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Feasibility study of a "Biological Fence" at the site of Shell Netherlands Refinery

Final report
Phase 2, extended monitoring

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Samenvatting
Dit eindrapport geeft de resultaten van het haalbaarheidsonderzoek 'biologische afrastering' op de locatie van de Shell Nederland Raffinaderij zoals dit in januari 1997 werd aangevangen.
Eerder, in november 1998, werden er drie biologische afrasteringen geplaatst en getest op hun verwijderingsvermogen voor aromatische samenstellingen en aardolie. De concentraties koolwaterstof in het grondwater namen af maar de variaties tussen de steekproefpunten binnen de afrastering maakten het trekken van een duidelijke conclusie erg moeilijk. Het resultaat was dat de haalbaarheidsstudie werd voortgezet zoals in dit rapport wordt beschreven. Er werd een workshop met externe experts gehouden, en de situatie wat betreft de contaminanten werd in januari 2001 geactualiseerd.
Een analyse van de contaminanten maakte duidelijk dat de afrasteringen biologisch actief waren en dat de concentraties in de afrasteringen na verloop van tijd verminderden.
Voor het opereren en de controle van biologische afrasteringen worden onder andere het gebruik van extra meetinstrumenten, zoals delta C metingen (isotopische ratio), bodemmonsteranalyse en aanpassing binnen het beheer van het systeem aanbevolen, b.v. het opvoeren van de stroomsnelheid van zuurstof en het achterwege laten van horizontale systemen.

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Gecontroleerde termen:
aardolie, aërobisch, biologische afrastering,
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Abstract
This final report gives the results of the feasibility study of a 'biological fence' at the site of Shell Netherlands Refinery, as started in January 1997.
Previously, three biological fences were installed in November 1998, and tested for their removal capacity of aromatic compounds and mineral oils. The hydrocarbon concentrations in the groundwater decreased, but variations between the sampling points within the fences made it very difficult to draw clear conclusion. As a result, the feasibility study was continued as described in this report. A workshop with external experts was held, and the contaminant situation was updated in January 2001.
Analysis of the contaminants demonstrated that the fences were biologically active, and that the concentrations in the fences decreased over time.
Recommendations for the operation and monitoring of biological fences include the use of extra monitoring tools, like delta C measurements (isotopic ratio), and soil sample analysis and adjustment in the system management, e.g. increase in oxygen flowrate and omission of horizontal systems.

Keywords
Controlled terms:
aerobic, biologic fence, BTEX aromatic compounds, mineral oil

Uncontrolled terms

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INHOUD

SAMENVATTING

Haalbaarheidsonderzoek van een "Biologische Afrastering"
op de locatie van Shell Nederland Raffinaderij

Inleiding
Dit is het eindrapport van de haalbaarheidsstudie 'Biologisch hekwerk"op de Shell Netherlands Refinery locatie, gestart in januari 1997.

Veel gebruikte methoden om verspreiding van verontreinigd grondwater te voorkomen, zijn pump & treat systemen en geohydrologische of civieltechnische isolatie. Een alternatief voor deze methoden zijn biologische afbraakprocessen. Het grondwater stroomt daarbij ongehinderd, terwijl de verontreinigingen in het grondwater in een biologisch geactiveerde zone worden afgebroken. Door deze afbraak wordt verspreiding van verontreinigingen voorkomen en worden daarmee risico's gereduceerd.

Biologische hekwerken
In de vorige fasen van deze haalbaarheidsstudie is een pilot locatie geselecteerd op het Shell Pernis terrein. Drie biologische hekwerken zijn op (semi) full scale langs de Eerste Petroleumhaven aangelegd en getest op hun verwijderingscapaciteit voor aromaten en minerale olie. Deze pilots zijn gebaseerd op toevoeging van zuurstof door luchtinjectie in de bodem op een diepte van circa 4 meter. Twee pilots bestaan uit horizontale injectiedrains, waarvan een in het (ongestoorde) oorspronkelijke bodemmateriaal ligt (pilot 1) en de ander in een grindkoffer is aangebracht (pilot 2). De derde pilot bestaat uit verticale injectiefilters die in het oorspronkelijke bodemmateriaal zijn aangebracht.

Eerder verkregen resultaten laten zien dat de concentratie aan koolwaterstoffen in het grondwater zijn gedaald (zie Nobis rapport 96-1-03), maar variaties in de analyses maakten het moeilijk om eenduidige conclusies te trekken. Daarom is besloten deze haalbaarheidsstudie te continueren in de vorm van een workshop met externe deskundigen en een nieuwe analyseronde om de verontreinigingssituatie na langdurigere behandeling vast te leggen.

Workshop
De werking van het bioscherm is geëvalueerd tijdens een workshop. Samen met de externe deskundigen werd geconcludeerd dat het zinvol is om door te gaan met het biologisch hekwerk, om de werking hiervan duidelijker aan te tonen.

Belangrijke punten en vragen die nog beantwoord moesten worden gedurende het project waren:
1. Zijn de drains op de juiste wijze geïnstalleerd (plaatsing en technische eisen)?
2. Is het debiet van de luchtinfiltratie hoog genoeg?
3. Kan een betere zuurstofoverdracht plaatsvinden?
4. Wat zijn de afbraaksnelheden?
5. Kan een massabalans worden opgesteld?
6. Stijghoogtes meten
7. Voorkeur voor flexibele verticale infiltratie systemen.

Werking van het biologisch hekwerk
De werking van de biologische schermen zijn sinds november 1998 gevolgd. De meest recente metingen van januari 2001 geven aan dat de gemiddelde zuurstofconcentraties in de meetdrains en peilbuizen is gestegen van 0,2 tot 1 mg/l. Deze gestegen concentraties zijn gunstig voor de aërobe afbraak van de aanwezige verontreinigingen.

De redoxpotentiaal is in de peilbuizen licht gestegen, wat ook duidt op meer geoxideerde condities (gunstig voor de afbraak van koolwaterstoffen). Deze stijging werd niet gemeten in de meetdrains, maar dit komt waarschijnlijk door onvoldoende doorspoeling van deze drains voorafgaand aan bemonstering.

Analyse van het grondwater naar verontreinigingen toonde aan dat de hekwerken actief waren omdat de concentraties van koolwaterstoffen daalden in de tijd. Deze conclusies zijn afkomstig uit metingen in het grondwater in de peilbuizen. De concentratie aan totale hoeveelheid koolwaterstoffen daalde in hekwerk 1 van 17.000 naar 9.000 µg/l, in hekwerk 2 van 3500 naar 1600 µg/l en in hekwerk 3 van 2000 naar 1000 µg/l. De resultaten uit de meetdrains zijn onbetrouwbaar, mogelijk door te weinig doorspoeling van deze drains.

In hekwerk 1 heeft de meeste afbraak van de verontreinigingen plaatsgevonden, maar dit was ook het hekwerk met de hoogste beginconcentraties aan koolwaterstoffen. Procentueel gezien was de afbraak in alle drie de hekwerken vergelijkbaar (50%).

Modellering

De gesimuleerde concentraties in pilot 1 and 3 waren lager dan de gemeten concentraties in het veld. De instromende concentraties zijn gedurende de duur van de pilot niet veranderd en de gemeten hogere concentraties zijn misschien het gevolg van een verminderde biologische afbraak sinds november 1999. Dit kan zijn veroorzaakt door veranderingen in de omgevingscondities, bv. dalende concentraties aan nutriënten zoals N en P. Een langzame zuurstofoverdracht of een te korte reactietijd tussen zuurstof en de verontreinigingen kunnen hier ook de oorzaak van zijn.

Technische vergelijking van de verschillende systemen

De flexibiliteit voor wat betreft de aanleg en luchtinjectie is hoog bij het gebruik van verticale filters en laag bij horizontale drains. Verticale filters blijken de meest kosteneffectieve techniek te zijn. Echter, bij aanwezigheid van gebouwen en/of ondergrondse infrastructuur kan een horizontaal geboorde drain het enige alternatief zijn.

Wanneer de aanvangsconcentraties mede in acht worden genomen, geven de drie hekwerken een vergelijkbare afbraak te zien van de aanwezige verontreinigingen. Gebaseerd op praktische ervaringen met verticale filters zijn deze aan te bevelen.

De kosten van biologische hekwerken zijn vergelijkbaar met die van conventionele systemen die zijn aangelegd op het terrein van Shell Pernis. Biologische hekwerken hebben echter minder negatieve milieueffecten (bijvoorbeeld laag verbruik van energie en grondstoffen, weinig emissies).

Optimalisatie

Aanbevelingen voor de optimalisatie in het systeem zijn:
- Verhoging van de flowrate;
- Intermitterende injectie van zuurstof;
- Weglaten van het horizontale injectie systeem.

Aanbevelingen voor de monitoring van biologische hekwerken, om de werkzaamheid ervan beter te voorspellen zijn verschillende analysetechnieken:
- Het gebruik van verbindingsspecifieke isotopen analyses;
- Bodem analyses.

Ontwerp biologisch hekwerk

Gecombineerde modellering van grondwaterstroming, stoftransport en biologische afbraak in de verzadigde zone is een goed hulpmiddel om de voorwaarden op te stellen voor een hekwerk, omdat het de informatie van verschillende processen combineert.

SUMMARY

Feasibility study of a "Biological Fence"
at the site of Shell Netherlands Refinery

Introduction
This final report gives the results of the feasibility study of a 'biological fence' at the site of Shell Netherlands Refinery, as started in January 1997.

Frequently used methods for preventing contaminated groundwater plumes from further spreading are pump and treat and geohydrological or geotechnical / engineering measures.
An alternative for these methods can be biological degradation processes. The groundwater flows freely, while the pollutants are degraded in an activated biological system. This concept is compatible with risk reduction and prevention of the spreading of pollutants.

Biological fences
In previous phases of this feasibility study, a specific pilot site was selected at the Shell Pernis site. Three biological fences were installed at this site in November 1998, and tested for their removal capacity for aromatic compounds and mineral oil. The pilots are based on air injection in soil at a depth of 4 m. Two fences consisted of horizontal infiltration drains in either the original soil material (fence 1) or in gravel (fence 2). The third fence had vertical infiltration filters that were installed in the original soil.

Previous results indicated that the hydrocarbon concentrations in the groundwater decreased (see Nobis report 96-1-03), but variations between the sampling points within the fences made it difficult to draw clear conclusion. As a result, the feasibility study was continued as described in this report. The continuation consisted of a workshop with external experts, and the contaminant situation was updated in January 2001.

Workshop
The performance of the biofences was evaluated in a workshop. External experts advised to continue the project, in order to better demonstrate the effectiveness of the biofences.

Important aspects and questions that needed to be addressed during the continuation of the project were:
1. Are the drains installed as expected (location and technical requirements)?
2. Is the infiltration flow high enough?
3. Is improvement of air distribution possible?
4. What are the degradation rates?
5. Can a mass balance be made?
6. Measure ground water levels
7. Preference for more flexible vertical infiltration systems

Performance
The biological fences have been operated since November 1998. The most recent measurements of January 2001 show that the concentration of oxygen in both the measuring drains and the monitoring wells increased from 0.2 to app. 1 mg/l in all fences. These higher concentrations are favourable for aerobic biodegradation.

A moderate increase in the redox potential in the monitoring wells was found, indicating that more oxidised conditions (favourable for hydrocarbon degradation) were present. This increase was not found in the measuring drains, most likely due to insufficient flushing during sampling.

Analysis of the contaminants demonstrated that the fences were biologically active, and that the concentrations in the fences decreased over time. These conclusions were drawn from the data of the monitoring wells. The concentrations of total hydrocarbons decreased in fence 1 from 17,000 to 9,000 µg/l, in fence 2 from 3,500 to 1,600 µg/l and in fence 3 from 2,000 to 1,000 µg/l. The data of the measuring drains gave less conclusive results, but this could be explained by insufficient flushing during sampling.

Based on the performance, fence 1(horizontal infiltration drain) showed the largest decrease in concentration, but this was also the fence with the highest initial contaminant concentration. When calculating the decrease in percentage, the three fences acted similar and showed 50 % reduction of the contaminants.

Modeling
The simulated concentrations in pilot 1 and 3 were much lower than the observed concentrations in the field. The input of concentrations did not increase, and the mismatching values for pilot 1 and 3 could be explained by decreased biological decay since November 1999. A change in environmental conditions for microbial degradation could be the reason for this. A possible explanation is a lack of nutrients (N, P). Nutrients can be needed in concentrations higher than Dutch soil can offer for complete microbial degradation, e.g. at hydrocarbon concentrations of higher than 1 mg/l. Also a slow oxygen transfer or a short reaction time in the fences could be the reason for this.

Technical comparison
The flexibility with respect to construction and air injection is high at fences with vertical filters. The flexibility of fences with horizontal injection drains is low. Based on the technical comparison the fence with vertical filters is the most cost-effective technique to construct and operate a full scale aerated biological fence. However, in the presence of buildings and infrastructure horizontal drilled drains can be the only alternative.

Taking the initial concentrations into account, and based on the performance, the three fences showed a similar decrease of the initial concentration. As practical experience has shown vertical filters to be more flexible, these type of biofences are preferred.

The costs of biological fences are comparable to conventional systems at the Shell Pernis site. Biological fences have less negative environmental influences than conventional techniques.

Optimisation
Recommendations for the adjustment in the system management include the increase in oxygen flowrate, intermittent supply and omission of horizontal infiltration systems.
Recommendations for the monitoring of biological fences to better understand its effectiveness include the use of extra monitoring tools, like delta C measurements (isotopic ratio), and soil sample analysis.

Design of a biological system

Combined modelling of groundwater flow, solute transport and degradation in the saturated zone is a powerful instrument to set up the conditions for the design of a biological fence. It puts together the information from the preliminary investigations about the various processes.

The implementation of biological fences for aerobic degradation of hydrocarbons can be improved when more knowledge is gained about transport of air in the underground and transfer of oxygen from air to groundwater.

CHAPTER 1

INTRODUCTION

In January 1997, NOBIS commissioned a feasibility study regarding a biological fence at the site of the Shell Netherlands Refinery with the aim of reducing pollution risks by applying biodegradability techniques.

The Shell Netherlands Refinery site is part of the Shell's overall Pernis site, which houses a refinery and storage facilities for petroleum products (Shell Netherlands Refinery: SNR), while the remainder houses chemical plants and storage facilities (Shell Netherlands Chemical: SNC). The site is generally covered with a layer of anthropomorphous soil, varying between 2 and 5 metres in thickness. This surface layer rests on a layer of clay, which contains an interbedded layer of sand at approximately 8 m below the surface. The first aquifer starts at a depth of approx. 20-25 m below the surface. At the boundaries of the site the phreatic groundwater flow (in the upper layer) is directed outward in the direction of the first and second "Petroleumhaven" docks and a polder area. The centre of the site is mainly characterised by infiltration into the water-bearing sequence. The site can be regarded as representative for industrial sites in the Botlek area.

At the site, 3 biological fences were installed in November 1998, and tested for their contaminant removal capacity. The situation is drawn in Appendix B. The overall aim of this project was to demonstrate the applicability and performance of an aerobic biofence. The fences were compared on hydrocarbon degradation, oxygen influx, construction, maintenance, performance of operation, flexibility and costs.

In the period December 1998 - November 1999 the fences showed a decrease of hydrocarbon concentrations in groundwater, but variations between the different sampling points within the fences made it very difficult to draw clear conclusions on biodegradation. The decrease is seen for volatile and non-volatile components, indicating that volatilisation was not the (major) explanation for the decrease. This decrease was found in all three fences, indicating that the fences performed similar. Results were evaluated in the report of stage 1 "Phase 4: Project evaluation" [Heijnen et al, 2000].

A few months after the evaluation, it was decided to continue this project, as a few questions remained unanswered. A workshop was held (6-6-2000) with external advisors to evaluate the system. Furthermore the goal of the current project was defined as: "Demonstration of aerobic degradation of the present pollutants as a result of the biofence".

This is the final report of the project, in which the contaminant situation was updated in January 2001, as the three biofences were not measured for their degree of contamination since January 2000. The results of the workshop, and the updated situation of the biofences are reported here. For all other information, the reader is referred to previous reports i.e. Heijenen et al, [2000].

CHAPTER 2

WORKSHOP

The minutes of the meeting (in Dutch) with the expert group are given in Appendix A. Their experiences regarding oxygen infiltration were used to evaluate the project.

General conclusions of the workshop are:
- Continuation of the project is advised, in order to better demonstrate the effectiveness of the biofences;
- Contact with experts during the project will be useful.

CHAPTER 3

OPERATION OF THE SYSTEM

Three different biofences were installed previously, and operated since December 1998. The following fences were installed (see also Appendix B):

Fence 1

Air injection through horizontal drains, installed by horizontal drilling.

Fence 2

Air injection through horizontal drains, installed by a drainage machine. The soil above the drain was replaced (100%) by gravel. At the column experiments the highest degradation rate was measured when 80% or more gravel was used as filling material. From this it is expected that fence 2 will perform best.

Fence 3

Air injection though 20 vertical injection filters installed by pulsing. The filters are placed in a serrated line. This design is expected to have a wide range of application.

The injection system was operated continuously with a flowrate of 26 to 54 m^3/hr, except for 3 weeks in May. Only one injection drain was used for fence 1 (horizontal fence), as in 1999.

The pressure in the drains remained constant, and was 0.2 and 0.3 for fence 1 and 3, respectively. The pressure in fence 2 (gravel fence) was higher, and varied from 1.2 to 1.8 bar. This was also found in 1999.
No major maintenance work was needed for the system, and the system was operated normally.

CHAPTER 4

MONITORING ACTIVITIES

4.1 Fieldwork

The fieldwork was carried out on the 24th and 25th of January 2001 by the Environment Technical Services of IWACO according to NNI-standards and/or regulations. The Environment Technical Services of IWACO is ISO-9001 and VCA certified.

The following activities were performed:
- measuring the hydraulic head in the measuring points;
- flushing monitoring wells (about 6 litres) and measuring drains;
- measuring pH, electrical conductivity and temperature of groundwater;
- measuring oxygen and redox potential of groundwater by using a flow cell and electrodes;
- sampling groundwater for chemical analyses.

Because of the sensitiveness of the oxygen and redox potential measurements, the equipment was calibrated at each fence before measurement. Duplicate samples were taken when needed.

The measuring drains could not be flushed within a limited amount of time, unlike the former flushing activities in 1998 and 1999 at the fences. The volume of each drain is about 200 litres, and it was planned to flush the drains with at least this volume. Real flushing volumes were 120-135, 50-70 and 160 litres for the drains of the fences 1, 2 and 3, respectively. Possible causes of the flush resistance of the tubes are:
- formation of precipitates ('clogging', e.g. by iron(hydr)oxides) inside the drain or the drain tubes;
- a kink in (some of) the tubes due to replacement of the tubes after removing the Fiber Optic Sensors (to measure hydrocarbon content) in August 2000, although support tubes were used during replacement. These sensors have been used in the previous phase of the project [Heijnen et al, 2000].

Flushing was needed to certify sampling the groundwater from outside the drain, and not (partially) stagnant water from inside the drain. The expectation is that at lower flushing volumes a part of the stagnant water is sampled, which is not representative for the bulk of the groundwater at that part of the fence.

In total 53 out of 60 measuring points were sampled. The following measuring wells were not sampled: 1A2, 1B3, 2A3, 2B1 and 3A1, 3A2 and 3A3. The first 4 wells did not give water because of a high flush resistance. The tubes 3A1-3A3 were not present anymore, as they could not be replaced after removal of the sensors.

4.2 Chemical analyses

The groundwater samples were analysed by the Environment Laboratory of IWACO Rotterdam (STERLAB certified), according to NNI-standards and/or regulations. All samples were analysed on the volatile aromatic hydrocarbons benzene, toluene, ethylbenzene and xylenes, the volatile fraction (C6-C12) and the non-volatile fraction (C10-C40) of mineral oil.

CHAPTER 5

RESULTS MONITORING & DISCUSSION

The obtained data are used to evaluate the current operation of the biofences. A validated solute transport model (Sorwaco) supports this evaluation. A distinction is made between data of the measuring drains and the monitoring wells.

5.1 General macroparameters

During sampling the pH, electric conductivity and temperature of the groundwater were determined. All values are considered as non-deviant (table 1).

Table 1. Characteristics of the groundwater at the site (January 2001).

	Minimum	Maximum
PH	6.7	7.3
Electrical Conductivity (µS/cm)	630	2000
Temperature (°C)	9.7	13.2

5.2 Hydraulic head

The measured groundwater levels are given in Appendix C, and are normalised to NAP-levels. In fences 1 and 3 the hydraulic gradient was 0.018 - 0.023 m/m. In fence 2 the average hydraulic gradient is 0.25 m/m (on May 7th 1999 the hydraulic gradient in fence 2 was about 0.13 m/m, at low tide as well as at high tide).

Based on the hydraulic gradient a difference was found between fence 2 on one hand, and fence 1 and 3 on the other hand. The difference in hydraulic head between the first and second measuring line of fence 2 was relatively small (5 cm), where the difference between the second and the third measuring line was much larger (45 cm). This higher hydraulic head at the third measuring line was similar to those of the other two fences, whereas the hydraulic head of the first and second measuring lines were not: 1.6 - 1.7 m NAP at fence 1 and 3 versus 2.1 - 2.2 m NAP at fence 2. The higher hydraulic head at fence 2 was probably caused by the lower conductivity of the soil at fence 2: more clay was present here. As the conductivity was lower and the hydraulic gradient was higher, it was assumed that the groundwater velocity (the product of gradient and conductivity) was similar to that of the fences 1 and 3.

All the fences showed a positive hydraulic gradient, which indicates that the groundwater in all fences flew towards the harbour during biosparging.

5.3 Oxygen supply

A lot of discussion in the previous phase focused on the suppletion and consumption of oxygen in the drain. The figures for all the single measuring points in the drain and the monitoring wells are given in Appendix D, and will be summarised and discussed with the following tables.

5.3.1 *Measuring drains (O_2)*

The average oxygen concentrations in the measuring drains A, B and C for the 3 fences were calculated using the results of the three sampling points at each drain (see Appendix B), and are given in table 2.

Table 2. Average oxygen concentration in measuring drains A, B and C for the 3 fences.

	November 1999			January 2001		
	Line A	Line B	Line C	Line A	Line B	Line C
Fence 1	7.90	0.82	0.16	7.44	0.92	1.08
Fence 2	0.20	2.50	0.21	1.05	1.41	1.08
Fence 3	1.42	0.20		ND	0.76	

ND not detected

Low concentrations of less than 0.2 mg/l as measured in November 1999 increased to 1 mg/l. These measurements indicate that oxygen was present in the measuring drains. The oxygen concentrations were still relatively low, except for fence 1, which had a high oxygen concentration (7.9 mg/l) in the upstream part.

5.3.2 *Monitoring wells (O_2)*

The average oxygen concentrations in the monitoring wells near A, B and C for the 3 fences were calculated using the results of the three sampling points at each drain (see Appendix B), and are given in table 3.

Table 3. Average oxygen concentration in monitoring wells near injection lines A, B and C.

	November 1999			January 2001		
	Line A	Line B	Line C	Line A	Line B	Line C
Fence 1	0.56	0.40	2.64	0.97	1.05	2.53
Fence 2	0.20	0.43	0.23	1.22	1.15	1.65
Fence 3	0.22	0.27	0.17	0.86	0.96	1.07

The oxygen levels in the field increased during the last year; this increase was small (average from 0.6 to 1.3 mg/l), but significant. The absolute increase was more pronounced in biofence 2 and 3 than in biofence 1.

The fact that increased oxygen concentrations were found in the monitoring wells can be a result of:

- A surplus of oxygen is added to the site, and therefore not all the added oxygen is used for biological processes;
- The concentration of contaminants decreased, as the soil in the fences became less polluted due to degradation. As a result, less oxygen is needed for the degradation of the remaining contaminants;
- The solid materials in the biofence became more oxidised, leaving more oxygen in the biofence;
- Previously present easy degradable substrates are degraded, and therefore less oxygen is needed for the degradation of the contaminants only;
- Microbial activity on both easy degradable substrates and contaminants has decreased as micro-organisms lack nutrients.

In conclusion, the measurements performed in January 2001 show that the concentration of oxygen in both the measuring drains and the monitoring wells increased from 0.2 to app. 1 mg/l in all fences. These higher concentrations are favourable for aerobic biodegradation.

