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IN SITU BIOREMEDIATION OF SOIL CONTAMI-
NATED WITH MONOCHLOROBENZENE AND
ANILINE

Summary report

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October 1998

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In situ bioremediation of soil contaminated
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Samenvatting

Dit is het samenvattende rapport van het NOBIS-project 'Biologische in situ sanering met een combinatie van afbreekbare verontreinigingen'. In dit project zijn de mogelijkheden van en de optimale condities voor de microbiologische afbraak van monochloorbenzeen en aniline en de combinatie van beide stoffen onderzocht.

De resultaten van dit onderzoek hebben geleid tot een voorstel voor een saneringsstrategie voor een deel van de site van de chemische industrie ICI Holland BV. In deze aanpak is het gebruik voorzien van zowel de van nature in de bodem aanwezige biologische afbraakpotentie als van gestimuleerde biologische afbraak.

Trefwoorden**Gecontroleerde termen:**

aniline, biological degradation, chlorobenzene

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Abstract

This is the summary report of the NOBIS project 'In situ bioremediation of soil contaminated with a combination of aniline and monochlorobenzene'. In this project, the possibilities of microbiological degradation of monochlorobenzene and aniline, and the optimum conditions for the process have been investigated.

The results of this research have led to a proposal for a remediation strategy for an area on the site of the chemical industry ICI Holland BV. Point of departure was the development of a low intensity, biological remedial and/or containment alternative.

Keywords**Controlled terms:**

aniline, biological degradation, chlorobenzene

Uncontrolled terms:

remediation strategy, research strategy

Project title

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CONTENTS

		SAMENVATTING	vi
		SUMMARY	xi
Chapter	1	INTRODUCTION	1
		1.1 Problem analysis and identification of bottlenecks	1
		1.2 Objectives of the NOBIS project	2
		1.3 Methodology	2
		1.4 Outline of the summary report	2
Chapter	2	CHARACTERIZATION OF THE SITE	3
		2.1 Introduction	3
		2.2 General information	3
		2.2.1 History	3
		2.2.2 Soil structure and hydrology	3
		2.3 Characterization of the subareas	6
		2.3.1 Source area in the top layer - characteristics	6
		2.3.2 Plume area in the top layer - characteristics	7
		2.3.3 (Secondary) Source area in the clay/sand layer - characteristics	8
		2.3.4 Plume area in the intermediary sandy layer - characteristics	8
		2.3.5 Aquifer	8
		2.4 Remarks with regard to the contamination target to be protected	8
Chapter	3	FEASIBILITY STUDY	11
		3.1 Introduction	11
		3.2 Literature search	11
		3.2.1 Objectives of the literature search	11
		3.2.2 Summary of the literature search	11
		3.2.3 Main conclusions of the literature search	12
		3.2.4 Evaluation of the literature research	12
		3.3 Summary of the field study	13
		3.3.1 Objectives	13
		3.3.2 Sampling	13
		3.3.3 Analysis of the results from the top layer	14
		3.3.4 Analysis of the results from the intermediary layer	19
		3.3.5 Overall conclusions of the field study	20
		3.3.6 Evaluation of the field study	21
		3.4 Laboratory study	22
		3.4.1 Objective of the laboratory research	22
		3.4.2 Summary of the laboratory study	22
		3.4.3 Evaluation of the microbiological laboratory study	23
Chapter	4	REMEDICATION/CONTAINMENT MEASURES	25
		4.1 Introduction	25
		4.2 Boundary conditions and remediation aims	25

	4.3	General notes on remediation techniques	26
	4.3.1	Applicability of remediation or containment measures	26
	4.3.2	Applicability of remediation and containment techniques	26
	4.3.3	Applicability of in situ techniques	26
	4.3.4	Applicability of biodegradation	27
	4.4	Measures regarding the source area in the top layer and clay/sand layer area	30
	4.4.1	Geohydrological containment by pumping and treatment aboveground	30
	4.4.2	Air sparging (aimed at both convective soil vapour transport and the stimulation of biodegradation)	31
	4.4.3	Air sparging in combination with nitrate infiltration	32
	4.5	Measures regarding the contaminant plume in the top layer	32
	4.5.1	Checking natural attenuation	32
	4.5.2	Bioscreen	33
	4.6	Intermediary sandy layer	33
	4.6.1	Geohydrological containment	34
	4.6.2	Stimulation of biodegradation	34
	4.7	Further elaboration of obvious measures	34
	4.8	Proposed remediation strategy	35
Chapter	5	CONCLUSIONS AND RECOMMENDATIONS	37
	5.1	Site characterization	37
	5.2	NOBIS investigation	37
	5.2.1	Literature search	37
	5.2.2	Field investigations	37
	5.2.3	Laboratory investigations	38
	5.3	Remediation measures and strategy	38
Appendix	A	LOCATION OF ICI HOLLAND BV AND CROSS-SECTION OF REGIONAL SOIL LAYERS	
Appendix	B1	CONTAMINATION CONTOURS OF MCB (1996)	
Appendix	B2	CONTAMINATION CONTOURS OF MCB (1995)	
Appendix	C1	CONTAMINATION CONTOURS OF AN (1996)	
Appendix	C2	CONTAMINATION CONTOURS OF AN (1995)	
Appendix	D	TOTAL LOADS OF MCB AND AN IN THE TOP LAYER	
Appendix	E1	HORIZONTAL FLUXES OF MCB AND AN	
Appendix	E2	VERTICAL FLUXES OF MCB AND AN	
Appendix	F	MONITORING AND SAMPLE STRATEGY: POSITION OF BOREHOLES AND FILTERS	
Appendix	G	COMPARISON OF REMEDIATION/CONTAINMENT OPTIONS	

Appendix	H	FURTHER ELABORATION OF OBVIOUS REMEDIATION MEASURES
Appendix	H1	PUMP AND TREAT IN THE SOURCE AREA OF THE TOP LAYER
Appendix	H2	PUMP AND TREAT IN THE INTERMEDIARY LAYER
Appendix	H3	BIOSCREEN(S) IN PLUME AREAS
Appendix	H4	MONITORING OF SPREADING (AND NATURAL ATTENUATION) IN PLUMES
Appendix	I1	ISO CONTOURS OF THE GROUNDWATER WITHDRAWAL IN THE TOP LAYER
Appendix	I2	GROUNDWATER WITHDRAWAL IN THE TOP LAYER AND FLOW PATHS
Appendix	J	DEEPWELL POSITION IN THE INTERMEDIARY SAND LAYER AND FLOW PATHS

SAMENVATTING

In situ bioremediation of soil contaminated with monochlorobenzene and aniline

Summary report

Dit rapport is het samenvattende rapport van het NOBIS-project 'Biologische in situ sanering met een combinatie van afbreekbare verontreinigingen'. Hoofddoelstelling van dit project is het vaststellen van de mogelijkheden voor biologische afbraak van monochloorbenzeen en aniline en de optimale omstandigheden voor dit afbraakproces.

Op een deel van de locatie van de chemische industrie ICI Holland BV te Rozenburg bevindt zich een bodemverontreiniging die hoofdzakelijk bestaat uit monochloorbenzeen (MCB) en aniline (AN). Om de vraag te kunnen beantwoorden of in situ bioremediatie in dit geval een geschikt saneringsconcept kan zijn, was (microbiologisch) onderzoek noodzakelijk. De resultaten van dit onderzoek zullen uiteindelijk de saneringsaanpak bepalen.

Het onderzoek is verdeeld in drie sub-fasen:

1. karakterisatie en monsternamen door middel van veldonderzoek;
2. literatuuronderzoek en laboratoriumexperimenten naar de omstandigheden waaronder biologische afbraak kan optreden;
3. interpretatie van resultaten en vertaling naar saneringsmogelijkheden.

Karakterisatie van de locatie

Tabel i geeft de bodemopbouw ter plaatse van de onderzoekslocatie weer.

Tabel i. Geschematiseerde bodemopbouw.

diepte (m -mv)	samenstelling	weerstand in dagen	doorlaatbaarheid in m ² /dag (kD)	geohydrologische eenheid
0 - 5	fijn zand, kleiig		5	ophooglaag
5 - 15	klei, zandig	4000		eerste scheidende laag
15 - 23	fijn zand, kleiig		55 tot 85	tussenzandlaag
23 - 25	klei, siltig, weinig	400		tweede scheidende laag (mogelijk niet overal aanwezig)
25 - 35	matig grof zand			eerste watervoerende pakket
35 - 45	klei, siltig			scheidende laag (hydrol. basis)

Totale verontreinigingsvrachten in de ophooglaag en de horizontale en verticale fluxen vanuit het brongebied naar de pluimgebieden zijn ingeschat. De resultaten zijn gepresenteerd in tabel ii, samen met de aangetroffen maximale verontreinigingsgehalten in de meest relevante bodemlagen.

Tabel ii. Concentraties, vrachten en fluxen van MCB en AN in de ophooglaag.

	vracht (kg)	totale radiale horiz. flux (kg/yr) van bron naar pluim	totale vert. flux (kg/yr)	max. conc. ophooglaag (µg/l)	max. conc. tussenzandlaag (µg/l)
MCB	1215	0,6	9,2	58.000	5.900
AN	8040	0,025	50,3	320.000	13

Waargenomen kan worden dat:

- de totale vracht aan AN hoger is dan die van MCB, maar dat horizontale verspreiding van MCB in een hoger tempo lijkt op te treden (of in het verleden in een hoger tempo is opgetreden) dan de verspreiding van AN.
- de verticale flux van AN in de richting van diepere bodemlagen groter is dan dezelfde flux van MCB. Toch worden in de tussenzandlaag erg lage concentraties AN (vergeleken met MCB) gevonden.
- horizontale fluxen maar een fractie van verticale fluxen zijn. Op jaarbasis bewegen zich maar enkele grammen aan MCB in de richting van de haven.

Hoe om te gaan met de 'lozing' van verontreinigingen via het grondwater op oppervlaktewater is een probleem wat speelt in vele projecten, waaronder enkele NOBIS-projecten. Een symposium over dit onderwerp zou een waardevol initiatief zijn voor NOBIS, eindgebruikers en bevoegde gezagen.

Belangrijkste conclusies van het literatuuronderzoek

In dit NOBIS-project is het literatuuronderzoek een nuttig instrument gebleken om de richting te bepalen van laboratorium- en veldonderzoek. Hierdoor kon het beschikbare budget en tijd voor het onderzoek optimaal worden benut.

De meest belangrijke conclusies van het literatuuronderzoek waren:

1. Biologische afbraak van chloorbenzenen (inclusief MCB) is aangetoond onder oxische omstandigheden.
2. Onder anoxische omstandigheden zijn geen gevallen van afbraak van MCB gevonden.
3. Biodegradatie van vergelijkbare aromatische verbindingen is aangetoond onder denitrificerende condities, zowel in aan- als afwezigheid van kleine hoeveelheden zuurstof, onder metaalreducerende condities, en onder sulfidogene en methanogene omstandigheden.
4. Mineralisatie van aniline is aangetoond onder oxische, denitrificerende, ijzer- en sulfaat-reducerende omstandigheden.
5. Mengsels van aromatische xenobiotische verbindingen kunnen zowel een stimulerend als een remmend effect hebben op elkaars biodegradatie.
6. Ophoping van (toxische) intermediären kan worden verwacht wanneer benzeenafbrekende organismen 'per ongeluk' monochloorbenzeen omzetten via de *ortho*-afbraakroute of de *meta*-route.

Resultaten van het veldonderzoek

In de *ophooglaag* lijkt verspreiding van MCB en AN voornamelijk in noordelijke en zuidelijke richting plaats te vinden. In westelijke en oostelijke richtingen lijkt verspreiding niet op te treden. In combinatie met de waarneming dat in deze richting duidelijk verhoogde zuurstofgehalten aangetroffen zijn (ca. 2 mg/l), kan dit een aanwijzing zijn voor optredende natuurlijke aërobe afbraak van AN en MCB.

Het lijkt erop dat in het brongebied van de ophooglaag zowel zuurstof-, nitraat- en sulfaatconsumptie heeft plaatsgevonden. Het gebruik van metalen als alternatieve elektronenacceptoren kan niet bewezen worden op basis van de veldgegevens. De waarnemingen wijzen op optredende anaërobe afbraakprocessen. Mogelijk wordt AN hier afgebroken.

In de *tussenzandlaag* heersen anaërobe omstandigheden. Er lijkt een verband te bestaan tussen de aanwezigheid van MCB/AN en de afwezigheid van sulfaat.

De verandering tussen de concentratieniveaus van MCB en AN zou kunnen wijzen op intrinsieke (anaërobe) afbraak van AN in de tussenzandlaag en de klei/zandlaag.

De indruk bestaat dat *het primaire doel van het veldonderzoek*: het evalueren van het **voorkomen van natuurlijke afbraak en de hierbij optredende processen**, bereikt is op een kosteneffectieve manier. Het gebruik van meer meetpunten (8 in de ophooglaag, 7 in de tussenzandlaag) zou geen relevant verschil hebben gemaakt voor wat betreft de interpretatie, terwijl minder meetpunten de interpretatie van de resultaten (onacceptabel) minder betrouwbaar zou hebben gemaakt. In een meer standaard situatie met grondwaterstroming in één richting en een duidelijk aanwijsbaar bron, pluim en schoon gebied, zou echter overwogen kunnen worden om het aantal meetpunten (per laag) terug te brengen tot 5 à 6.

De secundaire doelstelling: het bepalen van het mogelijke effect van natuurlijke afbraak op de verspreiding van verontreinigingen, is slechts deels bereikt.

Om de **orde van grootte van natuurlijke afbraak** en de gevolgen op verspreiding te kunnen bepalen, is additionele monitoring noodzakelijk: meer filters zouden periodiek moeten worden gemonitord over een periode van meerdere jaren.

Resultaten van het laboratoriumonderzoek

Op de verontreinigde locatie is microbiële activiteit gevonden, waaronder AN- en MCB-degraderende bacteriën. Afnemende afbraaksnelheden van MCB zijn gevonden bij afnemende zuurstofgehalten.

Additionele alternatieve elektronenacceptoren, zoals nitraat en sulfaat, verbeterden de afbraaksnelheid van MCB bij lage partiële zuurstofdrukken niet, ondanks het feit dat wat nitraat werd gereduceerd.

Afbraak van MCB vindt niet plaats onder anaërobe omstandigheden, noch in de aanwezigheid van alternatieve elektronenacceptoren, noch in de aanwezigheid van alternatieve elektronendonoren.

MCB en AN (indien separaat aanwezig) zijn niet toxisch tot concentraties van 10 mM. De aanwezigheid van AN lijkt een inhibiterend effect te hebben op de afbraaksnelheid van MCB.

Additionele koolstofbronnen en nutriënten bleken noch een positief noch een negatief effect te hebben op de afbraaksnelheid van MCB.

Voor een vergelijkbaar vervolgonderzoek zou het aan te bevelen zijn om meer metingen uit te voeren onder condities die beter vergelijkbaar zijn met de omstandigheden in het veld. Dit om een betere schatting van de afbraaksnelheden in het veld te kunnen maken. Een dergelijk onderzoek zou meer experimenten met grond en meer experimenten bij 'in situ' temperaturen (ongeveer 10 °C) moeten bevatten.

