NOBIS 96-3-04

NATURAL ATTENUATION AT THE COUPÉPOLDER LANDFILL? HYDROLOGICAL, GEOCHEMICAL AND BIOLOGICAL CHARACTERIZATION

Phase 2

drs. B. van Breukelen (Vrije Universiteit Amsterdam)
dr. W.F.M. Röling (Vrije Universiteit Amsterdam)
dr.ir. T.J. Heimovaara (IWACO B.V.)

September 1998

Gouda, CUR/NOBIS

Dutch Research Programme In-Situ Bioremediation

Auteursrechten
Alle rechten voorbehouden. Niets uit deze opgave mag worden verveelvoudigd, opgeslagen in een geautomatiseerd gegevensbestand of openbaar gemaakt, in enige vorm of op enige wijze, hetzij elektronisch, mechanisch, door fotokopieën, opnamen of op enige andere manier, zonder voorafgaande schriftelijke toestemming van CUR/NOBIS.
Het is toegestaan overeenkomstig artikel 15a Auteurswet 1912 gegevens uit deze uitgave te citeren in artikelen, scripties en boeken mits de bron op duidelijke wijze wordt vermeld, alsmede de aanduiding van de maker, indien deze in de bron voorkomt, "©"Natural attenuation at the Coupépolder landfill? Hydrological, geochemical and biological characterization - Phase 2", September 1998, CUR/NOBIS, Gouda."

Aansprakelijkheid
CUR/NOBIS en degenen die aan deze publicatie hebben meegewerkt, hebben een zo groot mogelijke zorgvuldigheid betracht bij het samenstellen van deze uitgave. Nochtans moet de mogelijkheid niet worden uitgesloten dat er toch fouten en onvolledigheden in deze uitgave voorkomen. Ieder gebruik van deze uitgave en gegevens daaruit is geheel voor eigen risico van de gebruiker en CUR/NOBIS sluit, mede ten behoeve van al degenen die aan deze uitgave hebben meegewerkt, iedere aansprakelijkheid uit voor schade die mocht voortvloeien uit het gebruik van deze uitgave en de daarin opgenomen gegevens, tenzij de schade mocht voortvloeien uit opzet of grove schuld zijdens CUR/NOBIS en/of degenen die aan deze uitgave hebben meegewerkt.

Copyrights
All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording and/or otherwise, without the prior written permission of CUR/NOBIS.
It is allowed, in accordance with article 15a Netherlands Copyright Act 1912, to quote data from this publication in order to be used in articles, essays and books, unless the source of the quotation, and, insofar as this has been published, the name of the author, are clearly mentioned, "©"Natural attenuation at the Coupépolder landfill? Hydrological, geochemical and biological characterization - Phase 2", September 1998, CUR/NOBIS, Gouda, The Netherlands."

Liability
CUR/NOBIS and all contributors to this publication have taken every possible care by the preparation of this publication. However, it can not be guaranteed that this publication is complete and/or free of faults. The use of this publication and data from this publication is entirely for the user's own risk and CUR/NOBIS hereby excludes any and all liability for any and all damage which may result from the use of this publication or data from this publication, except insofar as this damage is a result of intentional fault or gross negligence of CUR/NOBIS and/or the contributors.

Titel rapport
Natural attenuation at the Coupépolder landfill?
Hydrological, geochemical and biological
characterization
Phase 2

CUR/NOBIS rapportnummer
96-3-04

Project rapportnummer
96-3-04 phase 2

Auteur(s)
drs. B. van Breukelen
dr. W.F.M. Röling
dr.ir. T.J. Heimovaara

Aantal bladzijden
Rapport: 42
Bijlagen: 45

Uitvoerende organisatie(s) (Consortium)
IWACO B.V. (T.E. Hoencamp, MSc, 010-2865556)
Vrije Universiteit Amsterdam, Faculteit Biologie (dr. H.W. van Verseveld, 020-4447193)
Vrije Universiteit Amsterdam, Faculteit Aardwetenschappen (drs. J. Groen, 020-4447330)
Provincie Zuid-Holland, Dienst Water en Milieu (F.J. van der Ham, 070-4416611)

Uitgever
CUR/NOBIS, Gouda

Samenvatting

Dit rapport beschrijft de activiteiten die zijn uitgevoerd in fase 2 van het project waarin een poging wordt gewaagd om NA bij de stortplaats Coupépolder te karakteriseren. Binnen deze fase zijn alle historische en nieuwe gegevens geïnterpreteerd. De hydrogeologische ligging van de stortplaats is zodanig dat de verspreiding vanuit de stortplaats via de geulafzetting onder het noordelijk deel van de stortplaats naar het eerste watervoerende pakket plaatsvindt. De stort heeft de geulafzettingen en het watervoerende pakket direct onder de stort beïnvloed. Benedenstrooms is geen beïnvloeding aangetroffen, hoewel dit uit conservatieve transportberekeningen wel werd verwacht. Verdunning speelt naast afbraak een belangrijke rol, omdat de hoeveelheid percolaat dat uit de stort treedt klein is ten opzichte van de stroomsnelheid in het watervoerende pakket.
Microbiologische technieken, zoals de gram negatieve BIOLOG en de ontwikkeling van de degradatie specifieke BIOLOG plaat, zijn toegepast in dit onderzoek. Metabolische profielen zijn bepaald op monsters vanuit het stortlichaam, het grensvlak tussen de stort en de onderliggende bodem en de bodem onder het stortlichaam. De metabolische diversiteit was het hoogst binnen in het stortlichaam. Dit kan een aanwijzing zijn voor een grotere afbraakcapaciteit in het stortlichaam.

Trefwoorden
Gecontroleerde termen:
landfill, natural degradation

Vrije trefwoorden:

Titel project
Natural attenuation at the Coupépolder landfill?
Hydrological, geochemical and biological
characterization

Projectleiding
Provincie Zuid-Holland
(F.J. van der Ham, 070-4416611)

Dit rapport is verkrijgbaar bij:
CUR/NOBIS, Postbus 420, 2800 AK Gouda

Report title
Natural attenuation at the Coupépolder landfill?
Hydrological, geochemical and biological
characterization
Phase 2

CUR/NOBIS report number
96-3-04

Project report number
96-3-04 phase 2

Author(s)
drs. B. van Breukelen
dr. W.F.M. Röling
dr.ir. T.J. Heimovaara

Number of pages
Report: 42
Appendices: 45

Excecutive organisation(s) (Consortium)
IWACO B.V. (T.E. Hoencamp, MSc, 010-2865556)
Vrije Universiteit Amsterdam, Faculteit Biologie (dr. H.W. van Verseveld, 020-4447193)
Vrije Universiteit Amsterdam, Faculteit Aardwetenschappen (drs. J. Groen, 020-4447330)
Provincie Zuid-Holland, Dienst Water en Milieu (F.J. van der Ham, 070-4416611)

Publisher
CUR/NOBIS, Gouda

Abstract

This report describes the activities carried out in phase 2 of the project in which an attempt was made at characterizing NA at the Coupépolder. Within this phase all historical data together with additional measurements were interpreted. The hydrogeological setting of the landfill is such that the spread of landfill leachate will be via gully deposits below the northern part of the landfill to the underlying aquifer. The gully deposits and the aquifer directly below the aquifer have been influenced by the landfill leachate. Downstream no evidence has been found whereas using conservative transport modelling this was to be expected. Besides degradation, dilution probably plays an important role, the amount of leachate percolating from the landfill is small in comparison with the flow velocity in the aquifer.
Microbiological techniques such as the Gram Negative BIOLOG technique and the development of degradation specific BIOLOG plates have been applied in this phase. Metabolic profiles have been determined on samples from within the landfill, from the boundary between landfill and aquifer and from the aquifer directly below the landfill. The metabolic diversity was highest for the sample from within the landfill and much lower for the samples below. This may imply a larger degradation capacity in the landfill.

Keywords
Controlled terms:
landfill, natural degradation

Uncontrolled terms:

Project title
Natural attenuation at the Coupépolder landfill?
Hydrological, geochemical and biological
characterization

Projectmanagement
Provincie Zuid-Holland
(F.J. van der Ham, 070-4416611)

This report can be obtained by: CUR/NOBIS, PO Box 420, 2800 AK Gouda, The Netherlands
Dutch Research Programme In-Situ Bioremediation (NOBIS)

PREFACE

With this report, the second phase in the NOBIS project 'Feasibility project in situ bio restoration of landfills' project number 96-3-04, is closed. The aim of the project is to develop a method for determining the intrinsic degradation capacity of the soil and groundwater in order to assess how it affects environmental risks. This project is carried out by a consortium, consisting of Free University Amsterdam, Province of South-Holland and IWACO B.V.

September 1998

CONTENTS

SAMENVATTING

Natural attenuation at the Coupépolder landfill?
Hydrological, geochemical and biological characterization

Inleiding

De dreiging die voormalige stortplaatsen vormen voor het milieu vraagt veel aandacht van de huidige maatschappij. Op dit moment wordt geprobeerd deze dreiging op te heffen door een aantal maatregelen te treffen. Deze maatregelen zijn vaak een eeuwigdurende monitoring met daarbij zo nodig een eeuwigdurende beheersing. Deze oplossingen zijn echter zeer kostbaar.

De resultaten uit internationaal onderzoek aan een aantal stortplaatsen laten zien dat er bij stortplaatsen vaak minder verspreiding van verontreiniging optreedt dan in eerste instantie was verwacht [Christensen et al.,1994]. Een mogelijke verklaring voor dit fenomeen zou natuurlijke afbraak (NA) van de verontreiniging kunnen zijn.

Dit project wordt uitgevoerd in het kader van NOBIS en beoogt te onderzoeken of NA een significante bijdrage levert aan het beheersen van de verspreiding van verontreiniging uit stortplaatsen. Daarbij is het ook de bedoeling een generiek toepasbare methodiek te ontwikkelen waarmee het optreden van NA bij stortplaatsen kan worden gekarakteriseerd en gekwantificeerd. Daarbij wordt aansluiting gezocht bij overige ontwikkelingen binnen NOBIS op het gebied van NA.

Dit project omvat vier projectfasen:

- Fase 1: Een literatuurreview naar de state of the art rondom het karakteriseren van NA bij stortplaatsen. Deze fase is afgerond en gerapporteerd in een state of the art rapport [CUR/NOBIS, 1998].
- Fase 2: Het onderzoeken van de geochemie en geohydrologie bij een case (de stortplaats Coupépolder) en het opstarten van onderzoek naar de toepassing van microbiologische karakterisatiemethoden bij het beoordelen van NA bij stortplaatsen. De onderhavige rapportage vormt hier een onderdeel van.
- Fase 3: Het toepassen van de in fase 2 geteste microbiologische technieken om een aantal zones rondom de stortplaats te karakteriseren. Ook wordt hierbij getracht een koppeling te maken tussen de geohydrologische/geochemische benadering en de microbiologische benadering.
- Fase 4: De laatste fase van dit project betreft het uitwerken van de bevindingen in een generieke methodiek dat kan dienen als handvat om het NA-potentieel bij stortplaatsen te beoordelen.

Stortplaats Coupépolder

Beschrijving

De stortplaats Coupépolder ligt bij Alphen aan den Rijn in de provincie Zuid-Holland en heeft een oppervlakte van ongeveer 22 ha. Het is als stortplaats in gebruik geweest van 1959 tot 1985. Na sluiting van de stortplaats zijn milieubeschermende maatregelen getroffen, zoals:

- Het aanleggen van een ondergrondse ringdrainage.
- Op de taluds van de stortplaats zijn met bentoniet afdichtende lagen aangebracht.
- Om te voorkomen dat stortpercolaat in het oppervlaktewater kan stromen is er een damwand geplaatst.
- Om te voorkomen dat de aquifer stroomafwaarts van de stortplaats wordt verontreinigd is er een monitoringszone ingericht en zijn er maatregelen voorzien om bij een overschrijding van

de signaalwaarde in de monitoringszone een grondwaterbeheersing aan te leggen. Tot nu toe is de grondwaterbeheersing nog niet nodig gebleken.

Geologie

De geologische opbouw van de bodem bij de Coupépolder is als volgt:

- Ter plaatse van de stortplaats bevindt zich op een diepte van 40 tot 45 m -NAP de formatie van Kedichem. Dit is een kleipakket met een dikte van ongeveer 10 m en vormt daardoor voor deze studie de onderkant van ons systeem.
- Boven op de formatie van Kedichem zijn in een dikte van 32 tot 40 m de fluviatiele en eolische zanden van de formatie van Twente en de formatie van Kreftenheye te vinden.
- Op dit dikke zandpakket bevindt zich een compacte veenlaag, het Basisveen, met een dikte van 0,25 tot 1,8 m.
- Boven het Basisveen bevindt zich de formatie van Calais, bestaande uit een 8 tot 10 m dikke blauwgrijze en humeuze kleilaag.
- Tijdens de Duinkerken-fase hebben zich in dit gebied een groot aantal geulen ontwikkeld, die zich in de formatie van Calais hebben ingesneden. In deze insnijdingen bevinden zich nu geulafzettingen van zand, grind en leem. De stortplaats Coupépolder ligt boven op geulafzettingen die zijn afgezet door de Kromme Aar die nu ten westen en ten noorden van de stortplaats stroomt.

Geohydrologie

De geohydrologie wordt vooral beïnvloed door de nabijgelegen polders met bijbehorende polderpeilen en boezempeilen (Hollands Boezem). Daarbij heeft de ringdrainage rondom de stort ook een aanzienlijk effect.

Het peil van het freatisch grondwater in de stort varieert van -1,8 tot +0,9 m NAP. In het eerste watervoerende pakket onder de stort varieert het peil van -3,3 m tot -3,6 m NAP en in het tweede watervoerende pakket onder de formatie van Kedichem is het peil -4 m NAP. Hieruit kan dan worden geconcludeerd dat er een flux vanuit de stort naar de eerste aquifer zal zijn. Deze flux zal vooral plaatsvinden door de geulafzettingen. Tussen het eerste en tweede watervoerende pakket zal nauwelijks een flux zijn.

Geochemie en chemische invloed van de stortplaats op de omgeving

Om de geochemie en de mogelijke invloed van de stortplaats op de omgeving te kunnen beoordelen is een schematische onderverdeling van de stort en de ondergrond gemaakt. Hiertoe zijn verschillende zones gedefinieerd (zie ook Fig. 5 in bijlage A):

- Zone C1 is het deel van het eerste watervoerende pakket dat bovenstrooms van de stort zit.
- Zone C2 is het deel van het eerste watervoerende pakket dat zich direct onder de geulafzettingen onder de stort bevindt. Dit deel van het watervoerende pakket wordt als eerste beïnvloed door de stort.
- Zone C3 is het deel van het watervoerende pakket dat benedenstrooms van de stort zit. In deze zone is de monitoringslijn geïnstalleerd en op dit moment is dit deel nog niet beïnvloed door stortpercolaat.
- Zone C4 is het stortlichaam zelf. Hierin bevindt zich de bulk van de verontreiniging.
- Zone C5 is de afdeklaag tussen het stortlichaam en het eerste watervoerende pakket. Deze afdeklaag bestaat uit de kleien uit de formatie van Calais en de geulafzettingen uit de formatie van Duinkerken.

Om de gegevens in eerste instantie te beoordelen zijn alle beschikbare metingen op één hoop gegooid en zijn de zones als één geheel beoordeeld.

Zone C4: Het stortlichaam
Binnen het stortlichaam worden de hoogste concentraties aan verontreinigende stoffen gevonden. Er zijn zeer grote variaties. Op basis van de pH-waarden blijkt dat de stort in ieder geval vanaf 1988 in de methanogene fase is geweest. In het stortlichaam zijn er aanwijzingen voor ijzer-, nitraat- en sulfaatreductie. De elektrische geleidbaarheid (Ec) is hoog tot zeer hoog. Eén waarde (9.500 µS/cm) is dusdanig dat er sprake kan zijn van dichtheidsstroming.

Verontreinigingen die in het stortlichaam zijn aangetroffen zijn: BTEX en lage hoeveelheden gechloreerde alkanen. Metingen gedaan aan het percolaat in de ringdrainage (vanaf 1992) tonen ook verontreinigingen aan van phenol, cyanide, naftaleen en overige PAK's.

Zone C1: Bovenstrooms
Het watervoerende pakket bovenstrooms van de stortplaats is anaëroob. Uit metingen aan het grondwater blijkt dat er sprake is van een ijzer- en sulfaatreducerend milieu, hoewel de sulfaatreductie waarschijnlijk slechts gering is. Er is in de laatste meting één keer sprake geweest van een lichte overschrijding van de detectielimiet voor tolueen. Verder is geen verontreiniging aangetroffen.

Aanwijzingen voor de verspreiding van stortpercolaat
Door vergelijking van de waarnemingen uit de zones C1, C2 en C3 met de waarnemingen uit de zones C4 en C5 kan een invloed van de stortpercolaat op het watervoerende pakket worden aangetoond. Op basis van verontreinigingen kan niet echt een beïnvloeding worden aangetoond. Wel is er op basis van andere parameters sprake van een beïnvloeding. Deze parameters zijn onder andere ammonium en Kjeldahl-stikstof, redoxparameters, DOC, CZV en CO_2.

Het is niet mogelijk om een duidelijk redoxzonering aan te geven. Redenen hiervoor zijn dat het watervoerende pakket al ijzer- en sulfaatreducerend was en blijft. De methanogene zone is waarschijnlijk in de stort of direct eronder. Het niet of nauwelijks voorkomen van verontreinigingen onder de stort vormt een aanwijzing voor mogelijke NA.