5.4 **Redox measurements**

The oxygen measurements of January showed that more oxygen reached the groundwater in the reaction space in and downstream of the biofences. Theoretically, this results in an increased redox potential. The figures for all the single measuring points in the measuring drains and the monitoring wells are given in Appendix E, and are summarised and discussed with the following tables.

5.4.1 *Measuring drains (redox)*

The average redox potential in the measuring drains A, B and C for the 3 fences were calculated using the results of the three sampling points at each drain (see Appendix B), and are given in able 4.

Table 4. Average redox potential in the measuring drains A, B and C for the 3 fences.

	November 1999			January 2001		
	Line A	Line B	Line C	Line A	Line B	Line C
Fence 1	49	-126	-95	-40	-129	-112
Fence 2	-93	-167	-175	-101	-106	-184
Fence 3	-97	-133		ND	-136	

ND not detected

These redox measurements did not show an increase of the redox potential, as on average the redox potential even decreased from -105 to -115 mV only. This could be caused by a lack of flushing. Though the oxygen level was increased in the drains, this might be a temporally effect, caused by imperfect flushing activities. Oxygen level and redox potential should be correlated. An explanation of the lack of such a correlation could be that the increase in redox potential is a relatively slow process and will be retarded.

5.4.2 *Monitoring wells (redox)*

The average redox potential in the monitoring wells near A, B and C for the 3 fences were calculated using the results of the three sampling points at each drain (see Appendix B), and are given in table 5.

Table 5. Average redox potential in the monitoring wells near the injection lines A, B and C for the 3 fences.

	November 1999			January 2001		
	Line A	Line B	Line C	Line A	Line B	Line C
Fence 1	-111	-113	-113	-34	-49	-38
Fence 2	-138	-106	-136	-86	-53	-81
Fence 3	-90	-94	-105	-44	-82	-85

The redox potential in the monitoring wells showed a higher increase over time, compared to the data of the measuring drains. The average redox potential increased with approximately 50 mV (from -112 to -60 mV), which is in agreement with the increase in the oxygen concentrations in the monitoring wells. The highest difference was found in the following order: fence 1 > fence 2 > fence 3.

In conclusion, the measurements performed in January 2001 showed a moderate increase in the redox potential in the monitoring wells, indicating that more oxidised conditions (favourable for hydrocarbon degradation) were present. This increase was not found in the measuring drains, most likely due to insufficient flushing.

5.5 **Hydrocarbons**

The results of the hydrocarbon measurements in the drains and monitoring wells are given in Appendix F. The hydrocarbons were separated in volatile mineral oils (C6-C12), non-volatile mineral oils (C10-C40) and BTEX. The most important contaminants of the site were the volatile mineral oil components (C6-C12). In the past, concentrations up to 40 mg/l were measured in the monitoring wells. Non-volatile mineral oils were measured as well, but we found out that these data are unreliable. As a result, the data of the non-volatile mineral oils (C10-C40) are not discussed in this chapter, and Appendix G describes the reason for this. The other contaminants present at the site were aromatic compounds (BTEX). Only these 2 groups of contaminants are discussed, and the term total hydrocarbons is used for the sum of total volatile mineral oil (C6-C12) and BTEX.

5.5.1 *Measuring drains (hydrocarbons)*

Total hydrocarbons (HC)

The total concentrations of hydrocarbons (volatile mineral oil and BTEX) in the measuring drains are given in figure 1. Fence 1 started with the highest contamination in December 1998, and a reduction of 70% of the initial concentrations was achieved. The other 2 fences did not show such a high reduction, and since December 1999 the concentrations in the 3 fences were comparable. However, there was no alteration in total hydrocarbons from November 1999 to January 2001, the time period of this project, except for fence 3.

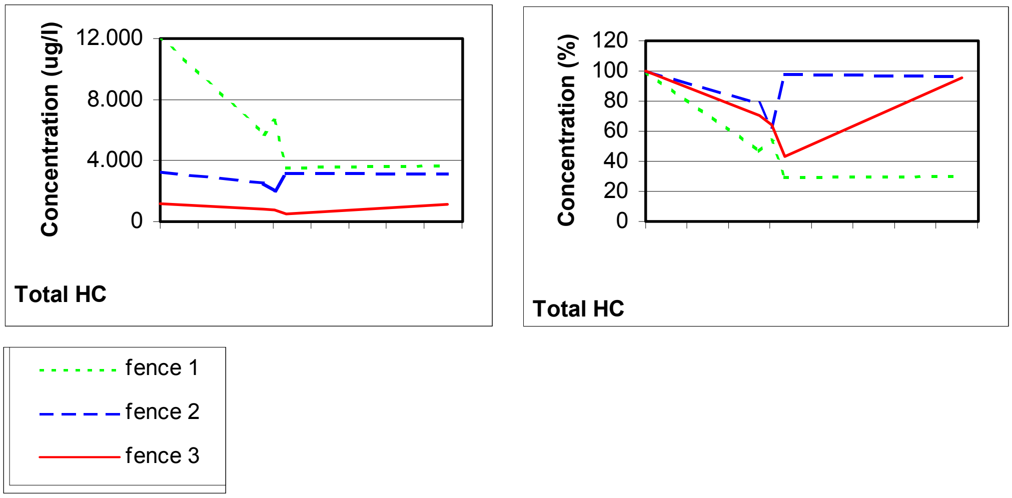


Fig. 1. Absolute (µg/l) and relative concentration (C/Co) of total hydrocarbons in the measuring drains.

Volatile mineral oils (C6-C12)

The volatile mineral oils were the main contaminants in the fences, and as a result the concentration profiles of C6-C12 (figure 2) are comparable to the results of total hydrocarbon (figure 1).

Fence 1 started with the highest contamination in December 1998, and a reduction of 70% of the initial concentrations was achieved. The other 2 fences did not show a reduction of the initial concentration, and since December 1999 the concentrations in the 3 fences were comparable. However, there was no decrease in total hydrocarbons from November 1999 to January 2001, except for fence 3. The absolute increase in fence 3 was not as dramatic as might be interpreted from figure 2, as the initial concentrations were very low. The absolute concentration of contaminants in fence 3 was still lower than in the other two fences

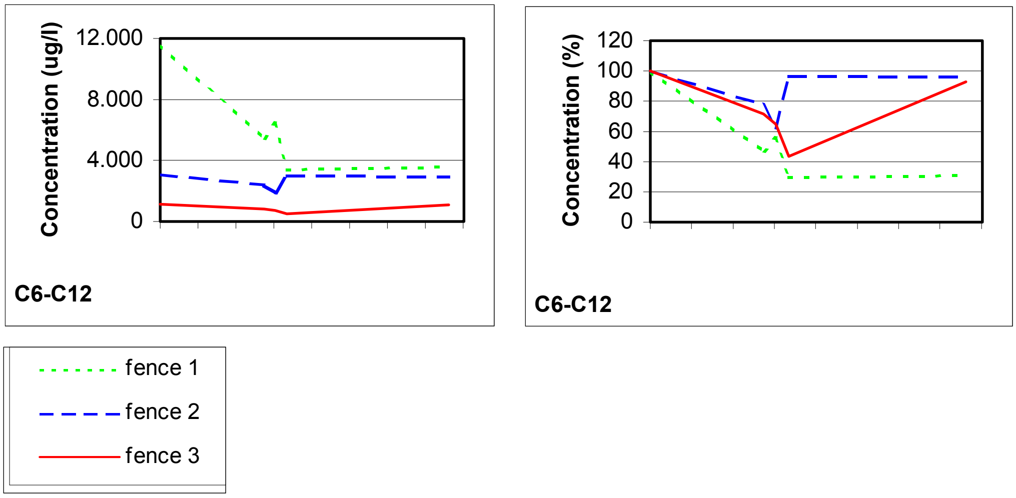


Fig. 2. Absolute (µg/l) and relative concentration (C/Co) of volatile mineral oils (C6-C12) in the measuring drains.

Figure 2 shows the average concentration per fence, but the concentration per line A, B or C of each fence was also calculated (table 6). This gives insight whether a more upstream part of a fence (line A) performs different from the lines downstream.

Table 6. Average C6-C12 concentrations (µg/l) in the measuring drains A, B and C for the 3 fences.

	November 1999			January 2001		
	Line A	Line B	Line C	Line A	Line B	Line C
Fence 1	414	3343	6433	1100	4100	4000
Fence 2	6533	1950	980	7700	1950	457
Fence 3	240	753		ND	1063	

ND not detected

The summarised C6-C12 concentrations per line showed a comparable stagnation or even an increase in concentrations as the summarised concentrations per fence. Decreasing concentrations were only observed in line C.

Table 7 shows the number of change in type of mineral oils in the measuring drains.

Table 7. Hydrocarbon fraction shift in the measuring drains.

	To lighter fractions *)	To heavier fractions *)	No change in pattern *)
Fence 1	2	4	3
Fence 2	5	0	4
Fence 3	2	0	4
Total	9	4	11

*) to lighter fractions C10-C12 and C8-C10 are decreasing and C6-C8 is increasing
to heavier fractions C10-C12 and C8-C10 are increasing and C6-C8 is decreasing
no change in pattern No (measurable) shift is observed.

From these amounts, it is concluded that 37% of the drains show a shift to lighter fractions (C8-C12 → C6-C8). It is hard to draw conclusions on biological degradation from these amounts, because of the fact that there is still a desorption of C10-C12 going on from the soil matrix in the pilots themselves. So C10-C12, but also other fractions, are supplemented.

BTEX

The concentrations BTEX were relatively low compared to the mineral oil concentrations; max. 600 µg/l BTEX in contrast to 15,000 µg/l C6-C12. The BTEX concentrations were decreasing in fence 1, constant in fence 2 and increasing in fence 3 (figure 3).

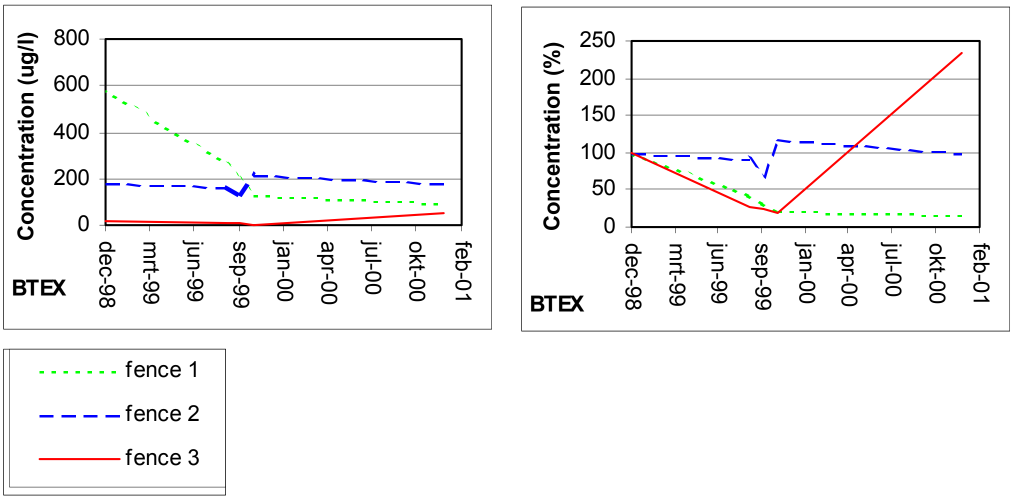


Fig. 3. Absolute (µg/l) and relative concentration (C/Co) of BTEX in the measuring drains.

The absolute increase in fence 3 was not as dramatic as might be interpreted from figure 3, as the initial concentrations were low. The absolute concentration of contaminants in fence 3 was still lower than in the other two fences. Apparently, concentrations fluctuate with 100%.

The data of the individual BTEX compounds are given in Appendix H. Based on the data from the measuring drains, fence 1 has the highest BTEX contamination, and the main contaminants are the xylenes, followed by ethylbenzene. The graphs with the relative concentrations show an increase in relative concentrations, especially in fence 3. As the concentrations were very low in this fence, these relative concentrations cannot be used. A reduction in xylene concentration of 75%, 55%, and 45% for fence 1, 2, and 3 respectively, has been observed.

The individual BTEX concentrations for each line per fence are given in table 8.

Table 8. Average BTEX concentrations (µg/l) in the measuring drains A, B and C for the 3 fences.

	November 1999			January 2001		
	Line A	Line B	Line C	Line A	Line B	Line C
Fence 1	18	43	320	33	89	117
Fence 2	613	49	34	585	34	8
Fence 3	247	5		ND	49	

ND not detected

Only high concentrations were found in fence 2, line A. On average, the concentrations were low.

5.5.2 *Monitoring wells (hydrocarbons)*

Total hydrocarbons (HC)

The total concentrations of hydrocarbons (volatile mineral oil and BTEX), measured in the monitoring wells (figure 4) showed that the total amount of hydrocarbons has decreased since the start of the fences.

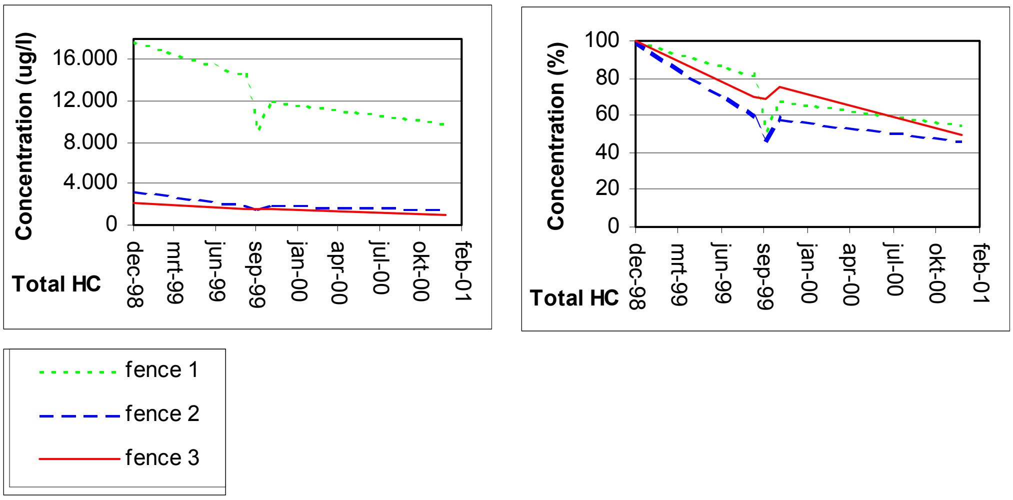


Fig. 4. Absolute (µg/l) and relative concentration (C/Co) of total hydrocarbons in the monitoring wells.

The initial concentration in fence 1 was much higher than in fence 2 and 3, however, the performance of the fences is compared. All the fences showed a reduction in total hydrocarbon of 50% since the start of the infiltration.
(Data from September 1999 in 3-8 have not been used, as these were extremely high, see Appendix F).

Volatile mineral oils (C6-C12)

The volatile mineral oils were the main contaminants in the fences, and as a result the concentration profiles of C6-C12 (Figure 5) were comparable to the results of total hydrocarbon (figure 5).

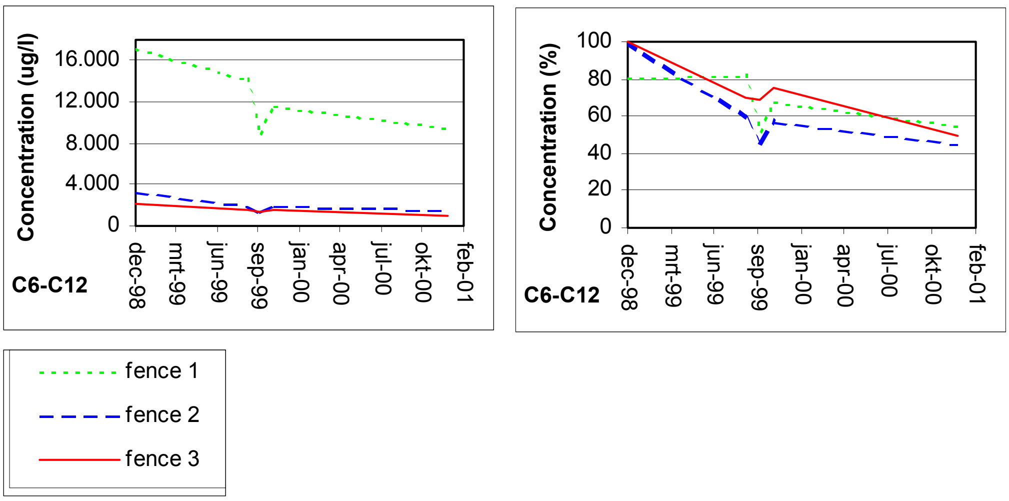


Fig. 5. Absolute (µg/l) and relative concentration (C/Co) of volatile mineral oils (C6-C12) in the monitoring wells.

The initial concentration in fence 1 was much higher than in fence 2 and 3, however, the performance of the fences can be compared. All the fences showed a reduction in total hydrocarbon of 50% since the start of the pilot tests. (Data from September 1999 in 3-8 have not been used, as these were extremely high, see Appendix F).

The concentrations in the individual lines per fence show a decrease in each line (table 9). The spatial variation in concentrations can be seen in this table as well.

Table 9. Average C6-C12 concentrations in the monitoring wells A, B and C for the 3 fences.

	November 1999			January 2001		
	Line A	Line B	Line C	Line A	Line B	Line C
Fence 1	16000	12533	9233	10467	9000	8967
Fence 2	2077	3637	907	2123	2757	503
Fence 3	2400	1390	1610	707	1400	1270

ND not detected

Table 10 shows the number of change in type of mineral oils in the measuring drains.

Table 10. Hydrocarbon fraction shift in the monitoring wells.

	To lighter fractions *)	To heavier fractions *)	No change in pattern *)
Fence 1	4	2	6
Fence 2	7	1	4
Fence 3	6	0	6
Total	17	3	11

* to lighter fractions C10-C12 and C8-C10 are decreasing and C6-C8 is increasing
to heavier fractions C10-C12 and C8-C10 are increasing and C6-C8 is decreasing
no change in pattern No (measurable) shift is observed

From these amounts, it is concluded that 37% of the drains show a shift to lighter fractions (C8-C12 $\rightarrow$ C6-C8). It is hard to draw conclusions on biological degradation from these amounts, because of the fact that there is still a desorption of C10-C12 going on from the soil matrix in the pilots themselves. So C10-C12, but also other fractions, are supplemented.

BTEX

The concentrations BTEX are relatively low compared to the mineral oil concentrations; max. 600 µg/l BTEX in contrast to 18,000 µg/l C6-C12. Compared to the initial concentrations, BTEX concentrations decreased in all the fences (figure 6).

The data of the individual BTEX compounds are given in Appendix I. Based on the data from the monitoring wells, fence 1 has the highest BTEX contamination, and the main contaminants are the xylenes, followed by ethylbenzene. The graphs with the relative concentrations show that the initial concentration of ethylbenzene and xylene are decreasing in all the fences. A reduction in xylene concentration of 50%, 90%, and 80% for fence 1, 2, and 3 respectively, has been observed.

The BTEX concentrations in the individual lines per fence are given in table 11. Fence 1 and 2 showed a decrease in BTEX concentrations, while the concentrations in fence 3 were significantly different.

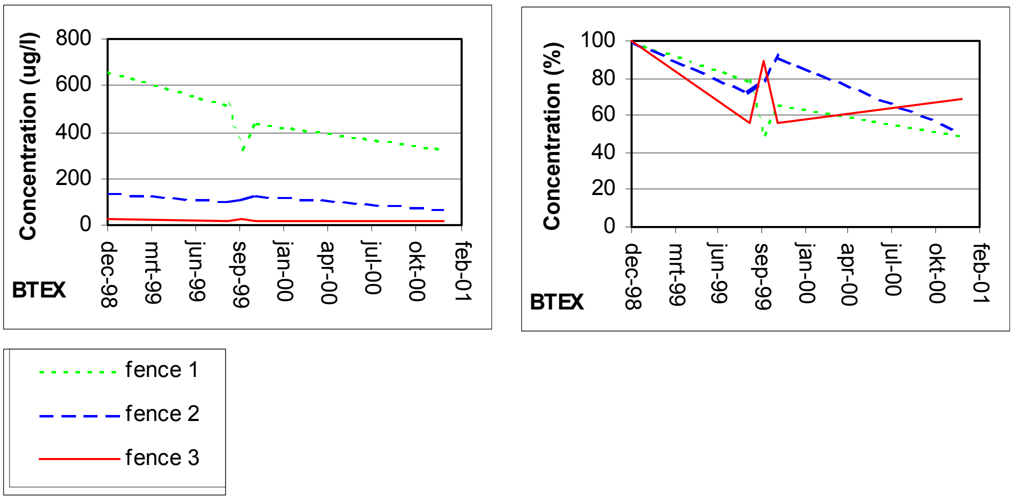


Fig. 6. Absolute (µg/l) and relative concentration (C/Co) of BTEX in the monitoring wells.

Table 11. Average BTEX concentrations (µg/l) in the monitoring wells A, B and C for the 3 fences.

	November 1999			January 2001		
	Line A	Line B	Line C	Line A	Line B	Line C
Fence 1	583	491	157	310	347	126
Fence 2	180	285	23	127	144	7
Fence 3	26	25	7	36	28	8

ND not detected

5.5.3 *Measuring drains vs. monitoring wells*

The concentrations of contaminants were generally higher in the monitoring wells than in the measuring drains. This could be due to a sampling effect, as the drains could not be flushed with groundwater as good as during previous analysis rounds (see chapter 2). Due to this incomplete flushing, we have doubts about the reliability of the measuring drains results.

The measured concentrations of C6-C12 in the monitoring drains fluctuated over time, making it hard to indicate a trend. When the data of each fence were averaged, the results of the monitoring wells showed an almost unanimously decrease in C6-C12 concentrations. This was also found for the BTEX data, especially for ethylbenzene and the xylenes.

CHAPTER 6

MODEL VALIDATION

6.1 New simulations

The existing solute transport model (Sorwaco, version 0.03) from 1999 was run to simulate the concentrations of mineral oil (C6-C12). The model simulates the concentration development by using a biological decay rate of respectively 0.65, 0.5 and 0.6 d^{-1} for fence 1, 2 and 3, respectively. These decay rates were fitted with previous measurements, taking into account the initial situation in 1998 and the situation in November 1999 [report stage 1, Project evaluation; Heijnen et al, 2000].

6.2 Results

In figure 7, 8 and 9 the measured concentration profile of hydrocarbons (C6-C12) is shown at different time periods in the monitoring wells. The simulated concentration development for January 2001 is plotted as well. The model suggests lower concentrations in January 2001 than actually measured.

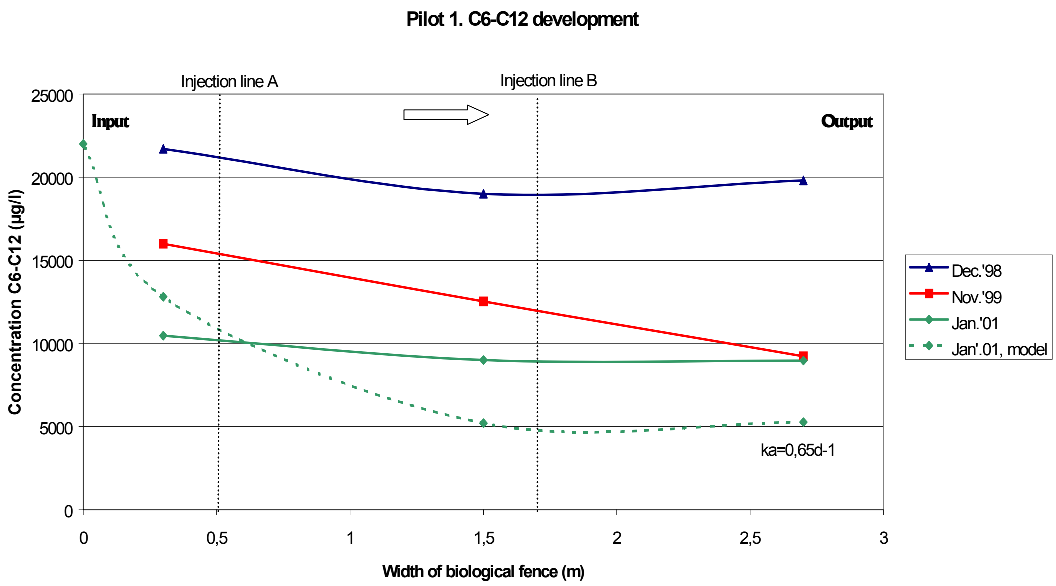


Fig. 7. C6-C12 data for fence 1.