Kortdurende, eenvoudige slurrytests zouden een snelle scan kunnen leveren van de mogelijkheden. Aanvullend zouden grondkolomtests kunnen worden gebruikt voor de meest relevante condities om het effect van diffusielimitatie te kunnen meenemen. Het gebruik van kleine kolommen met een korte recirculatietijd wordt geadviseerd.

Het gebruik van experimenten zonder grond (b.v. enrichments, chemostaten) wordt nog steeds aanbevolen in bijzondere gevallen waar een hoge graad van nauwkeurigheid gewenst is (b.v. bepaling van intermediären) en waar constante condities belangrijk zijn (vooral bij lage concentraties), of wanneer het wenselijk is dat de verkregen resultaten kunnen worden vergeleken met literatuurgegevens.

Conclusies met betrekking tot mogelijke saneringsmaatregelen en saneringsstrategie

Onderstaande technieken kunnen in principe worden toegepast op deze locatie binnen de bestaande randvoorwaarden (b.v. aanwezige infrastructuur, beleid):

1. convectief grondwatertransport (al dan niet met een bovengrondse waterzuivering), en/of
2. convectief bodemluchtransport en bovengrondse luchtzuivering, persluchtinjectie gecombineerd met bodemluchtexttractie en/of
3. biodegradatie, waarbij onderscheid kan worden gemaakt tussen:
 - a. natuurlijke afbraak;
 - b. gestimuleerde afbraak.

Conditie waaronder (gestimuleerde) afbraak als een saneringsmaatregel kan worden toegepast:

- a. de benodigde redoxomstandigheden dienen aëroob te zijn;
- b. de benodigde zuurstofconcentratie in het grondwater om volledige afbraak van MCB te bereiken is ≥ 2 mg/l;
- c. de hoogst bereikbare afbraaksnelheid voor MCB (onder ideale omstandigheden: 30 °C, zuurstofverzadiging, geen inhibitie als gevolg van AN, schudden) is ongeveer 20 mg MCB/kg grond/dag;
- d. het verwachte effect van de veldtemperatuur (12 °C) op de afbraaksnelheid is een 4 tot 7 keer lagere snelheid dan bij 30 °C;
- e. het verwachte effect van een lager zuurstofgehalte (2 mg O₂/l: minimum) op de afbraaksnelheid is een 1,7 maal lagere afbraaksnelheid dan bij zuurstofverzadiging;
- f. een combinatie van c, d en e leidt tot een geschatte *maximale* afbraaksnelheid *onder in situ condities* van ongeveer 2 mg/kg/dag. Deze afbraaksnelheid kan worden beschouwd als een maximum, omdat het gebaseerd is op een situatie met een optimale contact tussen de verschillende fasen. In een veldsituatie zal de afbraaksnelheid worden gelimiteerd door de diffusiesnelheid;
- g. remming van afbraak van MCB zal toenemen met toenemende AN-concentraties. Afbraaksnelheden voor MCB in aanwezigheid van 100.000 µg/l AN zullen afnemen tot slechts 20 % van de maximale afbraaksnelheid.

In theorie zouden bovenstaande gegevens een extensief biologisch concept (een bioscherm in de pluimgebieden) mogelijk maken. Voor deze specifieke locatie bleek grondwateronttrekking echter een meer kosteneffectieve saneringsmethode te zijn vanwege de aanwezigheid van een afvalwaterzuivering, waarvan is aangetoond dat deze zowel MCB als AN kan afbreken.

De volgende saneringsstrategie wordt aanbevolen:

1. Het overleggen van de resultaten van dit NOBIS-project inclusief de voorgestelde saneringsstrategie aan het bevoegd gezag en aan andere betrokken partijen om tot overeenstemming te komen voor wat betreft de saneringsaanpak. Of de Britannia-haven wel beschouwd moet worden als een bedreigd object zou hierin centraal moeten staan.
2. Installatie van onttrekkingsmiddelen in de ophooglaag en de tussenzandlaag.
3. Installatie van monitoringfilters in de ophooglaag in diverse richtingen. Uitvoering van een monitoringprogramma om het effect te meten van de grondwateronttrekking op de verspreiding(ssnelheid) van verontreinigingen en op het optreden van natuurlijke afbraak.
4. Monitoring in het watervoerende pakket om het effect van de grondwateronttrekking in de tussenzandlaag en op verspreiding naar dit pakket te controleren.

5. In een eventueel nog uit te voeren vervolgonderzoek naar de invloed van nitraattoedieningen op de afbraak van MCB en benzeen zou de locatie van ICI kunnen worden gebruikt als een testcase;
6. Na een relatief korte periode van intensieve monitoring (2 jaar) kunnen de verzamelde gegevens worden geïnterpreteerd en geëvalueerd, waarna de vervolgstategie overlegd dient te worden met het bevoegd gezag.
Vervolgmaatregelen kunnen variëren van beëindiging van verdere monitoring tot additionele maatregelen, zoals de installatie van een bioscherm.

SUMMARY

In situ bioremediation of soil contaminated with monochlorobenzene and aniline

Summary report

This is the summary report of the NOBIS project 'In situ bioremediation of soil contaminated with a combination of contaminants'. The overall goal of this project is to establish the possibilities of microbiological degradation of monochlorobenzene and aniline, and to identify the optimal conditions for the process.

An area on the site of the chemical industry ICI Holland BV (Rozenburg near Rotterdam) is contaminated mainly with monochlorobenzene (MCB) and aniline (AN). To answer the question whether in situ bioremediation is a suitable method for remediation, (microbiological) research was necessary. The results of this research will eventually determine the remediation strategy.

The research has been divided up into three sub-phases:

1. site characterization and sampling by means of a field investigation;
2. literature research and laboratory investigations to determine the conditions for biological degradation;
3. interpretation of the results and translation into remediation possibilities.

Site characterization

Table i presents the schematized soil structure at the investigated site.

Table i. Schematized soil structure.

regional depth (m -gl)	composition	resistance in days	conductivity in m ² /day (kD)	geohydrological unit
0 - 5	fine sand, clayey		5	top layer
5 - 15	clay, sandy	4000		first dividing layer
15 - 23	fine sand, clayey		55 to 85	intermediary sand layer
23 - 25	clay, silty or peat	400		second dividing layer (presence not clear)
25 - 35	(moderately) coarse sand			first aquifer
35 - 45	clay, silty			dividing layer (hydrological base)

Total loads of contaminants in the top layer and horizontal and vertical fluxes from the source area towards the plume areas have been estimated. The results are presented in table ii, together with the maximum concentrations found in the most relevant soil layers.

Table ii. Concentrations, loads and fluxes of MCB and AN in top layer.

	load (kg)	total radial hor. flux (kg/yr) source to plume	total vert. flux (kg/yr)	max. conc. top layer (µg/l)	max. conc. intermediary layer (µg/l)
MCB	1215	0.6	9.2	58,000	5,900
AN	8040	0.025	50.3	320,000	13

It can be observed that:

- the total load of AN is higher than that of MCB, but horizontal spreading of MCB seems to occur (or has occurred) at a faster rate than that of AN.
- the vertical flux of AN towards deeper soil layers is larger than the same flux for MCB. However, in the intermediary sand layer very low concentrations of AN (compared to MCB) have been found.
- horizontal fluxes are only a fraction of vertical fluxes. On a yearly basis only grams of MCB move towards the direction of the harbour.

Handling the 'discharge' of soil contaminants into surface water is a problem in many projects, including several NOBIS projects. A symposium on this issue would be a valuable initiative for NOBIS, end users and involved authorities.

Main conclusions literature search

In this NOBIS project the literature search proved to be a useful tool in directing laboratory and field research, thus optimising available research funds and time.

The most important conclusions of the literature research were:

1. Biological treatment of chlorobenzenes (including MCB) has been demonstrated under oxic circumstances.
2. No reports of the degradation of MCB under anoxic conditions have been found.
3. Biodegradation of related aromatics has been demonstrated under denitrifying conditions in both the absence and presence of small amounts of oxygen, under metal reducing conditions, and under sulphidogenic and methanogenic conditions.
4. Mineralization of aniline has been demonstrated under oxic, denitrifying, iron- and sulphate reducing conditions.
5. Mixtures of aromatic xenobiotic compounds can have both stimulating and inhibiting effects on their biodegradation.
6. Accumulation of (toxic) intermediates can be expected if benzene-degrading organisms accidentally degrade monochlorobenzene via the *ortho*-pathway or the *meta*-pathway.

Results of the field investigations

In the *top layer*, spreading of MCB and AN seems to occur mainly in northern and southern directions. In western and eastern directions, spread does not seem to occur. Combined with the observation that relevant amounts of oxygen have been found here (up to 2 mg/l), this could be an indication of occurring intrinsic aerobic degradation of AN and MCB.

It seems that in the source area of the top layer both oxygen, nitrate and sulphate consumption has taken place. The use of metals as alternative electron acceptors cannot be proven by the field data. Observations indicate occurring anaerobic degradation processes. Possibly AN is being degraded here.

In the *intermediary sand layer*, anaerobic circumstances prevail. There seems to be a correlation between the presence of MCB/AN and the absence of sulphate.

Given the changes in MCB and AN concentration levels, intrinsic (anaerobic) degradation of AN may occur in the intermediary and clay/sand layer.

We are under the impression that *the primary objective of the field study: evaluating the occurrence of natural attenuation and processes involved*, has been attained in a cost-effective manner. The use of more measuring points (8 in the top layer, 7 in the intermediary layer) would not have made a relevant difference in interpretation, while using fewer points would have made

the interpretation of the results (unacceptably) less reliable. However, in a more standard situation with a one-way groundwater flow and a well-defined source, plume and clean area, one might consider using 5 to 6 measuring points (for each layer).

The secondary objective: the determination of a possible effect of natural attenuation on the spread of contaminants, has only been reached partially.

To determine the **order of magnitude** of natural attenuation and its effect on spreading, additional monitoring is necessary: more filters would have to be monitored periodically for several years.

Results of the laboratory investigations

At the polluted site microbial activity was found, as well as AN and MCB degrading bacteria. Decreasing MCB degradation rates were found with decreasing oxygen concentrations.

Additional alternative electron acceptors such as nitrate and sulphate did not enhance the MCB degradation rate with low partial pressure of oxygen, despite the fact that some nitrate was reduced.

No degradation of MCB takes place under anaerobic conditions, neither in the presence of alternative electron acceptors, nor in the presence of alternative electron donors.

MCB and AN (if present separately) are not toxic up to concentrations of 10 mM. The presence of AN seems to have an inhibiting effect on the degradation rate of MCB.

Additional carbon sources and nutrients were not found to have neither a positive nor a negative effect on the degradation rate of MCB.

For a similar follow-up study we recommend that more measurements be taken under conditions more similar to those found in the field, so as to allow for a better estimate of degradation rates in a field situation. This would entail more experiments with soil, and more experiments at 'in situ' temperatures (approximately 10 °C).

Rapid, simple soil slurry tests could provide a quick scan of possibilities. Additionally, soil column tests could be used for the most relevant conditions, in order to include the effect of diffusion-limitation. We recommend the use of small columns with a short recirculation time.

Non-soil experiments (e.g. enrichments, chemostats) are still recommended in cases of special situations in which a high accuracy is desired (e.g. determination of intermediates) and in which constant conditions are important (especially with low concentrations), or in case it is desirable that the obtained results are comparable with the data in the literature.

Conclusions with regard to possible remediation measures and strategy

The following techniques can in principle be employed on this site within the existing boundary limits (e.g. present infrastructure, policy):

1. convective groundwater transport (possibly including aboveground groundwater treatment: pump and treat), and/or
2. convective soil vapour transport and aboveground soil vapour treatment, air sparging combined with soil vapour extraction and/or
3. biodegradation, at which a distinction may be made between:
 - a. natural attenuation;
 - b. stimulated degradation.

Conditions to apply (stimulated) degradation as a remediation measure are:

- a. the required redox condition is aerobic;
- b. the required oxygen concentration in the groundwater in order to obtain a complete degradation of MCB is ≥ 2 mg/l;
- c. the highest attainable degradation rate for MCB (under ideal circumstances: 30 °C, oxygen saturation, no inhibition as a result of AN, shaking) is approximately 20 mg MCB/kg soil/day;
- d. the expected effect of the field temperature (12 °C) on the degradation rate is a rate 4 - 7 times lower than at 30 °C;
- e. the expected effect of a lower oxygen level on the degradation rate is (2 mg O₂/l: minimum) a rate 1.7 times lower than at saturation levels;
- f. a combination of c, d and e leads to an estimated *maximum* degradation rate *at in-situ conditions* of approximately 2 mg/kg/day. This degradation rate is considered to be a maximum because it is based on a situation with an optimal contact between the different phases. In a field situation the degradation rate will be limited by the rate of diffusion;
- g. inhibition of MCB degradation will increase with increasing AN concentrations. Degradation rates of MCB at 100,000 µg/l AN will decrease to only 20 % of the maximum capacity.

In theory, these conditions would make a low intensity biological concept (a bioscreen in the plume areas) feasible. However, for this particular site, pump and treat turned out to be a more cost-effective remediation option because of the presence of an activated sludge waste water treatment which proved to degrade MCB and AN.

The following remediation strategy is recommended:

1. The presentation of the results of this NOBIS project including proposed remediation strategy to the authorities in charge and to the other parties involved, in order to come to a mutual agreement on the remediation approach. Whether Britannia Harbour is an 'endangered' object should be a central point of discussion.
2. Installation of pump and treat measures in the top layer and the intermediary sand layer.
3. Installation of monitoring filters in the top layer in several directions. Execution of a monitoring programme in order to measure the effect of the groundwater withdrawal on the spread of contaminants and on the occurrence of natural degradation.
4. Monitoring in the aquifer to check for a spread towards the aquifer and the effect of groundwater withdrawal in the intermediary sand layer.
5. The site of ICI could be used as a field test case in a follow-up study to investigate the influence of nitrate addition on MCB and benzene degradation.
6. After a relatively short period of extensive monitoring (2 years), the collected data should be interpreted and evaluated, after which the further strategy should be discussed with the competent authorities. Any subsequent measures can range from ending further monitoring to additional measures such as the installation of a bioscreen.

CHAPTER 1

INTRODUCTION

This is the summary report of the NOBIS project 'In situ bioremediation of soil contaminated with a combination of contaminants'. The overall goal of this NOBIS project is to establish the possibilities of microbiological degradation of monochlorobenzene and aniline, and to identify the optimal conditions for the process.

An area on the site of the chemical industry ICI Holland BV (Rozenburg near Rotterdam) is contaminated with a cocktail of contaminants which mainly consists of monochlorobenzene and aniline. To answer the question whether in situ bioremediation is a suitable method for remediation of the site, microbiological research was necessary. The bulk of this NOBIS project consists of microbiological laboratory experiments on soil and groundwater samples taken from the contaminated industrial site of ICI Holland.

In this report we will:

1. summarize and evaluate the results of the performed site and laboratory investigations;
2. evaluate the above-mentioned, describe possible remediation strategies for the site and recommend the best approach to be followed.

A more detailed description of the microbiological study and an overview of currently available knowledge on biodegradation processes of monochlorobenzene and aniline and the conditions under which degradation takes place is published separately in the NOBIS report 96-1-10: 'A microbiological study' (October 1998).