Uit de metingen komen een aantal sterke aanwijzingen naar voren voor het optreden van dichtheidsstroming in en onder de stort. In het midden van de monitoringslijn bij de diepste filters van de peilbuizen 3 en 4 worden verhoogde waarden aangetroffen voor de elektrische geleidbaarheid, chloride, sulfaat, alkaliniteit, methaan, TOC en CO_2.

Daarnaast zijn er de waargenomen hoge Ec-waarden in de stort en een geleidbaarheidssondering met een zeer lage weerstand.

Naar een conceptueel model van de stortplaats van de Coupépolder
Uitgangspunt voor het conceptueel model van de stortplaats is de grove schematisatie gepresenteerd in figuur 5 (zie bijlage A).

Op basis van de waterbalans, opgesteld in 1988, kan worden geconcludeerd dat de maximale flux vanuit de stort naar het eerste watervoerende pakket 0,78 mm/dag bedraagt. Hierbij moet wel worden gerealiseerd dat er sinds 1988 een aantal maatregelen zijn getroffen die deze flux beïnvloeden. Deze maatregelen leiden ertoe dat deze flux in ieder geval kleiner is geworden. De waterbalans uit 1988 moet worden verbeterd.

De stroomsnelheid in het eerste watervoerende pakket kan liggen tussen de 26 en 95 meter per jaar. Uitgaande van een zuiver convectief transport zonder menging betekent dit dat een eventuele pluim direct onder de formatie van Calais te vinden zou moeten zijn met een dikte van 1,95 tot 4,5 m. De aanwijzingen voor dichtheidsstroming wijzen op een tweede pluim vlak boven de formatie van Kedichem.

Microbiologische technieken

De meeste redoxprocessen in de bodem zijn microbiologisch gekatalyseerd. Het gevolg van de microbiële processen is de vorming van verschillende redoxzones. Bij de Coupépolder zijn mogelijke redoxzones: ijzerreducerend, sulfaatreducerend en methanogeen.

Onder en benedenstrooms van de stortplaats zijn lage concentraties van verontreinigingen aangetroffen. Aanwezigheid van verontreinigingen in het stortlichaam kan hebben geleid tot het ontstaan van verontreiniging afbrekende populaties micro-organismen in en onder het stortlichaam. Het is mogelijk om de afbraakcapaciteit te karakteriseren door DNA/RNA-profielen te onderzoeken of door met behulp van BIOLOG microtiter platen te kijken naar het metabolisch potentieel. Door het vergelijken van profielen uit de methogene zone met profielen uit zones stroomafwaarts kunnen conclusies met betrekking tot het afbraakpotentieel worden getrokken.

Optimalisatie van de Gram Negatieve BIOLOG platen

In fase 2 is vooral gekeken naar de BIOLOG methode. Elementen die zijn onderzocht waren de reproduceerbaarheid, optimale temperatuur, grootte van de enting, effecten van het al of niet toevoegen van additionele elektronenacceptoren, type reducerend agens en activiteitspecificiteit. De conclusie, die uit deze studie kan worden getrokken, is dat de analyse van de microbiële metabolische diversiteit nauwkeurig kan worden bepaald met behulp van BIOLOG microtiter platen. Verbeteringen die kunnen worden uitgevoerd zijn het toepassen van 10 ppm natriumsulfide als reducerend agens in plaats van natriumthioglycolaat en het incuberen van de platen bij 10 ^{o}C. De kleurreacties kunnen het beste worden bekeken na 4, 7, 14 en 28 dagen. Ook is het zo dat de BIOLOG platen zo snel mogelijk na het bemonsteren moeten worden ingezet. De gegevens kunnen eenvoudig worden verwerkt met behulp van de beschikbare BIOLOG software.

Ontwikkeling van biodegradatie specifieke microplaten

Toepassing van de standaard BIOLOG platen geeft informatie over het algemene microbiologische metabolische potentieel en niet specifiek voor het biodegradatiepotentieel. Toepassing van de BIOLOG MT microplaten, waaraan koolstofbronnen kunnen worden toegevoegd, maakt het mogelijk specifiek naar biodegradatie te kijken. In deze fase is gekeken hoe deze microtiter platen moeten worden gemaakt. Onderzocht is welke verdunningen moeten worden toegepast en hoelang het duurt voordat er reacties zijn waar te nemen.

Karakterisatie van de overgangszone tussen het stortlichaam en het onderliggende sediment

Eén van de hypothesen voor dit project was de aanname dat tussen stortlichaam en sediment een grenslaag ontstaat die kan fungeren als een hydrologische barrière en die misschien een verhoogde biologische activiteit heeft. In deze fase zijn kernen gestoken van deze grenslaag. Deze kernen zijn gekarakteriseerd met behulp van geochemische, microbiologische en elektronenmicroscopische technieken.

Geochemische karakterisatie

Het monster is kleiig en bevat meer zand aan de onderkant. Het kalkgehalte is hoog. Het monster oogt heterogeen; een aantal zwarte laagjes zijn waargenomen met humeuze materiaal, waarin zelfs plantstructuren zijn waar te nemen.

Wat opvalt aan de chemische analyses is dat het monster duidelijk is beïnvloed door stortpercolaat. De Fe^{2+} en Mn^{2+} zijn laag in vergelijking met de metingen in het stortlichaam (gedaan in 1988) en er is ook sulfaat aanwezig in het poriewater. Opvallend is de aanwezigheid van nitraat in het poriewater dat eigenlijk niet kan voorkomen onder deze omstandigheden. Misschien heeft er tijdens het bemonsteren toch wat oxidatie plaatsgevonden.

Elektronenmicroscopie

Uit de elektronenmicroscopie-opnamen blijkt dat er veel ijzersulfideneerslagen in het monster aanwezig zijn. Deze sulfidische neerslagen verklaren ook de zwarte kleur van het monster. De meeste zware metalen slaan neer onder sulfidische omstandigheden. De sulfideneerslagen in dit monster bevatten naast Fe alleen Zn als hoofdcomponent. Sulfideneerslag is dus een belangrijk proces, waarmee metalen uit het percolaat worden gefilterd. Sulfideneerslagen zijn zeer slecht oplosbaar.

Microbiologische karakterisatie

De metabolische profielen, verkregen met behulp van de BIOLOG GN microtiter platen, van de grenslaag en de lagen eronder en erboven zijn zeer verschillend. Het aantal positieve waarnemingen ligt het hoogste voor de laag boven het grenslaagje (in het stortlichaam) en is lager voor het laagje zelf en daaronder. Opvallend was dat sommige substraten, die worden gevormd bij de microbiële afbraak van organisch materiaal, niet worden verbruikt.

Verschillen in het potentieel om verontreinigingen af te breken zijn niet waargenomen. Dit kan mede veroorzaakt zijn doordat de monsters 2 maanden oud waren voordat ze ingezet zijn.

Onderzoek in fase 3 en fase 4

Coupépolder

De waterbalans voor de stortplaats moet worden aangepast aan de beschermingsmaatregelen bij de stort. Op basis van deze verbeterde waterbalans kan dan een betere schatting van de percolatiesnelheid worden gemaakt. Ook is het van belang om de effecten van de ringdrainage in het regionale waterstromingsmodel mee te nemen

In de volgende fase wordt getracht wat beter inzicht te krijgen in de geochemische processen op het grensvlak tussen stort en aquifer in de geulafzettingen. Ook zal het conceptueel model verder worden uitgewerkt en wat uitgebreidere berekeningen worden uitgevoerd.

Fase 3 zal vooral in het teken staan van het karakteriseren van het microbiologische potentieel. Hiertoe zullen zowel in het laboratorium als in het veld experimenten worden gedaan met microkosmossen. In het laboratorium worden ook experimenten ingezet met doorstroomcellen. Daarnaast wordt ook aandacht besteed aan het ontwikkelen en toepassen van DNA/RNA-karakterisatietechnieken. Wij zijn vooral op zoek naar verschillen in karakteristieken tussen stort, overgangszone en achtergrond. Hiertoe zal in het veld vooral gebruikt gaan worden gemaakt van zogeheten Multi Layer Sampling Microcosms (MLSMs).

Banisveld

Eén van de doelen van het project is het ontwikkelen van een generieke methodiek om stortplaatsen te karakteriseren. Om een generieke methode te ontwikkelen is het van belang om de ontwikkelingen te toetsen op een aantal stortplaatsen. Stortplaats Banisveld nabij Boxtel in Noord-Brabant is een geschikte case om de technieken die zijn ontwikkeld voor de Coupépolder toe te passen, omdat de geologische omstandigheden rondom deze stort sterk verschillen van de situatie bij de Coupépolder. Bovendien is ook van deze stortplaats een grote hoeveelheid gegevens beschikbaar.

SUMMARY

Natural attenuation at the Coupépolder landfill? Hydrological, geochemical and biological characterization

Introduction

The threat posed by old landfills to the environment is demanding considerable attention from present-day society. Various attempts are being made to overcome this threat by implementing a variety of measures. These measures frequently take the form of perpetual monitoring, combined with containment in perpetuity if necessary. Such solutions are, however, very expensive.

The results of international studies at a number of landfills show that at many of these sites there is less dispersion of pollutants than originally expected [Christensen et al., 1994]. A possible explanation for this phenomenon might lie in natural (intrinsic) degradation of the pollutants.

The present project is being carried out within the framework of NOBIS (Dutch Research Programme In-Situ Bioremediation) and is intended to examine whether intrinsic degradation is making a significant contribution towards containing the dispersion of pollution from landfills. A second objective is to develop a generically applicable methodology for characterizing and quantifying the occurrence of intrinsic degradation at landfills. It is also the intention that this work should be related to other developments under the NOBIS programme which relate to intrinsic degradation.

The project comprises 4 phases:

- Phase 1: A literature review into the state of the art of characterizing intrinsic degradation at landfills. This phase was completed and reported on in a state of the art report [CUR/NOBIS, 1998].
- Phase 2: A geochemical and geohydrological case study (the Coupépolder landfill) and the initiation of research into the application of microbiological characterization methods in assessing intrinsic degradation at landfills. The present report forms part of this study.
- Phase 3: Application of the microbiological techniques tested in Phase 2 to characterize a number of zones around the landfill site. It will be attempted to establish a link between the geohydrological/geochemical approach and the microbiological one.
- Phase 4: The final phase of the project will consist of translating the findings into a generic methodology which can serve as a guide for assessing the intrinsic degradation potential at landfill sites.

The Coupépolder landfill site

Description

The Coupépolder landfill site is located near the town of Alphen aan den Rijn in the Province of Zuid-Holland and covers an area of some 22 hectares. It was used as a landfill from 1959 to 1985. After the landfill was closed, a number of environmental-protection measures were implemented, including:

- The installation of an underground circular drainage system.
- The banks of the landfill have been provided with a bentonite sealing layer.
- A sheet-pile wall has been constructed to prevent landfill leachate from migrating into surface waters.

- To prevent the aquifer downgradient from the landfill from becoming polluted a monitoring zone has been set up and provisions have been made for installing a groundwater-containment system as soon as the signal value in the monitoring zones is exceeded. To date groundwater containment has not proved necessary.

Geology
The geological section below at the Coupépolder is as follows:

- At the landfill site the Kedichem Formation occurs at a depth of 40 - 45 m below NAP (Amsterdam Ordnance Datum = mean sea level). It is a sequence of clays approximately 10 m thick and consequently forms the base of the hydrogeological system for the purpose of the present study.
- The Kedichem Formation is overlain by fluviatile and aeolian sands of the Twente and Kreftenheye Formations with a thickness of 32 - 40 m.
- On top of this thick sand sequence is a compact layer of peat, the 'Basisveen', with a thickness of 0.25 - 1.8 m.
- The Basisveen is overlain by the Calais Formation which consists of a 8 - 10 m thick bluish-grey and humus-rich clay horizon.
- During the Duinkerken stage a large number of channels developed in this area which cut down into the Calais Formation. These washouts are now filled with channel deposits consisting of sand, grit and loam. The Coupépolder landfill is located on top of channel deposits deposited by the Kromme Aar River which at present flows to the west and the north of the landfill site.

Geohydrology
The geohydrology is influenced mainly by the nearby polders with their controlled maximum polder and 'Boezem' (polder outlet) water levels (Hollands Boezem datum). In addition, the circular drainage installed around the landfill site also exerts a considerable influence.

The level of the phreatic water in the landfill site is varies from -1.8 to +0.9 NAP. In the first aquifer underlying the site the level varies from -3.3 m to -3.6 m NAP and in the second aquifer, below the Kedichem Formation, the level is -4 m NAP. From this it can be concluded that there will be a flux from the landfill into the first aquifer. The flux will be mainly through the channel deposits. There will hardly be any flux at all between the first and second aquifers.

Geochemistry and chemical influence of the landfill on its surroundings
In order to assess the geochemistry and the possible influence of the landfill on its surroundings, a schematic subdivision was prepared of the landfill and the subsurface. In doing so a number of zones were defined (see Fig. 5 in appendix A):

- Zone C1 is that portion of the first aquifer which is upgradient from the landfill.
- Zone C2 is that portion of the first aquifer which is immediately below the channel deposits under the landfill. This is the part of the aquifer which will be influenced first by the landfill.
- Zone C3 is that portion of the first aquifer which is downgradient from the landfill. The fence of monitoring wells has been installed in this zone and to date this portion has not yet been influenced by landfill leachate.
- Zone C4 is the body of the landfill itself. It contains the bulk of the pollution.
- Zone C5 is the confining layer between the landfill and the first aquifer. It consists of clays of the Calais Formation and channel deposits of the Duinkerken Formation.

For the purpose of a first general assessment of the information all the available measurements have been combined and the zones evaluated as single units.
Zone C4: The landfill

The highest concentrations of pollutants are found within the landfill itself. There are, however, very large variations. From the pH values it is apparent that the landfill has in any case been in the methanogenic stage since 1988. There is evidence that iron, nitrate and sulphate reduction is taking place in the landfill. The electrical conductivity (Ec) is high to very high. One value (9,500 μS/cm) is so high as to suggest a possible density flow.

Pollutants found in the landfill include BTEX and low concentrations of chlorinated alkenes. Measurements performed on the leachate in the circular drainage (since 1992) also indicate pollution with phenol, cyanide, naphthalene and other PAHs.

Zone C1: Upgradient

The aquifer upgradient from the landfill is anaerobic. Measurement performed on the groundwater indicate iron- and sulphate-reducing conditions; although sulphate reduction is probably only slight. During the most recent measurements a single reading slightly exceeded the detection limit for toluene. No other evidence of pollution was found.

Indications of the dispersion of landfill leachate

By comparing the observations for zones C1, C2 and C3 with those for zones C4 and C5 it is possible to identify the influence (if any) of the landfill leachate on the aquifer. Going by the pollutants themselves there is no real sign of any influence. Other parameters do, however, suggest an effect. These parameter include ammonia and Kjeldahl nitrogen, redox parameters, DOC, CZV and CO_2.

It is not possible to identify a clear redox zonation. This is because the aquifer originally was already iron- and sulphate-reducing and remains so. The methanogenic zone is probably in the landfill or immediately below it. The virtual absence of pollutants below the landfill may be an indication that intrinsic degradation is taking place.

The measurements provide a number of strong indications for the presence of density flows in and below the landfill. In the centre of the monitoring fence at one of the deepest filters in piezometers 3 and 4, elevated values are encountered for electrical conductivity, chloride, sulphate, alkalinity, methane, TOC and CO_2.

In addition, there are also the high Ec values observed in the landfill and a conductivity test which indicated a very low resistance.

Towards a conceptual model of the Coupépolder landfill

The basis for setting up a conceptional model of the landfill is the rough schematization presented in figure 5 (see appendix A).

From the water flow balance drawn up in 1988 it can be concluded that the maximum flux from the landfill into the first aquifer is 0.78 mm/day. It should, however, be noted that since 1988 a number of measures have been implemented which influence this flux. These measures will have caused the flux to at least decrease. The 1988 water flow balance must be improved.

The flow rate in the first aquifer may be between 26 and 95 metres a year. Assuming purely convective transport with no mixing, this means that the thickness of the plume should be 1.95 - 4.5 m below the Calais Formation.

The indications of the presence of density flows suggest a second plume immediately above the Kedichem Formation.

Microbiological techniques

Most of the redox processes in the subsurface are microbially catalysed. The result of these microbial processes is the formation of a number of redox zones. At the Coupépolder the possible redox zones include: iron-reducing, sulphate-reducing and methanogenic.

Low concentrations of pollutants have been found below and downgradient from the landfill site. The presence of pollutants in the landfill could have lead to the creation of pollution-degrading populations of micro-organism in and below the landfill. It is possible to characterize the degradation capacity by examining DNA/RNA profiles or by using BIOLOG micro-titration plates to investigate the metabolic potential. By comparing the profiles for the methanogenic zone with the profiles for the zones further downgradient it will be possible to draw conclusions concerning the degradation potential.

Optimisation of the BIOLOG gram negative plates

In Phase 2, attention focused mainly on the BIOLOG method. Aspects investigated included reproducibility, optimum temperature, size of the spiking, effects of adding/withholding additional electron acceptors, types of reducing agents and activity specificity. The conclusion which can be drawn from this study is that BIOLOG micro-titration plates can be used to accurately analyse the microbial metabolic diversity. Possible improvements in the method include the use of 10 ppm sodium sulphide as the reducing agent instead of sodium thioglycolate, and incubating the plates at 10 ^oC. The colour reactions are best examined after 4, 7, 14 and 28 days. The samples must be analysed with the BIOLOG plates as soon as possible after the sampling. The data are readily processed using the available BIOLOG software.