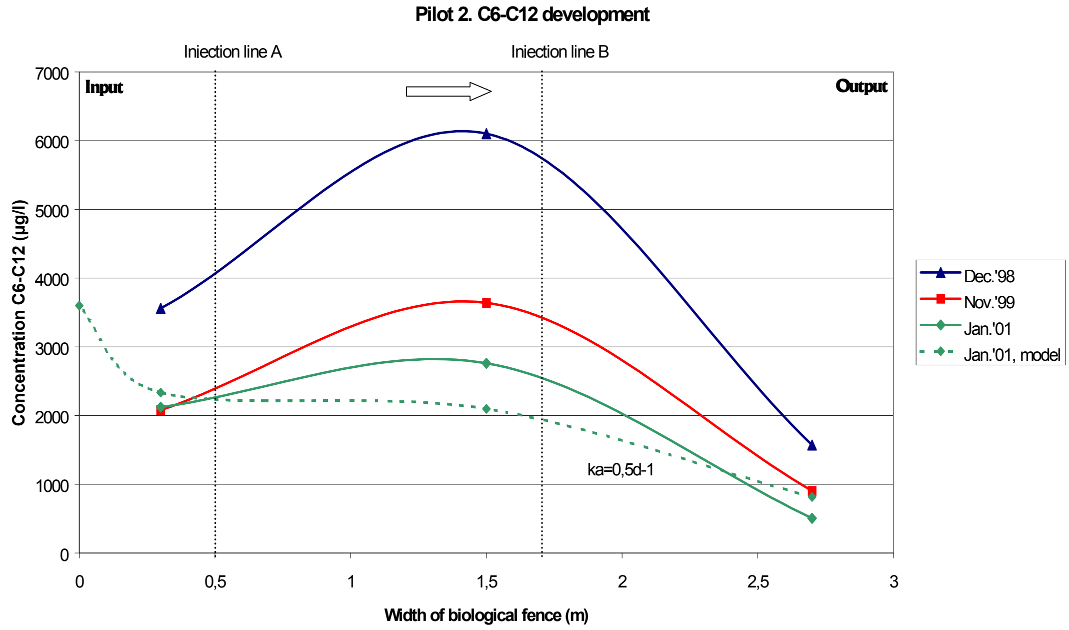


Fig. 8. C6-C12 data for fence 2.

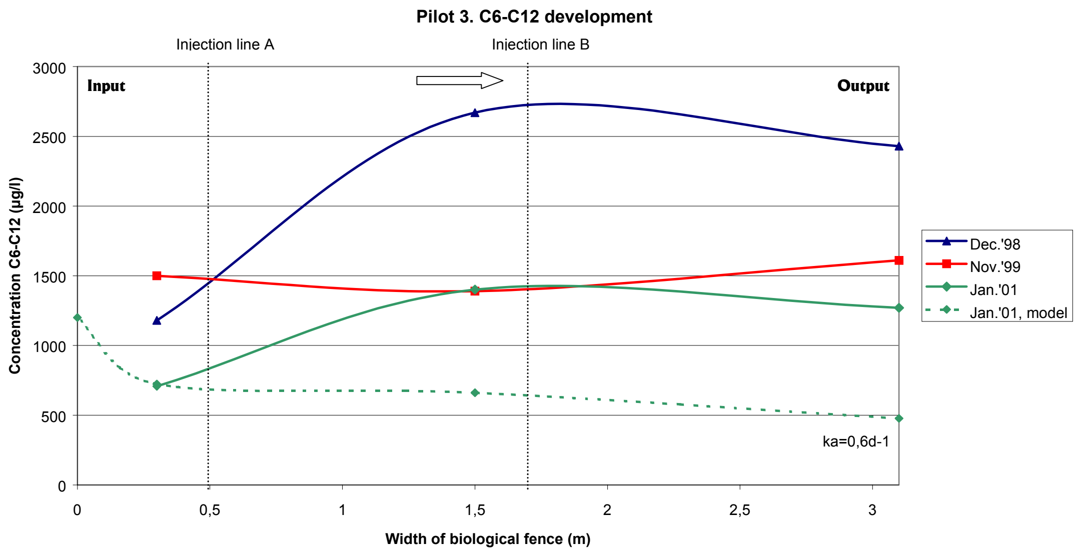


Fig. 9. C6-C12 data for fence 3.

Simulated values were plotted against measured values for January 2001 as well as for November 1999 in the figures 10, 11 and 12. The data of the monitoring wells have been used only, as we doubted the results of the measuring drains (see chapter 5). The following standard deviation was used to compare simulated values with measured values:

$$s = \sqrt{\frac{\sum((\text{measured } X_i / \text{simulated } Y_i) - 1)^2}{n}}$$

For this calculation, the measured concentration in filter 7 of pilot 3 in November 1999 was not used in the average value of the filter series 1-4-7. This concentration is an outcast in the series 1-4-7 as well as in the time series of filter 7 itself.

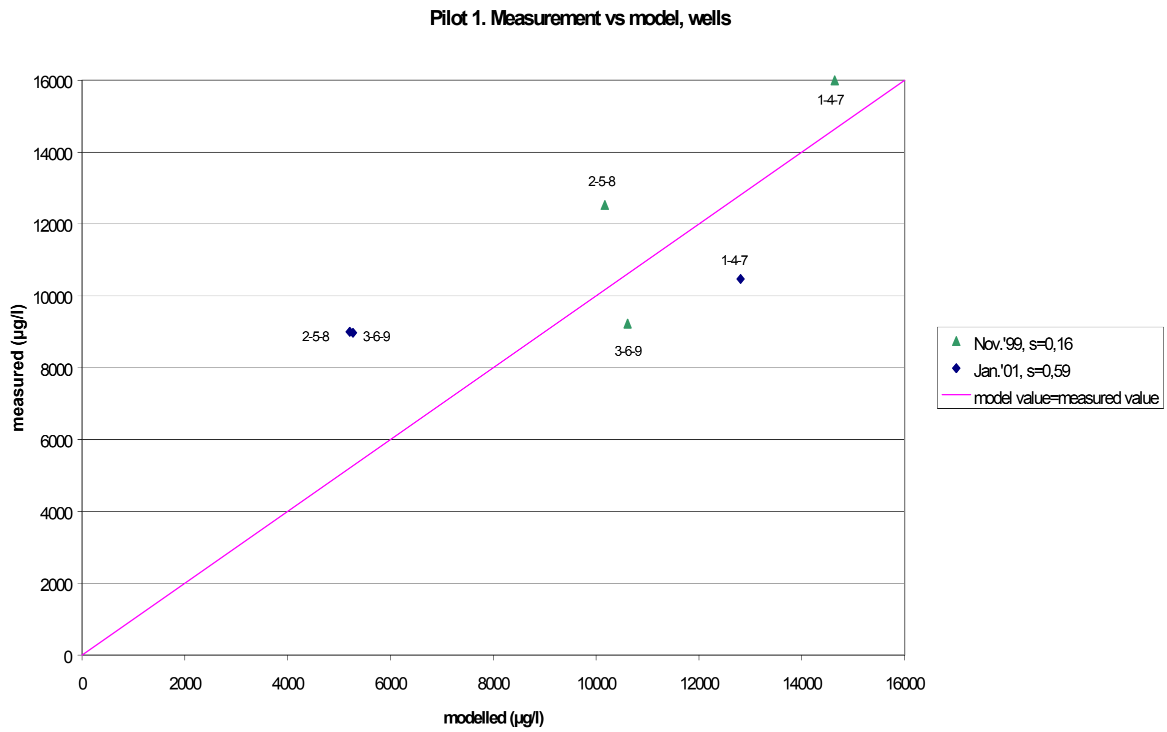


Fig. 10. Model versus measurements for C6-C12 at fence 1.

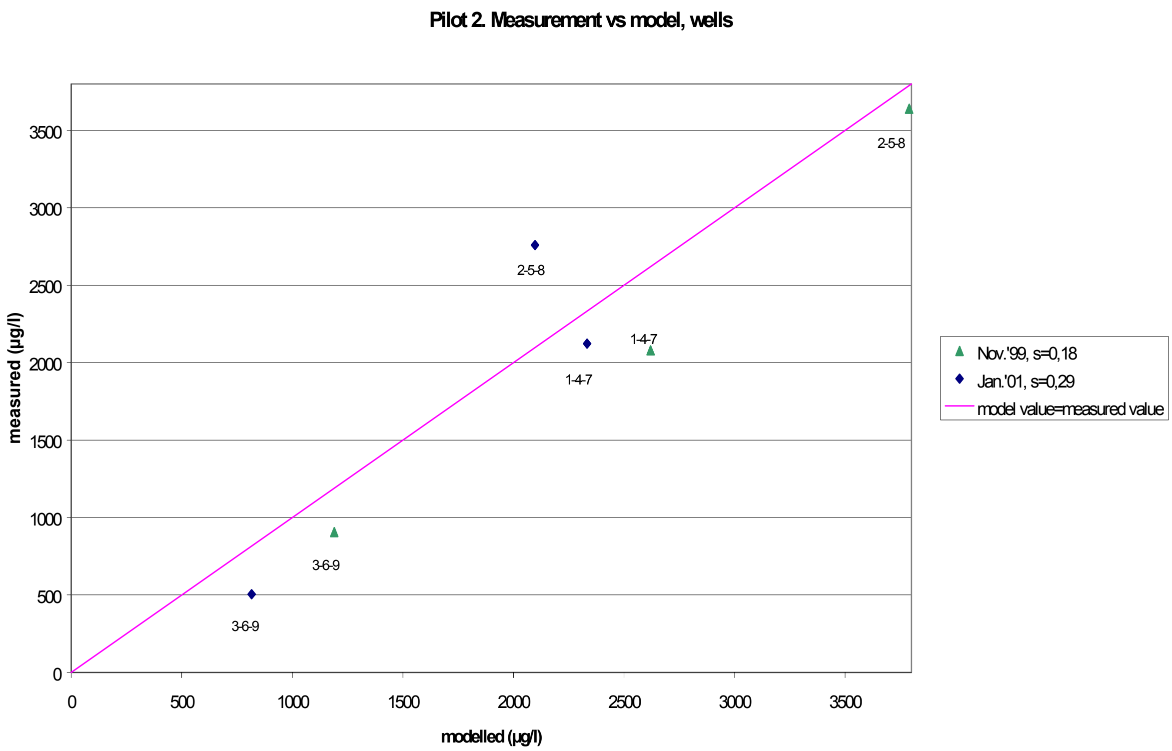


Fig. 11. Model versus measurements for C6-C12 at fence 2.

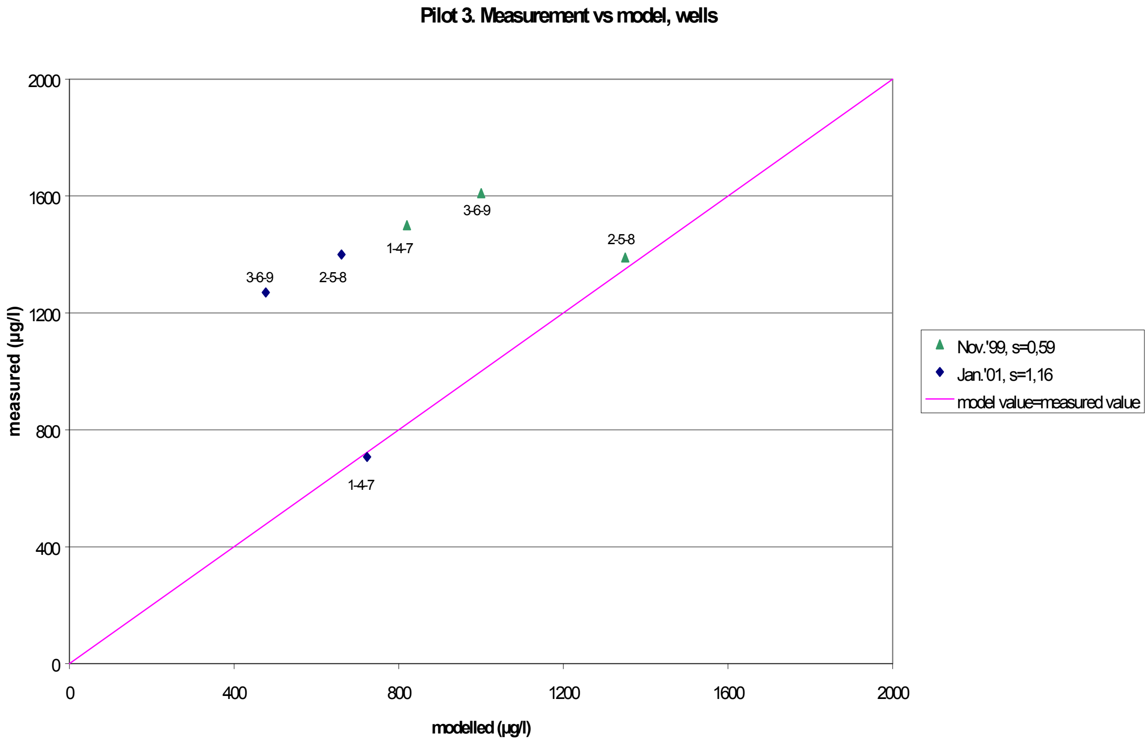


Fig. 12. Model versus measurements for C6-C12 at fence 3.

The standard deviations increased with a factor 3.7, 1.6 and 2.0, respectively for the pilots 1, 2 and 3. On these data it is concluded that pilot 2 is modelled reasonably, where the standard deviations for pilot 1 and 3 are unreasonably high.

6.3 Evaluation

The simulated concentrations in pilot 1 and 3 were much lower than the observed concentrations in the field. The input of concentrations did not increase (no concentration increase in upstream measuring points). The mismatching values for pilot 1 and 3 could be explained by decreased biological decay since November 1999. A change in environmental conditions for microbial degradation could be the reason for this. A possible explanation is a lack of nutrients (N, P). Nutrients can be needed in concentrations higher than Dutch soil can offer for complete microbial degradation, e.g. at hydrocarbon concentrations of about 5 mg/l or higher.

CHAPTER 7

OVERALL EVALUATION

Hydraulic gradient
Groundwater flew from the contaminated areas towards the harbour. The biofences appear therefore to be appropriately placed between contaminant source and environmental receptor (harbour).

Oxygen and redox potential
Significant concentrations of oxygen could be demonstrated in all the biofences. The applied amount of oxygen was not consumed as fast as in the start-up phase of the biofences, indicating that oxygen was not a limiting factor anymore. Oxygen concentrations were still very low in fence 2 and 3 in November 1999, whereas in January 2001 significant concentrations could be found in all fences. Oxygen changed from a limiting to a non-limiting factor in biofence 2 and 3, which could be caused by various processes that are difficult to interpret at this moment.

The input of hydrocarbon concentrations did not alter much over time, and the increase in oxygen concentration was most likely caused by internal biofence processes, such as:
- Oxidation of the solid material;
- Depletion of nutrients originating from solid matrix, thus limiting biodegradation;
- Other changes, i.e. changes in environmental communities, occurrence of preferential flow-paths, clogging of more reactive pores.

The increase in oxygen concentration is in agreement with an increasing redox potential.

Hydrocarbon concentrations
Volatile mineral oil (C6-C12) as well as BTEX concentrations decreased with 50% during passage through all three biofences, regardless large differences the influent and internal concentrations among the biofences. Most likely, the hydraulic retention time was similar in all three biofences. The similar removal in all biofences (in %) indicates that the reaction time (= hydraulic retention time) dominates the hydrocarbon removal, regardless hydrocarbon concentration and type of biofence. This rules out a possible limitation by nutrients as a cause of limited biodegradation, and a subsequent elevation of oxygen levels in the groundwater. Possibly temperature also limited the degradation.

The above argumentation is rather speculative. The way to obtain more quantitative information would be:
- Maintain operation of all biofences as before;
- Exclude all unreliable monitoring equipment from further monitoring;
- Ad some additional monitoring wells;
- Perform tracer SF6 studies, to get insight in the hydraulic retention time in the biofences. This will give information about the retention time in a biofence;
- Perform delta C measurements (isotopic ratio), to get more information about the quantitative performance of the biofences.

Oxygen concentrations and redox potentials were increasing, resulting in a more oxidised environment, thus becoming more fevourable for degradation of the hydrocarbons. This is in agreement with the results of the hydrocarbon measurement, as a decrease in concentration was found.

CHAPTER 8

CONCLUSIONS

Analysis data from monitoring wells demonstrated that the fences were biologically active, and that concentrations of the contaminants decreased over time.

The same conclusion could not be drawn from data of the measuring drains. This was most likely due to the limited flush volumes before sampling the measuring drains as a cause of a high flush resistance. This probably leads to less representative values for the measuring drains. Furthermore, the results of measuring drains and monitoring wells are difficult to compare, as each of them represents a different part of the soil: a vertical versus a horizontal part of the soil. As a result of the discrepancy between measuring drains and monitoring wells, the conclusions are drawn separately, and the conclusions of the monitoring wells are regarded as representative for the operation of the three biofences.

Monitoring wells

- Oxygen concentrations in the monitoring wells increased since November 1999 to values of 1.3 mg/l and higher;
- Redox potential values showed a moderate increase in the monitoring wells from -110 mV to -60 mV;
- Concentrations of contaminants were higher in the monitoring wells than in the measuring drains;
- Volatile mineral oils (C6-C12) were the main contaminants in the fences (16,000 µg/l);
- Volatile mineral oil (C6-C12) concentrations in the biofences decreased since the start of the infiltration to average concentrations of 9500, 1800, and 1100 µg/l for fence 1, 2, and 3, respectively;
- BTEX concentrations were relatively low compared to the mineral oil concentrations;
- BTEX concentrations in the biofences increased slightly, and average concentrations were 150 µg/l;
- Based on the hydrocarbon data, fence 1 showed the largest decrease in concentration; a decrease from 17,000 µg/l in December 1998 to 9,000 µg/l in January 2001 was observed. However, this was also the highest contaminated fence;
- The simulated data concentration development of C6-C12 showed a larger decrease from December 1998 to November 1999, than the measured data of November 1999 to January 2001. A lack of nutrients, slow oxygen transfer or a short reaction time in the fences could be the reason for this.

Measuring drains (results are less conclusive)

- Oxygen concentrations in the measuring drains increased sine November 1999 slightly to an average concentration of 1 mg/l, which is consistent with the increase in oxygen concentrations;
- Redox potential values did not increase, and remained at an average value of -110 mV;
- Volatile mineral oils (C6-C12) were the main contaminants in the fences;
- Volatile mineral oil (C6-C12) concentrations in the biofences were constant or even increased in fence 3. Average concentrations were 3100, 3200, and 1000 µg/l for fence1, 2, and 3, respectively;
- The concentrations BTEX were relatively low compared to the mineral oil concentrations;
- BTEX concentrations in the biofences remained fairly constant at an average concentration of 100 µg/l.

General conclusions

- The biofences are the first three pilots in Europe that have delivered quantitative data on their long term operation (2 years);
- The biofences are geohydrologically well placed between source and receptor (harbour);
- Stimulated aerobic degradation is applicable: The biofences remove about 50% of incoming contaminant concentrations. The limiting factor of the biodegradation rates in the biofences is not known;
- A low intensity system like Pernis needs to be monitored for a long time, to proof its effectiveness. Interpretation of concentration measurements when initially sorbed hydrocarbons are desorbed, are difficult;
- For future projects tracer and delta C measurements can give more quantitative information on performance.

CHAPTER 9

RECOMMENDATIONS FOR OPERATION AND MONITORING OF BIOFENCES

The project described in this report, focused on continuation of the previous phases, i.e. monitoring the degradation processes. Interpretation of the data and specifically understanding the differences between the three fences based on operation (practical) and performance (analysis data) is complicated. Based on the performance, fence 1 showed the largest decrease in concentration, but this was also the fence with the highest contamination. When calculating the decrease in percentage, the three fences acted similar. This was taken into account while recommending optimisation steps for biofences at other sites.

Based on the data obtained during this project, we feel that a good performance of the biofences was demonstrated. Decreasing hydrocarbon and increased oxygen concentrations were shown, and hydraulic head data showed that the fences were properly situated. Hence, we think that the operation and monitoring of similar biofences should focus on optimisation of the operation of the biofences, while using a vertical injection system, combined with additional monitoring tools.
The optimisation possibilities that were concluded at the workshop of June 2000, are discussed below:

Possible adjustments in the management of the system

Adjustment	Argumentation
Increase of the dynamics of oxygen addition / flow rate	Intermitting addition of air, combined with an increased injection rate. This will improve the mixing and dynamics of the system.
Addition of nutrients	Stimulation of microbial activity. Only usefull if nutrients are limited (has to be measured).
Vertical filters in gravel drain (in fence 2)	These are needed for a comparison between a 'clean' and contaminated fence.

Possible adjustments in the monitoring possibilities

Adjustment	Argumentation
Omitting measurements of hydrocarbons in drains	Experience has shown that the reliability of the hydrocarbon measurements in the drains are doubted.
Delta C measurements (isotopic ratio)	To get more insight in the degradation processes. This was relevant during the workshop in 2000, as the demonstration of biodegradation was not that clear at that time. These data gives information whether degradation occurs at the site, and is independent from the concentration of a certain compound.
Infiltration of SF6 as a conservative tracer	Gives information about the partition in the biofences and can be related with oxygen partition at the side. Results from our project have shown that increased concentrations of oxygen have been found, but information about the hydraulic retention time will still be valuable.
Measuring nutrients in groundwater	To check whether nutrients are a limiting factor.
Soil samples	Indication whether the concentration in the groundwater of the fences are influenced by the concentrations in the soil. Basically, this indicates the net flux of contaminants with the groundwater and the disturbance of soil contaminants.
Extra monitoring filters, also upstream of the infiltration zone (reference points)	Gives information about the dissolution from BTEX that is absorbed to the soil in the fences.
Analyses of oxygen in the drain	To check whether oxygen reaches the infiltration drain. Not needed if increased oxygen concentrations are found in the monitoring wells.
Mesocosms	To follow the reduction of contaminants in the fences without having the problem of heterogeneity.

LITERATUUR

Heijnen, M., T. F. Praamstra, H. Kuik, and I. A. Westerman. 2000. Biological fence at the site of Shell Netherlands Refinery: Project evaluation Nobis 96-1-3. Nobis.

APPENDIX A

MINUTES WORKSHOP

Besprekingsverslag

Onderwerp:
Workshop Biohek d.d. 6 juni 2000 te Gouda (SKB)

Steller:
Staps

Aanwezig:
Vermeulen, Satijn (SKB), Breukink, Praamstra (Iwaco), De Jongh (Shell), Schelwald (Gemeentelijk Havenbedrijf Rotterdam), Pijls (Tauw), Hullegie (HMVT), Vreeken (BMS), V.d. Velde (TTE), Vis (Ecotechniek), Rijnaarts (voorzitter) en Staps (TNO)

Samenvatting besprekingsverslag

Als inleiding voor de workshop werden de geschiedenis van het project en de projectervaringen gepresenteerd.

Vervolgens reageerden de vier externe deskundigen hierop. Belangrijke aspecten waren hierbij onder meer:

- liggen de drains daar waar ze worden verwacht en horizontaal?
- de algemene voorkeur voor verticale, meer flexibele systemen;
- het relatief lage injectiedebiet in combinatie met de continue beluchting;
- het verbeteren van de luchtverdeling;
- de afbraaksnelheid en de massabalans;
- het uitvoeren van stijghoogtemetingen.

Hierna werden vanuit het consortium mogelijkheden geschetst om inzicht te verkrijgen in het functioneren van het systeem en in mogelijkheden voor verdere optimalisatie (metingen en aanpassingen van de bedrijfsvoering)

Algemene conclusie van de workshop was dat continuering van het project zinvol is. Het consortium zal bij SKB een voorstel indienen voor het uitvoeren van twee vervolgfases:
1. een volgende monitoring ronde en het op stellen van een massabalans (af te sluiten met een go / no go moment);
2. vervolgonderzoek, eventueel na een optimalisatiestap.

De externe deskundigen zullen ook bij het vervolg van het project worden betrokken.

Introductie (Huub Rijnaarts)

De agenda voor de workshop is als volgt:
1. Introductie
2. Projectervaringen
3. Reactie externe deskundigen
4. Ideeën voortzetting onderzoek
5. Afsluitende discussie.