1.1 Problem analysis and identification of bottlenecks

An area on the site of ICI Holland BV, a company of the chemical industry seated in Rozenburg near Rotterdam, is contaminated with a cocktail of contaminants consisting mainly of monochlorobenzene and aniline.

The main aim of future remedial and/or containment measures will be to prevent any further spreading of contaminants due to the groundwater flow. Given the fact that monochlorobenzene (MCB) is the most mobile and most widely spread contaminant, attention will have to be focused on this compound.

Containment and/or (extensive) remediation measures based on biological techniques can be an attractive alternative to more conventional techniques:

- The intrinsic capacity of soil to remediate contaminants is used. By making use of this capacity in combination with the factor time, the soil quality can be restored with a limited effort and at limited costs.
- Drastic civil engineering measures or groundwater withdrawal will not be necessary.

The success of biological techniques will be determined by the magnitude of the intrinsic degradation and the possibilities to stimulate degradation on the site.

To arrive at a better estimate of these possibilities, the following questions will have to be answered:

- Does natural attenuation occur on the site?
- Are there sufficient electron acceptors present in the natural situation?
- What are the conditions under which degradation of MCB can occur?
- Does the presence of aniline have any effect on MCB degradation?
- What degradation kinetics is applicable to the site?
- What is the hydraulic conductivity of the present soil layers?

1.2 Objectives of the NOBIS project

The overall goal of this NOBIS project is to establish the possibilities of microbiological degradation of monochlorobenzene and aniline, and to identify the optimal conditions for the process.

The results of this research will eventually determine the remediation strategy for this part of the ICI site. Point of departure is the development of an extensive biological remedial and/or containment alternative.

1.3 Methodology

The research has been divided up into three subphases:

- A. a characterization of the soil, micro-organisms and contaminants by means of:
 - a literature study;
 - a field investigation.
- B. a laboratory investigation to determine the conditions for biological degradation.
- C. an interpretation and evaluation of results,
a translation into remediation alternatives and a global design of alternatives.

1.4 Outline of the summary report

This report contains following chapters:

- Chapter 2: Characterization of the site:
description of the soil layers, contamination loads and fluxes.
- Chapter 3: Feasibility study:
results and evaluation of the research performed.
- Chapter 4: Remediation/containment measures:
description and evaluation of possible remediation and containment techniques.
- Chapter 5: Conclusions and recommendations.

CHAPTER 2

CHARACTERIZATION OF THE SITE

2.1 Introduction

In this chapter, the site section of ICI Holland BV, a company of the chemical industry in Rozenburg near Rotterdam, will be described. The location of the ICI site can be found in appendix A.

2.2 General information

2.2.1 History

Until 1960, the ICI site was used for agricultural purposes. In order to render the area suitable for industrial use, it was raised by a 4 to 5 m thick layer of sand/sludge. The used dredgings originated from the 'Nieuwe Waterweg'. Several clay dikes were placed on the site in order to be able to contain the sand/sludge layer.

Sand piles were placed in order to improve the groundwater drainage in the top layer. On the ICI site section used for this NOBIS project, they were placed at a distance of 5 m from each other, and to a depth of 17 m -gl.

Since 1973, the ICI site section in question has been used for the production of components for polyurethane production. Soil and groundwater have been mainly contaminated with monochlorobenzene (MCB) and aniline (AN).

2.2.2 Soil structure and hydrology

Appendix A shows a cross-section of the surroundings of the ICI site on a larger scale. The local soil system can be schematized by five main soil layers, each with their own characteristics. This schematized soil structure has been presented in table 1. Represented kD -values originate from an 'Europort Botlek Belangen' study, cluster 4 (EBB: Europort Botlek Interest). The value for hydraulic resistance (c), originates from an earlier investigation on the site.

Table 1. Schematized soil structure.

regional depth (m -gl)	composition	resistance in days	conductivity in m^2/day (kD)	geohydrological unit
0 - 5	fine sand, clayey		5	top layer
5 - 15	clay, sandy	4000		first dividing layer (poorly permeable)
15 - 23	fine sand, clayey		55 to 85	intermediary sand layer
23 - 25	clay, silty or peat	400		second dividing layer (presence not clear)
25 - 35	(moderately) coarse sand			first aquifer
35 - 45	clay, silty			dividing layer (hydrological base)

Terrain level is approximately 4.7 m +NAP. Average groundwater level approximately 1 m -gl.

1. Top sand layer (0 to 5 m -gl)

The groundwater flow in the top layer is mainly determined by the surplus of rainfall. From the isohypses of the groundwater levels in the top layer, a radial flow from the centre towards the plume areas can be deduced.

The groundwater flow velocity seems to be highest in northern (towards Britannia Harbour) and southern directions. Assuming a fall in the groundwater level of 1/150 m/m and a conductivity 'k' of 1 m/day, the horizontal flow of the phreatic groundwater can be calculated at approximately 7 metres a year.

The radial flow can be influenced locally, depending on the presence of old clay dikes and on the resistance of the harbour quay.

Based on the measured differences in the groundwater levels between the deeper and shallow filters, a situation of groundwater infiltration can be expected. Based on a level difference ranging from 3.4 to 4 metres, the vertical flow can be calculated at approximately 0.3 m/yr.

It should be taken into account that the sand piles present in this layer form potential vertical routes of (fast) vertical migration. Older sand piles can lose the larger part of their draining capacity in the course of time as a result of clogging with small soil particles. The present draining capacity of these sand piles is unknown.

2. Clay/sand layer (5 to 15 m -gl)

The thickness of the clay/sand layer may vary at the location. This layer mainly consists of many thin alternating layers of clay and sand. On top of this layer, a thin layer of denser clay (former ground level) can be found here and there.

In view of the measured differences between the groundwater levels of the top layer and the deeper sandy layer, it is expected that there is a vertical flow (infiltration) of phreatic groundwater in this layer. The infiltration amount will be largely determined by the surplus of rainfall. Also refer to the remarks on sand piles.

3. Intermediary sandy layer (15 to 23 m -gl)

In this relatively well permeable layer, the groundwater flow is directed towards the Britannia Harbour, in a north-north-east direction. Based on a slope in the groundwater level of 1/1700 m/m and a *k*-value ranging from 1 to 10 m/day, the groundwater flow velocity is expected to be 4 to 7 metres a year. Measurements to determine the direction of the flow were carried out in a limited number of filters. Therefore, slight deviations should be taken into account.

In view of a difference in groundwater levels in the intermediary sandy layer and the first aquifer ranging from 0.1 to 0.2 metres, it can be expected that there is a (downward) infiltration rate of 0.1 m/yr.

4. Silty layer (23 to 25 m -gl)

This layer is supposed to form a natural barrier for the groundwater migration from the intermediary sandy layer towards the aquifer. However, it is not certain that this layer is present on the entire location. If gaps are present, vertical spread could be enhanced.

5. Aquifer (25 m -gl and deeper)

In this relatively well permeable layer, the groundwater flow on the regional scale is directed towards the south-west (note: this is directly opposite to the groundwater flow in the intermediary sandy layer). The groundwater velocity varies from approximately 4 m/yr (at the Britannia Harbour) to 11 m/yr (at the Seine Harbour, 1 km from the south of the ICI site).

Fig. 1. Conceptual model of the site.

2.3 Characterization of the subareas

Figure 1 shows a conceptual model of the site based on the degree of contamination and the soil stratification. In this conceptual model, five subareas were distinguished:

1. (primary) source area in the top layer;
2. plume area in the top layer;
3. (secondary) source area in the clay/sand layer;
4. plume area in the intermediary sandy layer;
5. aquifer.

For each subarea, the most important characteristics are presented in the following sections. Based on geohydrological data in combination with the properties of the contaminants and their present concentrations, an estimate of the following will be made for the relevant subareas:

- the present contaminant loads;
- the corresponding fluxes from a subarea in the direction of:
 - one of the other subareas;
 - the bordering (clean) parts of the ICI site;
 - the surface water.

2.3.1 Source area in the top layer - characteristics

Contaminations

In this area a cocktail of various contaminants can be found. Monochlorobenzene (MCB) and aniline (AN) are present in high concentrations. Because spills have caused soil contamination, it is most likely that MCB and AN are (at least partly) present as organic liquids. They can either be present as a mobile and dense non-aqueous phase liquid (DNAPL) or be found in a residual saturation: immobile organic product 'trapped' in pores by the interfacial tension.

Although up to now no pure product was found, it is likely that pure product is present around the old ground level (4 to 5.5 metres below present ground level) and this should be taken into account.

Occurrence and concentrations

The primary source area in the top layer has been defined as that part of the area where **MCB concentrations are higher than 100 µg/l**. This boundary line includes all known, suspected or potential spill-areas as well as the 100 µg/l iso contour of aniline.

This primary source area is approximately 15,000 m² large and lies fully within the boundaries of the investigated production location (see appendices B1: MCB contours and C1: AN contours).

The highest concentrations of MCB and AN found are 58,000 and 310,000 µg/l respectively (compare with maximum solubilities of 500,000 and 34,000,000 µg/l respectively).

Total loads

The total amounts of contaminants in the source area (unsaturated zone *not* included) have been estimated at:

MCB: 1215 kg;
AN: 8040 kg.

The assumptions taken in calculating these figures and (part of) the calculations are presented in appendix D.

Fluxes

Two fluxes can be distinguished:

1. **horizontal flux** from the source area towards the plume;
2. **vertical flux** from the source area down towards the clay/sand layer.

Ad 1: Horizontal flux

MCB: Horizontal flux of MCB from source to plume area per square metre a year has been calculated at 245 mg/m²/yr (refer to appendix E1).

Total horizontal flux for MCB from source area towards plume area can be calculated at approximately 0.6 kg MCB a year.

In the direction of the Britannia Harbour the flux is calculated at 0.12 kg a year.

AN: Only in the direction of the harbour and in southern direction relevant spread of AN seems to occur. Based on present AN concentrations, horizontal fluxes in these directions are estimated at 10 % of the MCB flux: 25 mg/m²/yr.

Ad 2: Vertical flux

The calculation of vertical, downward directed fluxes has been based on iso concentration contours and an average groundwater infiltration velocity of 0.3 m/yr. Refer to appendix E2 for the points of departure and figures used. It must be noted that due to the effect of pure product and sand piles, the presented fluxes may be underestimated.

MCB: For MCB, a total vertical flux of 9.2 kg/yr has been calculated.

AN: For AN, a total vertical flux of approximately 50 kg/yr has been calculated.

Presented vertical fluxes are rough estimates: the downward concentration development (in the clay/sand layer) is unknown and should be investigated further in order to be able to predict vertical loads with more certainty. If any further investigation to this subject is desired then it should include the draining capacity of the sand piles.

Other characteristics

The primary source area lies completely within the boundaries of the production plant. On this location strict security measures and operation procedures are being followed. This is of interest with regard to the selection of remediation measures.

2.3.2 Plume area in the top layer - characteristics

Contaminations

MCB is present in the plume area. In the northern and southern part of the location MCB and AN are both present.

Occurrence and concentrations

The plume area is presented by the area outside the 100 µg/l iso contour line in appendix B1. In the plume area, the contamination is either present dissolved in the aqueous phase, or sorbed at the soil solid matrix. No pure product is present. The contamination originates from the source area and has been dispersed by the groundwater flow.

Generally, concentrations equal to or below the detection limits (0.1 mg/l) will be present in soil.

Total loads

The size of the plume in the top layer is globally determined by the area between the 100 µg/l iso contours of MCB and the detection limit contour (0.1 µg/l) in the groundwater (also refer to appendix B1).

Based on the contamination contours, the total amount of contaminants in this area can be estimated at (refer to appendix D for calculations):

MCB: 6.1 kg

AN: 0.6 kg

Flux

Only fluxes from the source area towards the plume area are relevant: refer to 2.3.1.

2.3.3 (Secondary) Source area in the clay/sand layer - characteristics

Contaminations, occurrence and concentrations

About this layer there is relatively little information available. In the upper part, the MCB and AN concentrations of the soil are comparable with those in the top layer. No groundwater from this layer has been analysed. Consequently, nothing is known of any further penetration of the contamination into the depth of this aquifer.

2.3.4 Plume area in the intermediary sandy layer - characteristics

Contaminations, occurrence and concentrations

Only in two places situated directly below the location of the contaminant source in the top layer, high concentrations of MCB are found: 3,500 and 5,900 µg/l. The concentrations of aniline in the same filters are considerably lower: 2.5 and 13 µg/l.

Foci of attention

It is not completely certain whether a separating layer from 23 to 25 m -gl between the intermediary sandy layer and the aquifer is present.

2.3.5 Aquifer

Contaminations, occurrence and concentrations

Slightly elevated concentrations of MCB and AN were found at a depth of 30 m -gl.

Until now, only one drilling through the source was carried out in this aquifer. The filter that was placed was sampled only once. Slightly higher concentrations of aniline were encountered there compared with the intermediary sandy layer situated directly above. However, due to the fact that analyses have only been carried out once, it is impossible to decide whether this was a single raise due to the executed drillings or a trend in the concentrations in the aquifer as a result of a flow from the intermediary sandy layer.

The aquifer is considered to be the endangered object to be protected. This aspect is of course of importance in determining the urgency and necessity of the containment measures in the intermediary sandy layer to prevent a further spreading.

2.4 Remarks with regard to the contamination target to be protected

In this chapter we described the knowledge obtained from 'regular' site investigations.

Based on:

- the flux of contaminants in the top layer,
- the flux of contaminants in the deeper sandy layer,
- the possible presence of pure product in the source area,

the location under issue is considered to be an urgent case in accordance with the Dutch system for the determination of urgency. In this Dutch system, natural attenuation processes are not taken into account in the estimation of the flux.

Unknown aspects are:

- a. the amount of vertical spread towards the aquifer;
- b. the question whether contaminants *actually* spread in the top and intermediary sandy layer, or whether there is less spreading there than expected (e.g. as a result of intrinsic degradation).

Investigation of these aspects may result in the following conclusions:

1. Spreading has stopped, meaning that containment and monitoring will suffice. The competent authorities will have to be convinced of this.
2. Spreading occurs in the top layer and in the intermediary sandy layer. This leads to a 'discharge' into the harbour, be it a small-load discharge (< 1 kg/yr, see 2.3.1).
If one compares the efforts (energy, costs) to their environmental merit, it appears that any measures to fight this spreading will not be cost effective. This may be illustrated by a REC (Risk, Environmental merit, Costs) assessment or by the 'Environmental Benefit' concept of ICI.

Handling the 'discharge' of soil contaminants into surface water is a problem in many projects, including several NOBIS projects (e.g. KPE, EPON sites). A workshop on this issue would be a valuable initiative for NOBIS as well as for end users.

3. Spreading is significant or the authorities cannot be convinced that spreading is futile. Remediation measures should be examined.
The measures may differ from subsystem to subsystem. If e.g. the flux in the top layer is small compared to the natural attenuation occurring, while the spreading in the aquifer is significant, the measures may be limited to preventing the spreading in the aquifer.

As indicated in the previous sections, the fluxes and soil system are not fully characterized in the different subsystems. To decide whether additional characterization is necessary one should evaluate:

- a. the costs of investigating the spread (many relatively expensive deep drillings and an extensive monitoring plan);
- b. the costs of the measures to prevent a spread;
- c. the risk of still having to take measures after the investigation.

With regard to the ICI site, it was decided to first investigate the measures and their costs, which led to this NOBIS project.