Development of biodegradation-specific microplates

The use of the standard BIOLOG plates yields information on the general microbiological metabolic potential and not specifically on the biodegradation potential. The use of BIOLOG MT plates to which we can add carbon sources ourselves makes it possible to specifically look at biodegradation. In this phase, the procedures for making such micro-titration plates were investigated. The aspects examined included which dilutions should be used and how long it takes before it is possible to observe a reaction.

Characterization of the transition zone between the landfill and the underlying sediment

One of the hypotheses for this project centred on the assumption that between the landfill itself and the underlying sediments a boundary layer is formed which might act as a hydrological barrier and in which there may be elevated biological activity. In the present phase of the investigation, cores were obtained from this boundary layer. These cores have been examined by means of geochemical, microbiological and electron microscopy techniques.

Geochemical characteristics

The sample is clayey and contains more sand towards the base. The lime content is high. The sample appears heterogeneous and a number of thin black layers can be observed which are rich in humic material and in which even plant structures can be recognised

A noticeable result of the chemical analyses is that the sample has been clearly influenced by landfill leachate. Fe^{2+} and Mn^{2+} contents are low compared to measurements in the landfill itself (performed in 1988) while the pore water also contains sulphate. The further presence of nitrate in the pore water is also remarkable since it cannot really occur under these conditions. Perhaps some slight oxidation did take place during sampling.

Electron microscopy

The electron microscopy images indicate that the sample contains an abundance of iron sulphide precipitates. The presence of these sulphide precipitates also explains the black colour of the sample. Most heavy metals are precipitated under sulphidic conditions. The sulphide precipitates in the sample contain, apart from Fe, only Zn as a major component. Sulphide precipitation is therefore an important process by means of which metals are filtered out of the leachate. Sulphide precipitates are very insoluble.

Microbiological characterization

The metabolic profiles obtained with the aid of the BIOLOG GN micro-titration plates for the boundary layer are very different from those for the layers above and below it. The number of positive observations is highest in the layer immediately above the thin boundary layer (i.e. in the landfill) and then drops off in both the boundary layer and below it. A remarkable observation was that some of the substrates which are formed during the microbial degradation of organic material are not being consumed.

No differences were observed in the potential for degrading pollutants. This may partly be due to the fact that the samples were 2 months old before they were used.

Investigations in Phases 3 and 4

Coupépolder

The water flow balance at the landfill must be adjusted to take into account the protective measures at the site. Using this improved water flow balance it will be possible to make a better estimate of the percolation speed. It is also important to incorporate the effects of the circular drainage in the regional water flow model.

The next phase will be aimed at gaining a better understanding of the geochemical processes at the boundary layer between the landfill and the aquifer in the channel deposits. The conceptual model will also be further worked out and somewhat more extensive computations performed.

Phase 3 will be primarily concerned with characterizing the microbiological potential. To this end both field and laboratory experiments with microcosms will be carried out. In the laboratory further experiments will also be carried out with continuous flow cells. In addition, the development and application of DNA/RNA characterization techniques will also receive attention. We are primarily for differences in the characteristics of the landfill, transition zone and background. The main tool to be used in the field for this purpose will be so-called Multi-Layer Sampling Microcosms (MLSMs).

Banisveld

One of the aims of the project is to develop a generic methodology for characterizing landfills. In developing a generic method it is important to test the various developments at a number of landfill sites. The Banisveld landfill near Boxtel in the Province of Noord-Brabant is a suitable test case for applying the techniques for the Coupépolder, because the geological conditions at this landfill site are quite different from those at the Coupépolder. The is also a considerable amount of information available for the Banisveld landfill.

CHAPTER 1

INTRODUCTION

Old Municipal and other landfills present a potential threat to the environment and as such demand considerable attention from present day society. Now society aims to remove threats from landfills although the costs associated with the corresponding (more or less traditional) measures are enormous.

Recently, research on landfill plumes and other polluted soils and aquifers has shown that the spreading of pollution in the sub-soil is often less than expected [Christensen et al., 1994]. It appears that the concentration of the pollution decreases as a result of natural processes such as dilution, dispersion, evaporation, sorption and degradation. The combination of all possible processes that attenuate the pollution is called Natural Attenuation (NA).

Currently we are carrying out a project within the Dutch research program NOBIS titled: *'Feasibility project in situ bio restoration of landfills. NOBIS project 96-3-04'*. The goal of this project is to develop a methodology with which we can assess the potential of NA to control landfill leachate pollution plumes. The methodology is not meant to be a recipe how to apply NA, but more a set of guidelines. In addition, we hope to present guidelines on how to present and structure the information.

This report presents an overview of the data obtained in previous research and obtained during this project on the Dutch Landfill Coupépolder. A first rough conceptual model on the processes occurring at the landfill is given. In the following project phases, this conceptual model will be refined keeping the goal in mind how to assess the potential of NA to control the landfill leachate plume.

1.1 **Coupépolder as a case study**

In order to assess the potential of NA to control landfill leachate plumes we chose the former landfill Coupépolder near Alphen aan den Rijn as a case study. Several measures have been taken to prevent spreading of the pollution such as a subsurface ring drain and surface sealing with bentonite layers. For the deeper subsoil and first aquifer some measures are planned to be carried out if monitoring deems it necessary. Monitoring carried out since 1988 showed that the leachate is less polluted than might be expected [see IWACO reports from 1988 onwards] and we therefore assume attenuation is taking place.

There also have been reports of a 'black layer' found in cores at the boundary between the landfill and the underlying sediments. The hypothesis is that this layer is a result of increased biological activity due to sharp chemical gradients around this boundary. These gradients are the result differences between the material in the landfill and the original sediments. As such this layer could function as a natural biological screen.

Several reasons make Coupépolder an interesting case to study the background of NA in combination with landfills:

- The situation of Coupépolder is similar to many other landfills in the Netherlands.
- According to the initial plans, the control measures would last for eternity. It appears that NA can control the leachate from the landfill. If this is the truly the case, this will have a profound effect on the exact type of measures, if any!

1.2 **Approach in this project**

In this project, we aim to combine the more traditional hydrological and geo-chemical approach with more recent microbiological approaches. Special attention is given to data requirements, data analysis, data presentation, conceptual modelling, and the combination between data and modelling. This approach should result in a characterization of the potential of NA to control the leachate plume and an estimation of the rates of attenuation based on a smart monitoring of NA processes.

The project as a whole consists of four phases. A review of the available international literature and a visit to the Danish Technical University (dr. Thomas Christensen) was the first phase of this project. The results of the literature study can be seen as a state of the art and are summarized in the report ‘The intrinsic capacity of aquifers to degrade pollution from (old) landfills’ [CUR/NOBIS, 1998]. The review by Christensen [Christensen et al., 1994] from Denmark was the starting point for the state of the art report. The state of the art report presents the general processes that attenuate landfill leachate, the approaches for characterizing the processes and models to describe the behaviour of leachate.

The second phase consisted of confronting the existing data of the Coupépolder with the NA concepts in order to obtain a Conceptual view of the processes going on at the landfill. Additional data have been collected, especially concerning the redox conditions at the Coupépolder. Preliminary work has been carried out in order to obtain experience with novel microbiological techniques such as BIOLOG and DGGE. This report presents the first results of phase 2.

Phases 3 and 4 consist of integrating the microbiological techniques with the more traditional geochemical and geohydrological methodologies.

1.3 Layout of report

This report presents the first results of phase 2 and aims to present a first conceptual model (mental picture) of the Coupépolder and the processes occurring in the sediments surrounding the landfill. Characterization of the Coupépolder landfill started with reviewing the information of studies carried out in the last 10 years. Mainly the geology, hydrogeology and extent and type of contamination were investigated at that time. Within the present project, new data have been collected during sampling campaigns in 1997. Based on the literature study new parameters, representing the process conditions, and new characterization techniques are applied.

Besides the collection of additional information, a conceptual model describing behaviour and fate of the contaminants is under development. As a start groundwater flow is studied because groundwater is the carrier for contaminants. Then geochemical and, if possible, biological processes are included. This report describes the first steps in the development of the conceptual model. Proof of an impact of the landfill in the aquifer is found by looking at concentrations of redox parameters and macro parameters instead of trying to detect xenobiotic compounds.

Chapter 2 gives a general description of the topography, history and hydrogeology of the landfill. In chapter 3 possible geochemical and pollution effects of the surroundings are discussed using data collected in previous research and during this project. In addition, a rough model is presented of the landfill, in which the landfill is divided into five sections. The hydrological and geochemical processes are combined with a first conceptual model of the landfill in chapter 4. The following two chapters present the first results from the experiments carried out in order to develop and implement micriobiological characterization techniques.

Chapter 5 discusses the application of the BIOLOG GM microtiter plates for the microbiological characterization of the landfill sediment and water. Chapter 6 discusses the combined application of geochemical, electromicroscopy and microbiological techniques on samples taken from the expected location of the so-called black layer.
Finally, chapter 7 looks forward towards the next phase of the project.

CHAPTER 2

THE COUPÉPOLDER LANDFILL

2.1 Site description

The former Coupépolder landfill is situated northeast of Alphen aan den Rijn, between the Aar canal, the river Kromme Aar and the Zegerplas. The landfill is oriented from the northeast to the south-west (see Figs. 1 and 2 in appendix A). Landfilling at this site occurred between 1959 and 1985. A golf course was developed on top of the landfill after closing in 1985.

The former landfill has an area of about 22 ha. The length (from south to north) is approximately 850 m. The width varies between 200 and 300 m. The boundaries of the landfill are determined by the Aar canal in the south-east, the river Kromme Aar from the northwest to northeast and the Zegerplas in the south-west. The Zegerplas, the river Kromme Aar, and the Aar canal are connected and the levels correspond with the artificial polderlevel of the 'Rijnlandsboezem' which lies at -0.6 m NAP.

The houses closest to the landfill are farms and market gardens along the Aar canal, south-east of the landfill. Here we also find greenhouses. At 400 m to the northwest of the landfill lies the residential area 'Ridderveld'. The area west and northwest of the landfill between the Kromme Aar and 'Ridderveld' has a recreational use and harbours a midget golf course, a children’s farm, a park ('Heemgebied') and part of the golf course. The golf course extends in the polder 'Oudshoorn' north of the landfill. The polders further north and east of the Aar canal have an agricultural use (mainly pasture). An overview of the surroundings of the landfill is given in figure 2 (see appendix A).

2.2 History of the Coupépolder landfill

2.2.1 *Waste disposed of in the Coupépolder*

All information regarding the landfill history is based on research carried out for the Province of Zuid-Holland [IWACO, 1988a] The landfill was started in 1959. Permission was granted for the disposal of ordinary household, street, and agricultural refuse, ashes, demolition waste and comparable refuse (A license under the Dutch 'Hinderwet' was granted by Gedeputeerde Staten). The disposal of toxic compounds was forbidden. In 1973 permission was granted for extending the landfill area to the northeast part of the Coupépolder. In 1979 permission was granted for construction-, demolition waste, and other incombustible waste, as long as no hazardous chemical compounds leaches from the landfill.

The regional inspector reports some illegal activities [IWACO, 1988a] such as the landfill area being too large (landfill fronts), inadequate covering, the burning of refuse, and the dumping of illegal waste. These included household refuse (after 1978), shredder waste, bleaching powder, gypsum slurry, drilling fluids or circulation fluids, kitchen refuse from a hospital, sewage- and other slurry, and container waste of unspecified origin. In addition, it was observed that before waste disposal more soil had been removed from the south-east area than was allowed.

Incidentally, permission was granted by consultation to dispose of material outside of the license for a short period of time (few months) when no other treatment facility was available. This included shredder waste, kitchen waste from a hospital, and water treatment slurry.

Waste disposal stopped on the 1st of January 1985. The origin and type of about 5 % of the material in the landfill cannot be determined.

2.2.2 *Expansion history of the Coupépolder landfill*

A few low positioned parts (some under water) were filled between 1960 - 1972. Between 1972 - 1979 the landfill area was extended into the northeastern part of the Coupépolder. In the period 1979 - 1985, the maximal extension of the landfill had been reached.

2.2.3 *Areal distribution landfill materials*

The hill in the northern part of the landfill contains primarily household refuse. Household refuse is characterized by a compost like black matrix, in which all kinds of wrapping materials are mixed. High concentrations of methane and hydrogen sulphide were measured above holes that have been drilled on top and aside this hill. Unfortunately, obstructions inside the hill make it difficult to determine whether or not there are locations present in this part of the landfill that contain waste of a suspect origin. The flat part to the south of the 'hill' contains mainly construction-, and demolition waste (wood, bricks, and glass), and industrial waste (very diverging: tins, wrapping materials made of cardboard, car shredder, paper, straw, branches, etc.).

The thickness of the landfill is 14 m at the hill, and 3 to 6 m at the flat parts in the south. An extensive research using resistance-logs (from cone penetrations) and drillings did not provide clear evidence for the presence of illegally dumped barrels. Only one location (COB5, see Fig. 3 in appendix A) provided evidence of a barrel, wrought iron was found. Comparison of EM and magnetometric anomalies indicate the possible presence of a container inside the landfill body. An extensive discussion on the occurrence of EM anomalies in relation to drillings can be found in [IWACO, 1988c].

2.2.4 *Environmental measures taken at the former Coupépolder landfill*

In order to prevent environmental risks associated with the Coupépolder landfill a number of measures have been taken to prevent direct exposure to contamination. An overview of the described measures, implemented between 1988 and 1992, is given on figures 3, 4 and 5 (see appendix A).

2.2.5 *Subsurface ring drainage system*

A subsurface drainage systems has been constructed around the landfill. This drainage system is subdivided into three sections:

- section 'Aar canal';
- section 'Kromme Aar';
- section 'Heemgebied'.

All percolation to the sides of the landfill drains to this drainage system. The drains discharge towards a drain pump sump (drain pump sump 'Aar canal', 'Kromme Aar' and 'Heemgebied'). From these pump sumps the percolate is pumped via pipes and a central discharge measurement point towards a central pump sump. The percolate is pumped from this central pump sump to the municipal sewer system. The central discharge measurement system measures discharge from each section of the ring drainage system. Percolate can be sampled from each drainage section.

Sealing construction
The slopes of the landfill have been sealed with a sealing construction. The construction is from the top layers to the deeper layers:

- a layer of garden mould in two thickness. A thickness of 0.5 m where the surface is to be sown with grass and a thickness of 1 m in the planting sections in order to prevent damage to the sealing by deep rooting plants;
- a drainage layer of well condensed river sand with a thickness of 0.25 m, on top of the sand bentonite layer, except at the locations of the ditch that surrounds the landfill. Drains have been installed at regular distances of 25 m to facilitate future instalment of drains in the higher parts of the landfill;
- the sand-bentonite layer is a strongly condensed impermeable layer with a thickness of 0.25 m, containing a mixture of sand and 8 to 10 % bentonite. This layer forms a separation between the percolate draining from the landfill and the water in the ditch and water from precipitation that falls on the slopes;
- a support layer of a well draining sand with a minimal thickness of 0.3 m. The ring drainage system is installed in this support layer.

At the base of the slope, a ditch was dug around the landfill with its base on the sand-bentonite layer. This ditch discharges precipitation from the roads and the slopes.

Control measures for surface waters
A sheet pile wall was constructed between the northern section of the landfill and the Kromme Aar in order to prevent the flow of leachate from the landfill directly towards the Kromme Aar. At the same time, the sheet pile wall prevents drainage from the river to the drainage system.

Control measures for the subsurface water
If necessary, a geo-hydrological control system will be installed in the direct neighbourhood of the landfill in order to prevent uncontrollable pollution of the deep groundwater. This system consists of a monitoring system and a control system 100 m further downstream. The monitoring system is subdivided in a observation zone and a monitoring zone. Currently only the observation zone is in operation. This consists of five monitoring wells (01 to 05, see Fig. 3 in appendix A) each fitted with five screens in the first regional aquifer (-5, -25, -35 and -50 m). The monitoring zone will be installed based on results of measurements from the observation zone. The control system will be installed when the pollution has reached the monitoring zone. It will consist of 7 extraction wells with filters that extract water from the polluted regional aquifer. The flow rate of the extraction wells shall be 50 m^3/hour which makes the control complete.

2.3 **Hydrology**

2.3.1 *Geology*

Figure 5 (see appendix A) gives a schematic overview of the geology in the Coupépolder area. This area is part of the border of the North Sea basin with quaternary, tertiary and older sediments. Most important for this study are the quaternary sediments belonging to the lower-Pleistocene formation of Kedichem, the middle-Pleistocene formations of Kreftenheye and Twente and the holocene Westland formation.

The formation of Kedichem consists of deposits of the large rivers Rhine and Meuse and contains primarily clays and fine silty sands. The top of this formation is a continuous clay layer with a thickness of 5 to 10 m. For this study we have taken this to be the base of the described geological profile. The top of this layer at the Coupépolder lies at a depth of -40 to -45 m NAP. This was confirmed by geo-electrical measurements.
Above the formation of Kedichem we find moderately fine to coarse sandy deposits with an intercalation of gravel and loam. These deposits are wind borne sands of the formation of Twente

and fluvial sands of the formation Kreftenheye. The combined thickness of these formations ranges from 32 to 40 m.

