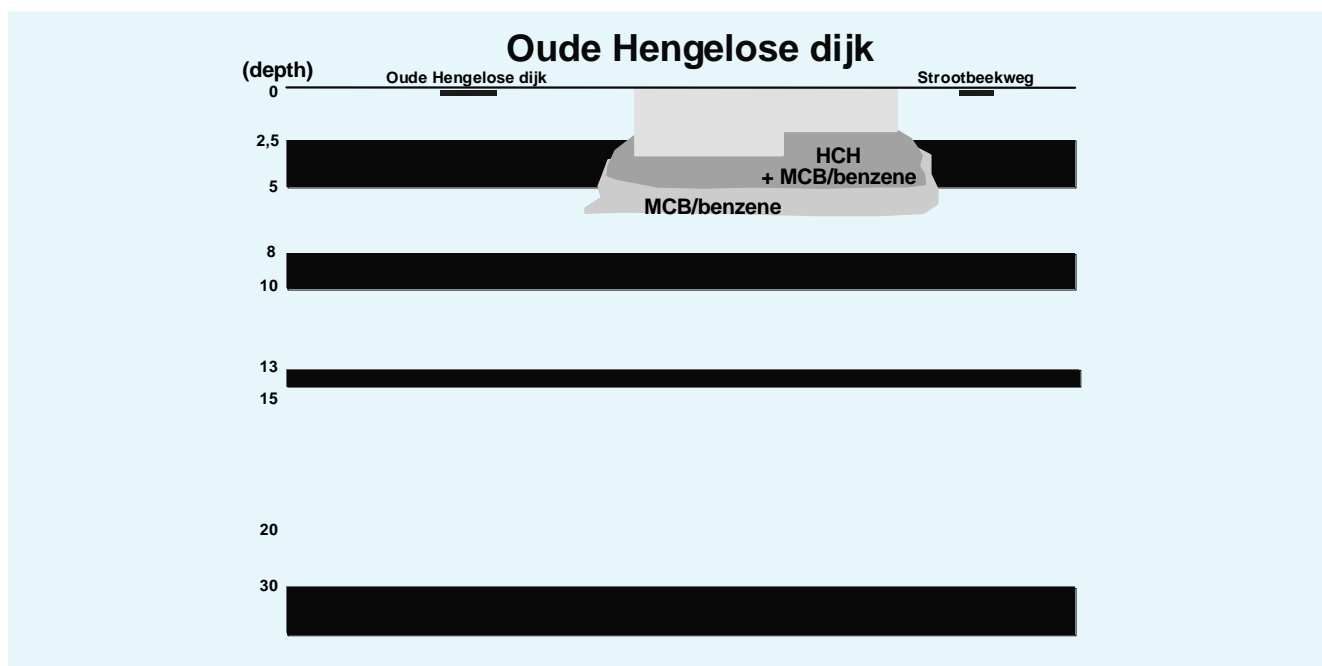


Figure 2. An overview of the non-industrial site in the eastern part of the Netherlands.

The redox potential characterisation of the source area of the first aquifer showed indications of iron- and sulphate reducing conditions. These low redox potential conditions are reported to be favourable for reductive dechlorination, but less favourable for the degradation of the formed intermediates. In the downstream part of the plume, iron-reducing conditions were found to be predominant. As intermediates of the dechlorination process were found, this indicates that intrinsic biodegradation of HCH does take place at this location.

Batch experiments

A laboratory microcosm study with sediment and groundwater of the non-industrial site was performed to confirm the intrinsic biodegradation of HCH. Depending on the contaminated site conditions, the *intrinsic anaerobic degradation* capacity of endogenous microorganisms may be sufficient to degrade HCH and the produced intermediates monochlorobenzene and benzene. In addition to the HCH already present in the soil samples, HCH was added. After an initial adsorption during the first three weeks, HCH-degradation started and monochlorobenzene and benzene were produced, see Figure 3.