CHAPTER 3

FEASIBILITY STUDY

3.1 Introduction

This chapter summarizes the results of the microbiological study and the additional field study. The investigations were focused on following questions:

1. Can MCB be degraded under natural conditions at the ICI location?
2. What effect does the presence of AN have on the degradation of MCB?
3. What effect do alternative electron donors like NO_3^- , Fe^{3+} and SO_4^{2-} have?
4. What is the relationship between the degradation rate of MCB and the oxygen concentration?

The investigations comprised:

1. literature search regarding properties and known degradation conditions of MCB and AN (see 3.2);
2. field study to determine (process) conditions for degradation in the field (see 3.3);
3. laboratory study to determine optimal conditions for degradation (see 3.4).

The results of the various substudies are summarized in the following sections (see 3.2 to 3.4). The results of each substudy are discussed in the form of: what was done, and what would we do the next time?

3.2 Literature search

3.2.1 Objectives of the literature search

The objective of the literature search was to gather information with regard to contaminants MCB and AN. Special attention was paid to:

- conditions under which degradation of MCB and AN has been reported;
- possible formation of (toxic) degradation products during degradation.

3.2.2 Summary of the literature search

This section is a summary of the complete literature search carried out, which is detailed separately in NOBIS report 96-1-10 'A microbiological study', October 1998.

Chlorobenzenes and related (halo)aromatic compounds

Many pure cultures are described that under *oxic conditions* are able to mineralize chlorinated benzenes to form CO_2 and cell carbon. Oxic degradation of related aromatic benzene proceeds via catechol through the *ortho*- or *meta*-pathway whereas (mono)chlorobenzene degradation proceeds via a modified *ortho*-pathway. Accumulation of (toxic) intermediates (chlorocatechol) can be expected if benzene-degrading organisms accidentally degrade (mono)chlorobenzene via the *ortho*-pathway or the *meta*-pathway. Where the monochlorobenzene concentration exceeded 3 - 4 mM (0.3 - 0.4 g/l), toxicity problems were observed in pure cultures.

Biological treatment of waste contaminated with chlorobenzenes has been demonstrated in waste gas, soil, and groundwater. In soil contaminated with monochlorobenzene and 1,2-, 1,3-, and 1,4-dichlorobenzene, degradation by indigenous microbes was achieved by biostimulation and aeration. Low quantities of organic material (straw) and nutrients were added to the soil to stimulate the indigenous population to degrade the chlorobenzenes. Within a period of 5 weeks more than 90 % of chlorobenzenes (1 - 6 mg/kg) was degraded.

Under *anoxic conditions*, polyhalogenated chlorobenzenes are used as electron acceptors by anaerobic bacteria. Reduction of polyhalogenated benzenes results in lower halogenated benzenes: chlorine substituents are replaced by hydrogen atoms. Higher halogenated benzenes are easier to reduce than lower halogenated benzenes, as a result of a more negative Gibbs free energy (ΔG^0). Reductive dechlorination of polychlorinated benzenes has been reported both under methanogenic and sulphidogenic conditions.

Biodegradation of related aromatics has been demonstrated under denitrifying conditions in both the absence and presence of small amounts of oxygen, under metal reducing conditions, and under sulphidogenic and methanogenic conditions.

However, no reports of the oxidation of monochlorobenzene under anoxic conditions were found.

Aniline

Mineralization of aniline has been demonstrated under oxic, denitrifying, iron- and sulphate reducing conditions. Aniline can serve as a carbon-, energy-, and nitrogen source. Long lag periods were observed in anaerobic enrichments of aniline-degrading bacteria (6 - 18 months). Toxicity was observed above aniline concentrations of 0.5 mM. Under oxic conditions an initial aniline-oxygenase converts aniline into catechol, which is further degraded via either the *ortho*- or the *meta*-pathway.

Bacterial degradation of mixtures of xenobiotic aromatic compounds

Mixtures of aromatic xenobiotic compounds can have both stimulating and inhibiting effects on their biodegradation. Metabolic pathways may be inhibited and misrouting of substrates may lead to toxic (suicidal) products. On the other hand, additional substrates may stimulate biodegradation of primary or secondary substrates as a result of an improved induction of certain pathways.

3.2.3 *Main conclusions of the literature search*

1. Biological treatment of chlorobenzenes (including MCB) has been demonstrated in waste gas, soil, and groundwater under oxic circumstances.
2. No reports of the degradation of MCB under anoxic conditions were found.
3. Biodegradation of related aromatics has been demonstrated under denitrifying conditions in both the absence and presence of small amounts of oxygen, under metal reducing conditions, and under sulphidogenic and methanogenic conditions.
4. Mineralization of aniline has been demonstrated under oxic, denitrifying, iron- and sulphate reducing conditions.
5. Mixtures of aromatic xenobiotic compounds can have both stimulatory and inhibitory effects on their biodegradation.
6. Accumulation of (toxic) intermediates can be expected if benzene-degrading organisms accidentally degrade monochlorobenzene via the *ortho*-pathway or the *meta*-pathway.

3.2.4 *Evaluation of the literature research*

When is a literature research necessary?

An extensive literature search would have to be carried out in case of:

- unknown substances and combinations of substances;
- unknown conditions for degradation.

If literature search results already are available (as is now the case for MCB and AN), it is sufficient to look only for recent publications in order to update existing knowledge.

A literature search is *unnecessary*, if degradation under the existing conditions is considered to be 'proven'. An example of this is the aerobic degradation of aromatics in sandy soil.

Before the ICI/NOBIS project, neither the effects of a combination of AN and MCB nor any anaerobic degradation conditions were known. In this NOBIS project the literature search has proved to be a useful tool to direct laboratory and field research, thus optimising available research funds and time. Based on the literature search results, in the laboratory and field studies more attention was paid to:

- the creation of (toxic) intermediates (chlorocatechols, benzene);
- degradation under a low oxygen pressure;
- degradation in the presence of nitrate (either with or without oxygen).

3.3 Summary of the field study

3.3.1 Objectives

Primary objective

The primary objective of the field study was to look for parameters that may indicate the occurrence of natural attenuation. Indications were obtained by a comparison of concentrations of contaminants, electron acceptors and redox conditions, measured in the source and plume areas on the one hand, and measured in a clean area (background concentrations) on the other hand.

Secondary objectives

The secondary objectives were:

1. to obtain soil and groundwater from the various layers for use in laboratory experiments;
2. to further characterize the soil layers by:
 - determination of soil structure and organic matter content;
 - determination of a possible effect of natural attenuation on the spread of contaminants.

3.3.2 Sampling

Soil sampling

Soil samples from the top sand and clay/sand layer were taken from four boreholes (borehole numbers 501, 601, 602 and 603) with a final depth of 7 m below ground level.

Additionally, two deep pulse drillings (801 and 802) were placed to collect soil from the deeper parts of the clay/sand layers and the intermediary sand layer: soil was taken from three different soil layers here.

This led to the sampling matrix presented in table 2. The positions of the boreholes are presented in appendix F.

Table 2. Soil sampling matrix (fig. 2a en fig. 2b represent borehole numbers).

	MCB (high conc.)	MCB and AN (high conc.)	MCB and AN (low conc.)	AN	clean area
top layer	802	801, 501	602	603	601
intermediary layer	802	801, 501	602	603	601
deeper sand layer	802	801	-	-	-

Groundwater sampling

In order to be able to sample the groundwater, monitoring filters have been placed in above-mentioned boreholes.

Minifilters MF 701 to MF 703 (17 m -gl) and filter 601 (5 m -gl) have been used to monitor background concentrations of relevant compounds in the intermediary and top sand layers. Additionally, filters 205, 208 and 9 (placed during previous investigations) were monitored to complete the monitoring matrix presented in table 3.

Table 3. Groundwater monitoring matrix.

	MCB	MCB and AN (high conc.)	MCB and AN (low conc.)	AN	upstream	downstream
top sand layer	208	501	602	603	-	601, 205
deeper sand layer	802	9	MF 702, MF 703	-	400	252, MF 701

In table 4 we have indicated measured parameters.

All filters on the location are presented in Appendix F. Filters used for monitoring activities are accentuated with green (monitoring filters top layer) and blue (monitoring filters intermediary sand layer) dots.

In figures 2a and 2b, values for the most important redox parameters: O₂, NO₃⁻, SO₄²⁻ and (possible) reaction product Fe²⁺ are given for each sampled filter. Given the relatively small number of monitoring points in the two layers, it was decided **not** to draw any iso concentration contour lines. However, from the drawings in figures 2a and 2b, concentration levels for each layer can be compared easily.

3.3.3 Analysis of the results from the top layer

Filters in the top layer at the production plant are more or less arranged in the form of a cross (see fig. 2a). The centre of the cross is the most polluted area of the location. In this centre lies filter 501.

In table 4 the results for this layer are presented in the west-east and north-south direction. For both directions filter 501 is taken as the centre of the imaginary x,y-axis and is therefore mentioned twice.

The results presented in table 4 and in figure 2a will be discussed in this section.

Before discussing the results, it must be noted that differences in parameter concentrations and/or correlation with MCB and/or AN concentrations could be indications for intrinsic biodegradation, but it should be kept in mind that other processes could also be involved, e.g. chemical equilibria or other biological processes than MCB and AN degradation.

Oxygen

From the west-east cross-section of the site it is clear that at the edges of the contamination plume, oxygen concentrations are higher than in the centre where no oxygen is found at all. For all filters with MCB and AN levels higher than 3700 µg/l and 16 µg/l respectively, no oxygen is present.

However, in filter 603 where moderate levels (1400 µg/l) of MCB can be found, oxygen levels are only slightly lower, or comparable to filters 10, 37 and 601 where no, or only a few micrograms of MCB are present.

NO₃⁻, NO₂⁻

Globally the same pattern can be observed for nitrate as for oxygen: in the presence of MCB and AN levels higher than 3.7 and 2.7 µg/l respectively, no nitrate is detected. Background levels measured in the (almost) clean filters 10 and 37 were 2.1 and 1.6 mg NO₃⁻/l respectively.

The relation between the presence of MCB/AN and the disappearance of NO₃⁻ seems to be stronger than the relation between MCB/AN and oxygen: in filter 601 oxygen can be found, whereas nitrate is not present.

NO₂⁻ is only detected in very small amounts (0.3 µg/l) in the centre of the contamination where very high MCB and AN concentrations are found. NO₂⁻ is a reaction product for occurring denitrification processes.

Sulphate, sulphide

The results do not show a clear relation between the presence of MCB (or AN) and the sulphate levels. In filters with no or very low MCB concentrations, sulphate levels range from 24 to 89 mg/l. This is comparable to levels found in filters with moderate MCB concentrations. Only in filters 208 and 501 that show very high MCB (≥ 10,000 µg/l) concentrations, sulphate concentrations seem to be lower compared to the background levels: 4 mg/l (at 10,000 µg/l MCB) and 11 mg/l (at 58,000 µg/l MCB).

Filters 208 and 501 are also the locations where sulphide has been found (1.7 and 0.4 mg/l respectively). Sulphide is a reaction product that will be formed as a result of occurring sulphate reduction.

Strangely enough a small amount of sulphide (0.3 mg/l) has also been found in the most northern filter 601 where very low amounts of MCB are present. This may be the result of a downstream transport or of occurring sulphate reduction.

Iron, manganese

In soils, iron is mainly present as solid FeOH₃. As Fe³⁺ dissolves poorly, only very low concentrations will be present in groundwater. Fe³⁺ can be reduced to Fe²⁺ which is highly soluble in water. Iron reduction will lead to an increase of the Fe²⁺ concentration in groundwater. Mn⁴⁺ is present as solid MnO₂. Manganese reduction will result in an increase of Mn²⁺ in groundwater.

From the west-east cross-section it is obvious that there is a correlation between the amount of MCB and the amounts of Fe(II) and Mn(total).

It should again be noted that the observed correlated concentrations may indicate a direct microbiologically based relation, but may also be due to geochemical processes.

(Bi)Carbonate

No relevant changes in bicarbonate levels could be detected.

Other indicators

Other measured indicators like DOC, COD, chloride, redox, pH and electric conductivity show more or less a correlation with present contamination levels. These parameters however should be considered as circumstantial evidence for occurring natural biodegradation at the site.

MCB and AN

Based on the additional information gathered in November 1996, new concentration contours have been drawn for MCB and AN in the top layer (refer to appendices B1 and C1 respectively). When compared to the situation up to November 1995 (refer to appendices B2 and C2), a spread seems to occur mainly in the northern and southern directions. In 1996, filters 10 (west of source area) and 37 (east of source area), showed lower concentrations than before. Combined with the observation that these filters contain relatively large amounts of oxygen, this could be an indication of considerable intrinsic (aerobic) degradation of both AN and MCB.

Table 4. Results from the top layer.

	direction: west > east			
filter	10	603	501	37
distance from centre (m)	-75	-55	0	55
depth (m)	0.4 - 2.4	3.7 - 4.7	3 - 4	1 - 3
main contaminants (µg/l)				
MCB	3.7	1,400	58,000	0
AN	2.7	13	320,000	0
benzene		29		
parameters (mg/l)				
O ₂ (average)	2.6	1.6	0	1.2
NO ₃ ⁻	2.1	0	0	1.6
NO ₂ ⁻	0	0	0.3	0
Mn		0.65	3.4	
Fe(II)	0.1	0.5	20	0
Fe(tot)	0.24	6.5	65	0.11
SO ₄ ²⁻	24	37	11	89
H ₂ S	0	0	0.4	0
bicarbonate		8.4		
Cl ⁻	59	61	135	15
NH ₄ ⁺		8.9		
COD		41	1,970	
DOC	4.2	15	960	3.3
redox (mV)				
redox (mV)	210	186	172	212
pH (-)				
pH (-)	7.73	7.5	8.14	7.7
Ec (µS/cm)				
Ec (µS/cm)	575	760	927	599
other contaminants (µg/l)				
DADPM	< 2	3,500		
phenylacetamide				
dichlorobenzene				
benzamide				
chlorophenols		0.06		
toluene				
TCCP				
dichlorobenzonitril	10			
dichlorobenzamide	2			
2-chloroaniline				

	direction: south > north			
205	208	602	501	601
-110	-80	-55	0	100
1.9 - 2.9	1.7 - 2.7	5.3 - 6.3	3 - 4	4 - 5
main contaminants (µg/l)				
3,700	10,000	7,900	58,000	4.9
16	145	7.3	320,000	16
	11	33	< 100	1.8
parameters (mg/l)				
0	0	0	0	2.1
0	0	0	0	0
0	0	0	0.3	0
		6.5		
1.1	1.3	4.9	20	0.3
14	2.2	170	65	10
28	4	37	11	58
0	1.7	0	0.4	0.3
		30		
72	120	1,600	135	85
		22		
		245	1,970	33
3.3	33	40	960	15
redox (mV)				
183	191	163	172	156
7.52	9.7	6.94	8.14	7.46
671	1,105	8,430	927	1,172
other contaminants (µg/l)				
< 2	160		13,000	
			400	
			90	
			100	
68	13	0.03		20
	15			0.2
	15	15		
	2.3			

Table 5. Results from the intermediary sandy layer.

filter	701	702	703	252	9	802	400
depth (m)	16 - 17	16 - 17	16 - 17	15 - 16	14.5 - 15.5	16 - 17	18 - 19
main contaminants (µg/l)							
MCB	0.3	0	0.3	0	5,900	3,500	2.3
AN	0	0	0	0	13	2.5	2.3
benzene						3,100	
parameters (µg/l)							
O ₂ (average)	0.4	0	0	0	0	0.1	0
NO ₃ ⁻	0	0	0	0	0	0	0
Mn	0.19	0.18	0.24		0.27		
Fe(II)	1.9	1.9	0.8	5.1	5	2.5	9.9
Fe(tot)	6.5	7.5	10	9.5	10	36	14
SO ₄ ²⁻	37	38	37	0	0	6	4.3
H ₂ S	0	0	0	0	0	0	0
bicarbonate	20	24	24		25		
Cl ⁻	240	320	495	330	380	205	315
NH ₄ ⁺	37	53	35		43		
COD	63	97	92		126		
DOC	26	42	38	36	61	23	81
redox (mV)							
redox (mV)	130	244	160	152	170	188	164
pH (-)							
pH (-)	7.27	7.25	7.27	7.23	7.39	7.3	7.16
Ec (µg/l)							
Ec (µg/l)	2,240	2,770	3,125	3,030	2,960	1,540	2,190
other contaminants (µg/l)							
DADPM				< 2	< 2	< 2	< 2
chlorophenols					47		
polyols						120	22,000

3.3.4 Analysis of the results from the intermediary layer

Filters in the deeper sand layer are globally located in a circle with filters 9 and 802 in the centre of the contamination. The exact location of the filters is given in figure 2b. In table 5, the results for these filters are presented.