These Pleistocene formations are covered by a 0.25 to 1.8 m thick layer of settled peat, the so-called 'basisveen'. This 'basisveen' is a continuous layer in large areas of Holland and thus also for the Coupépolder area.

On top of the 'basisveen' we find deposits of the formation of Calais. This is a 8 to 10 m thick layer containing primarily heavy blue-grey humus rich clays. Due to the rising sea levels these clays became more sandy to the top. In the late Holocene, the so-called 'Hollandveen' developed on top of the clays of the formation of Calais. This 'Hollandveen' has developed to a clayey peat layer with a thickness of about 1 m.

In the youngest Duinkerken phase, channels have developed which have carved into the above described formations while leaving sandy deposits. Some of the remaining rivers in the polders of Zuid-Holland are relicts of these channels. These channel deposits consist of fine layered sands or sandy clays that lie directly on the formation of Calais or in the deeper eroded parts directly on the Pleistocene sands. These channel deposits occur very locally and therefore are seldom found on the geological maps. The occurrence of these channel deposits below the Coupépolder landfill is of extreme importance for the spreading of the pollution.

The depth and location of above mentioned formations has been mapped using cone penetrations and electromagnetic measurements [IWACO, 1988a en b]. Characterization of the subsurface using resistance profiles gave excellent results. The clay layers in the upper 8 to 10 m of the soil exhibit low cone resistance (< 1 MPa), the channel deposits have a cone resistance between (1 - 10 MPa), and the sands of the formations of Twente and Kreftenheye have very high cone resistance (> 10 MPa). Interpretation of the cone resistance and EM measurements beyond the landfill showed that the northern and western parts of the landfill were indeed on top of the Holocene channel deposits. An overview of this situation can be found on figure 4 (see appendix A) in which the shaded section denotes the channel deposits.

The landfill lies on top of these deposits and has a thickness that varies between 3 to 6 m in the lower parts at the base of the hill up to 14 m at the top of the hill.

2.3.2 *Hydrogeology and groundwater flow*

In order to describe the hydrogeology we schematically divide the soil in a set of aquifers and impermeable layers. In this case we assume that water flows through the aquifers in a horizontal direction and in a vertical direction through the impermeable layers. The aquifers are characterized by the hydraulic conductivity (*k*-value) and a permeability value (*kD*-value) whereas the impermeable layers are characterized by a vertical hydraulic resistance value (*c*-value).

Anthropogenic influences have a large impact on the groundwater flow in the area. Most important are the polders, the fixed water-levels of the rivers and canals ('Hollands Boezem'), and the drains installed at the boundaries of the landfill.

The landfill body contains a phreatic groundwater table. Sometimes pseudo-groundwater tables are found. This phreatic layer consists of leachate and is recharged by infiltrating rainwater. The thickness of the saturated zone within the landfill is about 3 m. The average yearly precipitation surplus (precipitation minus evapotranspiration) in the area is approximately 360 mm/yr. The phreatic groundwater level is moderately flat with a small rise under the hill. The levels vary between -1.8 m NAP and +0.9 m NAP, with an average value of 0 m NAP. In the channel surrounding the landfill a water level of -1.9 m NAP is maintained. This open channel was replaced by a closed ring-drain in 1992, to prevent human contact of the outflowing leachate. The water level maintained in this system is -1.5 to -1.9 m NAP. The water levels of both the open and the closed drains have been and still are lower than the levels inside the landfill body, inducing an outflow of leachate from the landfill to these drains.

According to other research [IWACO, 1988b], the hydraulic conductivity of landfill bodies may vary strongly (0.1 - 1.0 m/day). It is assumed that the hydraulic conductivity is relatively low (0.3 m/day) at the hill, where household waste has been dumped, while the hydraulic conductivity is high at the locations where building-, and industrial waste has been dumped.

The natural aquitard, the combined 'basisveen' and clayey deposits from the formation of Calais, has a hydraulic resistance (*c*-value), which ranges from 30,000 days in the southern part (complete Holocene sequence) to 5,000 days and less in the northern part where the gully-deposits are found. These values were derived from dissipation tests [IWACO, 1988b].

The aquifer, in the Pleistocene sands of the formations of Twente and Kreftenheye, has a thickness ranging from 32 to 40 m. The *kD*-value is estimated from pumping-tests, and varies between 1,750 and 2,000 m^2/day according to pumping tests in Hazerswoude and Alphen aan den Rijn (TNO grondwaterkaart, 1988).

The groundwater level in the aquifer is decreases from -3.3 m NAP in the southern part to -3.9 m NAP in the northern part of the landfill. The difference in hydraulic head between the phreatic groundwater and the aquifer is about -3.6 m. Thus, besides an outflow of leachate to the sides, a vertical component of leachate outflow can result in the contamination of the aquifer beneath the landfill. Because of the lower *c*-values of the gully deposits in the north and the west, the bulk of the downward leachate flux is expected to occur in these deposits. The groundwater flow direction in the aquifer is northwards due to a hydraulic gradient of 1 : 1,000 m/m. The groundwater is flowing towards polders, where water levels of -5 to -6 m NAP are maintained. The flow-direction is not significantly influenced by groundwater extractions in the neighbourhood.

The formation of Kedichem beneath the aquifer, consisting of clay and fine clayey sands, has a *c*-value of 10,000 days [IWACO, 1992d]. The water level in the second aquifer below the formation of Kedichem is about -4 m NAP. Because of the high *c*-value and the low difference in water level between the two aquifers, vertical groundwater flow from the first to the second aquifer is marginal. Therefore the aquitard beneath the first aquifer was chosen to be the base of the conceptual model that has been developed for the Coupépolder landfill.

CHAPTER 3

GEOCHEMICAL CHARACTERIZATION OF THE COUPÉPOLDER LANDFILL

3.1 **Previous research**

Since 1981 the quality of the groundwater at the Coupépolder landfill has been studied. A large number of water samples (more than 150) have been taken from a number of filters (96). In addition, samples have been taken from the soil, the landfill, the surface waters etc. In 1992 IWACO published a report dealing with the groundwater quality of the landfill and the underlying aquifer [IWACO, 1992-3]. The goal of that investigation was to obtain an indication whether the aquifer beneath the landfill was influenced by pollutants from the landfill body.

Since 1992 additional data have been collected as part of the control measures taken to minimise the environmental risks. As part of the measures for the deep groundwater, monitoring is carried out using monitoring wells. Monitoring wells are installed upstream and downstream of the landfill. At the same time pollution levels of the closed drain surrounding the landfill are monitored. Here we give an updated overview of the pollution situation in the landfill and the underlying aquifer.

In this overview we adopt a similar zonation as was used in the study of 1992. In that study the landfill and underlying soil layers were divided in to five zones. The rationale behind this zonation is to make the interpretation of the results more easy as all data obtained from one zone are lumped together. The five zones are shown in figure 5 (see appendix A) and are:

- Zone C1: The part of the aquifer upstream of the landfill. This aquifer cannot be influenced by the landfill and as such serves as a reference for all measurements (background concentration values).
- Zone C2: The part of the aquifer beneath the landfill. Initially it was the idea to split this zone in to a section below the impermeable Holocene clay layer and a zone below the gully deposits. As the number of standpipes below the clay layer is relatively small and the residence time in the clay layer is much higher, this subdivision was not found to be very useful. If the landfill has an effect on the aquifer it should be found in this zone.
- Zone C3: This part of the aquifer is directly downstream of zone C2. As the groundwater flows from zone C2 to C3 it may be expected that zone C3 will ultimately be influenced by leachate from the landfill.
- Zone C4: This is the landfill itself. We expect to find the highest pollution in this zone.
- Zone C5: This is the layer between the aquifer and the landfill. This zone will be influenced by leachate from the landfill as the leachate migrates towards the aquifer. No filters have been installed in the clay layer because the extraction of water is expected to be very difficult.

The approach in which all data from all filters in a single zone are clustered is rather coarse. We have to expect heterogeneity, both in the landfill as well as in the subsoil. As a results the values obtained will cover a wide range and will have a high standard deviation. However it does give a general idea of the impact of the landfill on the aquifer.

An overview of the data is presented in table 1 (see appendix B). To summarize the data we can state that zone C1 is not influenced by the landfill and that zones C2, C3 and C5 are. As was expected zone C4 shows the highest concentrations.

3.2 Hydrochemical fieldwork performed during the present NOBIS study

The goal of the second phase of the NOBIS project was to characterize the landfill and to develop a conceptual model of the processes occurring around the landfill. The redox processes in the leachate plume are extremely important for the fate of the contaminants in the sub soil.

The landfill leachate contains a large amount of reduced species and as the leachate moves through lesser-reduced soil, it will tend to reduce the environment. Therefore we expect to find a range in redox conditions with the most reduced zones closest to the landfill and the least reduced zones further downstream in the zones not affected by the landfill leachate.

The inital fieldwork in this project was geared to obtain an idea of the extent of these redox processes at the Coupépolder landfill. The following activities were carried out:

1. In May 1997, groundwater samples from 16 of the 20 screens from the 5 monitoring wells downstream of the landfill were sampled and analysed for a number of parameters (see table 2 in appendix B which included the redox sensitive species oxygen, nitrate, Mn(II), Fe(II), sulphate, sulphide, methane. In addition electrical conductivity (Ec), temperature, pH, redox potential (Eh) and oxygen content were measured in situ at all 20 screens of the monitoring line (see table 2 in appendix B). Later in the same year (September 1997) 2 reference standpipes upstream of the landfill were also sampled and analysed for the same parameters.
2. In May 1997, the groundwater at six depths below the landfill was sampled with a multi-groundwater probe (MGWP1, by Delft Geotechnics, see table 2 in appendix B) and analysed for the same parameters as mentioned under the previous activity.
3. Alongside the multi-groundwater probe a cone penetration test has been carried out in order to obtain detailed information on the geology of the subsoil. This was necessary because it was preferred to obtain water samples from the sandy permeable layers and not from the clayey parts of the gully deposits. Water flow through the clayey layers is expected to be very small and clayey layers can induce local effects on the overall hydrochemistry. The interface between the gully deposits and the original aquifer was found to be at about -24 meters below the surface (= -19 m NAP), where the probe resistivities are all above the 10 MN/m^2.
4. In May 1997, a sediment sample was taken from the transition zone between the landfill and the underlying soil. This sample has been taken using a 'Begemann' coring which was carried out by Delft Geotechnics. This sediment sample has been characterized for grain size, C/N ratio, lime %, pore water chemistry, mineralogy using an analytical transmission electron microscope (AEM), and microbiological parameters discussed in table 4 in appendix B.

3.3 Hydrochemistry in the landfill

All data we have of the chemistry in the landfill originates from measurements carried out before 1988 and a few samples in 1990. Since then all investigations have focussed on the water quality in the other zones which might be impacted by the landfill.

At least since 1988, the landfill has been in the methanogenic phase. This can be deduced from the measured pH-values which have much higher values than those expected from acid phase leachate.

Locally we may expect other redox reactions to occur. Aerobic zones may occur at those locations that are in direct contact with the atmosphere or where oxygen rich rainwater enters the landfill. Nitrate reduction can occur because nitrate is found in measurable concentrations in all samples although below 3 mg/l. Iron reduction and manganese reduction occur (or have occurred) because Fe(II) and Mn(II) are measured to be above the detection limit at all locations with mean concentrations of 29 mg/l for Fe(II) and 1.8 mg/l for Mn(II). Sulphate-reduction is likely to take place because in 50 % of the samples analysed in 1988, sulphate concentrations were below the detection limit. One peak value of 600 mg/l sulphate indicates the possibility that gypsum has been dumped locally. No measurements of CO_2 and CH_4 have been performed in 1988. Alkalinity (bicarbonate and fatty acids) concentrations (ranging between 20 and 87 mmol/l) indicate an abundant fermentation and respiration of organic material.

Ec-values measured in the well screens which were positioned in the leachate plume in 1988 range between 1,241 and 9,490 μS/cm. The highest Ec-value of 9,490 μS/cm may be high enough to induce local density flow.

Concentration values of Anthropogenic Specific Organic Carbons (ASOCs) have been measured with screens inside the landfill body from 1988 and 1990 (only a few). The most important contaminants are the BTEX compounds benzene, toluene, ethylbenzene, and xylene with average concentrations of 11, 40, 65 and 263 μg/l respectively (see table 1 in appendix B). In more than 85 % of the samples the concentrations were above the detection limit. A large range of concentrations is observed, and the average values are strongly influenced by a few large peak values. The median values are below these averages. More than 85 % of the landfill body is polluted with modest concentrations of BTEX (n = 23).

The concentrations of chlorinated alkanes measured inside the landfill body are much less significant. The detection limit was not exceeded for the following compounds: dichloromethane, 1,2-dichloroethane, 1,1,2-trichloroethane and trans 1,2-dichloroethene. Only for 2 samples, 1,1-dichloroethane, and for 1 sample, cis 1,2-dichloroethene, exceeded the detection limit in a total of 69 samples from the total landfill area. Other chlorinated alkanes were found in very low concentrations in the range of a few μg/l if exceeding the detection limit at all. In order of importance these chlorinated alkanes are: trichloromethane, 1,1,1-trichlorethane, tetrachlorethene, trichloroethene and tetrachloromethane.

3.3.1 *Contaminants in landfill leachate: closed drain*

From 1993 onwards the water quality of the closed drain has been measured 3 or 6 times a year. Concentrations measured in the closed drain are considered to be more like real averages because this water is a mixture coming from a large contributing area. However, it is unclear to what extent this water is diluted by inflow of clean water from the surrounding Aar river/canal, fresh rainwater. It is also unclear to what extent the composition of the anaerobic leachate is changed by possible oxidation in the drain.

Review of the data obtained in 1996, revealed that in addition to the compounds measured in water from screens in 1988, the following contaminants are also present in the leachate (maximum concentrations are given in μg/l): phenol (2.8), cyanide (7), naphtalene (26) and other PAKs (less significant and much less mobile), 1,2,4-trimethylbenzene (12), 2-chlorotoluene (1.7), chlorobenzene (13) and chloroethane (240!).

3.3.2 *Heterogeneity in leachate concentration*

The measured concentrations of ASOCs are highly variable. The Ec and chloride concentrations also vary greatly, making dilution corrections difficult if not impossible. In general all compounds vary greatly in space. Sulfate concentrations are high at some places indicating a constant source of sulphate (probably gypsum), but are below the detection limit at 40 % of the locations. Thus sulphate/chloride ratios in the landfill vary greatly, which makes the interpretation of sulphate-reduction in the leachate very difficult. The variation in Fe(II) and Mn(II) concentrations is large.

3.4 **Quality and geochemistry of the aquifer upstream of the landfill**

The upstream groundwater (wells 16 and 17) is anaerobic, has an Ec of about 1,100 μS/cm and a neutral pH (7.1). The detection limit of the ASOCs is exceeded only once; in the most recent sampling a concentration of 2.4 μg/l toluene has been found.

The nitrate and oxygen concentrations are zero. Manganese (II) is not found above the detection limit which may indicate that no source for manganese is present, because dissolution of Mn(II) is thought to be favourable because iron-reduction (Fe(II) = 5 mg/l) is taking place. Sulphate concentrations are high (43 - 160 mg/l). Low sulphide concentrations (0.05 mg/l) indicate some sulphate-reduction. Alkalinity concentrations (4.2 - 7.4 mmol/l) are normal for these aquifers. The alkalinity corresponds with pristine water with bicarbonate at a pH of 7. However in this environment part of the alkalinity can be attributed to the contribution of fatty acids in the DOC. Unfortunately bicarbonate can not be estimated from equilibrium calculations based on the pH and the CO_2, because the measurement of dissolved CO_2 may be influenced by the fatty acids too.

3.5 **Indications for migration of landfill leachate**

Indications for the migration of landfill leachate can be obtained when the groundwater quality parameters measured in zones C2 (directly below the landfill) and C3 (downstream of the landfill) are compared with the groundwater quality measured in zone C1 (upstream) and zone C4 (the landfill itself). Appendix C gives plots of the concentrations, averages and standard deviations of a number of selected parameters. These plots give an indication of the spread in concentrations for each parameter.

There is some indication in zones C2 and C3 of an influence by landfill leachate. The temperature of the groundwater in zones C2 and C5 (about 20 ^oC) is significantly higher than the temperature zones C1 and C3 (about 12 ^oC). This could be an indication of an increased biological activity in zone C2 and C5. However, in order to be sure that these results are not an artefact of the sampling technique these temperature measurements need to be repeated. Other overall parameters which should be characteristic of landfill leachate are the electrical conductivity, the chloride concentration, the Total Organic Carbon content (TOC), and Kjeldahl nitrogen which is a measure of the total reduced nitrogen and the alkalinity. Following the redox zonation approach we look at the redox parameters, oxygen, nitrogen, Fe(II), Mn(II), sulphate, and methane. Figure 6 (see appendix A) gives a radar plot in which the concentrations in each zone can easily be compared with each other.

Using the plots in appendix C we find that the Ec is not a very good characterizing parameter for landfill leachate. The averages of the concentrations in zones C1, C2 and C3 do not differ much. However, the standard deviation does increase somewhat.

Chloride is a better characterizing parameter. In the pristine aquifer upstream the chloride has a relatively narrow concentration band. In the zones C2 and C3, the standard deviation is much higher and the average value of zone C2 is higher than zones C1 and C3.