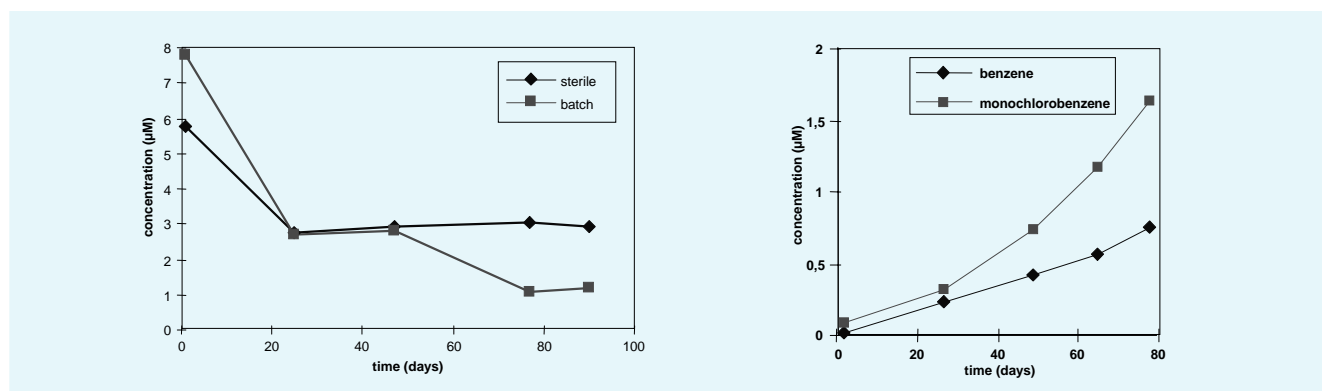


Figure 3. Intrinsic HCH-degradation and MCB and B production with subsurface solids and groundwater from a non-industrial site.

The biodegradation of the formed intermediates monochlorobenzene and benzene was tested under anaerobic conditions. After 4 months of incubation, no degradation of either monochlorobenzene or benzene was observed (results not shown). However, the addition of oxygen stimulated the degradation of monochlorobenzene or benzene (Figure 4).

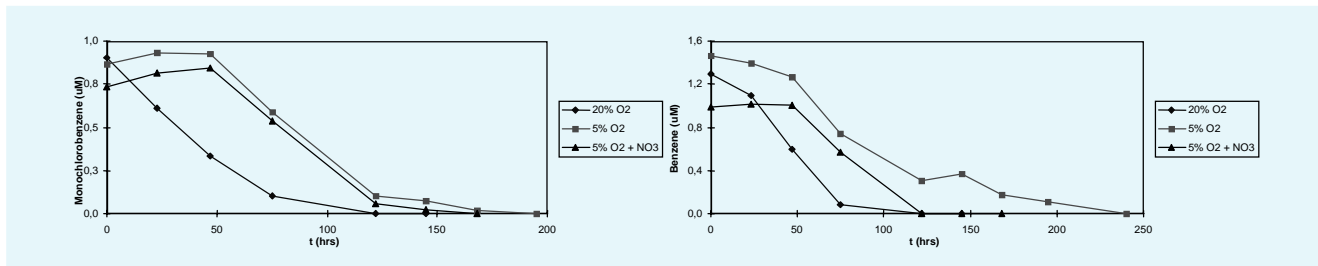


Figure 4. Aerobic degradation of monochlorobenzene and benzene.

The presence of 20% or 5% oxygen stimulated the degradation of monochlorobenzene or benzene. In the case of benzene, adding nitrate enhanced micro-aerobic degradation and we hypothesise that this occurs through anaerobic nitrate reducing conversion of formed oxidised products. This positive effect of the combination of small concentrations of oxygen and nitrate has been shown before, however, the responsible process has not been clarified yet (2, 6, 7).

Modelling

The site characterisation and the biodegradation studies showed that HCH is degraded into the intermediate products, and that HCH, MCB and B are hardly distributed into horizontal and vertical direction. Interpretation of the field data with computer codes Modflow and RT3D (adapted to HCH-bioconversion) was performed to predict the natural attenuation and the spreading of the contaminants at the site. However, various uncertainties (concentration measurements and groundwater flow rates) prevented a full assessment of the feasibility of natural attenuation at this site. Since no direct objects are at risk, it is proposed to monitor natural attenuation for several years.

Industrial site

Site description

This site is an industrial facility, where HCH has been produced and dissolved HCH compounds have formed a contaminated plume of 300 meter by 100 meter. This plume is moving away from the contaminated area into the direction of a nearby canal.

Field characterisation

At this site, three defined sandy aquifers can be defined as well down to a depth of 25 meter, and are separated by a peat-clay layer. The groundwater velocities are 7.5, 15 and 30-60 m.yr⁻¹ in the first, second and third aquifer, respectively. The groundwater direction (north north east) is towards a freshwater system, which forms the natural boundary of the site.

MCB, B, and CP were found as breakdown products of HCH in the core of the plume. In the first aquifer, benzene and chlorophenol appear to be removed during downstream transport in the direction of the water system, whereas the monochlorobenzene concentration remained fairly constant. In the second aquifer, the concentration of MCB, B, and CP showed no decline.

The redox potential characterisation of the source area of the first aquifer showed indications of sulphate reducing and methanogenic conditions. These low redox potential conditions are reported to be favourable for reductive dechlorination. In the downstream part of the plume, iron-reducing conditions were found to be predominant. The redox conditions in the second aquifer were less clearly defined, but can be characterised as reducing conditions.