Doel van de workshop is met behulp van externe deskundigen antwoord te krijgen op de volgende vragen:
- is continuering zinvol?
- zo ja:
  - wat kunnen zinvolle elementen bij continuering zijn?
  - is zo'n continuering voldoende interessant voor financiële ondersteuning door Shell GHR/ SKB (eventueel buiten workshop te behandelen)?
  - is een blijvende interactie met de groep van deskundigen wenselijk / mogelijk?

TNO zal als penvoerder van het eventuele vervolgproject een verslag van de workshop opstellen.

Projectervaringen (De Jongh, Praamstra, Vis)

Vanuit het projectteam wordt inzicht gegeven in de locatiespecifieke situatie en de aangelegde biologische hekwerken. Na de aanleg van de hekken is voor Shell veel meer bekend geworden over de geohydrologische situatie ter plaatse. Nu is bekend dat er lokaal veel minder water afstroomt dan er eerder werd aangenomen. Feitelijk beheerst het hekwerk slechts de eerste 10-15 m naast de haven. Voor de verontreinigingssituatie op de site is de relevantie van het hekwerk daarom beperkt, maar het is wel een ideale testlocatie (onder meer vanwege de aanwezigheid van een afscheidende laag). Binnen het Europoort-gebied geldt dat naarmate een locatie dichter bij zee ligt, in het algemeen minder klei aanwezig is en er daarom meer infiltratie van grondwater naar de haven zal plaatsvinden.

Ter plaatse van de hekken is een grondverontreiniging aanwezig, welke het beeld vertroebelt; resultaten kunnen nu pas in beeld komen nadat een substantieel deel van de grondverontreiniging is verwijderd.

Er bestaat een aantal onzekerheden met betrekking tot de aangelegde horizontale drains; mogelijk
- liggen deze
  - gedeeltelijk in klei
  - niet geheel horizontaal
- liggen de meetdrains niet recht boven de luchttoevoerdrains.

Ter optimalisatie van de luchtverdeling is in de drains een inhangring (∅ 25 mm) aanwezig. Hierin zitten 15 gaatjes (∅ 2 mm) over 30 m.

De verblijftijd van de verontreinigingen binnen de hekken wordt geschat op 35-50 dagen. Hoewel de redoxpotentiaal een structurele toename laat zien, is de verhoging van het O_2-gehalte tijdens de monitoring niet consistent.

Bacterietellingen zijn niet overwogen. Hieruit zou geen zinvolle informatie worden verkregen; een toename van 10^7 naar 10^8 zegt feitelijk niets Uitgangspunt was dat het systeem zou werken; basis is de aerobe afbraak van minerale olie. Uit eerder uitgevoerde kolomtesten is gebleken dat het grondwater voldoende ondersteunende nutrienten bevat voor biologische afbraak. In de kolommen werden ijzer-oxides waargenomen. Hierbij trad geen clogging op; wel verdergaande afbraak.

Algemene beeld is dat het systeem werkt; kolomproeven, modelberekeningen en afname van concentraties van verontreinigingen wijzen alle in dezelfde richting. Problemen vormen met name de aanwezige grondverontreiniging en het feit dat geen verhoging van zuurstofconcentraties wordt gemeten.

Resterende vragen met betrekking tot de toelichting van het consortium zijn onder meer:
- In hoeverre is lucht in de grindlaag aanwezig als weerstand? Helium stroomde wel goed door.
- Bestaat er weerstand tussen de drain en het grindkoffer?
- Bestaat er extra weerstand ten gevolge van de inhanger?
- Waarom is de weerstand in pilot 2 met grind relatief hoog?

Reactie externe deskundigen

Pijls
Doel van het systeem is tot O_2-verzadiging te komen. Controle hierop vindt plaats door O_2-metingen. Het is op deze locatie moeilijk gebleken om hieruit een consistent beeld te krijgen (wisselingen in ruimte en tijd). Tauw heeft de ervaring dat na enkele weken tot maanden het O_2-gehalte structureel toeneemt. Het feit dat dat hier niet plaatsvindt wordt mogelijk veroorzaakt door de O_2-verdeling:
- liggen de drains horizontaal?
- liggen de monitoringdrains daar waar verwacht, boven de toevoerdrains?
- ontsnapt er lucht door het grindkoffer?

Overwogen kan worden het meten op de drain zelf te richten: daar meetpunten aan te brengen en de verdeling van de lucht in beeld te krijgen.

Het injectiedebiet ligt laag: 0,3-0,8 m^3/uur, terwijl gebruikelijk is 5-20 à 30 m^3/uur om een voldoende groot beïnvloedingsgebied te verkrijgen. Dit is ook de ervaring van Hullegie (en tevens intermitteren). De combinatie van intermitteren en hoge debieten leidt tot drukgolven en grotere dynamiek in het systeem. Bedrijven als Biosoil en Mateboer werken ook met lage debieten, maar deze passen een dichter netwerk toe.
De reden waarom tot nu toe relatief lage debieten binnen het project zijn toegepast is:
- hiermee wordt het stripeffect zoveel mogelijk voorkomen (juist biologische afbraak wordt gestimuleerd)
- het systeem wordt zo extensief mogelijk bedreven.

Binnen de clusters van vijf verticale filters ontstaan er mogelijk voorkeursfilters. De voorkeur heeft het om de filters afzonderlijk te kunnen aansturen.

Pijls heeft uit de rapportages afgeleid dat het scherm lek is; de helft van de monitoringpunten geeft geen verlaging van de concentraties. Vanuit het consortium wordt dit genuanceerd: voor hekwerk 1 en 3 is dat niet de helft maar 30% en drie hiervan liggen stroomafwaarts en geven dus aan dat de input aan verontreinigingen plaatselijk is toegenomen. Aanvullende monitoringrondes zullen hier meer duidelijkheid in brengen.

Vreeken
Ziet de luchtverdeling als het grote probleem. De combinatie van lage debieten en een heterogene bodem zal voor de zuurstofverdeling waarschijnlijk leiden tot een onregelmatig verdelingspatroon. Waarschijnlijk heeft de inhanger weinig invloed; de lucht concentreert zich op enkele plaatsen met de minste weerstand. Een mogelijke oplossing zou kunnen bestaan uit een toepassing van een drain met hoge weerstand, waardoor een gelijkmatiger luchtuittreding wordt bewerkstelligd.

Ook voor het verticale systeem kan de luchtverdeling een probleem zijn. Hier spelen afsluitende lagen een grotere rol, hetgeen zou kunnen worden ondervangen door de toepassing van filters met hoge weerstand of filters op verschillende niveaus.

Indien van de huidige infrastructuur moet worden uitgegaan, wordt aanbevolen om te intermitteren met hoge debieten. In totaal is dan 50 m3/filter mogelijk. Deze hoeveelheid wordt nu verdeeld over acht strengen.

Er bestaan twijfels over de berekende afbraaksnelheid. Deze is mede gebaseerd op een aangenomen organisch stofgehalte verdelingscoëfficiënt in de bodem. Een directere methode is om deze snelheid vanuit het oliegehalte in de grond te bepalen.

Hullegie
Is in het algemeen niet gecharmeerd van horizontale systemen. Áls gekozen wordt voor een horizontaal systeem, dan beter kortere stukken achter elkaar (de hier toegepaste lengte van 30 m is lang; bij grotere debieten wordt toch het punt met de minste weerstand gezocht; 5 - 10 cm hoogteverschil heeft al grote invloed). Met een horizontale drain is ook hier weinig dynamiek te bewerkstelligen. Zijn de horizontale systemen nog wel zinvol?

Liever verticale filters op verschillende niveaus, intermitterend, met veel variatie in het onttrekkingsregime.

De mate van vrachtverwijdering is onbekend; wellicht is meer dan 90% uit de grond verwijderd. Hierbij is de verwijderingssnelheid van C6-C12 van een zelfde grootte-orde als die van componenten >C 12. Belangrijk is het bepalen van het werkelijke effect op de massa in de bodem; een massabalans maken om een beter fingerspitzengefühl te krijgen bij het systeem. Wellicht is nog maar een promille afgebroken? Dit wordt door anderen onwaarschijnlijk geacht.

Resterende vragen:
Zijn maatregelen noodzakelijk nabij de kade? Zou daar een nieuw hekwerk moeten worden geplaatst? De vraag is of het uittreden van verontreinigingen (transport vanuit grondwater richting oppervlaktewater) een probleem is; verwacht wordt dat ook buiten het grondwater afbraak zal plaatsvinden.

V.d Velde
V.d. Velde vraagt naar de uitvoering van stijghoogtemetingen. Er is niet gemeten aan de relatie luchtinjectie / drukopbouw. Deze metingen zouden interessant kunnen zijn, omdat ten gevolge van de luchttoevoer een zone kan ontstaan met verhoogde weerstand, waarbij de transportsnelheid kan afnemen ten opzichte van de natuurlijke situatie. Lucht zal immers de meest doorlatende plaatsen in beslag nemen. Hullegie heeft een dergelijk effect echter nooit waargenomen; het hydrologisch effect valt mee.

Onduidelijk is wat er ter plaatse van het grindkoffer gebeurt. Praamstra: mogelijk vindt hier minder O_2-overdracht plaats ten gevolge van de grotere diameter van luchtbellen. Overwogen kan worden om verticale filters in het grindkoffer te plaatsen.

Ideeën voortzetting onderzoek (Staps)

Vanuit het consortium worden onderwerpen gepresenteerd voor het vervolgonderzoek. Deze spitsen zich met name toe op langduriger monitoring en speciale metingen.

Langduriger monitoring
Motivatie voor langduriger monitoring:
- effectiviteit pas aantoonbaar op langere termijn (jaren);
- nalevering ten gevolge van het feit dat de hekken in verontreinigde grond staan;
- er zijn nog relatief weinig metingen uitgevoerd.

Zinvol wordt bovendien gezien het plaatsen van een extra monitoringfilter als blanco referentiepunt (stroomopwaarts van de hekken). Hierdoor kunnen de resultaten uit de biohekken worden vergelen met de situatie zonder luchttoevoer.

Speciale metingen
Uitgaande van de resterende vragen kunnen de speciale metingen worden toegespitst op het inzicht verkrijgen in de verspreiding van O_2 of in het aantonen van biodegradatie.

Verspreiding van O_2:
- SF6 als conservatieve tracer;
- plaatsen van sensoren voor continue metingen.

Voor het aantonen van biodegradatie zou de stabiele isotopen-methode (12C/13 C) kunnen worden ingezet.

Ten aanzien van de bedrijfsvoering wordt er van uitgegaan dat het huidige systeem blijft gehandhaafd om een zo goed mogelijke relatie tussen oorzaak en gevolg te behouden. Wel zijn beperkte aanpassingen mogelijk:
- aantal hekken;
- systeemconfiguratie;
- al dan niet intermitteren.

Na eventuele aanpassing kan weer een start-/stoptest worden uitgevoerd om inzicht te krijgen in de mate van respiratie binnen het aangepaste systeem.

Discussie

Satijn: interessant is de totale féasibility in relatie tot ander systemen; wat gebeurt er verderop (ook richting haven). Achter het hek gaat de afbraak nog door.

Het is zinvol om, hoewel het moeilijk zal zijn, in elk geval te trachten om een massabalans te maken.

Vermeulen: moet het projectjuist niet meer een andere kant worden opgestuurd; hoe kunnen we de technologie, in het kader van het optimaliseren, minimaliseren? Dit kan ook interessant zijn bij eventuele lekken in het scherm.

Het is zinvol om voorlopig met de huidige configuratie door te gaan en pas bij stagnatie de bedrijfsvoering aan te passen.

Conclusie

Ten aanzien van de besproken onderwerpen worden de volgende conclusies getrokken.

1. Continuering is zinvol.
2. Of continuering de financiële ondersteuning van de betrokken partijen waard is zal buiten deze workshop worden besproken.
3. Blijvende interactie met externe deskundigen: af en toe contact wordt door iedereen als zinvol gezien.
4. Vervolgafspraken:
    1. besprekingsverslag maken;
    2. intern overleg consortium voor vervolgonderzoek: 1 meetronde en opstellen massabalans;
    3. check met externe deskundigen;
    4. projectvoorstel indienen bij SKB (offerte voor fase 1, indicatie voor fase 2).

Vermeulen en Satijn zien een vervolg positief Hierbij wordt meegenomen dat er investeringen zijn gedaan. De algemene aanpak (workshop, betrokkenheid SKB, deelname externe deskundigen) en de open discussie is door alle betrokkenen als zeer positief ervaren.

Samenvatting van de voorstellen voor metingen:

- O_2-verdeling
- Meer meetpunten (incl. referentiepunt)
- Massabalans / afbraaksnelheid
- Stijghoogte / weerstand over filter
- Meten direct op de drains
- Isotopen (inzicht biodegradatie)
- SF6 (conservatieve tracer)

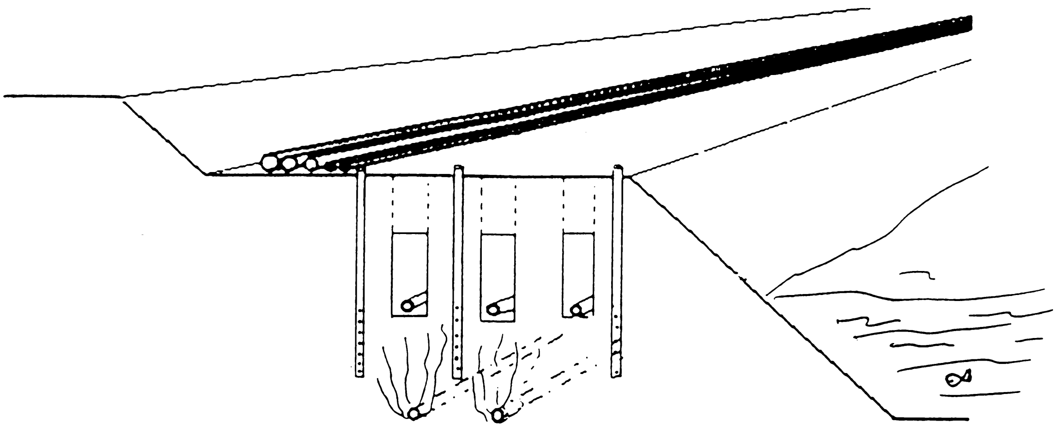
Samenvatting van de voorstellen voor aanpassing van de bedrijfsvoering:

- Verhoging injectiedebiet
- Intermitteren
- Verhoging dynamiek
- Minder clusteren
- Meer variatie over filters
- Filters op verschillende diepteniveaus
- Horizontaal systeem zinvol?
- Verticale filters in grindkoffer.

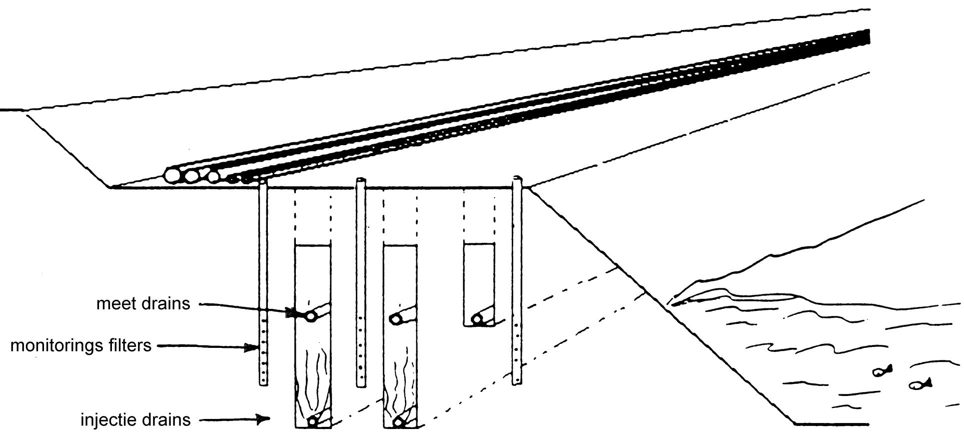
Buiten de vergadering is tussen SKB en TNO nog afgesproken dat het voorstel voor het vervolg-onderzoek in feite het eerste deel van de projectbeoordeling heeft doorlopen. De nu betrokken externe deskundigen zullen ook bij het vervolgtraject van de beoordeling worden betrokken.

APPENDIX B

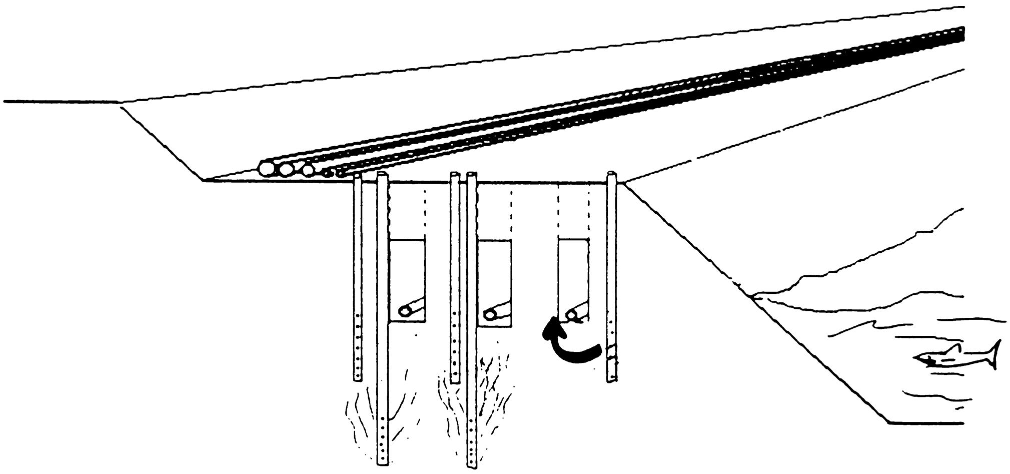
SAMPLING PORTS



Pilot 1



Pilot 2



Pilot 3

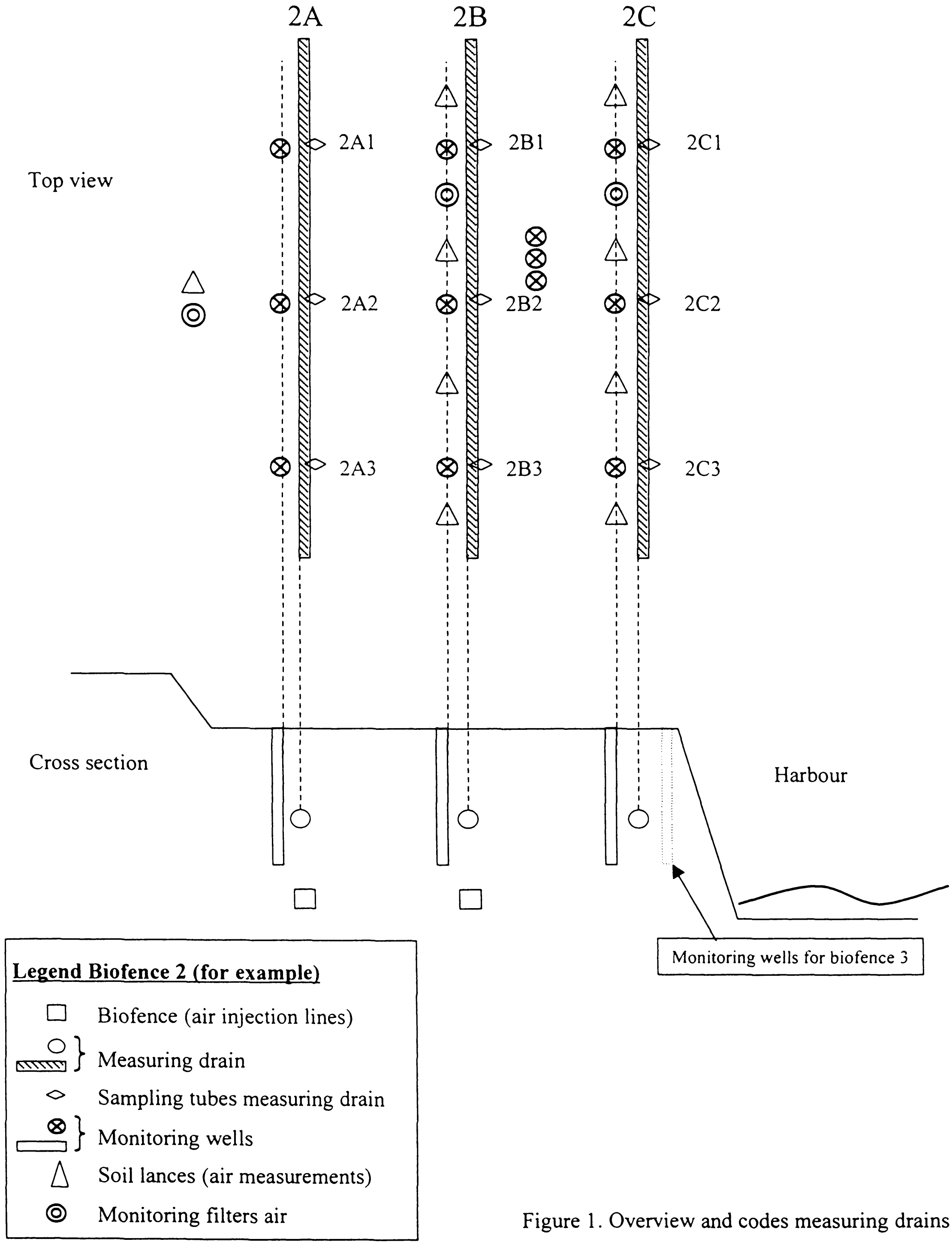


Figure 1. Overview and codes measuring drains

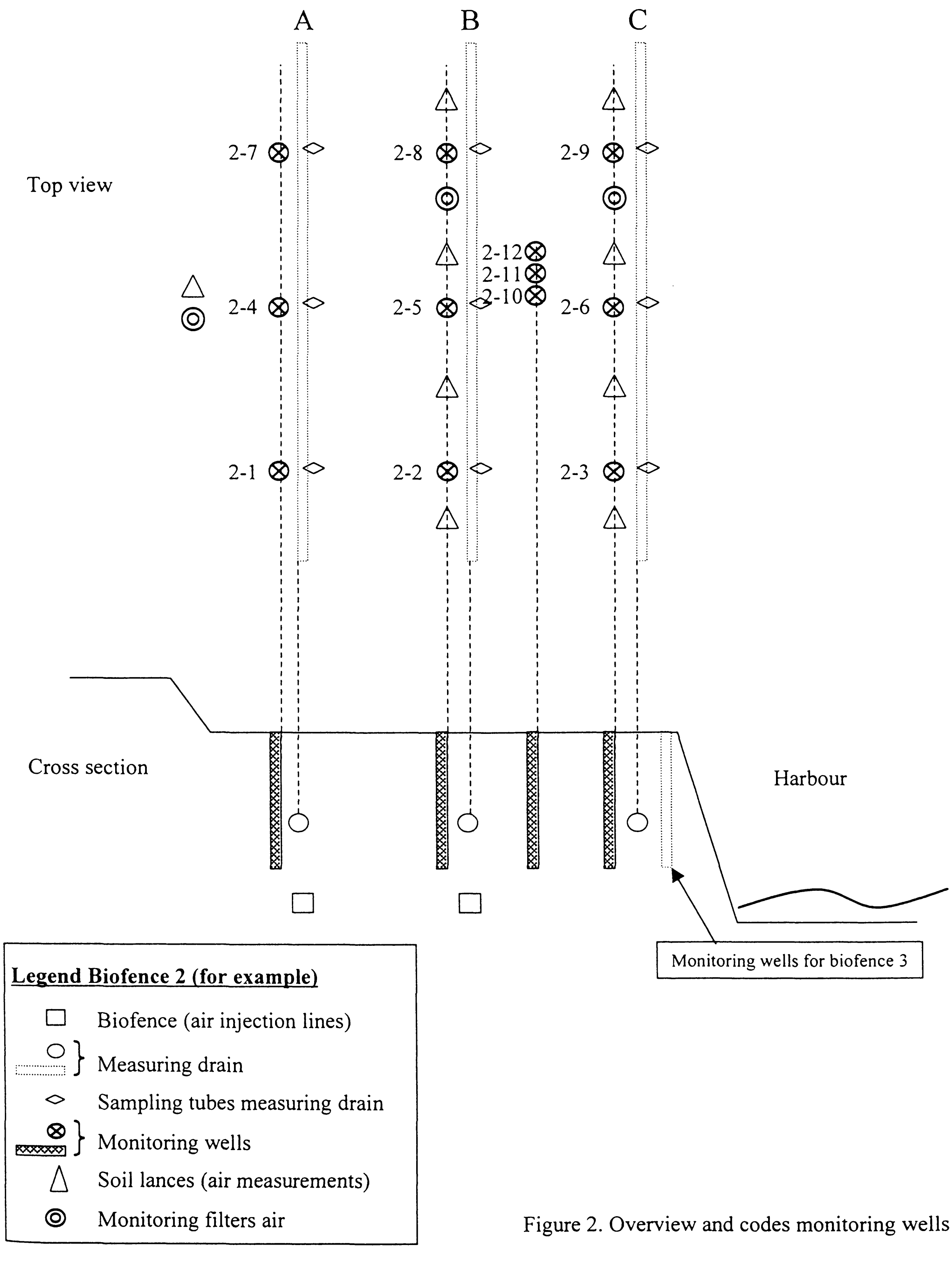


Figure 2. Overview and codes monitoring wells

APPENDIX C

GROUNDWATER LEVELS

Pilot 1

1-1	**1-4**	**1-7**
1,59	1,61	1,61
1-2	**1-5**	**1-8**
1,61	1,60	1,60
1-3	**1-6**	**1-9**
1,53	1,58	1,57
1-3 **dH** (m)	4-6 **dH** (m)	7-9 **dH** (m)
0,06	0,03	0,04
1-3 **i** (m/m)	4-6 **i** (m/m)	7-9 **i** (m/m)
0,025	0,0125	0,0167
avg **i** (m/m)		
0,0181		