The TOC concentration does not seem to be a very good characteristic for detecting the landfill leachate either. However, derived parameters such as the CO_2 concentration, Chemical Oxygen Demand (CZV), alkalinity, Kjeldahl nitrogen and ammonium all give similar results. Zone C2 shows clearly higher values than zones C1 and C3 and lower values than zone C4. All this points to an influx of organic matter from the landfill which may result in an enhanced biological activity in zone C2 and C4 when compared with zones C1 and C3.

Using a possible redox zonation as a characteristic for the leachate is not very easy in this situation. As was discussed before, the pristine aquifer has an anaerobic iron/sulphate reducing status, all samples from the pristine aquifer contain sulphate above the detection limit and in zones C2, C3 and C4 some samples are below the detection limit. This leads to the conclusion that sulphate reduction does occur but that it is very heterogeneously distributed. There is some evidence for iron reduction in zone C2 and C3 because the Fe(II) concentration is increased compared with the pristine aquifer, although the standard deviation is high. The latest results (measurements from October 1997) clearly show that zone C4 and directly below zone C5 is in a methanogenic phase. However, the presence of some methane in the pristine aquifer also provides evidence of (at least local) methanogenisis.

The ASOCs do not give a very good picture of the leachate plume because the concentrations are hardly increased. Along the flow direction from the landfill (zone C4) via the aquifer below the landfill (zone C2) towards the downstream aquifer water (zone C3), the BTEX compounds and in general the chlorinated alkanes show a decrease in average concentration and a decrease in percentage exceeding the detection limit. This could be an indication that some attenuating processes are active (dilution, sorption and degradation).

Summarizing we can state that there is a clear evidence for migration of leachate but the picture is not as clear as observed at other landfills [(landfill Vejen) Lyngkilde and Christensen, 1992a and 1992b; (landfill Grindsted) Bjerg et al., 1995].

3.6 **Density flow**

In order to obtain the geological overview, vertical geo-electrical souchings have been carried out. One measurement that deviated from others was vertical electrical sounding (VES25), [IWACO, 1988a]. This measurement shows a very low electrical resistance to a depth of 30 m with a value of about 8 Ω m. Normal values for the Pleistocene sands lie between 20 and 30 Ω m. Reason for these low values appears to be the high conductivity of the groundwater which was also confirmed by measurements in the filters of COB14-2 and COB14-1 (about 260 mS/m). This could be evidence of percolation from the landfill, the depth however is difficult to assess using this VES probing.

There are some strong indications for local density driven flow. Interpretation of the monitoring well data revealed that the lowest screens of monitoring wells 3 and 4 at respectively 50.5 and 49 m depth below the surface, have significantly higher chloride concentrations than the other screens being part of the monitoring line. Between November 1995 and May 1997 the wells were sampled three times. The chloride concentrations for the two screens varied between 300 and 500 mg/l during the three monitoring rounds performed. The other observation screens never showed chloride concentrations exceeding 190 mg/l (mean: 125 ± 34 mg/l).

Table 2 (see appendix B) and the figures in appendix D show results from all the filters of monitoring wells 03 and 04 and the multi groundwater sampling probe. The two lowest screens of well 03 and 05 show differences in water quality with respect to the other screens for approximate values of: Ec (3,100 vs. 1,300 μS/cm), alkalinity (22 vs. 8.25 mmol/l), sulphate (445 vs. 138 mg/l), methane (425 vs. 54 μg/l), TOC (33 | 14 mg/l), and CO_2 (405 vs. 82 mg/l). Concentrations of other redox parameters (sulphide, manganese, Fe(II)) were similar to the levels measured in the other screens.

Other indications that this water is in fact leachate from the landfill and has not an other source like relict sea water are:

1. the low concentrations of xylenes (4 hits < 0.4 μg/l) and 1,1-dichloroethane (1 hit) found;
2. the absence of high chloride concentrations in the other 3 lowest screens of the monitoring wells.

Inspection of the analysis on C6 - C8/C8 - C10/C10 - C12 fractions performed in November 1995 shown in figure 8 (see appendix A) presents another remarkable difference with the other screens. The fraction of the C6 - C8 was about 50 %, while the C8 - C10 and the C10 - C12 fraction were about 25 %. The other screens gave completely different results: the heavier fractions were dominant over the lighter fractions. These data suggest that degradation is taking place, in the landfill or inside this local density plume or both, explaining the high CO_2, HCO_3 and methane concentrations. Possible degradation is likely caused by fermentation and methanogenesis.

Proof of sulphate-reduction at these screens can not be given because of the high sulphate concentrations present and the sulphide concentrations below the detection limit. However, this does not rule out the presence of sulphate-reduction, since higher sulphate concentrations are observed in the landfill, and sulphide is likely to precipitate with Fe(II) to pyrite in this redox environment.

3.7 Conclusions and summary on the hydrochemistry and redox environment at the location

The leachate and the aquifer are both anaerobic and no nitrate is present. Heron [1994] states that natural biodegradation is limited when the electron acceptors oxygen and nitrate are absent. At the Vejen and Grindsted landfills the solid ferri(oxy)hydroxides appeared to be of importance as an electron acceptor in the respiration processes which break down the organic compounds including ASOCs in the leachate. The fieldwork that will carried out in the near future aims to give information on the presence of these minerals.

Observed Fe(II) concentrations are not really high which can have several causes:

- microbial catalysed Fe(III)-reduction is of limited importance;
- produced Fe(II) is precipitated along with sulfide as FeS, pyrite (FeS_2) and possibly siderite, lowering Fe(II) concentrations.

The data obtained until present do not provide clear evidence. Fe(II) concentrations are higher in the 'plume' than upstream indicating that active Fe(III)-reduction is taking place, thus supporting the first option. The landfill can be a source of Fe(II) due to reduction of Fe(III) present in the landfill. The Fe(II) dissolves and can then migrate with the leachate. This explanation is supported by the observation that no manganese (II) is measured upstream (probably because of no source), while this compound is measured in 68 % of the cases above the detection limit in the 'plume'. The Mn concentrations in the plume are similar to the lower end concentrations in the landfill. Sulphate concentrations upstream are high but sulphate is not used substantially as an electron-acceptor.

The TOC concentrations (peak values: 33 - 80 mg/, normally about 15 mg/l) are more or less equal to the Non Volatile Organic Matter (NVOC) concentrations. The TOC-values are somewhat lower than the NVOC (Non Volatile Organic Matter) concentrations at the Vejen landfill in Denmark (NVOC 15 - 130 mg/l).

Besides iron and sulphate reduction it is also possible that fermentation and methanogenesis could be important because the landfill leachate consists of a highly complex mixture of partly reduced and partly oxidised organic matter. Part of the CO_2 produced by biological processes is changed into bicarbonate at the neutral pH of 7. Thus the generally increased alkalinity in the plume is for the largest part an indirect product biological processes, and can have its source in the landfill or the aquifer itself. A minor part can be produced by calcite dissolution, which can occur when CO_2 dissolves calcite or by processes such as: nitrate-reduction and sulphate-reduction in the landfill or in the plume.

Therefore, we conclude that at the Coupépolder landfill attenuation of the landfill leachate does occur. It is a process of attenuation due to oxidation of the leachate by iron and sulphate reduction in the aquifer. However it can also be an attenuation due to an auto-oxidation of the leachate (i.e. fermentation).

CHAPTER 4

TOWARDS A CONCEPTUAL MODEL OF THE COUPÉPOLDER LANDFILL

4.1 Water balance of the landfill: estimating the downward leachate flux into the aquifer

4.1.1 *Water balance former Coupépolder landfill in 1988*

In 1988 a water balance was made for the former Coupépolder landfill. This section presents a short summary. The reader must realise that in 1988 many of the environmental control measures were not yet implemented. The slopes of the landfill were not sealed, the subsurface drainage system was not yet installed and there was no sheet pile wall between the landfill and the 'Kromme Aar'.

Instead there was an open drainage ditch around the landfill with a drainage base of -1.9 m NAP. The 1988 water balance is outlined in figure 7 (see appendix A) [IWACO, 1988b] and is summarized as follows:

Flux in

Effective infiltration amounted to 81,400 m^3/yr (370 mm · 22 ha).

Flux out

Based on measured electrical conductivity values, no significant flow from landfill to the boundary drain along the 'Heemgebied' (Ec = 1,000 μS/cm) occurred. The hypothesis is that a vertical flow to the aquifer occurred due to the more permeable sandy deposits in this area.

Based on the electrical conductivity in de other parts of the boundary drain (Ec = 2,500 μS/cm) it was estimated that 50 % of the water in the drain had the landfill (Ec = 4,000), and 50 % of the water had the Aar kanaal (Ec = 1,000) as their origins. Therefore this drain with a total drainage rate of 85,000 m^3/yr is estimated to drain the landfill with a drainage rate of 42,500 m^3/yr.

Based on electrical conductivity values, the flow from the landfill to the drain at the north between the landfill and the river Kromme Aar was insignificant. Rather, the flow was directly towards the river Kromme Aar.

This amount has been estimated in the first place by assuming that the flux along the length of this part of the drain is similar to the other parts of the drain but proportional to the length (15/40 · 42,500). This amounted to 16,000 m^3/yr. But because the head gradient between the groundwater in the landfill and the river was less (-0.60 m NAP) than the gradient between landfill and ring drain (-1.60 m NAP), the total amount was reduced and estimated to be 8,000 m^3/yr.

Flux towards aquifer

Using a mass-balance approach, all remaining water ought to flow towards the aquifer. The flow is calculated to be:

$$81{,}400 - (42{,}500 + 8{,}000) = 30{,}900 \ m^3/yr$$

As this amount comes from a surface area of 22 ha the resulting flux is 140 mm/yr which equals 0.38 mm/day.

In the solute transport calculations (STIWACO) this flux was separated into a flux through the Holocene sequence and a flux through the sandy deposits in the north. The assumption was made that the flux through the northern sandy deposits was 10 times higher than the flux through the Holocene clay layer. Combining this assumption with the lengths of the STIWACO transects (Holocene transect = 200 m; Gullies transect = 150 m; see table 2 in appendix B) allows us to estimate the size of the flux through the gully deposits:

$$200 \cdot 0.1X + 150X = 350 \cdot 0.38 \rightarrow X = 0.78 \text{ mm/day}$$

4.1.2 *Improving the water balance for the present project*

As can be seen in paragraph 2.2.4 a number of environmental measures has been carried out. These measures have a considerable impact on the water balance of the landfill and as such, the exercise carried out in 1988 must be repeated, but now for the new situation.

The groundwater level inside the landfill body varies between -1.8 and + 0.90 m NAP. Part of the phreatic leachate in the landfill body flows to the sub-surface drain surrounding the landfill, the rest flows downward via the gully deposits to the aquifer.

The Heem-area in the western part of the landfill has a water level of -1.90 m NAP, so water from the river Kromme Aar flows into the Heemgebied. The same amount of water is pumped out of this area back into the river Kromme Aar.

The discharge of the subsurface drain has been continuously recorded for the 3 drainage sections since early 1993. Water quality data of leachate in the drainage system has also been measured since 1993. Six times a year for major components and 3 times a year a very extensive analysis on organic contaminants is performed.

The concentration of leachate in the drain needs to be corrected for:

- Dilution by seepage from the Aar Canal.
- Dilution by seepage water of unclear origin. While constructing the drainage system unclear seepage which discharged to the drain (a few m^3/hour!) was found. This seepage probably still occurs.
- Dilution from some drains from the golf course that discharge to the closed drain (point 2 and 3: pers. comm. P. Miltenburg, PROMECO).
- Run-off from the slopes and the road alongside the landfill flows to the open drainage ditch which surrounds the landfill. Thus the surface area which infiltrates must be corrected for the surface area of the sealed slopes.

The water balance of the landfill can be refined using the following aspects:

- The evaporation of the grass growing on the golf course can be well estimated.
- Water used for irrigation of the grass, must be included in the inflow term, and should be estimated.
- The outflow of leachate towards the sides of the landfill can be more precisily assessed because the discharge of the closed drain system is accurately measured. The measured yearly average drainage value for 1993 to 1997 is 70,966 m^3/yr.

Although the barrier between the closed ring drain and the river Kromme Aar excludes dilution of the leachate in this part of the drain, the other parts of the drain are still diluted by water from the Aar canal, resulting in difficulties in estimating the contributions of the leachate and the Aar canal water in the drain. Using a similar approach as in 1988 based on a comparison of Ec-values could be a starting point.

A correction to the landfill area receiving precipitation must be made because the slope of the landfill has been made impermeable, thus precipitation falling on the slopes is discharged to the open drain which runs parallel to the closed drain. This correction can be made by decreasing the area receiving precipitation (22 ha) with the perimeter of the landfill multiplied by the width of the impermeable slope.

As mentioned before some unexplained seepage areas (a few m^3/hour) were encountered that discharges to the drain. It is important to know where the water in these seepage areas is coming from (probably the Aar canal). This will be further studied in phase 3 of the project.

4.2 **Water flow in the aquifer**

The hydraulic head in the aquifer ranges from -3.3 m NAP below the southern part of the landfill to -3.9 m below the northern part. As a result we see a difference in hydraulic head between the phreatic water in the landfill and the aquifer of about -3.6 m and as a result we expect a vertical flow. As was mentioned above, this flow occurs mostly in the gully deposits.

The water flow in the aquifer is in northern direction, with an average hydraulic gradient of 1 : 1,000 m/m. The water level in the polders to the north of the Coupépolder is kept at -5 to -6 m NAP. As a result water from the aquifer seeps in to these polders. There are no ground-water extractions in the neighbourhood of the landfill which distort the flow pattern.

The hydraulic head in the deeper (second) aquifer is -4 m NAP. The small difference between the first and second aquifer, combined with the very low permeability of the sediments of the formation of Kedichem makes the water flow from the first aquifer to the second, negligible.

4.3 **Solute transport**

Groundwater flow and solute transport models of the landfill
Since 1988 three groundwater or solute transport models have applied by IWACO to the landfill area:

- The first one was a 2D solute transport model (STIWACO), which was made for evaluating the migration of three key-parameters: chloride, zinc, and benzene [IWACO, 1988b].
- In order to assess the optimal arrangement of the monitoring network the models MOC (vertical transport) and PLUIM (horizontal transport) were integrated and the results were linked to MODISCO (an ARC/INFO based model), to calculate the interception probability of point emissions of mobile chemicals (benzene) for several monitoring well arrangements [IWACO, 1992-2].
- The third model (TRIWACO) was applied to find the optimal control variant for mastering the migration of pollutants. These control variants varied from 'pump and treat' systems, to partial containment (impermeable cover layers, vertical barriers, etc.), forced infiltration and immobilisation [IWACO, 1992b]. This model is the most sophisticated groundwater transport model available for the landfill area, and will be used as a starting point for the development of the solute transport model for the NOBIS-project.

The values of the parameters adopted in these models are presented in table 3 (see appendix B).

4.4 Simple calculations on water and solute transport

In order to obtain a rough idea of the water and solute transport rates in the different layers, we can apply some simple calculations.

These calculations are based on information on the following parameters and equations:

kD	(m^2 d^{-1})	transmissivity ($kD = K\ L$);
L	(m)	thickness of the aquifer;
Δx	(m)	distance over which the gradient in hydraulic head is calculated (flow distance);
K	(m d^{-1})	hydraulic conductivity;
c	(d)	vertical flow resistance ($c = \Delta x/K$);
v	(m d^{-1})	apparent groundwater velocity or volume flux density ($v = K\ dH/dx$, for vertical flow: $v = \Delta H/c$);
v_e	(m d^{-1})	effective groundwater velocity ($v_e = v/n$);
n	(-)	porosity;
i	(m/m)	hydraulic gradient.

Applying the above equations we can calculate a residence time for a certain soil layer:

T	(d)	residence time in a layer ($T = \Delta x/v_e = (\Delta x\ n)/(K\ \Delta H/\Delta x) = \Delta x\ c\ n/\Delta H$).

Transport through the gully-deposits
The flow velocity and the residence time through the sandy gully-deposits can be calculated with the following equations and parameter estimations (see also table 3 in appendix B):

n	0.3;
ΔH	3.6 m;
c	3,000 to 3,500 days;
L, Δx	the thickness of the gully deposits ranges from 10 to 17 m.

As a result the residence time in the gully deposits ranges between 2,500 and 5,000 days (6.8 to 13.7 years). The water fluxes range between $1.0 \cdot 10^{-3}$ and $1.2 \cdot 10^{-3}$ m/day (365 and 438 mm/yr).

The residence time in the Holocene cover layer can be calculated using the following parameter ranges:

n	0.3;
ΔH	3.6 m;
c	4,000 to 30,000 days;
Δx	8 - 10 m.

As a result the residence time in the Holocene cover layer ranges between 2,600 and 8,300 days (7.3 and 68.5 yr). The water flux through the Holocene cover layer ranges between 44 and 328 mm/yr.

Flow velocity in aquifer
The effective groundwater velocity in the aquifer is estimated using the following parameters:

L	32 - 40 m;
kD	1,750 - 2,000 m^2/d;
i	1 : 2,000 - 1 : 800;
n	0.3.

Combining these parameters with the equations given at the beginning of paragraph 4.4 results in an effective groundwater velocity in the aquifer that ranges between 26 and 95 m/yr.

Start time of plume migration
This parameter is very important when we try to estimate the current size of the plume originating from the landfill. However, it is very difficult to estimate this parameter as it is not exactly known what was dumped in the landfill and when it was dumped. We do know that landfilling started in 1959 and that household refuse was dumped since the beginning. Dumping of toxic compounds was forbidden, but there are reports of illegal dumping (possibly of toxic compounds). In 1973 the landfill was extended to the north east (i.e. to the gully deposits). Therefore we can assume a starting of leaching of organic matter from the landfill in the holocene clay layer around 1959 and the starting of leaching through the gully deposits in 1973.