Each parameter (electron acceptors, electron donors, (potential) reaction products) will be discussed in relation to the encountered contaminant concentrations.

Oxygen

In the laboratory analysis, oxygen was only detected in filter 701. During the sampling of filter 701 it was observed that large amounts of air bubbles were pumped up with the groundwater. Lowering the pump speed did not stop this. The measured oxygen level was probably caused by a leak in the filter hose. It can be concluded that there is no oxygen present in the deeper sand layer.

Nitrate

Nitrate was not found in concentrations exceeding the detection level.

Sulphate, sulphide

The background levels of sulphate in filters 701 to 703 can be averaged at 37 mg/l. The upstream filter 400 (4.3 mg/l sulphate) cannot be used as a reliable indicator for background concentrations as large amounts (22,000 µg/l) of propoxy compounds were encountered.

In the centre of the contamination (filter 9 with 5,900 µg/l MCB) no sulphate has been detected. Directly downstream in the clean filter 252 no sulphate was present either.

In areas with MCB (and smaller amounts of AN) there is a sulphate 'gap'. This is a strong indication that sulphate reduction is occurring. It is a possibility that the process of sulphate reduction did occur in the past but is presently limited by a shortage of sulphate.

Iron, manganese

Background concentrations of Fe(II) can be averaged at 0.15 mg/l. In filters 9 and 802 (relatively high MCB concentrations, smaller amounts of AN) Fe(II) concentrations of 5.0 and 2.5 mg/l respectively have been measured. Overall, the same conclusions can be drawn as for the top sand layer: the iron levels could be influenced both by chemical or biological causes.

The manganese concentration in the contamination centre is only slightly elevated against background concentrations.

Other indicators

The other measured values for the indicators DOC, COD, chloride, redox, pH and electric conductivity are more stable than in the top layer. This may be caused by the lower MCB concentrations and by a lower biological activity because of the absence of suitable electron acceptors.

MCB and AN

In the intermediary layer, AN concentrations are substantially lower than MCB (13 µg/l and 5,900 µg/l respectively). In the top layer, proportions are the other way around (58,000 µg/l and 320,000 µg/l respectively). Given the comparable mobility of MCB and AN, this could be an indication of intrinsic anaerobic degradation of AN in the clay/sand layer.

3.3.5 Overall conclusions of the field study

Top layer

Spread of MCB and AN seems to occur mainly in northern and southern directions. In western and eastern directions, no spread seems to occur, which is possibly a result of occurring intrinsic degradation. Combined with the observation that relatively large amounts of oxygen have been found here, this could be an indication of occurring intrinsic aerobic degradation of AN and MCB.

At the contaminated site it seems that oxygen, nitrate as well as sulphate consumption has taken place in the source area of the top layer. It cannot be proven from the field data that metals have served as alternative electron acceptors but this should nevertheless be taken into account for the microbiological laboratory research.

Observations indicate the occurrence of anaerobic degradation processes. AN is possibly being degraded here. The literature research (see 3.2) which showed that anaerobic degradation of AN is possible under varying redox conditions, supports this possibility.

Intermediary sand layer

In the intermediary sand layer, anaerobic circumstances prevail. There seems to be a correlation between the presence of MCB/AN and the absence of sulphate.

Based on changes in the concentration levels for MCB and AN, intrinsic (anaerobic) degradation of AN may occur in the intermediary and clay/sand layer.

3.3.6 *Evaluation of the field study*

A field study aimed at detecting biological processes occurring naturally in the soil is certainly useful, because this is the only way in which it can be determined whether the field conditions are suitable for natural or stimulated biodegradation. A field study can yield information in basically three different ways:

1. It may reveal signs of the occurrence of natural biological processes and can therefore direct the laboratory study. Important information may be derived especially from the presence or absence of electron acceptors.
2. It may yield important information for the final process design (e.g. stratification, organic carbon levels).
3. It may provide insight in the order of magnitude of natural attenuation and the extent to which this affects spreading.

We think that biological parameters should be measured in an early stage of the research. Until now, this has only been done to a small degree.

In this stage, various conditions (redox condition, the presence of electron acceptors, pH and macro chemistry) would have to be investigated in:

- the source area;
- the plume area;
- a clean area.

The extent of the field study and the choice of parameters would depend on:

- the properties of the contaminant concerned;
- the soil structure (especially its stratification);
- the existing knowledge and experience;
- the budget.

In this NOBIS project, 8 groundwater measuring points in the top layer and 7 measuring points in the intermediary sand layer have been employed. We are under the impression that:

- the primary objective of the field study: evaluating the **occurrence of natural attenuation and processes involved**, has been attained in a cost-effective manner. More measuring points would not have made a relevant difference in the interpretation and fewer measuring points would have made the interpretation of the results (unacceptably) less reliable. However, in a more standard situation with a one-way groundwater flow, a well defined source, plume and clean area, it could be considered to use 5 to 6 measuring points (for each layer). This should be regarded to be the absolute minimum.
- the secondary objective: determining any possible effects of natural attenuation on the spread of contaminants, has only been attained partially. Conclusions on the spread of contaminants have been drawn, based on the differences in appendices B1/B2 and C1/C2 respectively. However, the differences between the contours drawn are based on a very limited number of observations: for only 4 points a set of two analysis results with a very short monitoring interval were available. To determine the **order of magnitude** of natural attenuation and its effect on spreading, additional and relatively

extensive monitoring is desirable: more filters will have to be monitored periodically over a period of several years.

Quantification of intrinsic biodegradation processes through field measurements alone is difficult because of the long monitoring periods, the often slow processes and complex interactions and sometimes unknown mechanisms.

In this NOBIS project a quantification of biodegradation rates will therefore mainly have to be deduced from microbiological laboratory experiments, conducted on soil samples from the site under investigation. The results of this research will be given and discussed in next paragraph.

3.4 Laboratory study

3.4.1 *Objective of the laboratory research*

The overall objective of the laboratory study was to determine the usability and optimum conditions of a certain biodegradation variant to be applied at the site under investigation. The practical approach, results and conclusions of this laboratory research are reported separately in the NOBIS report 96-1-10, 'A microbiological study', October 1998.

The main questions in the laboratory study and their answers are shortly described in next paragraph.

3.4.2 *Summary of the laboratory study*

This section summarizes the results given in the NOBIS report 96-1-10, 'A microbiological study', October 1998.

The main questions in the laboratory study and their answers are shortly described below.

1. Are viable microbes present at the polluted site, and are these indigenous microbes capable of degrading monochlorobenzene?
At the polluted site microbial activity was found, as well as aniline and monochlorobenzene degrading bacteria.
2. How toxic are monochlorobenzene and aniline to these bacteria?
Monochlorobenzene and aniline are not toxic up to concentrations of 10 mM.
3. Do additional carbon sources and nutrients enhance the degradation rate of monochlorobenzene?
Additional carbon sources and nutrients were observed to have neither a positive nor a negative effect on the degradation rate of monochlorobenzene.
4. What is the effect of the co-contaminant aniline on the degradation rate of monochlorobenzene?
Aniline does have a variable, sometimes inhibiting effect on the degradation rate of monochlorobenzene.
5. Does degradation of monochlorobenzene take place under anaerobic conditions in the absence or presence of alternative electron acceptors such as nitrate, metals, sulphate and carbon dioxide?
No degradation of monochlorobenzene takes place under anaerobic conditions. Neither in presence of alternative electron acceptors nor in the presence of alternative electron donors.
6. Is the degradation rate of monochlorobenzene influenced by low partial pressures of oxygen?
Decreasing monochlorobenzene degradation rates were found with decreasing oxygen concentrations.

7. Do additional alternative electron acceptors such as nitrate and sulphate enhance the monochlorobenzene degradation under low oxygen concentrations?

Additional alternative electron acceptors such as nitrate and sulphate did not enhance the monochlorobenzene degradation rate with low partial pressure of oxygen, despite the fact that some nitrate was reduced.

3.4.3 *Evaluation of the microbiological laboratory study*

This evaluation was executed from a practical and applicational point of view with regard to soil remediation.

Evaluation of the research strategy

In order to determine the employability and optimum conditions of a biodegradation variant to be applied at the site, various conditions needed to be investigated, because it was not known whether MCB could be degraded under the conditions existing at this site. Therefore, a step-by-step approach was followed:

Step 1: A rapid screening of the possibilities ('does it occur or not').

In cases of which it was strongly suspected that biodegradation could occur under certain conditions, or if biodegradation under such conditions had been demonstrated to occur, these conditions were further investigated in the next step.

Step 2: Refinement step.

Steps 1 and 2 were carried out both alternately and simultaneously. For example, with regard to biodegradation under oxic conditions a refinement step was immediately carried out based on known data.

The ICI study was for the most part carried out in the way that microbiologists are used to: experiments with inoculated systems were carried out, using both soil and non-soil systems. The standard temperature was 30 °C.

This microbiological approach has advantages in that standard methods are employed, obtained data can be compared with other studies and (values from) literature, and the methods employed are more accurate.

It would be preferable, from the point of view of the agency remediating the soil, if data obtained from experiments could be used directly in the field situation.

Consequently, experiments would have to be carried out with soil and at the in situ temperature (approximately 12 °C), to the extent possible.

This has, however, a disadvantage in that the experiments carried out can be less easily compared with literature data or with the results of other types of tests. Furthermore, during experiments with soil it is harder to maintain certain environmental conditions and to measure intermediates.

Laboratory results: What did we use?

The following laboratory study data were finally used for the elaboration of a remediation concept for the site under investigation (see also 4.3.4):

1. experiments intended to rapidly screen conditions in order to discover whether or not degradation occurs under these conditions;
2. experiments intended to measure degradation rates and estimate maximum degradation rates.

Next, the maximum rates were compared with the minimally required rate in the field (which depends on the remedial aims, the soil properties, and the degree to which the soil is contaminated).

What would we do differently or additionally?

- Measuring the maximum degradation rate in a soil suspension or in a column containing a stirred sample *at the in situ field temperature*.
- Adaptation and repetition of the column test.
The test carried out during the investigation, involving an aerobic and an anaerobic soil column, yielded results deviating from the expectation on the basis of the results of the microbiological study.

Adaptations should be aimed at:

- shortening the residence time in the column (e.g. by using short, wider columns);
- making it easier to work under anoxic conditions.

The following could still be done as a check:

- a test under (more or less) in situ conditions to check whether the degradation rates under ideal conditions more or less correspond to those occurring in the field.
This could either be done in the laboratory with larger undisturbed columns or in the field in a small pilot plant.

Recommendations for the strategy of a feasibility study

In view of the above findings, we recommend the following strategy for a feasibility study:

1. Additional measurements under in situ conditions (e.g. more experiments with soil at 12 °C).
2. More tests of the following types:

<i>laboratory test</i>	<i>advantages</i>	<i>disadvantages</i>
a. slurry	relatively homogeneous, simple, rapid, standard	soil structure no longer intact
b. soil column	soil structure maintained quick overall result	conditions vary locally conditions not easily comparable difficult to interpret detailed mechanisms

3. Fewer non-soil experiments (enrichments, chemostats).

However, we recommend to carry out non-soil experiments in case promising data for these have been found in the literature, such as for rapid batch experiments or in special situations if:

- extensive details are necessary (e.g. determination of intermediates);
- constant conditions are important (especially in the case of low concentrations);
- it is desirable that the obtained results are comparable with data from the literature or publications.

CHAPTER 4

REMEDIATION/CONTAINMENT MEASURES

4.1 Introduction

This chapter sketches possible remediation and containment measures from a technical point of view. The following subjects are successively discussed in the subsections:

- the boundary conditions, objectives, and site-specific conditions (see 4.2);
- the general notes on remediation measures (see 4.3);
- the measures to be taken in subareas:
 - source area in top layer and clay/sand layer (see 4.4);
 - plume in the top layer (see 4.5);
 - plume in the intermediary sandy layer (see 4.6);With the deeper aquifer being regarded as a protected object, no measures are planned for this aquifer;
- a selection of the most effective and reliable measures (see 4.7);
- the compilation of measures to be taken in the subareas, so as to arrive at an optimal remediation strategy (see 4.8).

4.2 Boundary conditions and remediation aims

This section discusses the assumptions, boundary conditions, objectives and site-specific conditions with regard to the remediation of the ICI site under investigation:

- a. The site should meet the requirements formulated in consultation with the authorities in charge, the land owners and the present user (ICI). Given the ongoing changes in environmental policy, the outcome of this discussion is uncertain. There seems to be a trend towards a more site- and contamination-specific approach. However, for the case at hand, we adopted the relatively strict and old policy as a starting point (see also f):
 - ***no spread in the direction of the harbour or aquifer;***
 - ***measures should at least fit within the Isolation, Containment, Monitoring (ICM) framework;***
 - ***containment/monitoring of pure product (sinking layers).***
- b. Continuation of the current use in the coming years.
Therefore:
 - ***time is not a critical factor.***
- c. Measures should not interfere with the company's operations.
Therefore:
 - ***earth moving is not feasible;***
 - ***it is preferred that no measures be taken at the plant.***
- d. Minimum investments (now and in the future).
- e. The site should (eventually) be suitable for other industrial purposes.
- f. In view of the current legal framework and the site-specific conditions, it is sufficient to contain the contaminations (ICM variant) at the site.
In view of the long period available, it may be considered to include cost-effective remediation measures of a low intensity in this variant. These measures should aim at improving the soil quality to allow for the site to be used for other industrial purposes as well.

4.3 General notes on remediation techniques

This section contains some general notes on the applicability of remediation techniques at the site.