Filter	TT in mNAP	Hydr. head TT	Hydr. head mNAP
1-1	3,30	1,71	1,59
1-2	3,41	1,80	1,61
1-3	3,37	1,84	1,53
1-4	3,33	1,72	1,61
1-5	3,33	1,73	1,60
1-6	3,40	1,82	1,58
1-7	3,37	1,76	1,61
1-8	3,37	1,77	1,60
1-9	3,37	1,80	1,57
1-10	3,30	3,10	0,20
1-11	3,29	1,72	1,57
1-12	3,32	1,73	1,59

Pilot 2

2-1	**2-4**	**2-7**
-	2,20	2,18
2-2	**2-5**	**2-8**
2,00	2,15	2,12
2-3	**2-6**	**2-9**
1,66	1,63	1,64
2-3 **dH** (m)	4-6 **dH** (m)	7-9 **dH** (m)
0,34	0,57	0,54
1-3 **i** (m/m)	4-6 **i** (m/m)	7-9 **i** (m/m)
0,283	0,238	0,225
avg **i** (m/m)		
0,2486		

Filter	TT in mNAP	Hydr. head TT	Hydr. head mNAP
2-1	3,45	-	-
2-2	3,48	1,48	2,00
2-3	3,51	1,85	1,66
2-4	3,39	1,19	2,20
2-5	3,43	1,28	2,15
2-6	3,43	1,80	1,63
2-7	3,37	1,19	2,18
2-8	3,37	1,25	2,12
2-9	3,46	1,82	1,64
2-10	3,37	3,21	0,16
2-11	3,40	1,45	1,95
2-12	3,39	1,40	1,99

Pilot 3

3-1	**3-4**	**3-7**
1,72	1,67	1,67
3-2	**3-5**	**3-8**
1,68	1,65	1,65
3-3	**3-6**	**3-9**
1,62	1,63	1,62
1-3 **dH** (m)	4-6 **dH** (m)	7-9 **dH** (m)
0,10	0,04	0,05
1-3 **i** (m/m)	4-6 **i** (m/m)	7-9 **i** (m/m)
0,036	0,014	0,018

avg **i** (m/m)
0,0226

Filter	TT in mNAP	Hydr. head TT	Hydr. head mNAP
3-1	3,34	1,62	1,72
3-2	3,33	1,65	1,68
3-3	3,36	1,74	1,62
3-4	3,34	1,67	1,67
3-5	3,37	1,72	1,65
3-6	3,33	1,70	1,63
3-7	3,39	1,72	1,67
3-8	3,44	1,79	1,65
3-9	3,42	1,80	1,62
3-10	3,31	3,05	0,26
3-11	3,32	1,71	1,61
3-12	3,33	1,69	1,64

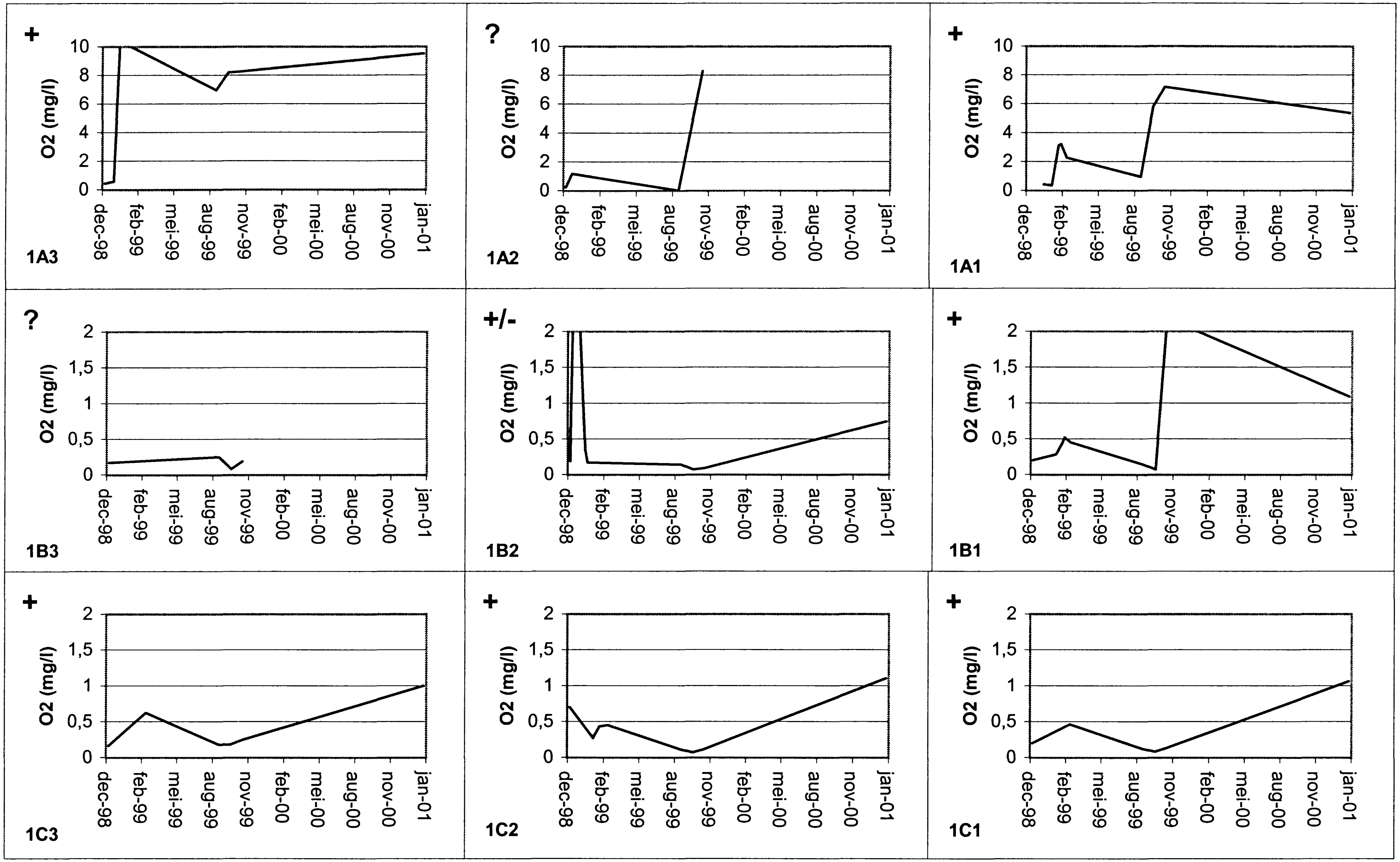
APPENDIX D

OXYGEN PROFILES

Measure drains

O_2 measurements

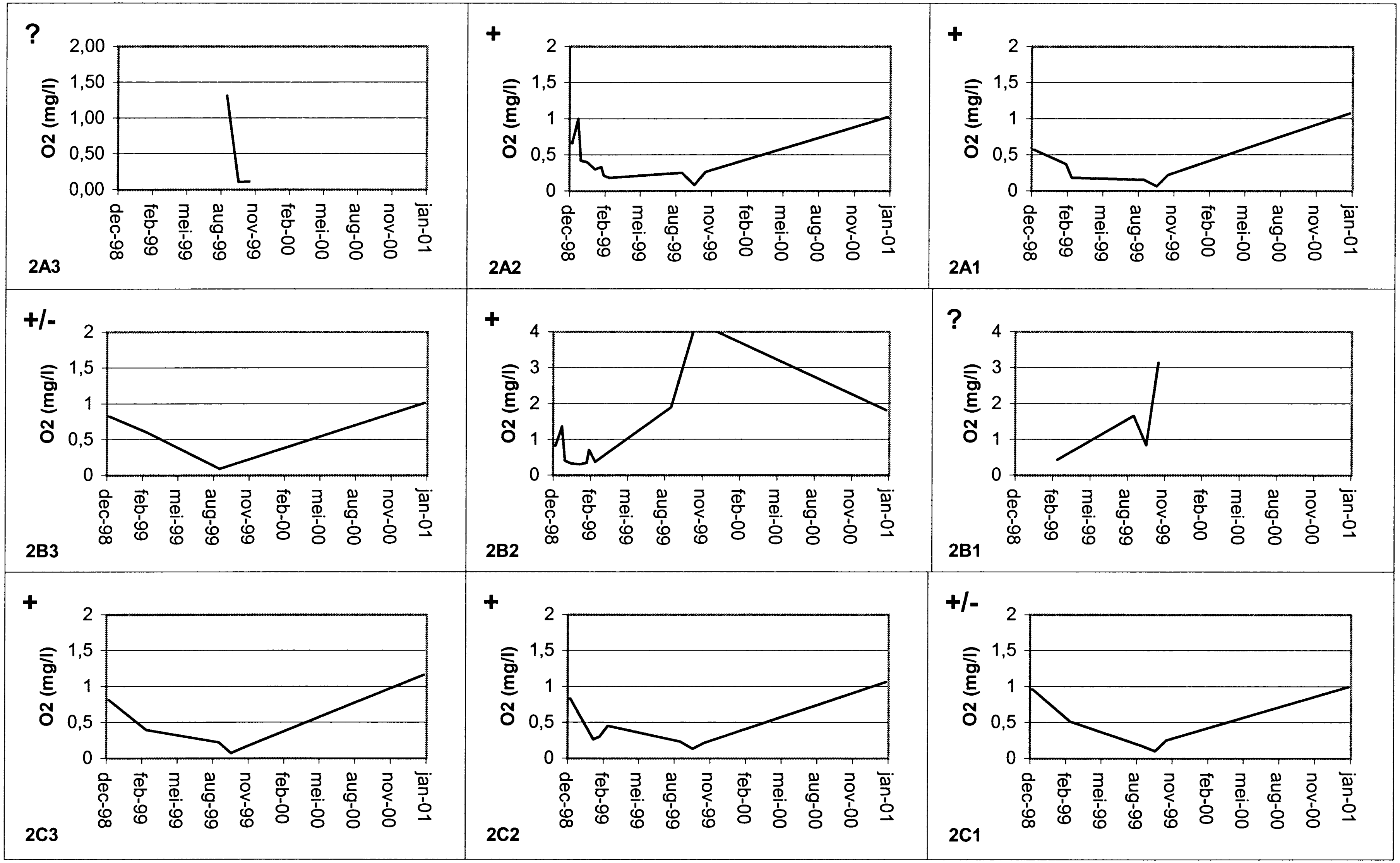
Fence 1



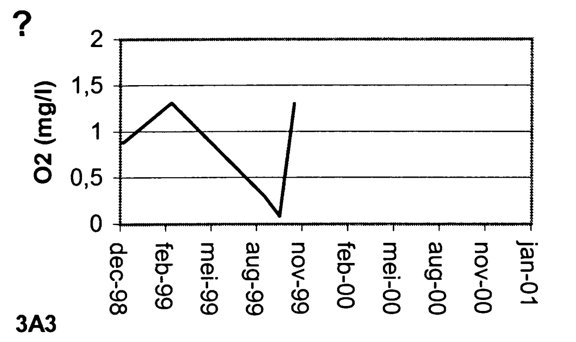
Measure drains

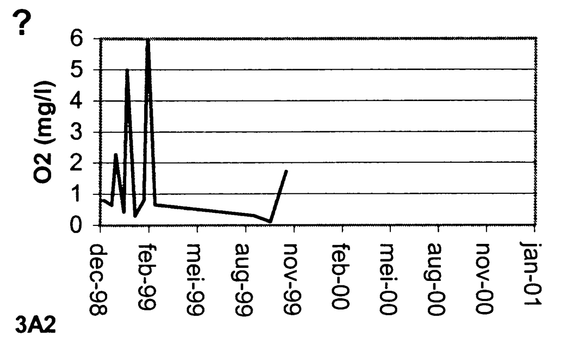
O_2 measurements

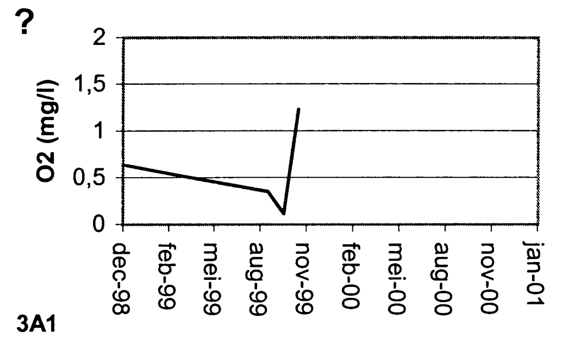
Fence 2

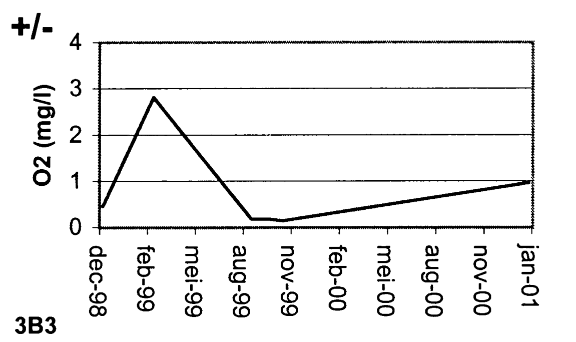


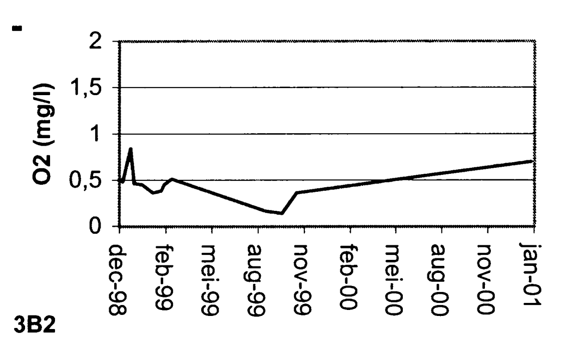
Measure drains — O_2 measurements — Fence 3

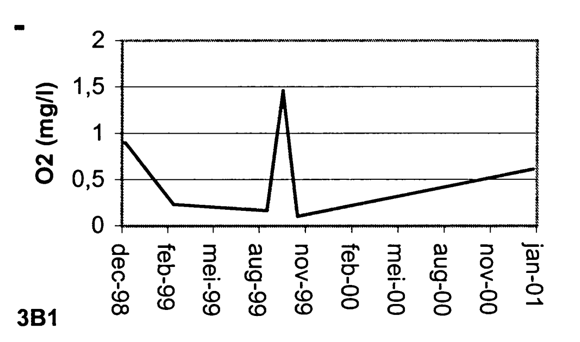




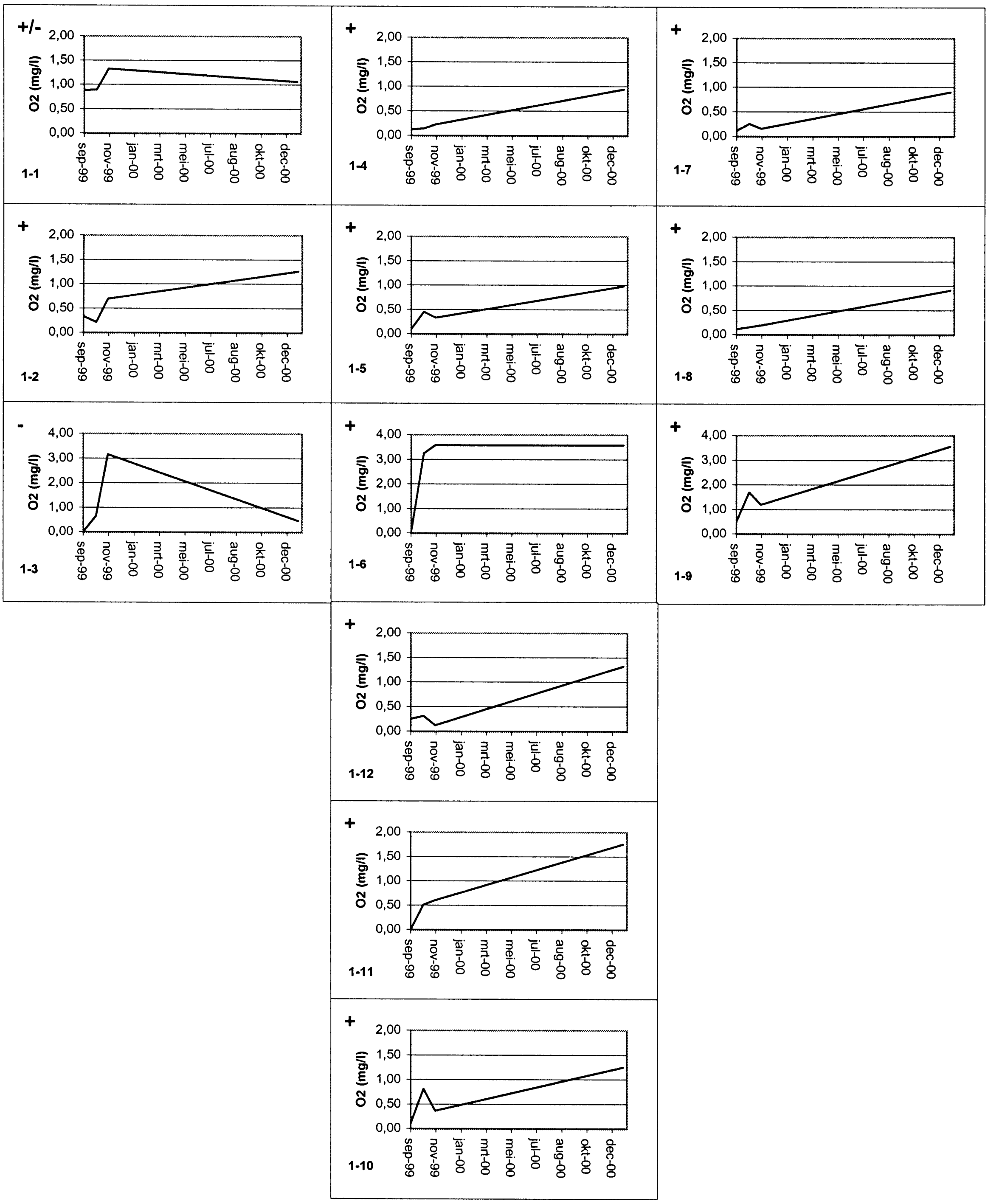




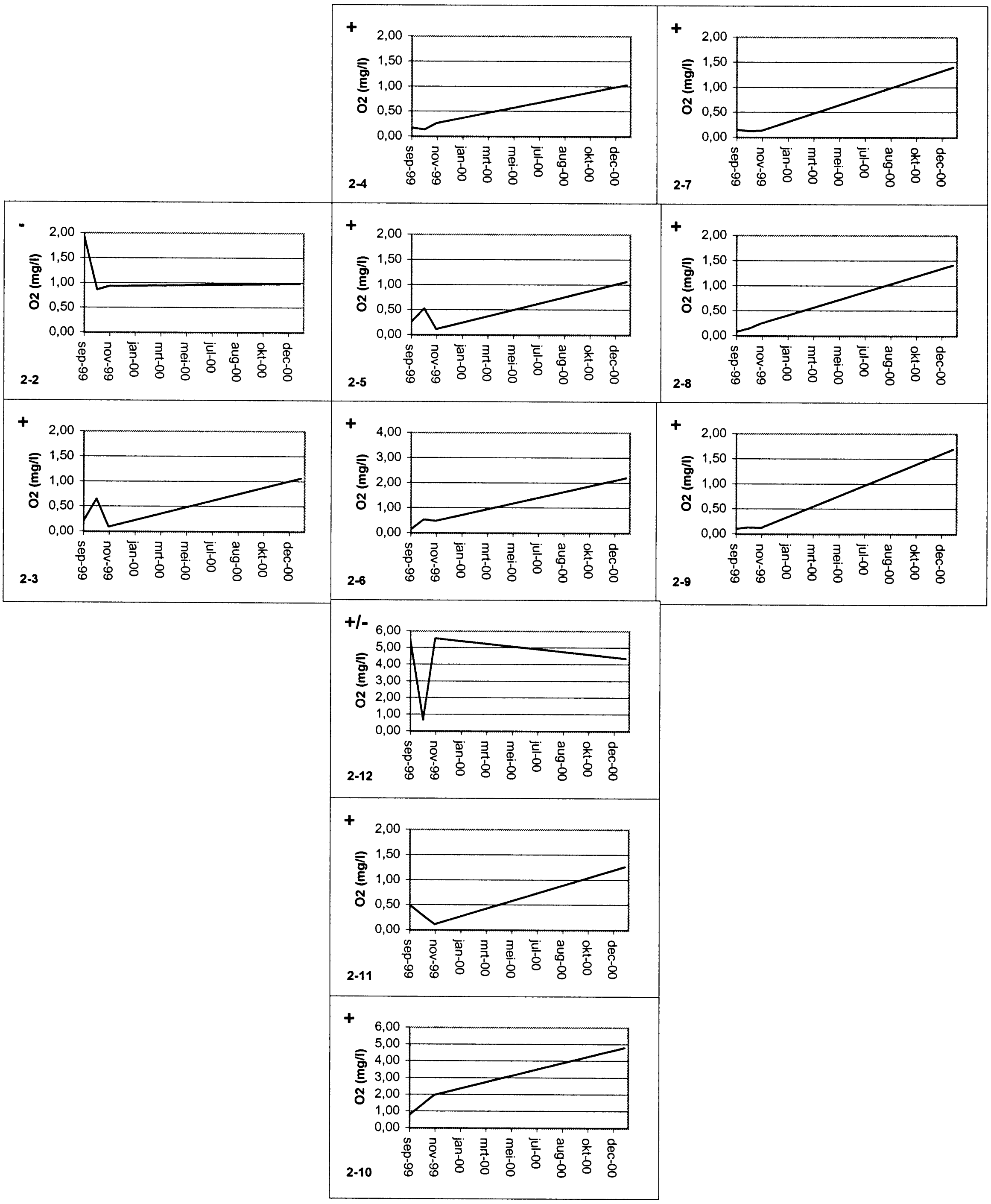




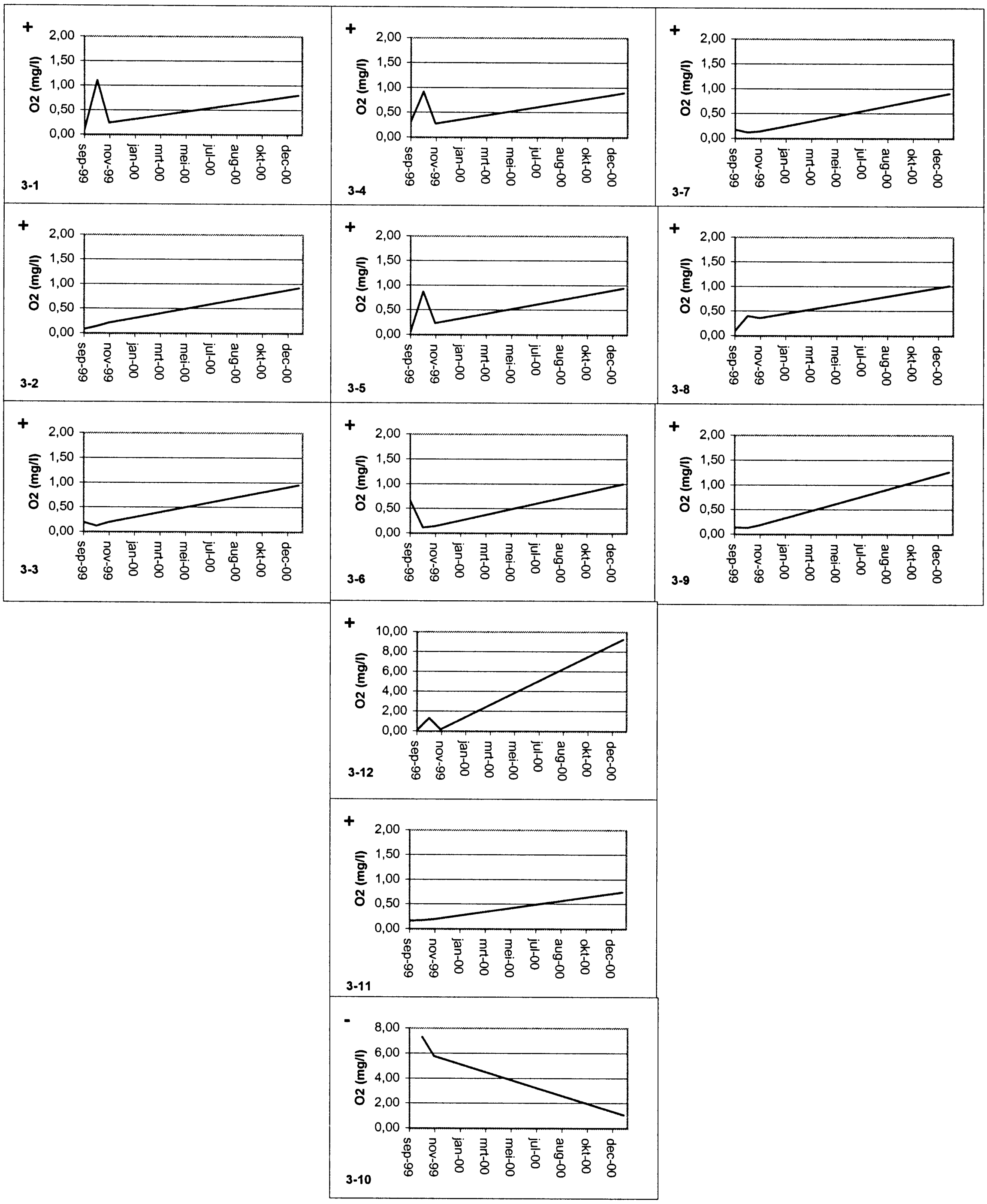
Monitoring wells O_2 measurements Fence 1