In the STIWACO model the start time of leaching was set at 1973. Assuming a residence time in the gully-deposits of ten years combined with the following start times for the plume migration resulted in the following distances (assuming an effective groundwater velocity of 31 m/yr):

- 1973 = (24 - 10) · 31 = 430 meters in 1997 (10 years in cover layer);
- 1979 = (18 - 10) · 31 = 250 meters in 1997;
- 1985 = (12 - 10) · 31 = 60 meters in 1997.

As demonstrated there are large uncertainties in all parameters we used to estimate the plume migration. Especially the uncertainties in the start time of plume migration, the residence time in the Holocene cover layer and the gully deposits, and the flow velocity in the aquifer are important. In addition it is very well possible that the water flux and hydraulic gradient in and around the landfill have changed due to the landfilling. The migration in the aquifer is relatively very fast (26 - 95 m/year). So minor differences in the start time and the *c*-values result in large differences in the position of the plume front.

The plume is also subjected to bio geochemical processes which tend to retard the migration of the plume. In the above presented calculations we considered the plume to move as fast as the water does so it can be considered as a worst case approach.

Thickness plume
The thickness of the plume can be estimated if we assume that no mixing occurs between the water originally flowing in the aquifer and water flowing in to the aquifer from the landfill. The relative thickness of the plume is then equal to the proportion of the flux contributed by the landfill to the total flux in the landfill.

Contribution from landfill to aquifer: $F_1 = \mathit{flux} \cdot \mathit{length\ transect} = 0.133\ \mathrm{m^2/day}$.
Contribution of flux through aquifer: $F_2 = kD \cdot I = 0.9 - 2.25\ \mathrm{m^2/day}$.
Thickness plume: $D_{\mathrm{plume}}/D_{\mathrm{aquifer}} = F_1/(F_1 + F_2) \rightarrow D_{\mathrm{plume}} = 1.95 - 4.5$ m.

Thus, the plume will be very thin.

CHAPTER 5

MICROBIOLOGY

5.1 Introduction: microbiological processes and the degradation of xenobiotics (ASOCs)

5.1.1 *Microbially mediated redox processes*

Most redox processes in the soil are biologically mediated. These biological processes result in the development of a sequence in redox zones such as observed underneath and downstream two Danish landfills [CUR/NOBIS, 1998]. Generally, the order of the redox zones is from redox reactions yielding a low amount of energy to redox reactions yielding a high amount of energy. We expect that the redox zonation of the Coupépolder landfill is partially similar to what has been found at other landfills:

- in and underneath the landfill a methanogenic zone;
- further down stream an iron-reducing zone;
- possibly between these zones a small sulphate reducing zone which might be detected with some luck by drilling.

Results so far indicate that leachate upstream the landfill is already anaerobic and very likely iron-reducing or even sulphate reducing, thus denitrifying and aerobic zones are not present. Because the same hydrogeologic situation continues downstream of the landfill denitrifying and aerobic zones are not expected downstream either.

5.1.2 *Degradation of xenobiotics*

As mentioned before low concentrations of xenobiotics have been encountered underneath the landfill. Downstream no significant elevations in concentrations have been found so far. The presence of xenobiotics underneath the landfill may have led to the establishment of a xenobiotic-degrading population.

We hope to measure the biodegradation potential at the methanogenic zone as well as to relate this potential to the microbial population composition. Sediment further downstream may not have had prior contact with xenobiotics, and sediment upstream certainly has not. There, biodegradation potential for xenobiotics could be absent. Presence of biodegradation potential indicates the natural capacity for xenobiotic degradation.

Incubation of sediment spiked with xenobiotics is expected to especially stimulate the xenobiotic-degrading micro-organisms, which can be identified by detecting DNA/RNA profiles using nucleic acid based analysis in combination with comparison to DNA/RNA profiles from unspiked samples.

5.2 Microbial methods: developments and improvements

So far, most microbiological research effort in this project has been put in the application of BIOLOG microtiter plates (see [CUR/NOBIS, 1998] for explanation). The main reason for this, is that the use of BIOLOG plates requires metabolic active bacteria, thus good methods should be available immediately at the start of the experiments. In contrast to DNA analysis it is not possible to freeze samples for BIOLOG analysis later on because freezing might kill or inactivate micro-organisms.

Methods for analysing the metabolic capacities/diversity of samples were developed for the regular BIOLOG plates, using the gram-negative micro-organisms specific plates (BIOLOG GN).

Also a start has been made with the development of a biodegradation specific plate, using xenobiotics as the carbon source.

5.2.1 *Metabolic profiles using the general BIOLOG GN microtiter plates*

Most experiments were performed using material from what we expected to be the so-called 'black layer' (see chapter 1 for introduction and chapters 2 and 6 for more detail). In addition some samples from the layers above and below the black layer were used, as well as oligotrophic artificial medium (OAM medium) [Ludvigsen et al., 1996] 1 : 100 inoculated with sample and incubated anaerobically at 10 ^oC.

For inoculation in BIOLOG plates samples were suspended in anaerobic suspension medium (10 mM $NaHCO_3$, 0.4 % NaCl, 0.015 % sodium thioglycolate, 0.00015 % methylene green, 0.01 % phytagel), prepared according to BIOLOG instructions. Suspensions and microplate inoculations were performed in an anaerobic glove box (N_2 atmosphere). Microplates were incubated in anaerobic jars and usually incubated at 10 ^oC. Color changes were followed in time by transferring the jars to an anaerobic glove box, removing the plates from the jar and noting which wells had turned purple (indicative of tetrazolium dye reduction).

Similarities between two microplates were calculated by using the simple matching method (number of wells which either react positive or negative in both plates divided by the total number of substrate containing wells (95)).

Reproducibility

Reproducibility was checked by making two independent suspensions of the black layer (1 g sample in 100 ml of suspension medium) on the same day and inoculating this suspension into BIOLOG GN plates. Color reactions were checked after incubating for 3, 7, 10, 14, 21 and 28 days. Reproducibility was very high, the similarity based on simple matching was 93 % on average. Only measurement on the 10th day had a lower similarity (87 %). In total 70 on the one and 74 wells on the other plate had reacted positive after 28 days. After 3, 7, 10, 14 and 21 days respectively, 38, 68, 78, 85 and 93 % of the final number of positive wells (thus on day 28) had reacted.

Reproducibility was also checked by preparing and inoculating suspensions from the same soil sample on different days. Development of metabolic profiles were quite different in time. The numbers of positive wells in three independent experiments after incubating for 21 days were 57, 65 - 66 (the duplo experiment (see above)) and 38. Similarities in metabolic profiles between experiment 1 and 3 was 72 % and between experiment 2 and 3 65 %. Samples were stored at 4 ^oC (freezing is thought to damage cells). From literature we learned that changes in microbial populations (checked by culture methods and phospholipid fatty acid analysis) are common during storage of subsurface samples. This indicates that microbial changes occur during sample storage and therefore BIOLOG analysis as well as microcosms experiments should be performed as soon as possible after sampling.

Samples subcultivated in OAM medium (in which 1 g of sample was added to 100 ml medium, thus sample 1 : 100 diluted) before BIOLOG analysis (where the OAM medium was diluted 1 : 10, thus the orginal sample 1 : 1,000 diluted) showed far less positive wells than samples directly inoculated into BIOLOG (in a sample (g) to medium (ml) ratio of 1 : 100 or 1 : 1,000) plates, despite that final inoculation ratios are similar. This is indicative of the selectivity (and unsuitability) of culturing methods. Similarities were 75 % for the 'black layer' and 62 % for the layer below the black layer.

Effect of temperature

To select an appropriate temperature for incubation, plates were incubated at 10 °C (groundwater temperature), room temperature and 37 °C. Fastest reactions occurred at 10 °C, 16 positive wells were noted after incubating for 4 days, 42 after 7 days and 57 after 31 days. Reactions still occurred between 52 days and 66 days of incubation.

Development at room temperature was much slower, after 4 days 15 wells had reacted, and only 2 more wells showed a reaction between 4 and 7 days, after 31 days 64 wells had reacted. After 31 days the profiles at 10 °C and room temperature were for 77 % similar, patterns after 4 and 7 days differed very much from each other.Only two wells coloured at 37 °C, while the plate dried out. Based on these results, 10 °C was chosen as the most suitable temperature for BIOLOG plate incubations.

Effect of inoculum size

From the black layer 1 : 100, 1 : 1,000 and 1 : 10,000 dilutions were inoculated in BIOLOG plates. Upon dilution from 1 : 100 to 1 : 1,000 only a few wells did not react any more in the 1 : 1,000 dilution, while dilution to 1 : 10,000 resulted in a slightly larger decrease in positive wells. Reactions for the 1 : 100 dilution were faster than in the more diluted samples. For the 1 : 1,000 3 wells reacted positive which did not react in the 1 : 100 dilution. The 1 : 1,000 and 1 : 10,000 showed 85 % and 88 % similarity to the 28 day 1 : 100 dilution plate.

Since the negative control (well A1, containing no substrate) remained negative during incubation, a 1 : 100 dilution is most suitable. However, the minimum dilution which can be used depends on the sample. When a 1 : 100 dilution of the layer above the black layer was plated, all wells including the negative control, turned purple. This could be due to the presence of substrates or reducing agents derived from the sediment in the 1 : 100 dilution. Using a dilution 1 : 1,000 solved this problem. By plating serial diluted samples, a MPN-BIOLOG (Most Probable Number-BIOLOG) can be performed to indicate which dilution is suitable for a certain substrate.

Effect of electron acceptors additions

The effect of aerobic conditions and the addition of electron-acceptors (5 mM KNO_3 or 1 mM Fe(III)Cl, or leaving out 10 mM $NaHCO_3$) was tested. Under aerobic conditions far less wells (34) reacted compared to the anaerobic plate (57). With the exception of three wells, all the wells that reacted under aerobic conditions also reacted under anaerobic conditions. Iron addition resulted in precipitation and no reactions in the plate after 3 weeks. Addition of nitrate or leaving out carbonate gave a profile comparable to a normally prepared plate (similarities: 91 respectively 93 %), with a few wells not responding (respectively 9 and 5 out of 38 in the normal plate) and 4 extra in case of the carbonate omission.

Thus the addition of electron-acceptors seems not to be advantageous and normal suspension medium should be used.

Effect of reducing agent

BIOLOG recommends the use of 150 mg sodium thioglycolate per litre as reducing agent (oxygen scavenger) in the anaerobic suspension medium. However sodium thioglycolate contains carbon and thus is it a potential substrate, furthermore it is unnatural. In anaerobic medium also often sodium sulphide is used as reducing agent. The use of sodium sulphide has been tested in microplates. Results showed that too high concentrations of sodium sulphide resulted in direct tetrozolium dye reduction by the sulphide. At 40 ppm an anaerobic medium was obtained and no tetrazolium reduction by the sulphide itself was observed. BIOLOG results were similar to suspension medium with sodium thioglycolate.

Specificity for microbial activities

In principle the reactions in the plates might not be due to microbial activities but to enzymatic activities or chemical activities. This was tested by filtering through a 0.2 μm filter which removes (most) micro-organisms and treatment with organic solvent which inactivates micro-organisms and enzymes, and therefore only chemical activities were measured. Since after 14 days no reactions in BIOLOG GN plates had occurred this indicates that reactions are indeed due to microbial activities.

Concluding remarks

BIOLOG analysis of microbial metabolic diversity can be performed accurately with anaerobic GN plates. Analysis should be performed as soon as possible after samples have been collected. Optimal conditions for preparation and incubation can be achieved by using the suspension medium as described by the BIOLOG company, but with 40 ppm sodium sulphide replacing the thioglycolate, and incubating anaerobically at 10 ^{o}C. Plates should be monitored in time; after 4, 7, 14 and 28 days.

A database can easily be made by using the BIOLOG software. This allows the comparison of newly obtained metabolic profiles to profiles already in the database. When profiles in the database have a relation to a certain biodegradation potential, a relation between profiles might indicate that this biodegradation potential is also present at the sampled location.

5.2.2 *Development of biodegradation specific microplates*

The general BIOLOG plate is suitable for measuring (changes in) general microbial metabolic potential, but does not yield information on the biodegradation potential. For measuring biodegradation potential, we have to use the BIOLOG MT microplate (microplate with redox chemistry without carbon sources added) to which we add carbon sources ourselves. Suitable carbon source are xenobiotics, (possible) intermediates of xenobiotic degradation and landfill specific carbon sources. During development, it is also important to assess the possible toxicity of a substrate [CUR/NOBIS, 1998].

To set up a biodegradation specific plate, in first instance the following substrates were tested: the xenobiotics; trichloroethylene, 1,2-dichloroethane, xylene, phenol, toluene, biphenylol, dimethylphenol, and possible intermediates and closely related substrates; gentisate, p-toluic acid, gallic acid, p-coumaric acid, caffeic acid, ferulic acid, 4-hydroxybenzoic acid, benzoic acid, proto-catechuate, syringic acid, salicyclic acid, vanillic acid and phloroglucinol.

Several attempts have been made so far to test these substrates. In the first attempt, per substrate a dilution range (100, 50, 25, 12, 6 and 3 ppm) was made in duplicate. The first range was inoculated with suspension medium inoculated with a 1 to 10 diluted sample from 4 week old OAM medium (100 ml) inoculated with a piece of black layer (1 g). The second range served as a positive control/toxicity test, it was inoculated with from the old OAM medium fresh OAM medium. This medium contained 250 ppm acetate and 250 ppm glucose. However even after 4 weeks no reactions were observed in the range which was meant to be a positive control/toxicity test. This was probably due to too low concentrations of substrates in the OAM medium. For BIOLOG plates a substrate concentration of 2 g/l is advised, but in principle 200 ppm will do.

The experiment was repeated with a duplicate substrate concentration range of 330, 80 and 0 ppm and inoculated with suspension medium in which material from the black layer was suspended. In the toxicity test suspension medium supplemented with 2 g/l glucose was used. This time colour/redox reactions were observed in the toxicity test for all 0 and 80 ppm concentrations, as well as most 330 ppm concentrations, after 7 days. For 2 substrates (biphenylol and salicylic acid) no positive results were observed after 25 days, while 3 substrates (phenol, dimethylphenol and phloroglucinol) resulted in inhibition of dye reduction, since a colour reaction at 330 ppm was only noted after 11 days.

Reaction with xenobiotics as sole carbon source were observed after 7 days for 330 ppm benzoic acid (as coenzyme A-linked form the central metabolite in aromatic compound degradation), after 11 days for phenol and after 14 days for gentisate and p-coumaric acid. These results are hopeful for the development of a biodegradation specific plate. A new plate with higher concentration of xenobiotics (2,000, 1,000, 500, 250 ppm) has been prepared and inoculated with a cell suspension of the black layer. As might be expected, the more xenobiotic added in the toxicity test, the slower the response. Only a few wells with 2,000 ppm reacted within 7 days and slightly more than halve had reacted after 14 days.

In wells with xenobiotic added as the sole source of carbon a different profile developed from the previously observed. This might be due to the fact that accidentally the sample had been exposed to air and higher temperature for a few days, and thus the microbial composition might have changed. The number of positive wells with xenobiotics as sole source of substrate was strongly dependent on its concentration. The lowest concentration (250 ppm) gave slightly more positive results (11 out of 16 after 14 days) than the 500 ppm (10 out of 16) and far more positive results than the 1,000 ppm (7 out of 16) and 2,000 ppm (5 out of 16).

Xenobiotics that reacted positive at the higher concentrations were also utilised at the lower concentrations. Only for syringic acid a positive reaction was observed at 1,000 ppm but not at 500 ppm and 250 ppm. Thus, in general a concentration of 250 ppm is suitable for use in biodegradation plates.

CHAPTER 6

CHARACTERIZATION OF THE TRANSITION ZONE BETWEEN THE LANDFILL AND THE UNDERLYING SEDIMENT: 'THE BLACK LAYER'

6.1 Motive and sampling

In a previous investigation, a report was made of a 'black layer' between the landfill and the underlying sediments at COB14 (J. Groen, personal communication). The hypothesis is that this layer has important properties that may be important for the attenuation of the landfill leachate. In order to test this hypothesis a sediment sample was taken from the interface between the landfill and the sediment where the landfill is situated on top the gully deposits. The sample had a length of 1.44 m and a diameter of 3 cm. It was thought that this 'black layer' may have properties such as:

- a hydraulic barrier;
- an active layer were much breakdown of contaminants/organic compounds takes place.

The sample was taken with a Begemann core. The Begemann coring was successful, but the work water (tap water) involved may have influenced the pore water in the sample by diffusive exchange through the 'stocking'. In addition microbiological contamination may have occurred.

6.2 Geochemical characterization

6.2.1 *Sedimentological description of the sediment sample*

The sample can be characterized as a light clayey soil, being more sandy towards the bottom (see table 1 in appendix B). This sample differs from the sample observed at COB14 which was sandy. In fact, COB14 is the only location where it has been observed that the landfill is directly positioned upon sandy material. At all other locations including this one, the gully-deposits are clayey at the interface with the landfill. The sample has a high lime content (15.2 - 17.7 %) and a C/N ratio ranging between 15 and 16.5.