4.3.1 *Applicability of remediation or containment measures*

Evaluation step 1

In step 1, we consider the applicability of (1) remediation measures and (2) containment measures:

1. Measures intended to improve the soil quality in the contaminated (sub)area. These measures concern the entire subarea. A distinction can be made between:
 - a high-intensity remediation strategy: a remediation project carried out within a short period of time which involves a lot of effort (a dense network of filters, alternation and combination of techniques, high flow rates, high energy consumption);
 - a low-intensity remediation strategy: a remediation project utilising the factor time and the self-purifying capacity of soil. This entails a limited effort (a less dense network, simpler techniques, lower flow rates, low energy consumption). The boundary condition to be met by this remediation strategy is the containment of the contamination.
2. Measures intended to prevent any spreading from a contaminated (sub)area by interrupting the route of exposure. Containment measures would involve a zone or screen around the area.

Conclusion of evaluation step 1

Due to site-specific conditions (the required continuation of the company's operations and the time available) and the nature of the contaminated soil system, a remediation strategy of a high intensity is not feasible at this site.

4.3.2 *Applicability of remediation and containment techniques*

Evaluation step 2

Next, we consider the applicability of remediation and containment techniques. A distinction may be made between:

1. civil-engineering or geotechnical measures. These would involve either a removal by moving the soil or an isolation using sheet-pile walls.
2. in situ techniques stimulate the removal of contaminants from the soil and groundwater without removing the soil itself. This definition also includes groundwater and soil vapour withdrawal, although an aboveground water and air treatment will often be necessary.

Conclusion of evaluation step 2

Civil-engineering or geotechnical measures are not feasible and/or too expensive under the specific conditions of the site (required continuation of the company's operations).

4.3.3 *Applicability of in situ techniques*

Evaluation step 3

Here we consider the possibilities of the application of in situ techniques, consisting of either removal or containment, by means of:

1. convective groundwater transport (possibly including aboveground groundwater treatment: pump and treat), and/or
2. convective soil vapour transport and aboveground soil vapour treatment, air sparging combined with soil vapour extraction, and/or

3. biodegradation, at which a distinction may be made between:
 - a. natural attenuation;
 - b. stimulated degradation.

Sub b.

Conditions can be enhanced by:

- the supply of nutrients and electron acceptors and/or electron donors in the water phase (infiltration, often combined with pump and treat); this is in principle technically feasible both in the case of aerobic and anaerobic degradation;
- supply of oxygen by air sparging. This is only relevant to aerobic degradation:
 - in the top soil, this is technically feasible (and a technology that has been successfully applied in the past) and the most cost-effective method for the supply of oxygen (in case a stimulation of aerobic degradation is decided on);
 - in the deeper layers, this is likely to be technically feasible and cost-effective. The interim results of the KPE project are positive. If this option is chosen, a phased installation is preferable (i.e. an installation on part of the site, testing, evaluation, and adaptation and extension of the plant).

Conclusion of evaluation step 3

Basically, the above techniques can be applied, and doing so would not be contrary to any of the boundary conditions. The various aspects of these techniques would have to be further investigated per subarea.

Because too few facts were known about the aspects of biodegradation, its applicability was investigated within the NOBIS project (see 4.3.4).

4.3.4 Applicability of biodegradation

Evaluation step 4

The degree to which biodegradation can be applied as a containment/remediation measure is discussed here.

Anaerobic degradation of MCB

Laboratory results indicate that anaerobic degradation of MCB is not possible under iron reducing, sulphate reducing, denitrifying and dehalorespiring conditions. **If it should be possible, laboratory results certainly did not show what is necessary to stimulate it.** Anaerobic degradation of MCB will therefore not be considered as a remediation option.

Aerobic degradation of monochlorobenzene

Indigenous activity

Activity of indigenous MCB degrading microbes under aerobic conditions has been proven in experiments with soil slurries (refer to the NOBIS report 96-1-10, 'A microbiological study', section 4.1). Incubation occurred at approximately 55,000 µg/l MCB, which was comparable to the highest concentration found in the groundwater on the site (measuring point 501) in the fieldwork phase.

Activity as a function of the oxygen level

Results from experiments (both soil- and sludge enrichments) show a correlation between the oxygen levels and degradation rates.

At partial pressures of 0.2 and 0.1 atmosphere oxygen (measured in the headspace) degradation of MCB was complete. In slurry experiments with soil from measuring points 602 and 603 an MCB degradation rate of 23 mg·kg⁻¹·day⁻¹ was measured (oxygen saturation, refer to section 4.1

of the NOBIS report 96-1-10 'A microbiological study'). These populations encountered 40 and 7 times (respectively) the concentrations they were used to in the field situation.

Soil taken from filter 601 showed a lower degradation rate of $17 \text{ mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$. This can be explained by the fact that field concentrations of MCB for soil and groundwater at this measuring point are very low (0.1 mg MCB/kg and $4.9 \mu\text{g MCB/l}$ respectively). Apparently the biological population in this soil was not fully adapted to the more than 10,000 times higher concentrations during the laboratory test.

The above-mentioned degradation rate of approximately $20 \text{ mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ for MCB can be considered to be the maximum degradation rate because of the ideal circumstances (shaking, oxygen saturation, $30 \text{ }^\circ\text{C}$) during the tests.

In an *in situ* field situation this rate will not be reached, due to the lower temperature, lower oxygen levels and a lesser soil/water contact. First we will discuss the effect of the oxygen level.

At $5 \text{ mg O}_2/\text{l}$ (0.1 atm) the degradation rate is about 20 % lower than the degradation rate at $10 \text{ mg O}_2/\text{l}$ (0.2 atm. , saturation level).

At lower partial oxygen pressures (0.02 and 0.005 atm.) *incomplete degradation* of MCB occurs and strong evidence for the formation of intermediates exists. Chlorobenzenediol which is strongly related to chlorocatechol has been detected. Chlorobenzenediol and chlorocatechol are both intermediates in the degradation pathway of MCB (see references in 'A microbiological study'). Relevant experiments can be found in the NOBIS report 96-1-10 'A microbiological study', section 4.6.1.

Since formation of large concentrations of chlorocatechols and/or chlorobenzenediols could have a toxic effect on the biodegrading capacities of bacterial populations present in the soil, the formation of these intermediates in a field situation should be avoided. Possible toxic effects and incomplete degradation of MCB should be avoided by maintaining an oxygen level that is high enough in the area that is to be treated.

Thus, a remaining question is: what oxygen level is high enough?

From the results presented in section 4.7 of the NOBIS report 96-1-10 'A microbiological study', it can be concluded that at 3 % oxygen (0.03 atm.) complete degradation of MCB occurs. This level is therefore considered to be safe. In a field situation, oxygen will be measured in the aqueous phase. It can be calculated that at a partial pressure of 0.03 atm. oxygen in the headspace, $1.5 \text{ mg O}_2/\text{l}$ (at $30 \text{ }^\circ\text{C}$) must have been present in the aqueous phase.

For the design of a remediation concept, a safe minimal concentration of approximately 2 to 3 mg/l oxygen within an 'active zone' will have to be considered. At these concentrations, degradation rates are expected to be approximately 40 % lower than at oxygen saturation levels (refer to table 13 of the NOBIS report 96-1-10 'A microbiological study').

The effect of the temperature on MCB degradation

A degradation rate 4 to 7 times lower at the *in situ* field temperature ($12 \text{ }^\circ\text{C}$) compared to the laboratory temperature of $30 \text{ }^\circ\text{C}$ can be deduced from a comparison of the presented degradation rates (in $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g protein}^{-1}$) for sludge enrichments in tables 13 and 14 of the NOBIS report 96-1-10 'A microbiological study'. Degradation rates in soil enrichments at $12 \text{ }^\circ\text{C}$ (oxygen saturation) were too low for reliable measurements.

The effect of MCB, AN, and combinations of MCB and AN on degradation rates

Concentrations of MCB and AN (**not combined**) up to 10 mM (= 1,126,000 µg/l MCB and 931,000 µg/l AN) showed no effect on degradation rates. However, the lag-phase increased with increasing concentrations. If biodegradation of similar high concentrations is to be stimulated in the field, a lag-phase of at least several months has to be taken into account.

If MCB and AN are **both present**, a relevant inhibition of MCB degradation in the soil is to be expected for AN concentrations over 50,000 µg/l. This conclusion has been drawn from the presented results in table 10 of the NOBIS report 96-1-10 'A microbiological study', section 4.4.1.

With approximately 50,000 µg/l AN present, experiments with batch soil-enrichments show 66 % of the MCB degradation rate without AN. With approximately 100,000 µg/l and 200,000 µg/l AN present respectively, the degradation rate drops further to 20 % and 15 % (respectively) of the maximum capacity.

For the centre of the combined MCB and AN contamination (around filter 501: 58,000 µg/l MCB combined with 320,000 µg AN/l present) this implies that biodegradation will only proceed at a very slow rate and after a long lag-phase which would take at least several months, possibly more.

In the centre of the contamination, high AN concentrations will slow down MCB degradation to a level which makes biodegradation not a suitable remediation alternative for this part of the site. Present contaminants will have to be contained and removed at a later stage, or will have to be reduced first by means of conventional techniques, if they pose an unacceptable risk.

The effect of (micro)nutrients and carbon source

The addition of a carbon source (yeast extract) and vitamins did not enhance biodegradation (also refer to section 4.3 of the NOBIS report 96-1-10 'A microbiological study').

When applying a biologically based remediation strategy, no nutrient addition will be necessary on short notice. For long term strategies (especially intensive ones) it is advisable to periodically monitor for macronutrients. Micro-nutrients could be measured incidentally. In case of depletion, nutrient addition should be applied.

The effect of additional alternative electron acceptors at low oxygen concentrations

Addition of sulphate showed no effect on MCB degradation. Results for nitrate addition were not clear. Initial nitrate levels decreased slightly, and brown-colouring (indication for catechol formation) was not observed. This could indicate complete MCB degradation at low oxygen concentrations. However, within the context of this research the effect of nitrate combined with low oxygen concentrations could not be investigated thoroughly. The possibilities for degradation in the presence of nitrate may be further investigated in other research projects.

Conclusion of evaluation step 4

The main conclusions with regard to the possibilities to apply biodegradation as a containment/remediation measure are summarized below:

- a. the required redox condition is aerobic;
- b. the required oxygen concentration in the groundwater in order to obtain a complete degradation is ≥ 2 mg/l;
- c. the highest attainable degradation rate for MCB (under ideal circumstances: 30 °C, oxygen saturation, no inhibition as a result of AN, shaking) is approximately 20 mg MCB/kg soil/day;
- d. the expected effect of the field temperature (12 °C) on the degradation rate is a rate 4 - 7 times lower than at 30 °C;

- e. the expected effect of a lower oxygen level on the degradation rate (2 mg/l: minimum) is a rate 1.7 times lower than at saturation levels;
- f. a combination of c, d and e leads to an estimated *maximum* degradation rate *at in situ conditions* of approximately 2 mg/kg/day. This degradation rate is considered to be a maximum because it is based on a situation with an optimal contact between the different phases. In a field situation the degradation rate will be limited by the rate of diffusion;
- g. no inhibition is expected in the case of concentrations of MCB and AN up to 1 g/l (separately present!);
- h. inhibition of MCB degradation will increase with increasing AN concentrations. Degradation rates of MCB at 100,000 µg/l AN will decrease to only 20 % of maximal capacity. In the contamination centre, high AN concentrations will slow down MCB degradation to a level which makes biodegradation not a suitable remediation alternative for this part of the site. Present contaminants will have to be contained and removed at a later stadium, or will have to be reduced first by means of conventional techniques;
- i. in the short term, no nutrients need to be supplied; however, monitoring is necessary;
- j. the possibilities for degradation of MCB in the presence of nitrate should be further investigated.

4.4 Measures regarding the source area in the top layer and clay/sand layer area

Objective

Minimum objective:

- containment of the contamination to prevent spreading towards the aquifer.

Other (secondary) objectives may be:

- containment to prevent spreading in the top layer;
- containment to prevent spreading through the intermediary sandy layer;
- remediation of the source area.

Possible measures:

- geohydrological containment by pumping and aboveground treatment.

Possibly in combination with:

- air sparging (aimed at both convective soil vapour transport and the stimulation of biodegradation);
- air sparging combined with nitrate infiltration.

Natural attenuation or bioremediation of a low intensity is **not possible**, because this occurs too slowly in the centre of the source area where concentrations of MCB and AN exceed 10,000 µg/l. In the next few decades the risk of spreading would not be eliminated if these techniques were used.

4.4.1 *Geohydrological containment by pumping and treatment aboveground*

Vertical migration has occurred due to infiltration and possibly also by density-dependent flow. Groundwater extraction would interrupt this path.

Options:

a. ***Extraction in the source areas of the top layer and clay/sand layer***

This would have a remediating effect, because high concentrations would be eliminated. However, it would probably require a relatively dense network on the production location itself to prevent further vertical and horizontal spreading. Initially, relatively intensive extraction should occur, and the concentrations would be high. After some years, the intensity could be lowered by intermittent pumping of groundwater.

b. ***Extraction in the intermediary sandy layer, just below the source areas with a limited number of deepwells***

This would be an effective containment but there would hardly be any remediating effect. A disadvantage of this method would be that contaminants would be attracted from the topsoil.

An obvious system would be to use option a at a few locations where the concentrations are highest, in combination with option b.

Aspects to which attention should be paid during the remediation measures:

- a comparison between the types of extraction means (vertically or by horizontally driven bores);
- the risk of settlement and how to eliminate this risk;
- the number and positions of extraction means, desired location versus accessibility;
- the possibilities for treatment, existing treatment plant;
- a specification of costs.

4.4.2 *Air sparging (aimed at both convective soil vapour transport and the stimulation of bio-degradation)*

It is not feasible to install an intensive air sparging system in the top layer because of the plant's infrastructure present.

Non-intensive removal of the contamination by air sparging (intermittently and with a low density injection filter network) would occur too slowly and would probably not eliminate the risk of spreading downwards by the groundwater flow. Moreover, if only air sparging were applied in the source area, pure product might be mobilised and then sink further. Therefore, air sparging in the source area as a single measure will not be further considered.

Air sparging **in combination with** geohydrological containment may have the following advantages:

- a. mobilisation of pure product, which is then removed by groundwater extraction;
- b. convective removal by stripping;
- c. stimulation of aerobic degradation.

As a result of air sparging, the pump and treat containment system would have an increased remediating effect. This measure should be therefore be considered as an additional measure.

Air sparging can be applied in three different systems:

1. a system in the source area at 'hot spots', aimed at a, b, and c;
2. a less dense network or a screen in the top layer at the border of the source area (concentrations approximately 100 µg/l) in order to stimulate aerobic degradation;
3. a system in the intermediary sandy layer below the source area, especially aimed at aerobic degradation (injected air would travel upwards in the source area).

Aspects to which attention should be paid during further elaboration

In the stage of an evaluation/designing, the following should still be investigated:

- the number and positions of injection and extraction means; the desired location versus accessibility;
- the possibilities for treating extracted soil vapour and the cost involved;
- a specification of the cost.

4.4.3 *Air sparging in combination with nitrate infiltration*

In addition to air sparging (see the notes on air sparging presented in 4.4.2), it might be possible to stimulate degradation with the addition of nitrate under micro-aerophilic conditions. However, it must be noted that the occurrence and the order of magnitude of degradation under these conditions has not yet been determined.

Nitrate dosing at very low costs and a relatively high degradation rate would have to be necessary in the source area in order to obtain a bonus with regard to the above remediation and containment variants. However, it is currently unknown whether degradation can occur under these conditions.