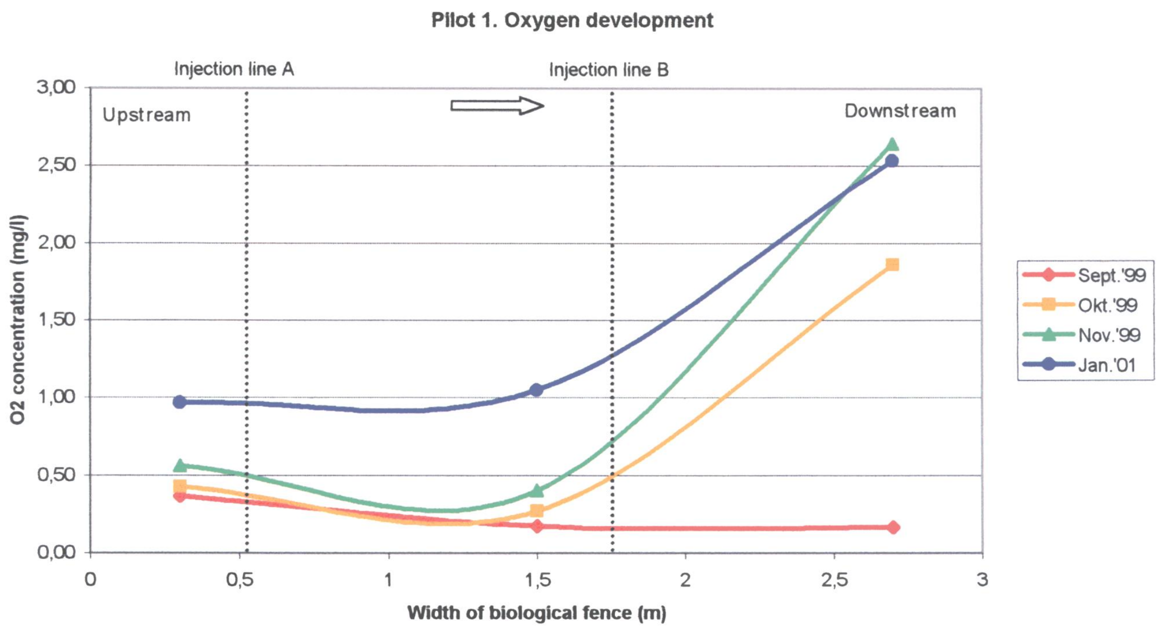


Monitoring wells O_2 measurements Fence 2

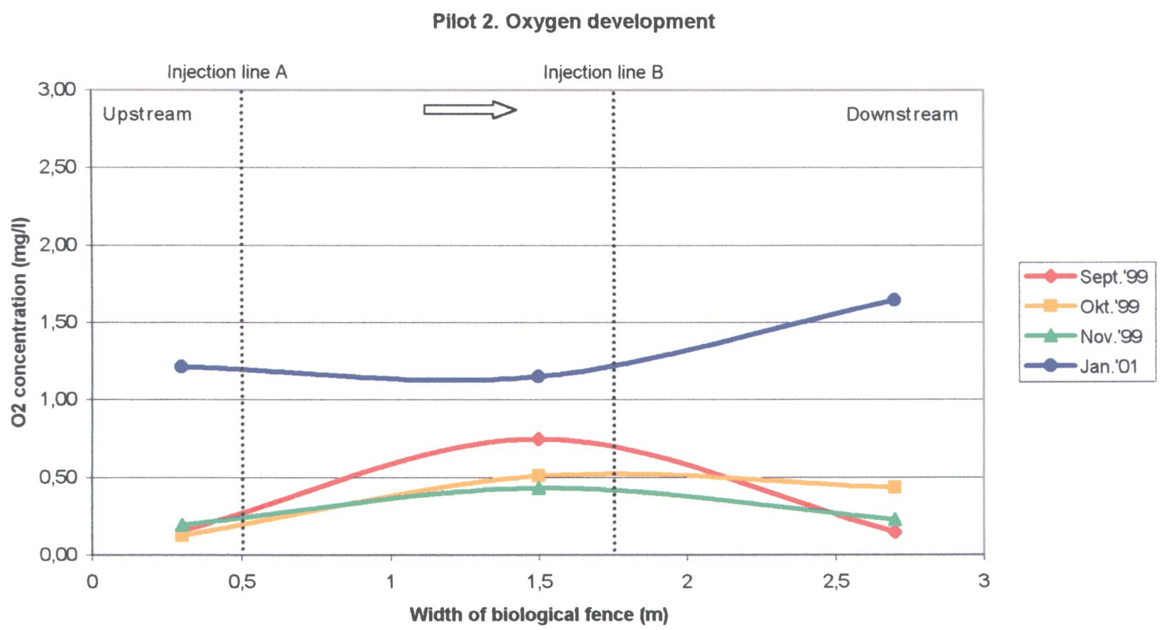


Monitoring wells O_2 measurements Fence 3

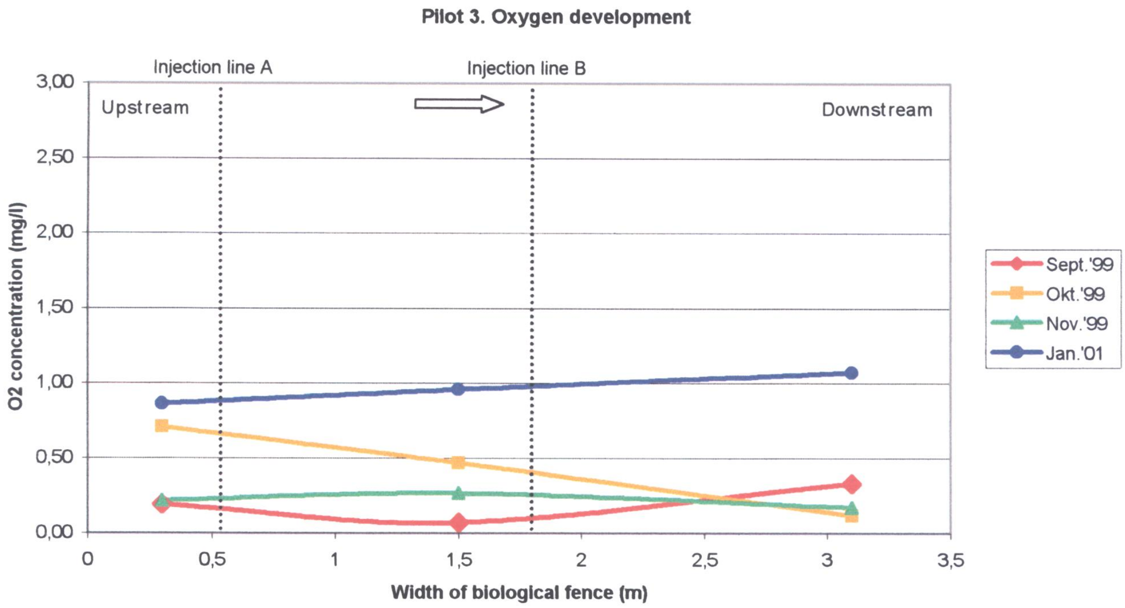




Pilot 1. Oxygen development
Injection line A
Injection line B
Upstream
Downstream
O2 concentration (mg/l)
3,00
2,50
2,00
1,50
1,00
0,50
0,00
0
0,5
1
1,5
2
2,5
3
Width of biological fence (m)
Sept.'99
Okt.'99
Nov.'99
Jan.'01



Pilot 2. Oxygen development
Injection line A
Injection line B
Upstream
Downstream
O2 concentration (mg/l)
3,00
2,50
2,00
1,50
1,00
0,50
0,00
0
0,5
1
1,5
2
2,5
3
Width of biological fence (m)
Sept.'99
Okt.'99
Nov.'99
Jan.'01

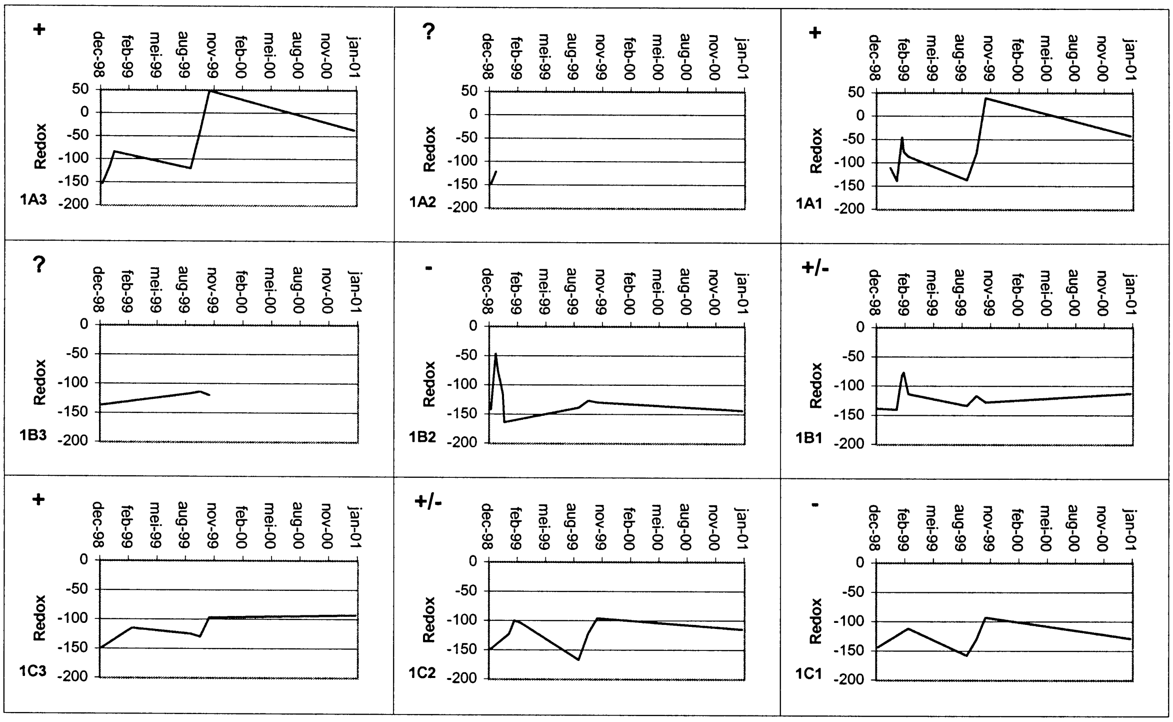


Pilot 3. Oxygen development
Injection line A
Injection line B
Upstream
Downstream
3,00
2,50
2,00
1,50
1,00
0,50
0,00
O2 concentration (mg/l)
0
0,5
1
1,5
2
2,5
3
3,5
Width of biological fence (m)
Sept.'99
Okt.'99
Nov.'99
Jan.'01

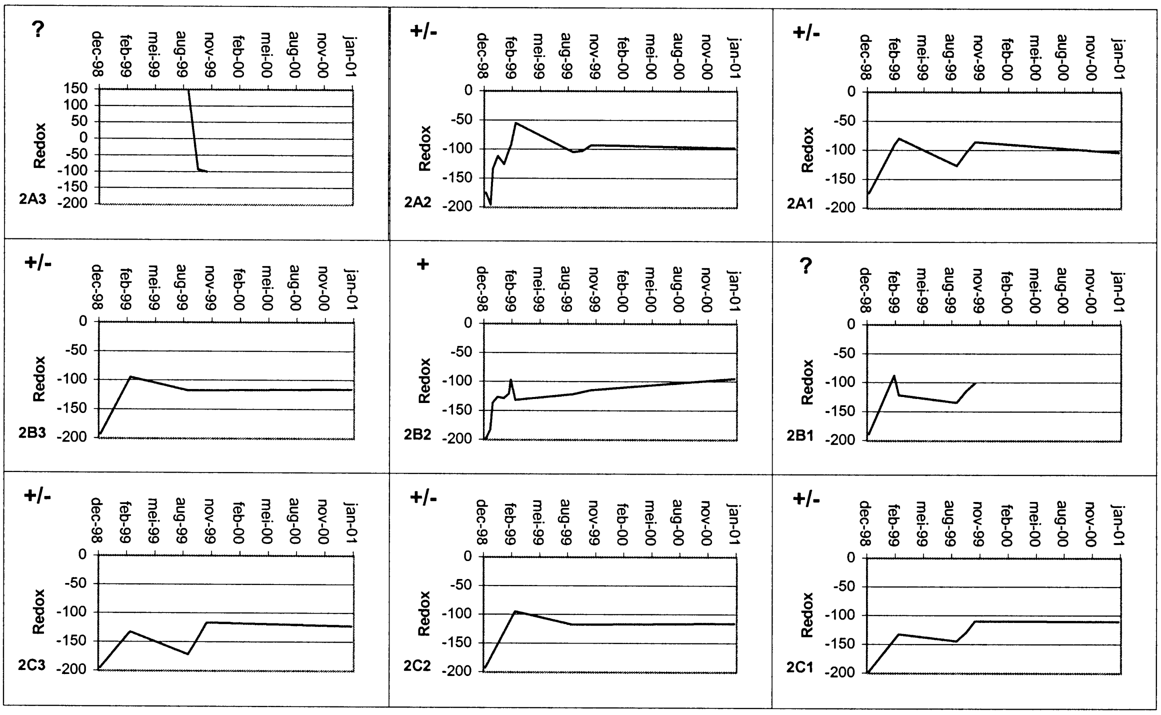
APPENDIX E

REDOX PROFILES

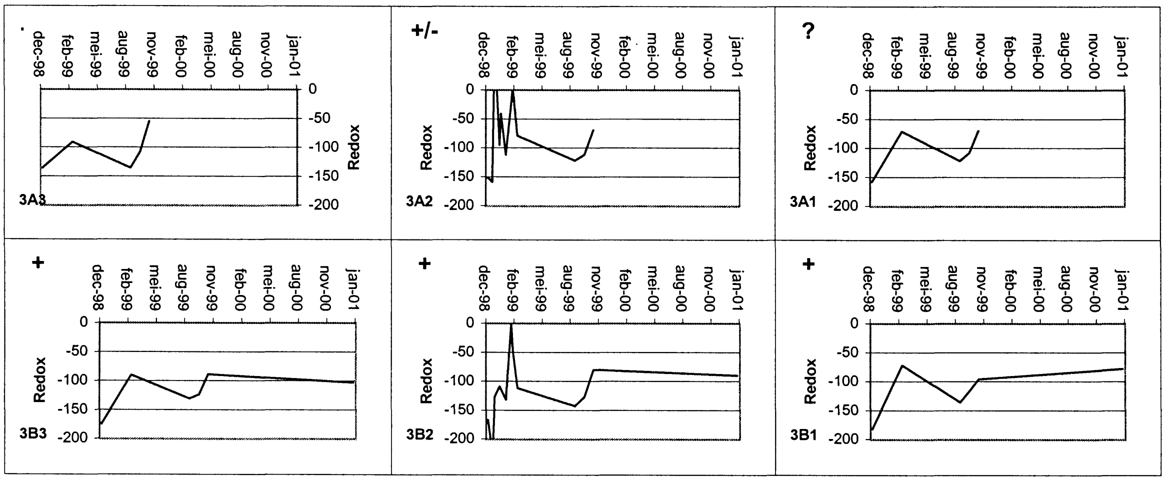
Measuring drains Redox measurements Fence 1



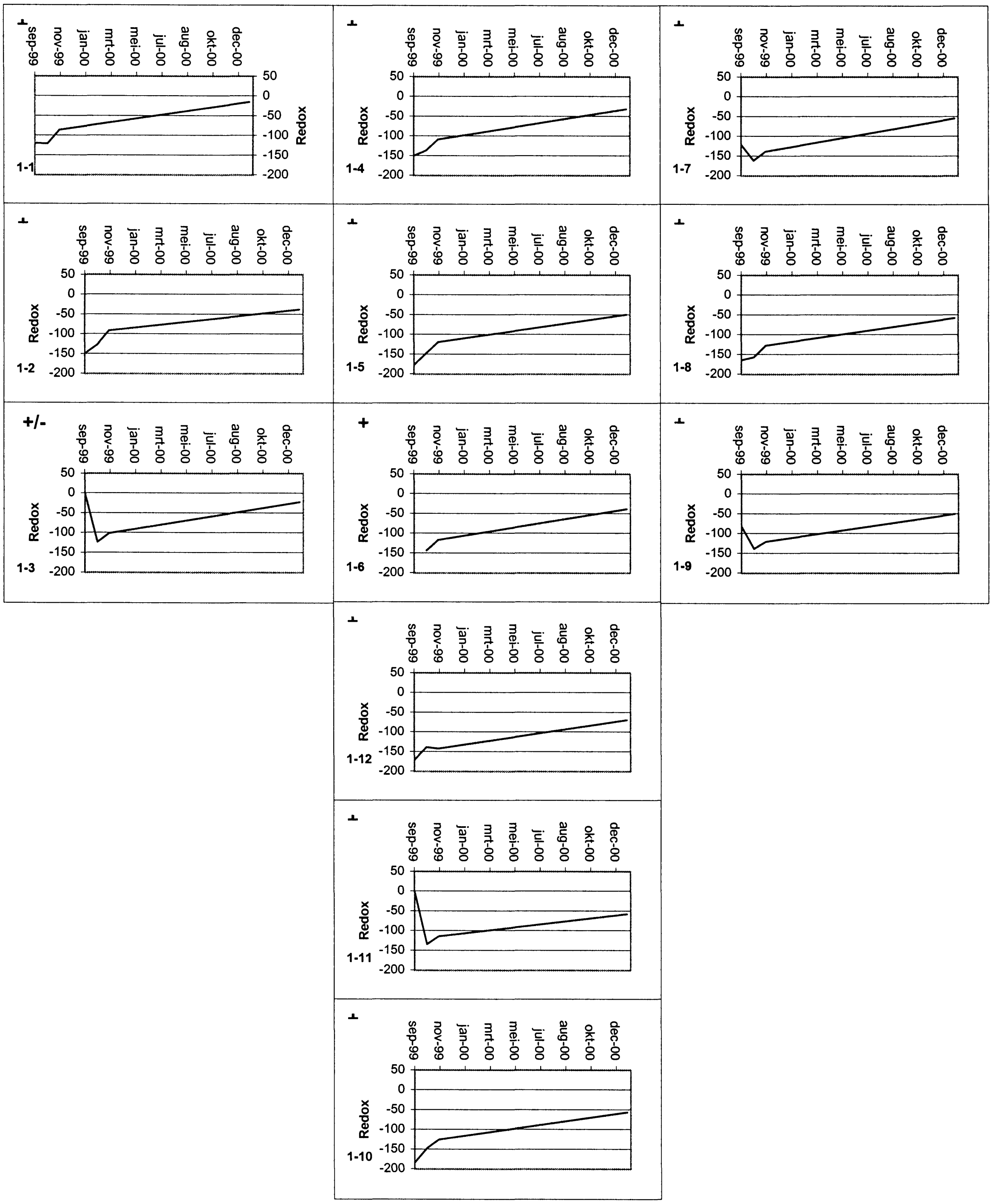
Measuring drains Redox measurements Fence 2



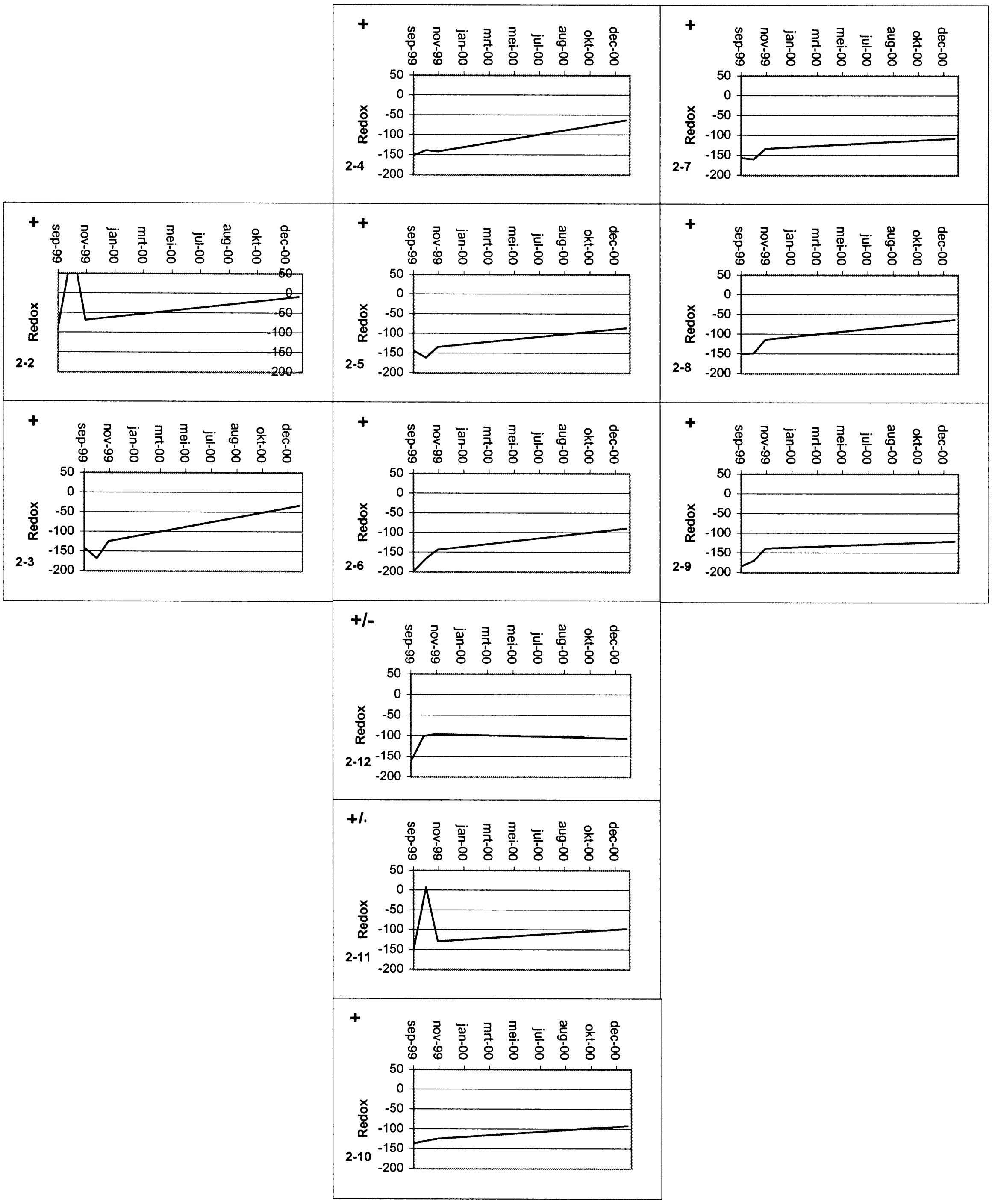
Measuring drains | Redox measurements | Fence 3