The sample has a heterogeneous appearance. Over the entire length several black layers were observed with a thickness of a few centimetres. These layers consisted of humic material and even plant leaves were observed. At least at one location black mineral precipitates were observed (described in the section geochemistry). The colour of the sample ranged from 2.5 Y 2-6/0 (Munsell color chart).

6.2.2 *Hydrochemistry*

The results of the hydrochemical analysis of the sample are presented in table 4 (see appendix B). The sample is clearly influenced by the landfill leachate. The Ec (2,660) and ammonium concentrations (165 - 222 mg/l) are somewhat below average for the landfill leachate. Fe^{2+} and Mn^{2+} concentrations are very low with respect to the concentrations measured in leachate in 1988 (see table 1 in appendix B). Sulphate is still present in the pore water (4.6 - 19.9 mg/l). Most remarkable are the nitrate concentrations of 3.8 - 7.7 mg/l which were not expected. If these data are valid the pore water is not really methanogenic, but several redox reactions may occur simultaneously. However, the nitrate and sulphate concentrations in combination with the low concentrations of manganese(II) and iron(II) may also be due to possible oxidation of the samples during sampling and analysis.

6.3 **Geochemistry**

6.3.1 *Electron microscopy*

Two samples from the black layers in the core section were selected for analysis in an analytical transmission electron microscope (AEM). The samples were air-dried at room temperature and embedded in epoxy and subsequently thin-sectioned using a procedure developed specifically for analysis of individual particles and fine grained geochemical specimens [Bradley et al., 1986]. The sections (< 100 nm thick) were transferred to thin carbon (< 20 nm thick) substrates supported on a Cu grid. The grids were examined with a 200 KeV AEM equipped with a solid state X-ray detector. Structural and crystallographic properties of individual grains were examined using high resolution imaging and electron diffraction. Compositions were determined using energy despersive spectrometry.

6.3.2 *Results*

As can be seen in the electron micrographs in appendix E abundant quartz grains, clay particles, and discrete iron sulphide precipitates are observed. The wide spread distribution of fine grained iron sulphide particles explains the black colour of the samples. The clay minerals have a smectite-like and an illite-like composition and exhibit 20 Å and 10 Å fringes respectively. The heavy metal concentration of the individual clay particles are generally below the detection limit (< 5 % (m/m)). Some clay particles contain traces of Cr and Ti. SAED (Surface Area Electron Diffraction) reveals that the sulphide recipitates consist of both amorphous and crystallised structures. The approximate Fe/S stoichiometry ranges from 0.3 tot 1.0. The d-spacing of the crystallised structures are not a good match for pyrite (FeS_2), but coincide with those for greigite (Fe_3S_4) and mackinawite (FeS). Most iron sulphide precipitates contain Zn as a major compound. Other heavy metals have not been detected in these structures.

The micro-analytical results clearly reveal that the prevailing conditions just beneath the landfill (c.q. in the landfill-soil interface) are sulphidic. In a sulphidic environment the distribution of most heavy metals like Cu, Ni, Pb, and Zn is controlled primarily by the formation of/co-precipitation with highly insoluble sulphides. Hence, sulphide-precipitation is an important mechanism by which landfill leachate is attenuated from these metals by this interface. Since heavy metals are virtually absent in this layer, with the exception of Zn, the results strongly suggest that the actual emission of heavy metals from the landfill is very limited.

6.4 **Microbial characterization of the black layer and the surrounding layers**

Metabolic profiles (obtained with BIOLOG GN plates) from the black layer and layers above and below it were very different from each other. Most positive wells were observed in the layer above the black layer (74 wells after 21 days compared to 65 and 53 for the black layer and layer below it, respectively). Similarities of the black layer with the layers above and below it were 73 and 72 % after 7 days and 75 % each after 21 days, respectively. Surprising was that several of the substrates (acetic acid, formic acid, butyric acid) which are formed during microbial degradation of organic waste in landfills were not used.

Degradation and toxicity of several xenobiotics and (closely related) degradation intermediates was tested at 330 - 500 ppm for the three layers. The idea was that the black layer contains the micro-organisms involved in xenobiotic biodegradation. Thus, less toxic effects and more degradation potential might be expected. However, results of 14 day old biodegradation plates do not support this. After 7 days no colour reaction was observed in the toxicity test for three out of 15 substrates (p-aminobenzoic acid, gentisate and benzoic acid), while for both the layer above and below only p-aminobenzoic acid was inhibitory. After 14 days toxicity tests with gentisate and benzoic acid turned positive for the black layer. Degradation was observed for TCE and benzoic acid in all three layers but also for coumaric acid in the black layer and layer above the black layer. Additionally, gentisate and phenol were used in the black layer, while caffeic acid and syringic acid were utilized only in the layer above the black layer. Redox reactions with 4-hydroxy benzoic acid and proto-catechuate were observed for the lower layer.

However, it should be noted that biodegradation plates were made 2 months after samples were taken and thus microbial composition might have changed (see above). More importantly, while preparing this report we found that the type of drilling used can cause contamination of the sample. Thus, the measurements are of limited value.

DNA has been isolated from the samples and can be amplified directly with eubacterial specific primers. Unfortunately the negative control also gave a positive result during PCR, this makes the interpretation of the results very difficult. This problem has to be solved first.

6.5 **Conclusions**

The sample investigated was probably not similar to the material found at COB14. No indications were found that this layer may have special characteristics formed in situ due to possible inflow of materials from the landfill, except from in situ precipitated minerals (FeS and ZnS).

The BIOLOG characterization showed that the layer above the 'black layer' had the most metabolic activitiy. Clear differences in the potential to degrade xenobiotics were not found. This could have been caused by the fact that the samples were 2 months old before the BIOLOG experiments were carried out.

CHAPTER 7

RESEARCH PROGRAM FOR THE NEXT PERIOD

7.1 **Hydrology and geochemistry**

7.1.1 *Hydrology*

The TRIWACO model from 1988 will be updated. The model will be converted to a Micro-Fem model. The water balance and the downward flux to the aquifer will be more precisely assessed. The closed drain will be introduced in the model (using a top system similar to a ditch). Migration through the gully-deposits can perhaps be modelled in more detail, and the overall the network can be refined. In order to be able to carry out this refinement additional data is required.

In order to estimate the outflow of leachate to the subsurface drain the quantity measured must be corrected for dilution with water from other sources than the landfill. In 1988, this correction was carried out using the electrical conductivity values of the contribution waters. Because the situation has changed considerably since 1988, these conductivity values have to be measured again.

The evaporation from the surface of the landfill can be estimated using the values known for grass cover. More important however is the estimation of the amount of water applied as irrigation. This information must be obtained from the manager of the golf course.

7.1.2 *Geochemistry*

Increasing the sample density along the profile which runs parallel to the groundwater flow direction in the aquifer and intersects MGWP 1 and observation well 03 will extend the hydro-chemical information. For the compilation of a cross section parallel to the groundwater flow additional samples are required. Samples from one or two locations beneath the landfill and samples beyond the observation wells in the direction of the road to the north of the downstream of the landfill have been taken in September and October 1997.

Geochemical parameters

Geochemical parameters of the aquifer will be determined on samples taken from four locations: upstream, below the landfill and at two locations downstream. The same parameters will be analysed as presented in table 4 (see appendix B). In addition information on the chemical and mineralogical composition (pyrite, ferrihydroxides, Oxidation capacity (OXC)) will be determined by chemical extraction techniques [IWACO, 1997].

Samples must also be taken from the leachate in the landfill. The OXC and reduction capacity RDC of these samples also has to be measured.

Modelling of solute- and reactive transport

The MICROFEM model will give insight on water flow that is more detailed. Interpretation of leachate contaminant concentrations may be improved by using the quality data of PROMECO. Different numerical and analytical models will be used to improve our knowledge of the processes occurring at the landfill. One of these processes is density flow. The migration of the leachate can be estimated with the simple models such as BIOSCREEN, CHEMPATH or SORWACO.

Hydrogeochemical processes may be modelled with PHREEQC along a central flow path to give some insight in these environments. However, the data seem too complex and heterogeneous to be fitted.

In general before attempting to model the processes a detailed analysis will be made on the data and parameter requirements of the numerical models so that the consequences of missing parameters or not very well parameterised values is well understood.

7.2 **Microbiology**

In October 1997, four drillings have been placed in and near the landfill (up- and downstream), both sediment and ground water have been collected for the laboratory micro-cosms as well as for direct microbial measurements on the material. Results will be combined with the results of the geochemical and hydrological experiments (see previous chapters).

7.2.1 *Measurements on drilling material*

Redox zones

Material from the drillings will be used directly for bioassays (measurement of methanogenesis, iron/manganese reduction and denitrification activities, using similar methodologies as Christensen, see [CUR/NOBIS, 1998]).These results combined with the results of the geo-chemical analysis this gives us information on the redox processes presently occurring at a specific locations in the landfill.

Microbial populations and activities

Nucleic acid analysis (16S rDNA amplification, followed by DGGE) and BIOLOG plate assays (using normal plates and if possible also a biodegradation specific plate) on microbial populations of both sediment and ground water will be performed. This gives among others an indication whether the composition and activities of microbial populations in groundwater are similar to those of sediment. If so, sampling groundwater (much easier than collecting sediment) could be sufficient to monitor microbial population composition and activities in the future.

Measurement of xenobiotic degradation in laboratory micro-cosms

Aim is to establish whether biodegradation potential is available at the position of a drilling as well as gathering an indication of biodegradation parameters for use in mathematical models. Furthermore the measured biodegradation will be related to (changes in) microbial populations (via nucleic acid analysis) and metabolic activities (measured in BIOLOG microplates) analysis performed prior (see above) and after the experiment. Per drilling, three cosms will be prepared in way resembling the method of Christensen:

- Active microcosm, not spiked with xenobiotics.
- Active microcosm, spiked with xenobiotics.
- Inactivated microcosm, spiked with xenobiotics. The micro-organisms will be killed be auto-claving the flasks at three consecutive days, after which the xenobiotics will be added.

Ratio sediment to groundwater will be 1 ml (about 2 g) wet sediment per 1ml groundwater, which is a more natural situation than that used by Christensen, where 1,300 ml groundwater was added per kg sediment. Cosm 1 will be prepared in 100 ml flasks, 2 en 3 in 500 ml flasks.

The cosms will be spiked so that the final concentration for each xenobiotic will be 100 μg/l. Based on previously encountered xenobiotics at the Coupépolder landfill (see chapter 5), the solution that will be used for spiking will consist of benzene, toluene, ethylbenzene, xylene, naphthalene, trichloroeth(yl)ene, trichloromethane and tetrachloorethane.

Cosms 2 and 3 will be sampled in time to measure degradation of xenobiotics via GC analysis of concentrations as well as TOC analysis. 11 ml groundwater samples will be taken after 0, 3, 7, 14, 21, 28, 35 and 42 days. To maintain a constant ratio sediment to groundwater an equal volume of fresh groundwater will be added after sampling. At the end of the experiment, or when xenobiotics are depleted earlier, sediment and/or groundwater of cosm 1 (unspiked) and cosm 3 (spiked) will be analysed for microbial populations (biodegradation specific and normal BIOLOG plate analysis, nucleir acid analysis). Differences in DGGE-profiles of PCR-amplified DNA will give an indication which micro-organisms (as band position in DGGE-gel) are involved in biodegradation.

7.2.2 *Flow through column*

A flow through column will likely provide a better simulation of the natural situation than laboratory or in situ cosms, due to the simulation of ground water flow. In the next period one experiment will be performed with as main goal to gain experience with this type of columns. During the experiment samples will be collected for GC-analysis of xenobiotic concentrations and results will be compared to the corresponding batch. At the end of the experiment sediment will be collected and divided in fractions. Ground water will be extracted from these fractions to measure the gradient in xenobiotic concentrations. Nucleic acid and BIOLOG analysis will also be performed on these fractions to establish whether there is heterogeneity in the column. Also underneath the landfill a gradient is likely to be present and different substrate concentrations might result in different microbial populations.

Set up will be as follows; material from below the landfill (expected to be methanogenic) will be used, a column with diameter 4.1 cm and 32 cm long will be filled with sediment (about 400 ml, assumed to contain 30 % water). Groundwater will be led through the column at about 12 ml/day (equal to 10 m/year groundwater flow), corresponding to a residence time of 10 days. Effluent will be collected. Groundwater will be spiked with the same compounds as for the cosms, also a conservative tracer will be added to measure the real residence time. The column probably has to be rinsed first with spiked groundwater to account for sorption.

7.3 **Multi-Layer Sampling Microcosms (MLSMs)**

7.3.1 *Introduction*

Initially it was the idea to make use of In Situ Microcosms (ISMs) in order to estimate biological attenuation potential and attenuation rates. The ISMs used by the group of Christensen in Denmark [Nielsen et al., 1996] are not very practical for the Coupépolder landfill because the aquifer in which these microcosms are to be installed is too deep. Because of this aspect and because the ISMs excludes all direct contact with the aquifer after being installed we thought it is better to do the experiments in flow through columns using aquifer sediment and aquifer water.

However, we still would like to do some experiments in situ as field experiments give us different insights than laboratory experiments. A recent and very promising development is the application of Multi-layer Sampling Microcosms (MLSMs) described in a recent review [Mandelbaum et al., 1997]. This development opens up a wide range of possibilities which are going to be explored in this project.

7.3.2 *Description and operation of the MLSMs*

The MLSMs is a dialysis cell that is lowered in a screen of a sampling well. Generally, a sequence of multiple criss-crossed dialysis cells is used. Flexible Viton® seals that fit flush to the inner diameter of the screened well divide the cells into groups. The dialysis cell is fitted with dialysis membranes (0.2 µm pore size) to confine the micro-organisms under study to the dialysis cell. When the dialysis cell filled with demineralized water is inserted in the groundwater, dissolved salts and contaminants diffuse through the membrane. After a certain period, the water in the dialysis cell will be in equilibrium with the ground water outside the cell.

The cells are retrieved after a certain period. As the retrieval time is very short, the effect of disturbance in the sampling well is negligible because the main transport process in the cell is diffusion controlled. In the laboratory the cells are opened and the water can be analysed.
Application of MLSMs is very flexible. The cells can be filled with sediment to look at properties of the sediment. It is also possible to fill the cells with a sorbing material to quantitatively sample the groundwater. Other modifications or adaptations could be using different membranes to sample the groundwater selectively for different compounds.

7.3.3 *Application in this project*

We intend to apply groups of MLSMs in sampling filters. Each group is fitted with a combination of different MLSMs, i.e. one filled with demineralised water and a conservative tracer, one filled with demineralised water and sediment and perhaps one or more fitted with different membranes.

Upon retrieval, after leaving the MLSMs in the field for a certain (and yet to be determined) period, the MLSMs will be taken to the laboratory and analysed. The idea is to combine geochemical measurements and microbiological experiments similar to the ones presented in the previous sections.

7.4 **Extension of the project with the Banisveld landfill**

The aquifer below the Coupépolder landfill is anaerobic. The oxidation capacity of the aquifer depends on the sources of Fe(III) and sulphate. In addition attenuation due fermentation in the landfill leachate can also be of importance.

Because the Coupépolder landfill is in a relatively complex setting (sandy aquifer below a holocene cover-layer with peat layer etc.), we propose to broaden the current project with the Banisveld landfill near Boxel in Noord-Brabant. The aquifers below the Banisveld landfill are less anaerobic and as such will have a larger oxidation capacity and the aquifer primarily consists of sandy materials.

The preliminary work at Banisveld has been carried out in the last couple of months. We propose to carry the research planned for phase 3 onwards for both Coupépolder and Banisveld in parallel. The attention at both landfills will be focussed on anaerobic degradation and fermentation.

REFERENCES

Bjerg, P.L., K. Rügge, J. Pedersen and T.H. Christensen, 1995.
Distribution etc.
Environ. Sci. Tech., 29 (5): 1387-1394, 1995.

Bradley, J.P. and D.E. Brownlee, 1986.
Science 231: 1542-1544, 1986.

Christensen, T.H., P. Kjeldsen, H.-J. Albrechtsen, P.H. Nielsen, P.L. Bjerg and P.E. Holm, 1994.
Attenuation of landfill leachate pollutants in aquifers.
Crit. Rev. Environ. Sci. Technol., 1994.

CUR/NOBIS, 1998.
The intrinsic capacity of aquifers to degrade pollution from (old) landfills - Phase 1.
CUR/NOBIS report 96-3-04, Gouda, September 1998.

Heron, G., 1994.
Redox buffering in landfill leachate contaminated aquifers.
PhD-thesis, 1994.

IWACO, 1988a.
Vervolgonderzoek Coupépolder Alphen aan den Rijn. Interimrapport Fase 1a, Tekst en Bijlagen.
IWACO, October 1988.

IWACO, 1988b.
Vervolgonderzoek Coupépolder Alphen aan den Rijn. Fase 1b, Deel 1: Risico-evaluatie.
IWACO, October 1988.

IWACO, 1988c.
Bodemonderzoek Coupépolder Alphen aan den Rijn.
IWACO, GEO-LOGIC-projectnummer 6616, May 1988.

IWACO, 1989.
Notitie beheersmaatregelen vuilstort Coupépolder.
IWACO, September 1989.

IWACO, 1991a.
Notitie: Beheersmaatregelen taluds Coupépolder Alphen aan den Rijn.
IWACO-projectnummer 1024850, June 1991.

IWACO, 1991b.
Opsporing en verwijdering van containers in de vuilstort Coupépolder te Alphen aan den Rijn.
IWACO, December 1991.