An investigation into the degradation under these conditions could be carried out in a field situation, e.g. concurrently with a further microbiological study as part of a follow-up study.

4.5 **Measures regarding the contaminant plume in the top layer**

Objective

Primary objective:

- containment of the plume.

A secondary objective could be:

- remediation of the slightly contaminated plume area (concentrations < 100 µg/l).

Possible measures:

- checking whether natural attenuation occurs (monitoring of spreading and parameters);
- a bioscreen, somewhere in the plume.

Not recommended

(Either because of the high costs while only a low load would be removed or because it would be an everlasting measure):

- groundwater extraction in the plume area (this would also attract contaminants from the source);
- intensive remediation by stripping or biodegradation.

Note

When discussing measures for the plume area, it must be noted that measures taken in the source area (see 4.4) would affect the plume area: the flux from the source area (supply from the plume) would strongly decrease.

4.5.1 *Checking natural attenuation*

The best way of checking whether natural attenuation occurs is measuring the contaminant concentrations and the most relevant process parameters in a row of filters located close to each other. These filters should be installed in a flow path running through the plume from the source area.

If natural attenuation occurs, this would of course be a highly cost-effective containment method. If no natural attenuation is found to occur, at least the rate of spreading would be measured accurately.

Aspects to which attention should be paid during further design

The exact position of the filters, their number, their distance from each other, the package of contaminants to be monitored, cost, and the policy regarding natural attenuation.

4.5.2 Bioscreen

The installation of a bioscreen could be considered in the spots where natural attenuation insufficiently prevents MCB and AN from spreading.

The conditions in this bioscreen would have to correspond with those required for biodegradation as detailed in 4.3.4, which were derived from the NOBIS report 96-1-10 'A microbiological study'. In 4.3.3, the use of pressurized air was already mentioned as the most cost-effective method to install a bioscreen.

The degradation rate required in the screen to neutralise the inflowing contaminants depends on the:

- flow rate of the groundwater;
- contaminant concentrations in the inflowing groundwater;
- thickness of the screen.

The flow rate and the contaminant concentrations in the inflowing groundwater depend on the position of the screen. The thickness of the screen depends (in the case of oxygen supply by air sparging) on the:

- radius of the influence of air sparging;
- distances between filters.

In an earlier stage of this project, a sample calculation was carried out to demonstrate that, in theory, such a screen stimulates degradation to a sufficient degree and thus prevents spreading.

Aspects to which attention should be paid during further design:

- when combining extraction measures in the source area: check whether the installation of a bioscreen would still be useful;
- the background concentration of oxygen in the plume makes it useful to consider a phased installation of air sparging filters:
 1. initially, the filters should be as far apart as possible;
 2. if it turns out that the oxygen concentrations are not sufficiently affected between two filters, only then should additional filters be installed;
- the determination of the exact position of the screen, and a specification of the cost.

4.6 Intermediary sandy layer

Objective:

- prevention of spreading.

Possible measures:

- geohydrological containment;
- containment by stimulating biodegradation.

Not recommended:

- a further investigation into the occurrence of natural attenuation: natural attenuation is probably too slow for MCB because of the anaerobic environment.

4.6.1 *Geohydrological containment*

In 4.4.1 (geohydrological containment by pumping and aboveground treatment), this measure was already mentioned.

The implementation of containment could be reached by installing one or two deepwells immediately behind the source areas, directly below the clay/sand layer. This way, an effective containment could probably be achieved, but it should be taken into account that it would have hardly a remediating effect.

Aspects to which attention should be paid during further elaboration:

- the number and positions of the extraction means: desired location versus accessibility;
- effects on the aquifer;
- possibilities for treatment;
- costs.

4.6.2 *Stimulation of biodegradation*

In order to make it possible for the above measure to be of a permanent nature, it should be considered to apply air sparging in the area between the clay/sand layer and the intermediary sandy layer.

Given the preliminary results of the KPE project, relatively long radii of influence seem to be achievable in the package of the clay/sand layer, partly because of the horizontal stratification in this package. During an elaboration, the results of this project could be used.

Aspects to which attention should be paid during a further elaboration:

- the position of the pressurized air filters;
- the effects of making an anaerobic environment aerobic;
- the cost.

4.7 **Further elaboration of obvious measures**

A comparison of the discussed measures in the previous sections 4.4 to 4.6 with regard to most important aspects:

- costs (investments and yearly costs),
- reliability (is it 'proven' technology and is it likely to work?),
- feasibility (is installation possible on a site in operation?),
- flexibility (can the system be easily adjusted?),
- degree of containment and/or removal of contaminants,

has been made. This overview is presented in appendix G.

From this comparison it can be concluded that 4 measures have a 'high score' on before mentioned aspects:

- a. monitoring of spreading (and natural attenuation) in plumes;
- b. pump and treat in the source area of the top layer;
- c. pump and treat in the intermediary sand layer;
- d. bioscreen(s) in the plume areas.

A further elaboration of these measures with regard to '*aspects to which attention should be paid during further design*' as mentioned in 4.4 to 4.6 was necessary to be able to compose the optimal remediation strategy. These further elaborations can be found in appendices H1 to H4.

For this site, pump and treat turned out to be a more obvious remediation variant than it may be for other sites, because of the presence of:

1. an aboveground industrial waste water treatment plant (active sludge). The sludge from this plant has been used in laboratory experiments and has been found to degrade MCB and AN very effectively. It has enough capacity to deal with an extra amount of water.
2. a sewer system with enough capacity to transport extra amounts of water from the polluted production plant towards the waste water treatment plant.

Groundwater treatment and (to a lesser extent) transport generally make up the major part of involved costs when applying pump and treat measures. The presence of the sewer system and an industrial waste water treatment plant, combined with the fact that pump and treat is a 'proven' and accepted technology, justifies further elaboration of pump and treat measures in both the top layer and the intermediary sand layer.

4.8 Proposed remediation strategy

In this section conclusions and suggestions concerning the further approach of the remediation strategy on the ICI site will be given.

We propose:

- to present the results of this NOBIS project, including the proposed remediation strategy, to the competent authorities and other parties involved, in order to arrive at a mutual agreement on the remediation approach. Whether Britannia Harbour is an object to be protected should be focused on in the discussions;
- the installation of pump and treat measures on short notice: two horizontal drains in the top layer (see appendices H1, I1 and I2) and one deepwell in the intermediary sand layer (see appendices H2 and J);
- the installation of a row of monitoring filters in the top layer in the western, northern and (north)eastern directions. We also propose the execution of a monitoring schedule in order to measure the effect of the groundwater withdrawal on the spread of contaminants and on the occurring natural degradation in the top layer;
- monitoring the filter in the aquifer to check for spread towards the aquifer and the effect of groundwater withdrawal in the intermediary sand layer;
- a project proposal to investigate the influence of nitrate addition in the presence of low oxygen tensions on MCB and benzene degradation with the Universities of Groningen and Wageningen, TNO and Tauw (in preparation). The site of ICI could be used as a field test case;

- to interpret and evaluate the data collected after a relatively short period of monitoring (2 years), after which the further strategy should be discussed with the competent authorities. Further strategy could involve a wide range of activities:
 - decreasing or even ending monitoring activities;
 - (temporary) continuation of monitoring activities;
 - increasing monitoring activities;
 - taking additional measures:
 - installation of extra groundwater extraction filters in the top layer;
 - installation of a bioscreen (top layer) combined with nitrate injection;
 - installation of a bioscreen in the intermediary sand layer;
 - (based on the final results of the NOBIS/KPE project which will be available by then)
 - installation of an additional deepwell in the aquifer.

These additional measures have all been mentioned in previous sections and have been elaborated on to a certain extent. Any need for further elaboration and comparison of these additional measures depends on the future results of the proposed monitoring and remediation activities and on a combination of other developments (in remediation policy, technical developments, ICI location strategy, et cetera) that reach beyond the scope of this NOBIS project.

CONCLUSIONS AND RECOMMENDATIONS

5.1 Site characterization

Estimates of total loads of contaminants in the top layer and horizontal and vertical fluxes from the source areas towards the plume areas have been made in 2.3.

The calculation of contamination fluxes and loads provided a clear insight in the contamination situation and specific problems and this subsequently led to a more effective remediation strategy. For the ICI site, it was observed that the horizontal contamination fluxes amount to only a fraction of the vertical fluxes.

Based on the obtained results in this project, we conclude that on the investigated site, vertical migration poses a larger threat to the environment than horizontal migration and that remediation efforts should primarily be aimed at preventing vertical spread rather than horizontal spread.

On a yearly basis, only grams of MCB move towards the direction of the harbour. If this plume would eventually reach the harbours surface water, undetectable amounts of MCB would be 'discharged'.

In view of the efforts (energy, costs) versus the environmental merit, it seems that measures to fight any horizontal spread towards surface water not cost-effective. This can be further illustrated by a REC (Risk, Environmental merit, Costs) assessment or by the 'Environmental Benefit' concept of ICI.

Handling 'discharge' of contaminations into surface water as a result of convective flow and diffusion from soil contamination is a problem with many projects and with several NOBIS projects (e.g. KPE, EPON sites). It is strongly recommended to organise a symposium on how to deal with this issue. We believe that this would be a valuable initiative for NOBIS, end users and the authorities involved (e.g. water quality administrators).

5.2 NOBIS investigation

5.2.1 Literature search

The most important conclusions of the literature review are reported in 3.2.3.

Prior to the ICI/NOBIS project, neither the effects of a combination of AN and MCB nor any anaerobic degradation conditions were known. In this NOBIS project, the literature search has proved to be a useful tool to direct laboratory and field research, thus optimising available research funds and time.

5.2.2 Field investigations

Reported overall conclusions in 3.3.5 have been based on the usage of 8 groundwater measuring points in the top layer and 7 measuring points in the intermediary sand layer. We are under the impression that:

- *the primary objective* of the field study: evaluating the **occurrence of natural attenuation and processes involved**, has been attained in a cost-effective manner. More measuring points would not have made a relevant difference in interpretation, fewer points would have made the interpretation of the results (unacceptably) less reliable.

However, in a more standard situation with a one-way groundwater flow, a well defined source, plume and clean area, one could consider to use 5 to 6 measuring points (for each layer). This should be regarded to be the absolute minimum.

- *the secondary objective*: determining any possible effects of natural attenuation on the spread of contaminants, has only been attained partially.

Conclusions on the spread of contaminants have been drawn, based on a very limited number of observations: for only 4 points a set of two analysis results with a very short monitoring interval were available. To determine the **order of magnitude** of natural attenuation and its effect on spreading, additional and relatively extensive monitoring is desirable: more filters will have to be monitored periodically over a period of several years.

5.2.3 *Laboratory investigations*

The overall conclusions are reported in 3.4.1.

The laboratory investigations have provided us with useful information concerning the (im)possibilities of MCB and AN degradation. We now have a good qualitative impression of the required conditions and, to some extent, we can even make a quantitative estimate of the effect of the presence of electron acceptors, electron donors, and the co-contaminant AN on the degradation of MCB.

However, in trying to translate laboratory results into field conditions, more experiments that approach these field conditions would have been useful.

For a similar follow-up study we would therefore recommend more measurements that better approach the field conditions. This means more experiments with soil, and more experiments at 'in situ' temperatures (approximately 10 °C).

Field conditions could be approached more by increasing the number of relatively rapid and simple soil slurry tests. This will provide a quick scan of possibilities. Additionally, soil column tests could be used for the most relevant conditions in order to include the effect of heterogeneities and diffusion-limitation. We recommend the use of small columns with a short recirculation time.

Non-soil experiments (e.g. enrichments, chemostats) are still recommended:

1. in case promising data were found in the literature;
2. in the case of rapid batch experiments;
3. in case of special situations, for instance:
 - when a high degree of accuracy is desired (e.g. determination of intermediates);
 - when constant conditions are important (especially with low concentrations);
 - when it is desirable that the results obtained are comparable with the data from literature or publications.

5.3 **Remediation measures and strategy**

The conditions under which to apply (stimulated) degradation as a remediation measure are presented in 4.3.4.

In theory, these conditions would render a low intensity biological concept (e.g. a bioscreen in the plume areas) feasible. However, for this particular site, pump and treat turned out to be a more cost-effective remediation option because of the presence of an activated sludge waste water treatment which proved to degrade MCB and AN.

We believe that the remediation strategy for the ICI site proposed in 4.8 is flexible and built up around a technically secure and predictable core of pump and treat measures which have worked well in other cases and which will be highly cost-effective in this case due to the presence of a large active sludge waste water treatment system.

We consider the proposed additional monitoring measures and the phased approach leaving room for additional future remediation measures and the usage of naturally occurring biodegradation on the site the best way to reach an optimum between costs and environmental merit within the requirements as formulated by the competent authorities (both now and in the future).

Although the core of the proposed measures are not 'biologically based', this NOBIS project has led to a more fundamental insight in possibilities regarding biological degradation of MCB and AN. In turn, this insight has led to a remediation strategy in which biological processes both in the field and in the waste water treatment are being used in order to achieve an optimum between available funds and environmental merit.

Therefore, we can safely say that at least one of the NOBIS objectives: making better use of biodegrading capacities, has certainly been achieved through this project.

APPENDIX A

**LOCATION OF ICI HOLLAND BV AND CROSS-SECTION
OF REGIONAL SOIL LAYERS**

APPENDIX B1

CONTAMINATION CONTOURS OF MCB (1996)

APPENDIX B2

CONTAMINATION CONTOURS OF MCB (1995)

APPENDIX C1

CONTAMINATION CONTOURS OF AN (1996)

APPENDIX C2

CONTAMINATION CONTOURS OF AN (1995)

APPENDIX D

TOTAL LOADS OF MCB AND AN IN THE TOP LAYER

Points of departure and assumptions:

- contaminated saturated zone = 4 metres;
- porosity = 0.35;
- soil density 1700 kg/m³;
- K_{oc} MCB = 150 dm³/kg;
- K_{oc} AN = 200 dm³/kg;
- f_{om} : fraction of organic matter = 0.02;
- f_{oc} : fraction of organic carbon = 0.006 · f_{om} = 0.012;
- assumption of equilibrium: $C_{soil} = K_{oc} \cdot f_{oc} \cdot C_{groundwater}$;
- assumption: concentrations do not vary with height.

Table D1. Load of monochlorobenzene in plume and source area of the top layer.

conc. in ground-water (µg/l)	average conc. in groundwater (µg/l)	average conc. in soil (mg/kg)	area (m ²)	total: g. water (kg)	total: soil (kg)
0 - 100 (plume)	50	0.090	10000	0.7	6.1
100 - 1000	300	0.54	5275	2.2	19
1000 - 10000	3000	5.4	7650	57	281
> 10000	30000	54	2075	87	762
				147	1068

Table D2. Load of aniline in the plume and source area of the top layer.

conc. in ground-water (µg/l)	average conc. in groundwater (µg/l)	average conc. in soil (mg/kg)	area (m ²)	total: g. water (kg)	total: soil (kg)
0 - 100	50	0.12	7000	0.49	5.7
100 - 1000	300	0.72	1875	0.78	9.2
1000 - 10000	3000	7.2	2250	27	110
> 10000	100,000	240	4730	165.5	7720
				194	7845

APPENDIX E1

HORIZONTAL FLUXES OF MCB AND AN

MCB

The groundwater flow velocity in the filling layer varies locally. In order to be able to calculate the yearly amount of contaminants per square metre of soil from the source area into the plume area (flux), we have assumed the following:

v : average flow velocity (all directions): 7 m/yr
 A : area of flow towards plume: 2500 m²
 C_{in} : inflowing concentration of MCB from the source: 100 µg/l
 Θ : pore volume: 35 %
 Φ_{MCB} : total flux from the source to the plume area per square metre per year

$$\Phi_{MCB} = C_{in} \cdot \Theta \cdot v = 245 \text{ mg/m}^2/\text{yr}$$

In the direction of the Britannia Harbour a flow occurs over an area of 125 m (width) by 4 m (depth). The total flux in this direction can be calculated at 0.12 kg/yr. The assumed groundwater flow velocity of 7 m/yr in this direction could be underestimated, but even if it is several times higher, the flux in the direction of the harbour will still be less than 1 kilogramme a year.