Monitoring wells Redox measurements Fence 1



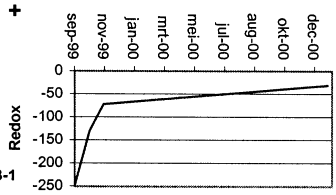
Monitoring wells   Redox measurements   Fence 2



Monitoring wells | Redox measurements | Fence 3

+

3-1



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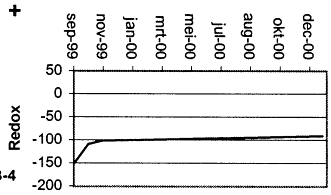

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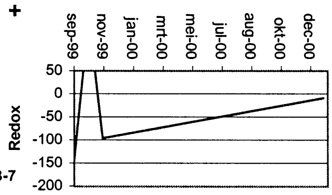

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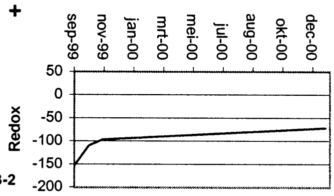

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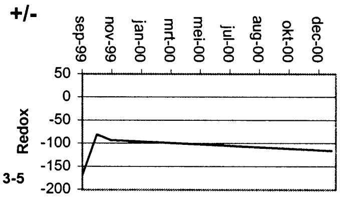

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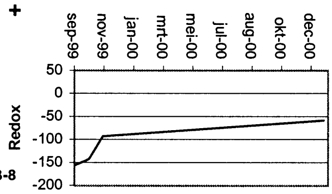

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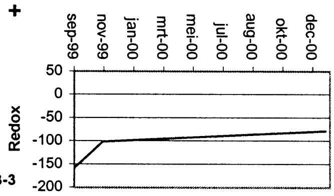

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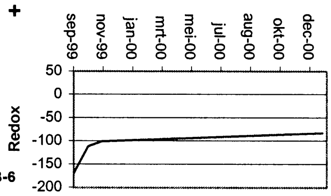

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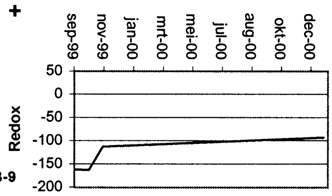

+/-

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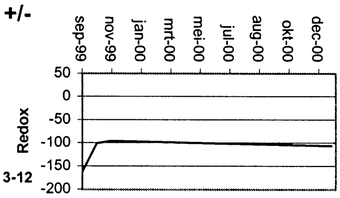

+/-

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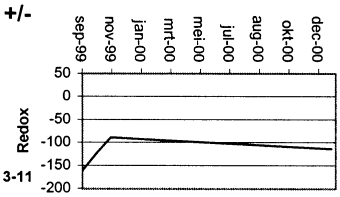

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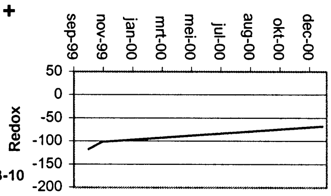
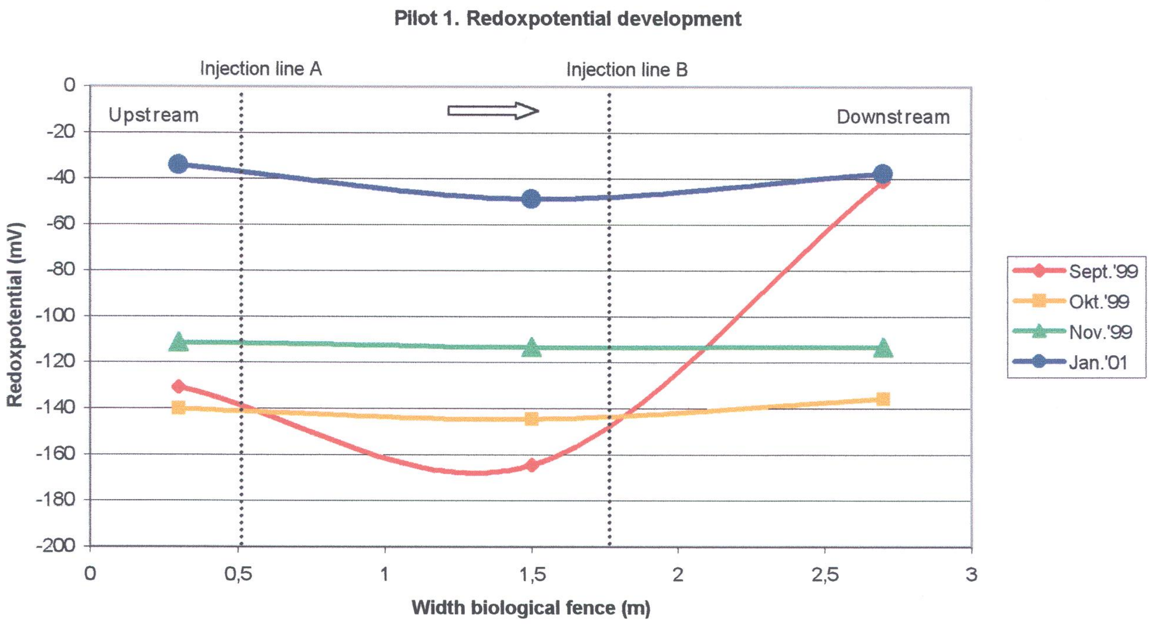
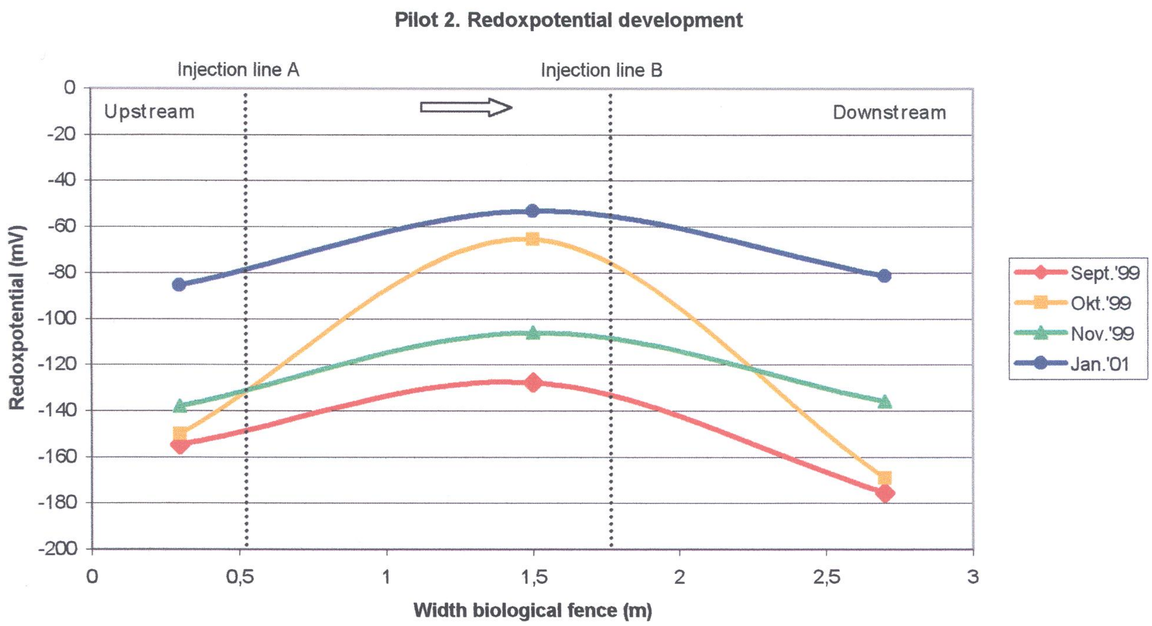
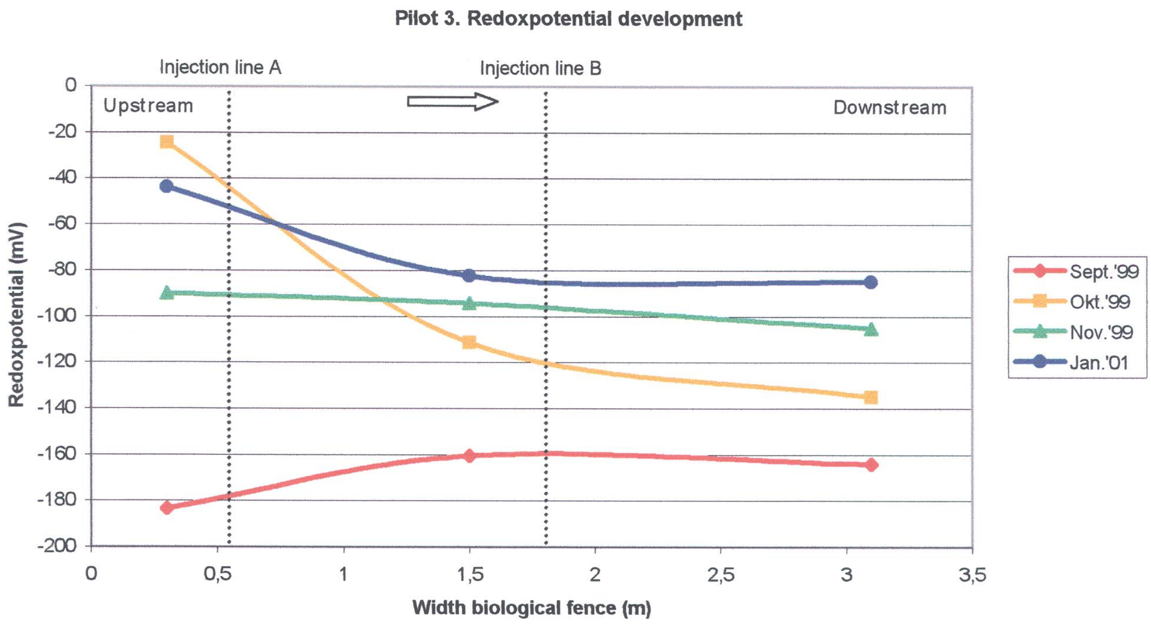



Pilot 1. Redoxpotential development
Injection line A
Injection line B
Upstream
Downstream
Redoxpotential (mV)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
0
0,5
1
1,5
2
2,5
3
Width biological fence (m)
Sept.'99
Okt.'99
Nov.'99
Jan.'01


Pilot 2. Redoxpotential development
Injection line A
Injection line B
Upstream
Downstream
Redoxpotential (mV)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
0
0,5
1
1,5
2
2,5
3
Width biological fence (m)
Sept.'99
Okt.'99
Nov.'99
Jan.'01

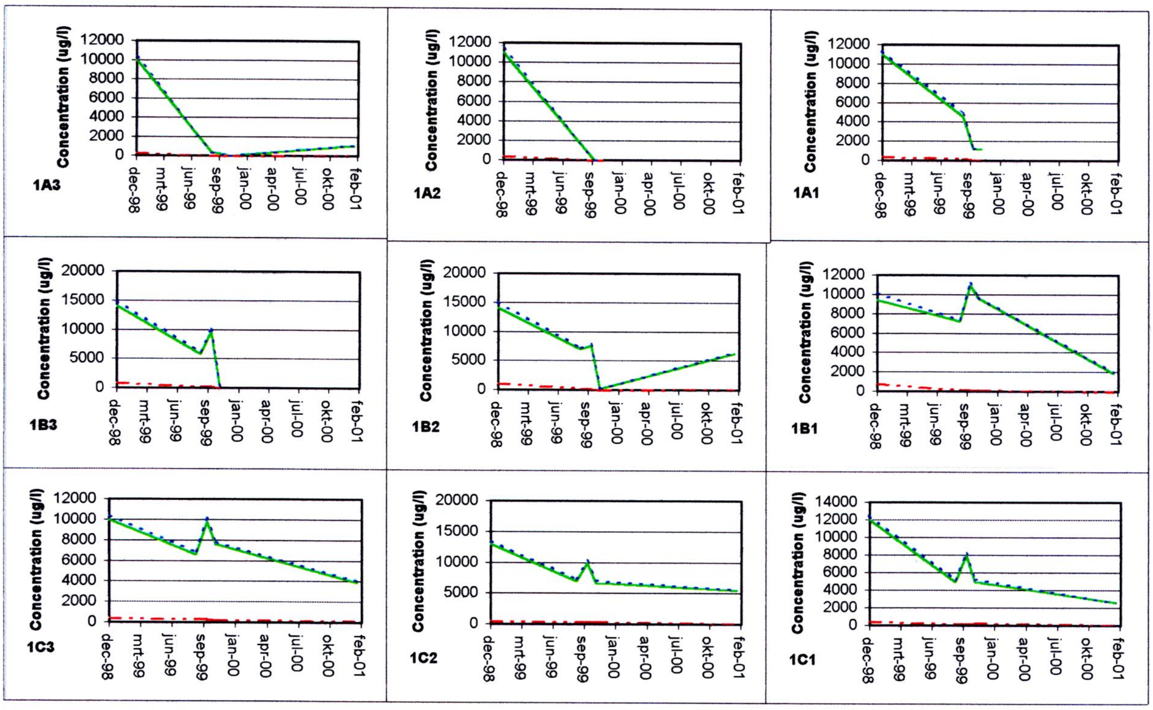


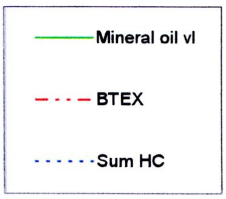
Pilot 3. Redoxpotential development
Injection line A
Injection line B
Upstream
Downstream
Redoxpotential (mV)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
0
0,5
1
1,5
2
2,5
3
3,5
Width biological fence (m)
Sept.'99
Okt.'99
Nov.'99
Jan.'01