Both aquifers showed an average DOC concentration of 27 mg.l⁻¹, indicating the presence of sufficient electron donor capacity for reductive dechlorination. Intermediates of the dechlorination process were found indicating that intrinsic biodegradation of HCH does take place at this location.

Batch experiments

A laboratory microcosm study with sediment and groundwater of the site was performed to confirm intrinsic biodegradation of HCH, and to test the feasibility of a combined intrinsic and stimulated *in situ* bioremediation. Depending on the contaminated site conditions, the *intrinsic anaerobic degradation* capacity of endogenous microorganisms may be sufficient to degrade HCH, or the degradation has to be stimulated via the addition of electron donors. If there is no or an insufficient intrinsic biodegradation capacity for monochlorobenzene and benzene, stimulation of this degradation via an *activated aeration* step is necessary.

Enhanced HCH degradation through the addition of various electron donors was tested. In addition to the HCH already present in the soil samples, extra HCH was added, and the desired conversion to monochlorobenzene and benzene was demonstrated, see Figure 5.

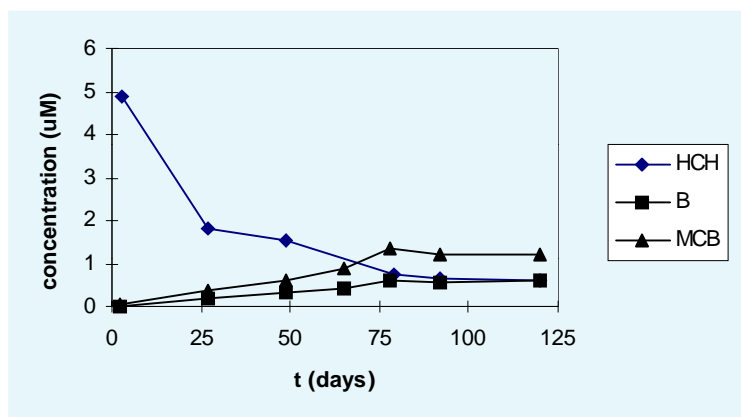


Figure 5. HCH degradation with subsurface solids and groundwater from an industrial site.

All the tested conditions showed degradation of HCH and production of benzene and monochlorobenzene. The addition of either compost percolate or landfill leachate II (rich in fatty acids) showed a rapid degradation of HCH, whereas other additions (lactate and landfill leachate I) showed an inhibitory effect, compared to no addition, see Table 1.

Table 1. First order HCH-degradation rates k (d^{-1})

Addition	k (d^{-1})
-	0,0116 - 0,0170
Compost percolate	0,0074 - 0,0123
Landfill leachate I (rich in VFA)	0,0001 - 0,0055
Landfill leachate II (poor in VFA)	0,0115 - 0,0215
Lactate	0,0052 - 0,0074

The biodegradation of the formed intermediates monochlorobenzene and benzene was tested under anaerobic conditions. After 4 months of incubation, no degradation of either monochlorobenzene or benzene was observed (results not shown). However, the addition of oxygen stimulated the degradation of monochlorobenzene or benzene, like with the material from the non-industrial site (Figure 4).

Implementation of a pilot/full scale system at the industrial site, and integration in the redevelopment of the site

The results of the site characterisation and biodegradation studies have shown that it is possible to stimulate HCH degradation through the addition of an electron donor and the degradation of MCB and B via aerobic degradation. This concept is currently implemented at the industrial site, in conjunction with other redevelopment activities.

At the industrial site, a container terminal will be constructed at the border of the canal, forming the boundary of the site. This canal needs to be protected against HCH contamination, and therefore removal of HCH from the discharging groundwater is needed.

In the redevelopment of the site, infiltration facilities will be made to create an anaerobic infiltration (activated) zone in which the HCH will be transformed into MCB and B. Aerobic conditions are required for the degradation of MCB and B, so the anaerobic infiltration zone is followed by an aerobic step. The combination of a bioremediation system, and the redevelopment of the site as a container terminal control the specific design of the system.

The design, implementation, and first tracer results will be presented at the conference.

Conclusion

At the non-industrial site, the site characterisation and the biodegradation studies showed that HCH is degraded into monochlorobenzene or benzene. Modelling could not clearly predict the fate of the contaminants at the site, and it is proposed to monitor natural attenuation for several years and use that information to better quantify the protectiveness of monitored natural attenuation (MNA) and to design the definitive approach.

At the industrial site, the site characterisation and the biodegradation studies showed that HCH is degraded into monochlorobenzene or benzene, but the degradation processes are not fast enough to prevent the contamination of a canal with HCH. The batch experiments have shown that the degradation process of HCH can be stimulated via the addition of an electron donor, followed by aerobic degradation of the formed intermediates (monochloro)benzene. The redevelopment of the site needs a specific design of the bioremediation system, and the system is currently being implemented at the site.

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