IWACO, 1992-1.
Rapportage fase 1: Beheersmaatregelen.
IWACO-projectnummer 1024850, June 1992.

IWACO, 1992-2.
Rapportage fase 2: Ontwerp monitoringssysteem.
IWACO-projectnummer 1024850, May 1992.

IWACO, 1992-3.
Rapportage fase 3: Nazorg: technische en organisatorische aspecten; ontwerp beslismodel.
IWACO-projectnummer 1024850, June 1992.

IWACO, 1992a.
Deelrapportage 1: Beheersmaatregelen voor taluds en oppervlaktewater.
IWACO-projectnummer 1024850, August 1992.

IWACO, 1992b.
Deelrapportage 2: Beheersmaatregelen voor het diepe grondwater.
IWACO-projectnummer 1024850, August 1992.

IWACO, 1992c.
Deelrapportage 3: Signaalwaarden.
IWACO-projectnummer 1024850, August 1992.

IWACO, 1992d.
Deelrapportage 4: Ontwerp monitoringssysteem en technische beslismodel.
IWACO-projectnummer 1024850, August 1992.

IWACO, 1992e.
Deelrapportage 5: Ontwerp beslismodel, organisatorische aspecten.
IWACO-projectnummer 1024850, August 1992.

IWACO, 1992f.
Samenvattende rapportage: Onderzoek monitoring en beheersmaatregelen stort Coupépolder Alphen aan den Rijn.
IWACO-projectnummer 1024850, August 1992.

IWACO, 1997.
Rapportage: Nazorgplan Coupépolder te Alphen aan den Rijn (ZH/020/0007).
IWACO-projectnummer 1052020, March 1997.

Ludvigsen, L., H.-J. Albrechtsen, G. Heron, P.L. Bjerg and T.H. Christensen, 1996.
Anaerobic microbial redox processes in a landfill leachate contaminated aquifer (Grindsted, Denmark.
J. Contaminant Hydrology, 1996.

Lyngkilde, J. and T.H. Christensen, 1992a.
Redox zones of a landfill leachate pollution plume (Vejen, Denmark).
J. of Contam. Hydrol., 10: 273-289, 1992.

Lyngkilde, J. and T.H. Christensen, 1992b.
Fate of organic compounds in the redox zones of a landfill leachate pollution plume (Vejen, Denmark).
J. of Contam. Hydrol., 10: 291-307, 1992.

Mandelbaum, R.T., D. Ronen and M.R. Shati, 1997.
In situ microcosms in aquifer bioremediation studies.
FEMS Microbiology Reviews, 1997.

Nielsen, P.H., T.H. Christensen, H.-J. Albrechtsen and R.W. Gilham, 1996.
Performance of the in situ microcosm technique for measuring the degradation of organic chemicals in aquifers.
Ground Water Monitoring and Remediation, 16: 130-140, 1996.

Other literature

Appelo, T. and D. Postma, 1993.
Geochemistry, Groundwater and Pollution.

Germani, M.S., J.P. Bradley and D.E. Brownlee, 1990.
Automated thin-film analyses of hydrated interplanetary dust particles in the analytical electron microscope.
Earth and Plantary Science Letters, 101: 162-179, 1990.

Kjeldsen, P., 1993.
Groundwater pollution source characterization of an old landfill.
Journal of Hydrology, 142: 349-371, 1993.

Locher, W.P. and H. Bakker, 1990.
Bodemkunde van Nederland, deel 1.

RGD, 1970.
Toelichting bij de geologische kaart van Nederland (1 : 50.000): blad Gorinchem Oost, kaartblad 38 O.
Auteur: Van Staalduinen, Rijksgelogische Dienst, Haarlem, 1970.

RGD, 1979.
Toelichting bij de geologische kaart van Nederland (1 : 600.000): blad Rotterdam West, kaartblad 37 W.
Auteur: Verbraeck, Rijksgelogische Dienst, Haarlem, 1979.

Stuyfzand, P.J., 1993.
Hydrochemistry and hydrology of the coastal dune area of the western Netherlands.

APPENDIX A

FIGURES

Fig. 1. Overview of the surroundings (topographic map).
Fig. 2. Enlargement of the figure 1, including reference standpipes 16 en 17.
Fig. 3. Overview of landfill, including all sampling points until now.
Fig. 4. Overview of measures taken in order to prevent spreading of the landfill leachate.
Fig. 5. Geological cross section of the landfill and the underlying aquifers. Location of zones C1 to C5.
Fig. 6. Radar plots of selected parameters showing impact of landfill (zone C4) on other zones.
Fig. 7. Summary of the water balance in 1988.
Fig. 8. Fractions (%) C6 - C8 (bottom), C8 - C10 (middle) and C10 - C12 (top).

Fig. 6. Radar plots of selected parameters showing impact of landfill (zone C4) on other zones.

Fig. 7. Summary of the water balance in 1988.

Fig. 8. Fractions (%) C6 - C8 (bottom), C8 - C10 (middle) and C10 - C12 (top).

APPENDIX B

TABLES

Table 1. Statistics of combined measurements in zones C1, C2, C3, C4 and C5.

parameter name	count of measurements					count < detection limit					average value				
	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5
1,1,1-trichloorethaan	9	17	74	15	7	9	15	68	5	6	0,50	0,59	0,54	0,96	0,53
1,1,2-trichloorethaan	8	9	61	1	4	8	9	61	1	4	0,50	0,50	0,50	0,50	0,50
1,1-dichloorethaan	9	17	74	15	7	9	17	72	15	7	1,17	1,38	0,87	2,00	1,57
1,2-dichloorethaan	9	17	74	15	7	9	17	74	14	7	0,50	0,50	0,51	0,50	0,50
ammonium als N	14	19	78	15	8	0	0	0	0	0	13,30	72,94	12,13	294,00	58,61
anorganisch koolstof (IC)	1		4			0		0			63,00		125,00		
arseen (hydride techniek)	3					3					2,00				
B.Z.V. (20 °C - 5 dagen)		2	1	1	2		2	1	0	1		5,00	5,00	9,00	8,00
barium (ICP)	3	2	1	1	2	3	0	0	0	0	50,00	535,00	90,00	470,00	1400,00
barium (ICP-USV)		1			1		0			0		1400,00			910,00
benzeen	14	20	101	18	10	14	15	100	2	3	0,20	0,48	0,20	11,75	2,34
bicarbonaat		1			1		0			0		3200,00			3200,00
BTEX (totaal)	7	7	81		2	6	6	74		1	1,03	1,00	1,03		3,35
C.Z.V.	8	5	44	2	4	0	0	0	0	0	44,38	158,20	44,55	1833,00	376,25
badmium (grafiet oven)	3					3					0,50				
cadmium (ICP-USV)	1					1					0,40				
calcium (ICP)	6	14	34	13	4	0	0	0	0	0	84,67	205,50	152,71	360,00	718,75
carbonaat		1			1		1			1		0,50			0,50
chloride	3	7	5	6	7	0	0	0	0	0	136,67	350,00	105,40	701,67	944,29
chloride (HPLC)	11	15	97	14	4	0	0	0	0	0	123,64	232,47	146,79	671,79	747,50
chroom (grafiet oven)	3					2					2,20				
chroom (ICP-USV)	1					1					1,00				
cis 1,2-dichlooretheen	9	17	74	15	7	9	17	73	15	7	1,00	1,26	0,53	2,00	1,49
dichloormethaan	9	17	74	15	7	9	17	74	15	7	7,44	3,71	1,18	3,20	6,86
EOX	3	5	4	4	5	3	4	4	0	3	1,00	1,14	1,00	18,50	2,74
ethylbenzeen	14	20	101	18	10	14	12	97	2	5	0,20	1,65	0,27	64,91	0,34

parameter name	count of measurements					count < detection limit					average value				
fenol-index (NEN 6670)	4	13	17	18	8	3	6	14	2	4	1,28	2,92	1,18	42,76	2,23
fosfaat (totaal) als P	3	14	31	13	4	0	0	0	0	0	2,55	1,58	1,59	0,54	0,95
fractie C10- C12	2		20			1		4			35,00		42,50		
fractie C6 - C8	2		20			1		6			7,50		15,75		
fractie C8 - C10	2		20			1		4			15,00		25,25		
geleidingsver. (veld)	5		60			0		0			1302,80		1400,60		
geleidingsvermogen (25°C)	7	14	27	13	4	0	0	0	0	0	1163,86	1558,50	1350,00	3475,31	4200,00
ijzer (ICP)		5	16		1		0	0		0		12580,00	8456,25		45000,00
ijzer(II)	3	14	31	13	4	0	0	0	0	0	7,90	15,97	11,06	30,98	22,33
kalium (ICP)	6	17	34	17	7	0	0	2	0	2	17,17	66,00	17,70	300,53	54,07
kalium (vlam)	3	2	1	1	2	0	0	0	0	0	13,97	205,00	19,00	300,00	63,00
Kjeldahl-stikstof als N	10	22	75	18	11	1	0	2	1	0	10,58	84,14	17,48	308,78	62,18
kooldioxide (vrij)	2	6	16		2	0	0	0		0	45,50	294,17	122,38		1400,00
koper (grafiet oven)	3	2	1	1	2	3	0	0	0	1	2,00	4,00	6,80	15,00	9,00
koper (ICP-USV)	1					0					13,00				
lood (grafiet oven)	3	2	1	1	2	3	2	1	1	2	5,00	5,00	5,00	5,00	5,00
lood (ICP-USV)	1					1					5,00				
magnesium (ICP)	6	14	31	13	4	0	0	0	0	0	36,00	77,21	44,68	174,38	100,25
mangaan (ICP)	3	14	31	13	4	2	1	9	0	0	0,63	1,64	0,74	1,80	2,50
methaan	2	6	19		2	0	0	0		0	225,00	1608,88	110,21		3290,00
min. olie (IR) NEN 6675	3	2	1	1	2	3	2	1	0	2	50,00	50,00	50,00	310,00	50,00
min. olie vluchtig (GC)	2		20			1		4			6,80		8,82		
natrium (ICP)	6	14	31	13	4	0	0	0	0	0	80,83	142,36	91,26	514,54	536,25
nikkel (grafiet oven)	3					3					10,00				
nikkel (ICP-USV)	1					1					5,00				
nitraat als N (HPLC)	3	14	28	13	4	2	6	16	0	2	0,23	0,44	0,52	1,41	1,32
nitriet als N (HPLC)	3	14	28	13	4	3	11	24	8	2	0,04	0,03	0,03	0,01	0,03
pH	4	6	20		2	0	0	0		0	7,15	7,17	6,78		6,60

parameter name	count of measurements					count < detection limit					average value				
pH (veld)	5		60			0		0			7,00		6,95		
redoxpotentiaal (Eh)			20					0					85,72		
sulfaat	3	2	1	1	2	0	0	1	0	0	106,00	21,50	1,00	3,70	150,95
sulfaat (HPLC)	6	14	34	13	4	1	1	1	6	1	80,83	79,93	130,93	89,92	167,25
sulfide (vrij)	2	6	19		2	0	6	16		2	0,06	0,05	0,05		0,05
temperatuur	5	5	60		1	0	0	0		0	12,50	19,80	12,80		21,00
tetrabroommethaan	1	8	13	14	3	1	8	13	14	3	0,20	0,20	0,20	0,20	0,20
tetrachlooretheen	9	17	74	15	7	9	17	72	11	7	0,50	0,50	0,51	1,19	0,50
tetrachloormethaan	9	17	74	15	7	9	17	72	14	6	0,50	0,50	0,53	0,60	0,56
TOC	2	6	19		2	0	0	0		0	15,00	21,33	16,13		62,00
tolueen	14	20	101	18	10	13	14	97	1	3	0,36	1,53	0,27	39,89	0,97
trans 1,2-dichlooretheen	9	17	74	15	7	9	17	74	15	7	1,00	1,26	0,52	2,00	1,50
trichlooretheen	9	17	74	15	7	9	17	74	11	7	0,50	0,50	0,50	1,15	0,50
trichloormethaan	9	17	74	15	7	9	12	67	4	6	0,50	0,92	0,69	2,09	0,74
xylenen	14	20	101	18	10	14	11	85	2	4	0,29	4,98	0,40	263,19	2,62
zink (ICP)	3	2	1	1	2	3	2	1	1	2	100,00	100,00	100,00	100,00	100,00
zink (ICP-USV)	7	1	62			7	0	17			5,00	5,50	19,18		
zuurstofgehalte	2	1	36		1	1	1	16		1	0,06	0,01	0,58		0,01
zuurverbruik (alkaliteit)	7	13	35	12	3	0	0	0	0	0	6,33	17,38	10,17	58,39	42,12

Table 3. Parameter values used for previous modelling excercises.

Model/ Investigation	**Landfill**	**Holocene (Local)**	**Holocene (Regional)**	**Gullies**	**Aquifer (Local)**	**Aquifer (Regional)**	**Kedichem Formation**	**Second Aquifer**	**Dispersivity long. | vert.**
STIWACO	KD = 0.32 c = 800; D = 5 (-5 : 0) L.T.[*1] = 350 m	KD = 0.02 c = 20,000; D = 10 (-10 : 0) L.T. = 200 m		KD = 1.70 c = 300; D = 10 (-10 : 0) L.T. = 150 m	KD = 1,200 c = 1.25; D = 30 (-40 : - 10)				5 m | 1 m
MOC/PLUIM/ MODISCO	**k = 0.5** KD = 1 - 10 K = 0.1 - 1 D = 3 - 6 <> 14	c = 4,000 D = 6 - 8 **c = 3,500**	c = 2,500 - 10,000	c = 1,500 - 3,000 **c = 3,500** flux = 1 mm/d	KD = 1,800	KD = 1,800 - 3,600 KD = 500 - 4,000 (text) D = 35 m			
TRIWACO[*2]	K = 0.1 - 1 h = -1.9 - + 0.9 => 0 m flux = 4 m^3/ uur	D = 8 - 10 **c = 4,000**	c = 250 - 5,000 **c = 4,000** **2 partial areas:** **c = 500 (NE)** **c = 2,000 (E)**	**c = 3,000**	KD = 1,750 - 2,000 => **1,800** **D = 30** D =35 H = -3.3 - 3.9 => - 3.6	KD = 1,000 - 3,000 **KD = 1,800** **1 partial area = 3,600** **D = 30**	D = 10 **c = 10,000**	D = 190 **KD = 2,500** H = -4 m	
Dissipation experiments		max: c = 30,000		c = 5,000 or less					

[*1] L.T. = Length Transect.

[*2] TRIWACO data are based on studies of ICW (1976) and TNO/DGV (1980).

Table 4. Soil and water analysis sediment beneath landfill (May 1997).
Depth 6.00 - 7.45 m - surface landfill.

depth from top	**81 - 145** [*4]	**49 - 81 cm** [*4]	**0 - 22 cm** [*4]
	sediment parameters (weight %)		
lime %	17.7	15.9	15.2
clay %[*5]	29.1	23.5	19.5
silt %[*5]	50.2	37.2	30.3
sand %[*5]	20.7	39.3	50.2
classification (Dutch) (RGD, Stiboka)	lichte klei	zware zavel	zware zavel
nitrogen %	0.365	0.285	0.169
carbon %	5.48	4.56	2.79
C/N	15	16	16.5
CEC[*6] (meq/100 g)	39.6	32.4	23.4
	hydrochemistry (mg/l)[*1*2]		
Ec (lab)	2,660	-	-
pH (Sentron)	7.93	7.93	7.84
Eh (Sentron)	-46.3	-48.0	-44.0
Na^+	79.7	115	129
K^+	66.3	62.0	40.5
Mg^{2+}	37.8	26.4	23.8
Ca^{2+}	87.0	110	56.5
NH_4^+	222	207	165
Si^{4+}	4.68	5.07	4.67
Al^{3+}	1.51	1.85	3.11
Fe^{2+}	< 0.3	0.51	< 1.0
Mn^{2+}	0.26	< 0.3	< 1.0
Cl^-	234	321	551
HCO_3^-	1,536	1,389	-
CO_3^{2-}	-	284	-
SO_4^{2-}	11.8	19.9	4.6
NO_3^{2-}	5.9	3.8	7.5
PO_4^{3-}	1.4	3.7	1.2
sum pos.	24.91	25.73	20.57
sum neg.	32.10	41.76	15.75
error [*3]	-13 %	-24 %	+13 %

[*1] Sediment samples were centrifuged in the ultracentrifuge (30,000 rpm, 10 °C, 30 min.).

[*2] The pore water chemistry may be influenced by a diffusive exchange with the work water used during the Begemann drilling. This work water is tap water (pers. comm. van de Velde, GD).

[*3] Differences in the electroneutrality-balance can be due to errors in the calibration line.

[*4] Samples are not completely mixed, thus analyses are not completely representative of the given intervals.

[*5] Fractions were determined with the Fritsch laser-particle sizer (Sed-Lab, Faculty Earth Sciences, Free University). The boundaries between the clay and silt fractions and the silt and sand fractions is determined at 8 μm (corresponds to 2 μm with the pipette method) and 63 μm respectively.

[*6] CEC is calculated as: CEC (meq/100 g) = 0.7 · (% clay) + 3.5 · (% C).

APPENDIX C

GRAPHICAL OVERVIEW OF STATISTICS OF SELECTED PARAMETERS PER ZONE

APPENDIX D

GRAPHICAL OVERVIEW FOR 1997 MEASUREMENTS (MGWP 1 AND MONITORING LINE)

APPENDIX E

ELECTRON MICROGRAPHS