APPENDIX F

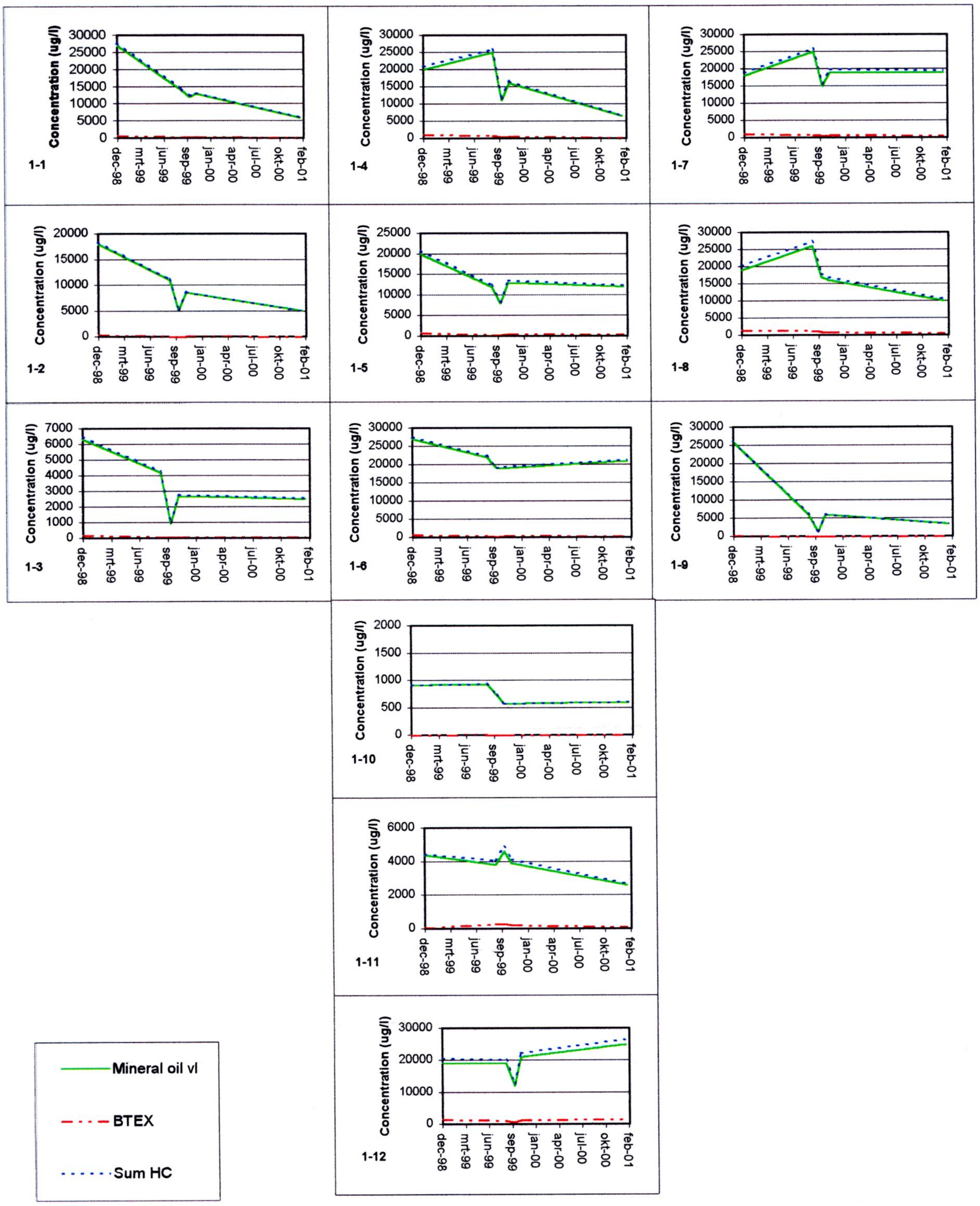
HYDROCARBON PROFILES

Measuring drains | Measurements seperate components | Fence 1

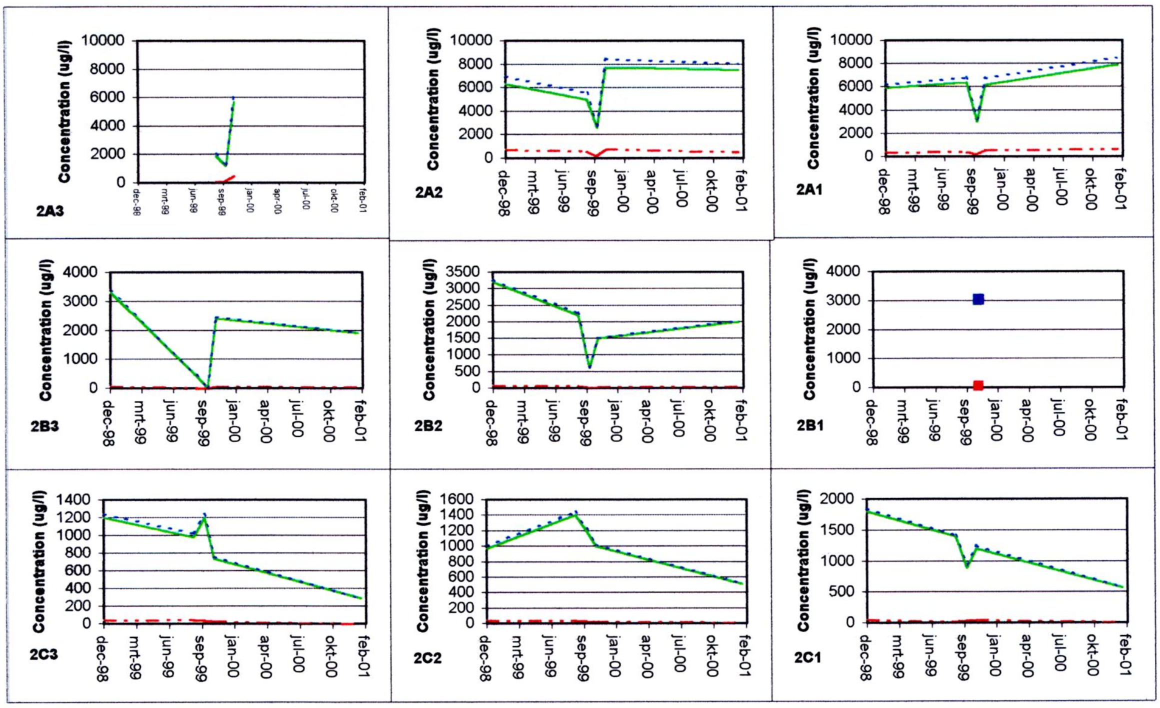


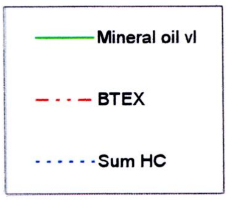


Monitoring wells Measurements seperate components Fence 1

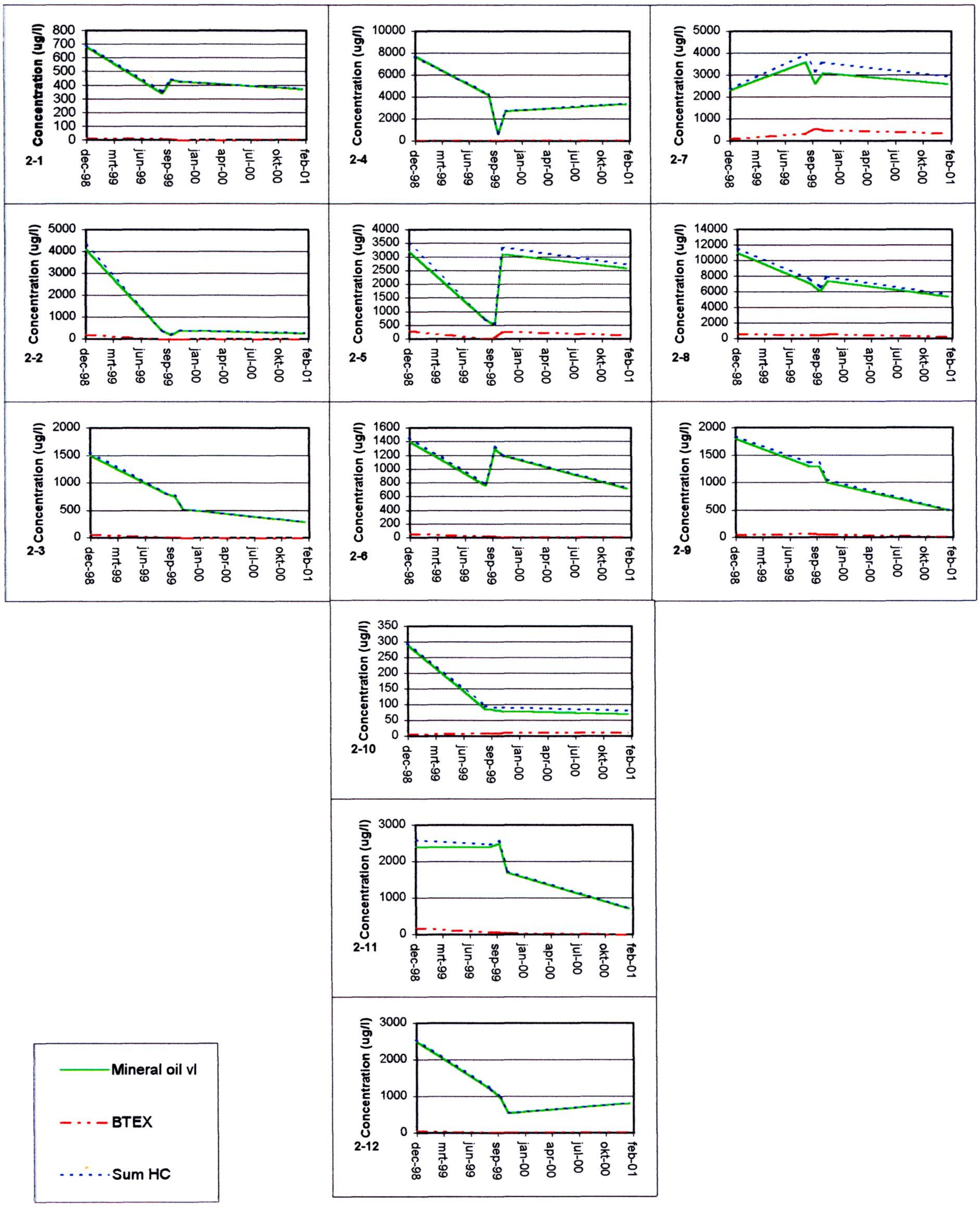


Measuring drains Measurements seperate components Fence 2

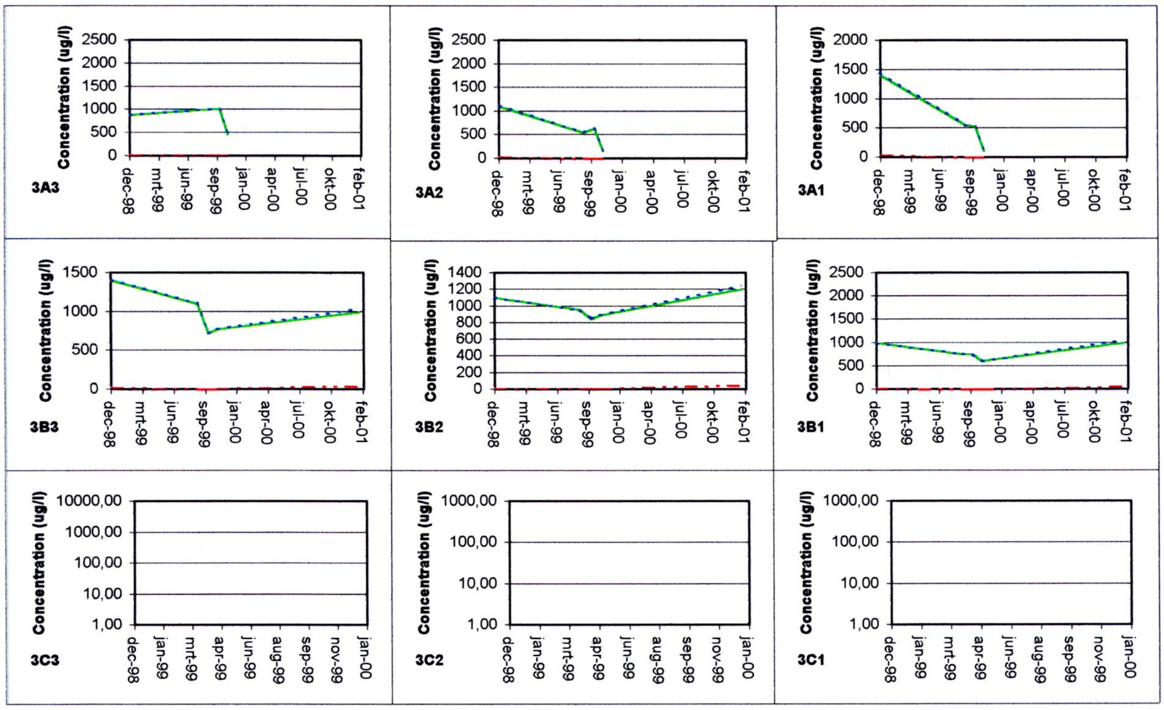


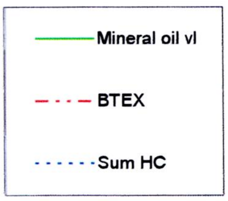


Monitoring wells   Measurements seperate components   Fence 2

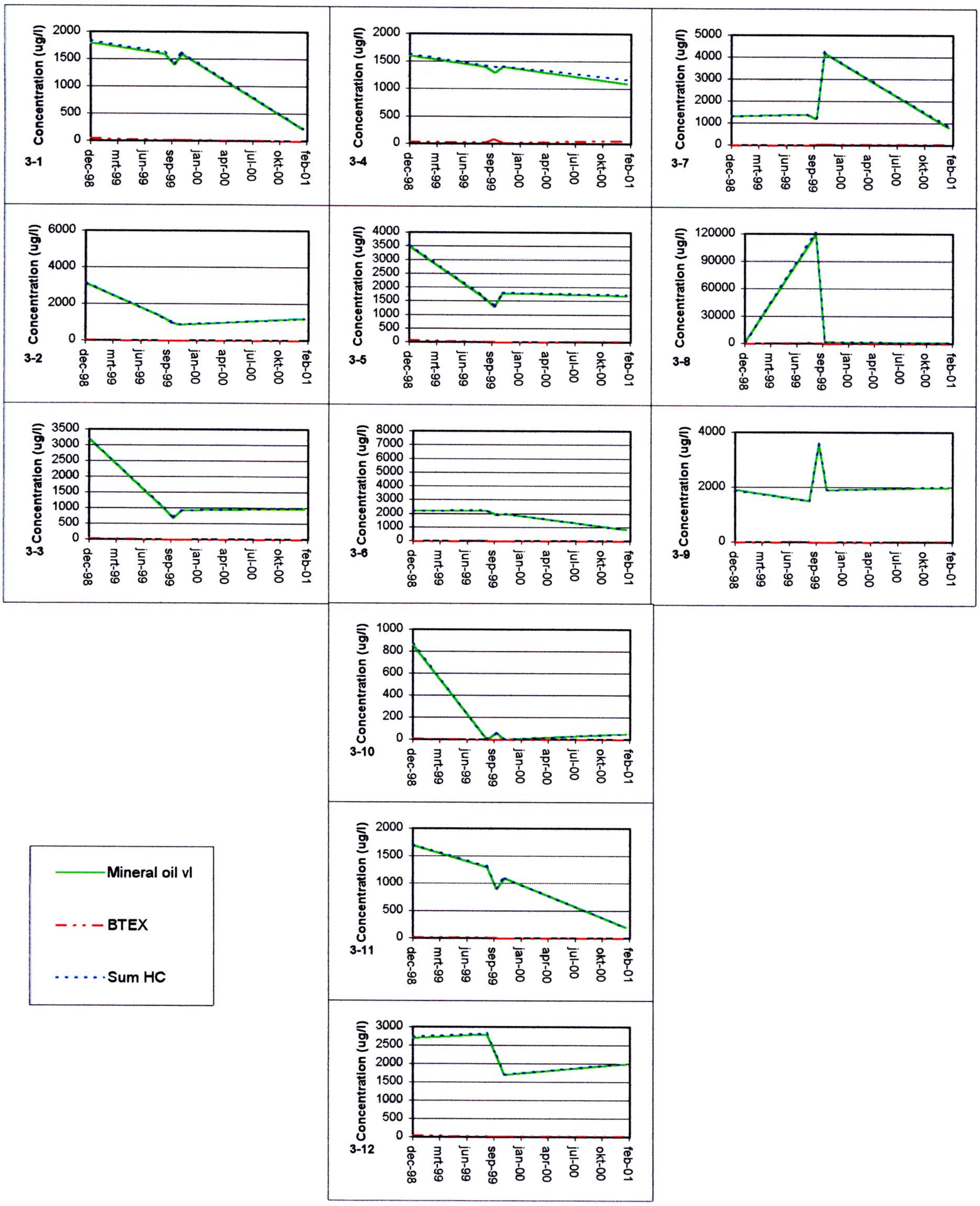


Measuring drains Measurements seperate components Fence 3





Monitoring wells   Measurements seperate components   Fence 3



APPENDIX G

EXPLANATIONS FOR THE UNRELIABLE NON-VOLATILE MINERAL OIL (C10-C40) DATA

The Dutch standard NEN 6678 is used for the analyses of C10 - C40. Conform the NEN, the sample bottle is filled for three quarters. Petroleum ether is added in the bottle in the laboratory, so that the whole sample can be adapted. In this way, disturbance by heterogeneity (like free product in a floating layer) is prevented. After extraction and purification with florisil, the different compounds in the sample are separated by a GC and detected with a flame ionisation detector (FID). The components are quantified using the RIVM standard (a mixture of gasoline and motor oil).

For the analyses of volatile mineral oil (C6 - C12) no standards (NEN) are present. De methodology IWACO applies, corresponds with NEN 6407 (determination of BTEX). A bottle is completely filled in the field. In the lab, a vial is filled, and dilution when needed. The samples are directly analysed by means of on-line Purge and Trap followed by GC-FID. The components are quantified with an internal standard (fluorbenzene).

The goal of the analyses of C10 - C40 is the determination of the amount of oil that is present in the harbour area. The partially filling of the bottle and the extraction with petroleum ether is not the most suitable technique for the fraction C10 - C12 (volatilisation of components will occur). However, this is the compromise that is contracted in the NEN for the determination of mineral oil over the total fraction C10-C40.

The samples of Shell Pernis contain mainly the volatile part of mineral oil, and differences can occur in the data of C10 - C12 when both techniques are used, see table G1.

Table G1. Fraction of C10-C12, calculated from both measurements (C6-C12 and C10-C40).

	Fence 1		Fence 2		Fence 3	
	Mineral oil (vl) C10-C12	Mineral oil (nv) C10-C14	Mineral oil (vl) C10-C12	Mineral oil (nv) C10-C14	Mineral oil (vl) C10-C12	Mineral oil (nv) C10-C14
Dec-98	4200	390	340	2700	990	540
Sep-99	6600	1140	153	270	880	805
Okt-99	7150	0	176	2400	630	344
Nov-99	3245	1045	194	8400	800	459
Jan-01	0	0	166	1500	88	1015

The C10-C12 data (calculated from C6-C12 data) are larger than the C10-C14 data (calculated from C10-C40 data). This demonstrates that sampling and analyses of the C10-C40 data has resulted in a loss of the smaller mineral oils.

Considering the above, the results for C10 - C12 of the volatile mineral oil method is more reliable than the non-volatile oil method. We think that when sampling for C10 - C40, completely filled bottles should be used in future, though this is contrary to the NEN.

As a result, the interpretation of the mineral oil data is focused on the C6-C12 fraction of the mineral oils. Furthermore, the mineral oils present in the fences consisted mainly of the C6-C12 fraction:

- in pilot 1 an average of 96% (filters) en 88% (drains) of C10-C40 consists of the fraction C10-C12;
- in pilot 2 an average of 75% (filters) en 91% (drains) of C10-C40 consists of the fraction C10-C12;
- in pilot 3 an average of 59% (filters) en 87% (drains) of C10-C12. From the chromatogram it is obvious that in this case a large amount consists of C14-C18. Even C20-C26 is present in amounts of 5-15% of the total. It seems the type of mineral oil in pilot 3 is slightly different from the other pilots.

NB: It has to be pointed out that the mentioned amount of C10-C14 from the C10-C40 analyses is flattering, for a part of C10-C14 is volatilised which causes a lower share of C10-C14 to C10-C40.

APPENDIX H

RESULTS OF BTEX DATA IN MEASURING DRAINS

Measuring Drains

Benzene

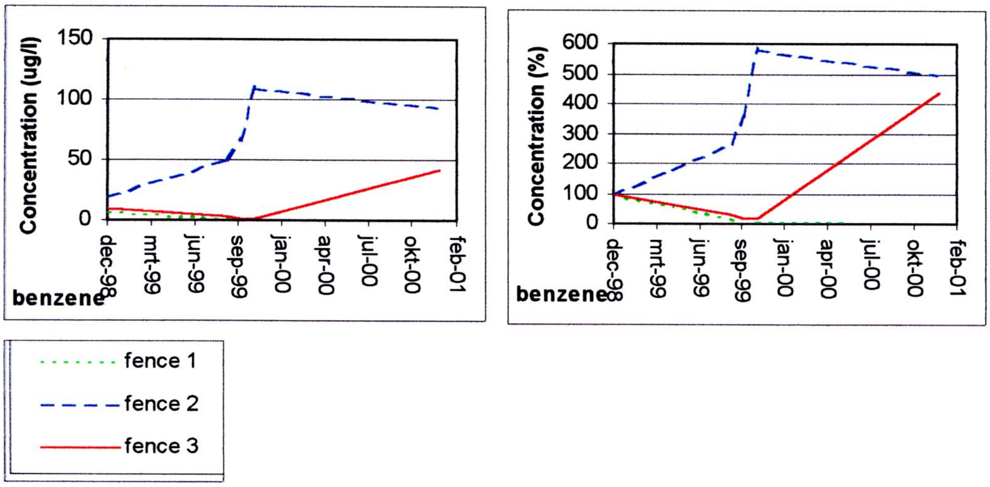


Figure . Absolute (μg/l) and relative concentration (C/Co) of benzene in the measuring drains.

Toluene

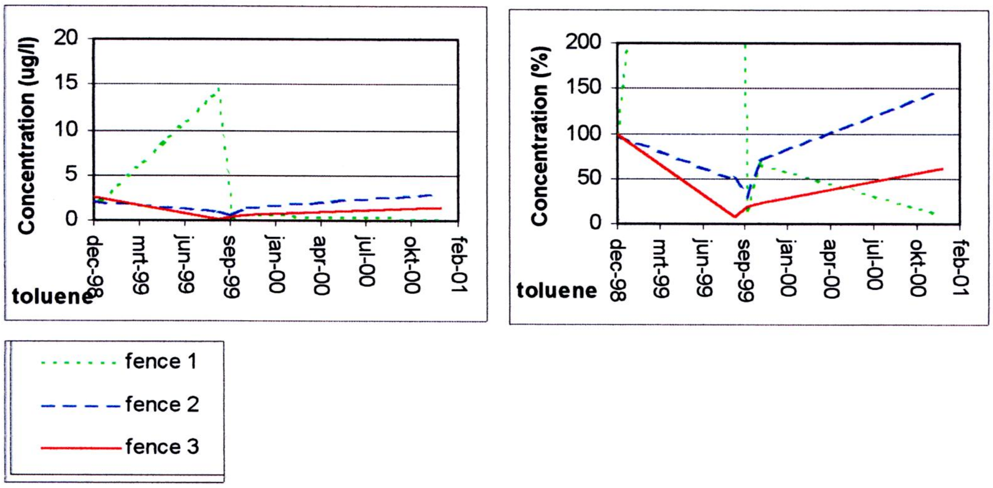


Figure . Absolute (μg/l) and relative concentration (C/Co) of toluene in the measuring drains.

Ethylbenzene

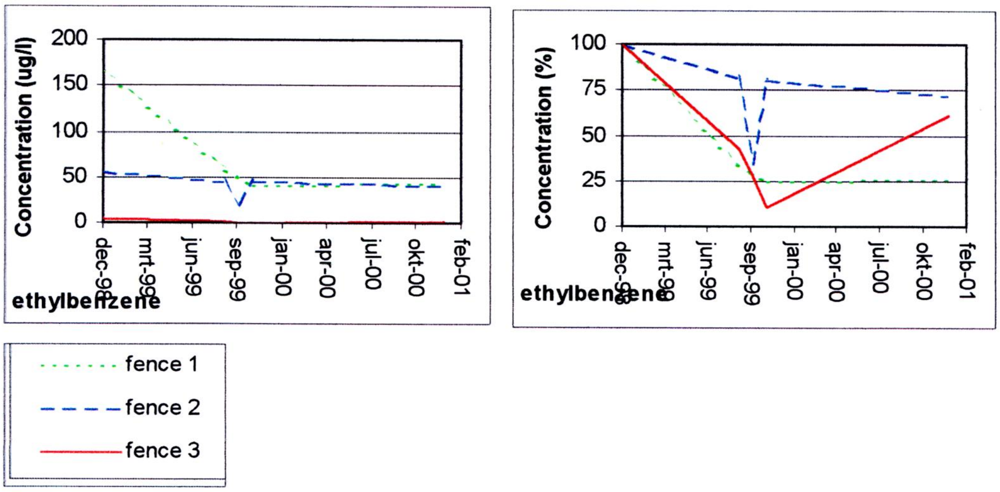


Figure . Absolute (μg/l) and relative concentration (C/Co) of ethylbenzene in the measuring drains.

Xylene

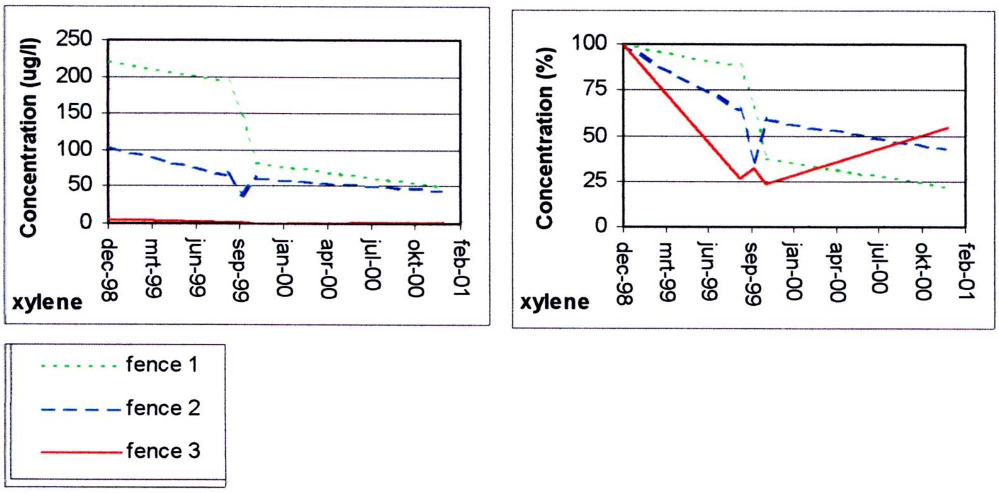


Figure . Absolute (μg/l) and relative concentration (C/Co) of the xylenes in the measuring drains.

BIJLAGE I

RESULTS OF BTEX DATA IN MONITORING WELLS

Monitoring Wells

Benzene

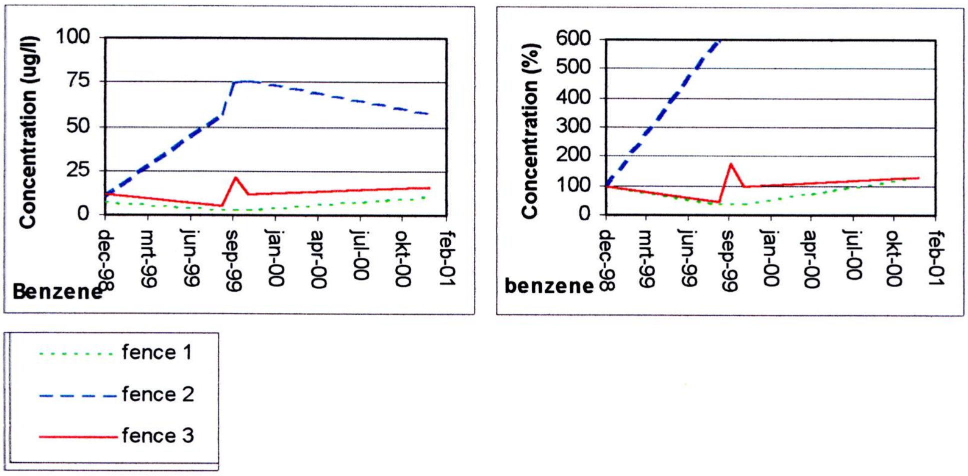


Figure . Absolute (µg/l) and relative concentration (C/Co) of benzene in the monitoring wells.

Toluene

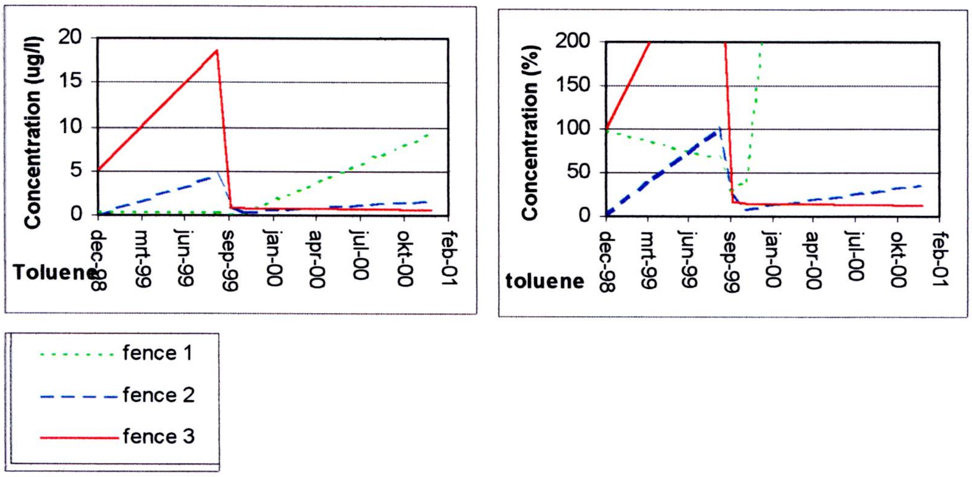


Figure . Absolute (µg/l) and relative concentration (C/Co) of toluene in the monitoring wells.

Ethylbenzene

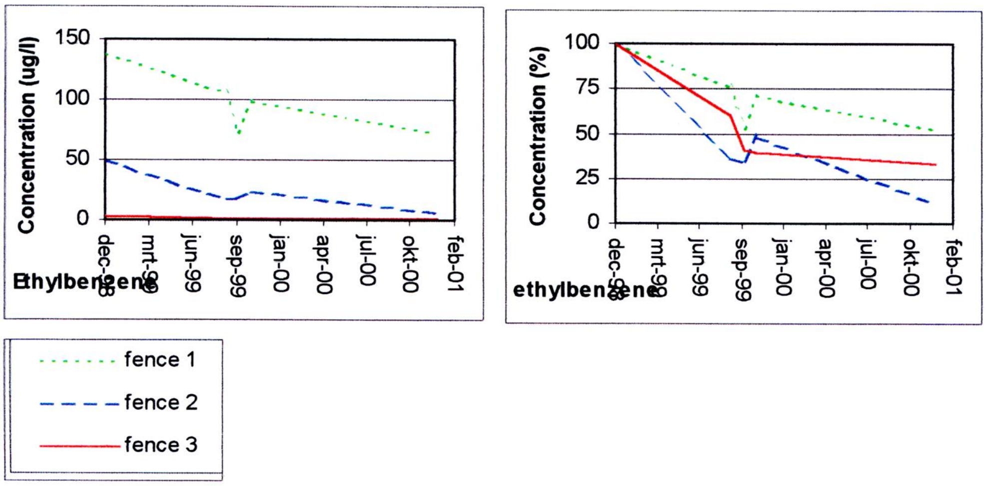


Figure . Absolute (μg/l) and relative concentration (C/Co) of ethylbenzene in the monitoring wells.

Xylenes

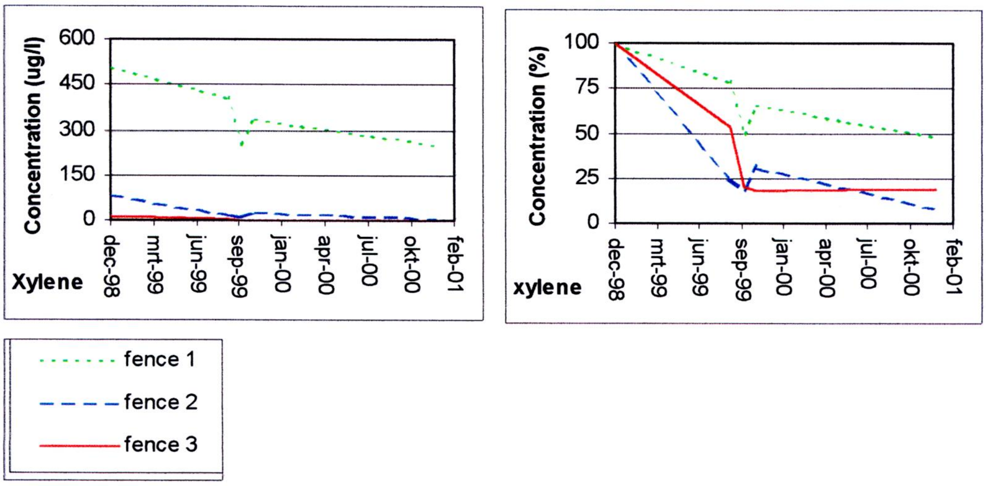


Figure . Absolute (μg/l) and relative concentration (C/Co) of the xylenes in the monitoring wells.