The total load at the boundary between the source area and the surrounding territory (plume area) can be calculated at 0.61 kg/yr for the entire location (approximately 625 by 4 m).

Aniline

The same procedure can be followed for aniline, although a relevant spread of AN only seems to occur in the direction of the harbour and in the southern direction. At the 100 µg/l iso contour line for MCB (= the defined border between the source area and the plume area at the location) C_{in} for AN is about 10 % of the MCB concentrations. This means fluxes in these directions will lie in the order of magnitude of 10 grams aniline a year (25 mg/m²/yr).

APPENDIX E2

VERTICAL FLUXES OF MCB AND AN

Points of departure (also refer to appendix E1):

v_{inf} : groundwater infiltration velocity = 0.3 m/yr

Table E2.1. Monochlorobenzene.

conc. in ground-water ($\mu\text{g/l}$)	average conc. in groundwater ($\mu\text{g/l}$)	area (m^2)	flux ($\text{mg/m}^2/\text{yr}$)	total: flux (kg/yr)
0 - 100	50	10000	5.25	0.05
100 - 1000	300	5275	31.5	0.17
1000 - 10000	3000	7650	315	2.41
> 10000	30,000	2075	3150	6.54
				9.2 kg MCB/yr

Table E2.2. Aniline.

conc. in ground-water ($\mu\text{g/l}$)	average conc. in groundwater ($\mu\text{g/l}$)	area (m^2)	flux ($\text{mg/m}^2/\text{yr}$)	total: flux (kg/yr)
0 - 100	50	7000	5.25	0.036
100 - 1000	300	1875	31.5	0.059
1000 - 10000	3000	2250	315	0.709
> 10000	100,000	4730	10500	49.6
				50.3 kg AN/yr

APPENDIX F

**MONITORING AND SAMPLE STRATEGY: POSITION OF
BOREHOLES AND FILTERS**

APPENDIX G

COMPARISON OF REMEDIATION/CONTAINMENT OPTIONS

Table G1. Overview and comparison of remediation/containment options.

measures in top layer	area ⁱ	investment costs (indexed ⁱⁱ)	yearly costs (indexed ⁱⁱ)	reliability ⁱⁱⁱ	feasibility on site in operation ^{iv}	flexibility of system ^v	degree of containment ^{vi}	degree of removal ^{vii}
1. natural attenuation (monitoring): see appendix H4	plume	100	100	o	++	--	++	+
2. limited groundwater extraction (excluding extern. treatment): see appendix H1	source	400	150	+	o	+	+	++
3. bioscreen: air sparging (linear approach): see appendix H3	plume	750	200	o/+	+	+	++	-
4. groundwater extraction (excluding external treatment): see appendix H1 and 4.4.1	source and plume	1650	300	+	--	+	++	++
5. bioremediation: air sparging (area approach): see 4.4.2	plume	1750	350	o	-	o	--	++
6. bioscreen: nitrate injection (linear approach): see 4.5.2	source and plume	?	?	--*	+	+	++	-
measures in intermediate sandy layer	area	investment costs	yearly costs	reliability	feasibility on site in operation	flexibility	containment	removal
1. groundwater extraction: see app. H2	plume	400	150	+	++	+	++	+
2. bioscreen: air sparging (linear approach): see 4.6.2	plume	1850	225	-	o	o/+	++	-
3. air sparging directly under source area (area approach): see 4.6.2	plume	1850	225	o	o	o/+	--	++

i: source area: concentrations over 100 µg/l, presence of pure product can't be excluded

ii: cost for monitoring natural attenuation are set at 100; costs of other measures are indexed to those of natural attenuation

iii: is it a 'proven' technology?

iv: is installation possible and/or are there any risks involved for the production plant (during installation, operation, maintenance)

v: can the system easily be adjusted by e.g. making it more or less intensive?

vi: will the measurement prevent further spread?

vii: will the measurement reduce the load of contaminants?

*: possibilities need to be investigated further

Legend: ++: very high (very positive)

+ : high (positive)

o: moderate (neutral)

-: low (negative)

--: very low (very negative)

APPENDIX H

FURTHER ELABORATION OF OBVIOUS REMEDIATION MEASURES

APPENDIX H1

PUMP AND TREAT IN THE SOURCE AREA OF THE TOP LAYER

The following aspects should be known in order to be able to determine any further remediation strategy and the measures to be taken (also refer to 4.4.1):

1. *Types of extraction means*

A comparison of the vertically placed filters and drains installed by horizontally driven bores renders a slight preference for the installation of horizontal drains. Horizontal drains are cheaper, need lesser maintenance and operate more precisely than vertical filters. In addition, activities on the production location do not need to be disturbed by the installation of horizontal drains. Underground infrastructure should be well known before applying any horizontal drillings.

However, both extraction means yield the same volumes of extracted groundwater and cause the same drop in the groundwater level (see under 2).

2. *Extraction system and volumes*

In order to be able to remediate the source area, two horizontal drains (each 40 m long) will have to be installed at a depth of approximately 3.5 m -gl. The distance between drains will have to be 15 m. The extraction volume has been calculated at 0.5 to 1.0 m³/hour. The groundwater level will drop 1 m. The iso contours of the calculated groundwater levels are presented in appendix I1. The expected initial concentrations are:

MCB: 50,000 to 60,000 µg/l;

AN: 200,000 to 300,000 µg/l.

A similar system with vertical filters would have to comprise of 2 strings with 40 vertical filters each (1 m from centre to centre), and a filter length of 3 to 5 m -gl. The extraction volumes and the drop in the groundwater level will be comparable to those in the horizontal system.

3. *The effects of the groundwater withdrawal on contaminations*

Groundwater flow paths are presented in appendix I2. Calculations have been performed assuming a one-way northern flow direction (towards Britannia Harbour). From the calculated flow patterns it can be concluded that the influence of the extraction measures reaches up to the northern border of the production location. As a result of this:

- contaminants will no longer spread from the production location (and source area) towards the Britannia Harbour;
- contaminants outside the production location (plume area) will spread towards the Britannia Harbour.

As a result of a lower groundwater table, infiltration from the source area towards the clay/sand layer and the intermediary sand layer cannot be prevented. On the other hand, a reduction in infiltration velocity from 0.3 m/yr to 0.22 m/yr will be achieved. In addition, the contamination levels in the centre of the source area will decrease with time. The combination of both these effects will substantially reduce the total vertical flux of contaminations.

4. *Risk of settlement*

As a result of a lower groundwater level, settlement can occur. This has been calculated at 9 mm, assuming a worst case scenario and a groundwater extraction in the intermediary sand layer (refer to appendix H2). Given the fact that naturally caused fluctuations in the groundwater level already exist, settlement will already have occurred to some extent. Damages as a result of settlement are not expected.

5. *Possibilities for groundwater treatment*

An aboveground industrial waste water treatment plant (active sludge) is present elsewhere on the ICI site. The sludge from this plant has been used in laboratory experiments and has been found to degrade MCB and AN very effectively. The plant has enough capacity to deal with the extra amount of water (approximately 1 m³/hr) and MCB/AN loads.

A sewer system is present, also with enough capacity to transport this extra amount of water from the polluted production plant towards the waste water treatment plant.

In short, no relevant investments have to be made for transport and purification of extracted groundwater.

APPENDIX H2

PUMP AND TREAT IN THE INTERMEDIARY LAYER

1. *Extraction system and volumes*

A containment of contaminations in the intermediary sand layer can be achieved by installing one deepwell with a filter at 15 to 20 m -gl.

The recommended location for this deepwell is just north of the production plant (refer to appendix H1). The extraction volume has been calculated at 0.5 m³/hour. The initial concentrations for AN and MCB are expected to be < 10 µg/l, but will increase with time when the highest concentrations, originating from the source area around filter 9, reach the deepwell.

2. *The effect of groundwater withdrawal*

In appendix J, the area of influence has been calculated. It is recommended to perform additional measurements in the newly placed filters in the intermediary sand layer in order to determine the direction and the magnitude of the flow in this layer more accurately.

In the calculations, it was assumed that a dividing layer between the intermediary sand layer and the aquifer was present at the site. In case of any 'gaps' in this layer, a spread could still occur towards the aquifer, despite the groundwater withdrawal in the intermediary layer. It is therefore recommended to monitor the concentration levels in the aquifer.

3. *Risk of settlement*

Refer to appendix H1.

4. *Possibilities for groundwater treatment*

Initial concentrations will probably be so low that no treatment will be necessary before discharge. When concentrations exceed a certain level, the groundwater can be discharged into the sewer system to be treated in the industrial waste water treatment plant (refer to appendix H1).

APPENDIX H3

BIOSCREEN(S) IN PLUME AREAS

The installation of a bioscreen on the north side of the production location will remove the flux from the source area and prevent further spread towards the harbour.

Filters would have to be placed as deep as possible: 5.5 m -gl, which is 4 m under the groundwater level. In situations with high oxygen demands, the effective radius of influence (ROI) would have to be kept within 3 metres at least. Prior to full installation, the ROI should be tested in a field situation.

However, in view of the fact that natural oxygen levels of 1.5 to 2 mg/l were detected in this area, and that it is relatively clean (oxygen demand will not be very high here), and that oxygen levels would have to be increased only slightly, the effective ROI of an air sparging filter can be estimated at 4 metres. This leads to a total number of 16 injection filters.

The following assumptions were made:

- the inflowing groundwater concentrations are 1000 µg MCB/l (worst case scenario);
- a porosity of 0.35;
- a groundwater flow of 7 m/yr;
- a soil density of 1700 kg/m³;
- a bioscreen thickness of 4 metres.

Based on these assumptions, the necessary degradation rate in this zone can be calculated at 360 µg/kg/yr (1 µg/kg/day).

In 4.3.4 a maximal degradation rate of 2000 µg/kg/day was calculated. This is an indication that even when compensating for the less favourable circumstances in the bioscreen (compared to the laboratory conditions) the degradation capacity within the bioscreen should be large enough to neutralise inflowing concentrations.

However, we recommend to investigate the spread of contaminants and the natural attenuation in this area (refer to appendix H4) before installing a bioscreen. Spread is expected to be minimal, particularly in combination with the groundwater withdrawal in the source area (refer to appendix H1), and this is the reason why the environmental merit and cost-effectiveness of the bioscreen in the plume area will be very low.

APPENDIX H4

MONITORING OF SPREADING (AND NATURAL ATTENUATION) IN PLUMES

1. *Monitoring the horizontal spread and natural attenuation*

The best way of checking whether spread and natural attenuation occur is by measuring contaminant concentrations and the most relevant process parameters in a row of filters located close to each other.

It is best to carry out any such measurements on the west and northeast side of the investigated site because of:

- the accessibility and available space;
- the fact that in this area a decrease has already been measured compared with earlier measurements (filters 10 and 37 on the northeast side and west side, respectively);
- the fact that the optimum conditions are located here:
 - low concentrations of MCB and AN (< 100 µg/l);
 - a low flow rate;
 - a background concentration of oxygen;
 - no endangered objects in the immediate vicinity.

According to present data natural attenuation on its own does not seem to be sufficient to prevent further spread on the northern side (towards the Britannia Harbour). Therefore, it is an option to place a row of filters here as well in order to determine the contamination fluxes towards the harbour. This data would be useful in case the authorities would like to see more detailed information about the low fluxes towards the harbour.

On the west and northeast-side of the location, initially two sets of five filters should have to be installed in a flow path running from the source area through the plume, all at the same depth, preferably just above the old groundlevel: 5 m -gl. The distance between these filters should be approximately 3 metres. Existing filters could be incorporated in the monitoring 'line' of filters.

2. *The monitoring frequency and analysis package*

All filters should initially be monitored every six months for: MCB, AN, oxygen, pH and electric conductivity.

In addition, the two outer filters should be monitored for: DOC, Fe²⁺, NO₃⁻, SO₄²⁻ and Cl⁻.

Groundwater levels in all filters should also be measured in order to be able to determine the local groundwater flow more accurately and to make a distinction between the effect of the groundwater flow and natural attenuation.

Depending on the outcome and evaluation of the first results, it can be decided to continue, expand or reduce the monitoring efforts. It is expected that within a relatively short period of time (approximately 2 years), quantitative data of the occurring spread and natural attenuation will be available. Further actions (ranging from no more monitoring to additional remediation measures) would have to be based on this data and would have to be in consultation with the authorities.

3. *Monitoring the vertical spread towards the aquifer*

The exact degree to which spreading occurs towards the aquifer is unknown (see 2.3).

A choice should be made between:

- a. investigating this further, which involves deep drillings, extensive monitoring and calculations of spreading. This will entail relatively high costs and will not reduce the risk of measures still having to be taken afterwards;
- b. taking measures to prevent spreading right away.

This option calls for a comparison of the costs of a further investigation to those of taking measures. In appendix H2 the measures for the intermediary sand layer are presented. Because of the presence of a water treatment plant, the costs for these measures are not much higher than the installation of monitoring wells.

These measures will also influence and possibly prevent spread towards the aquifer. However, because it is not certain whether a dividing layer between the aquifer and the intermediary sand layer is present on the site, it cannot be fully excluded that despite groundwater withdrawal in the intermediary layer, an unacceptable spread towards the aquifer will occur.

We therefore advise to monitor MCB concentrations in the aquifer. In case of unacceptable spread, additional groundwater withdrawal should be considered.

4. Costs

If natural attenuation occurs in the top layer and can be quantified on site, this would of course be a highly cost-effective containment method. If no natural attenuation is found to occur, at least the rate of spreading would be measured accurately.

We regard monitoring in this case to be a useful instrument with low investment costs and a high potential, certainly when it is being combined with groundwater withdrawal in the contamination source.

5. *Policy regarding natural attenuation*

Last but not least, when applying natural attenuation as a containment technique, much effort should be invested in the dialogue with the competent authorities. Recent changes in the Dutch policy regarding soil remediation leave more room for site-specific approaches. The first cases of authorities approving of remediation strategies involving natural attenuation are a fact now. However, natural attenuation is a relatively new aspect for the Dutch situation and knowledge about the subject will vary locally. In some cases authorities may have to be informed, instructed and convinced of the applicability of natural attenuation.

APPENDIX I1

ISO CONTOURS OF THE GROUNDWATER WITHDRAWAL IN THE TOP LAYER

APPENDIX I2

GROUNDWATER WITHDRAWAL IN THE TOP LAYER AND FLOW PATHS

APPENDIX J

DEEPWELL POSITION IN THE INTERMEDIARY SAND LAYER AND FLOW PATHS