

## NATURAL ATTENUATION OF ORGANIC CONTAMINANTS AT THE INTERFACE BETWEEN GROUNDWATER AND SURFACE WATER

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### Abstract

Soil remediation in practice often consists of the application of extensive techniques for the active removal of the contamination source and remediation of the plume. Object of risk are often surface water systems. There are strong indications that the interface between groundwater and surface water plays an important role in the natural degradation of organic contaminants (NA-interface). This is especially the case for mobile contaminants that are persistent in an anaerobic (subsurface) environment, but mineralized relatively easy under more oxidized environmental conditions (e.g., benzene, the light aliphatic fraction of mineral oil). This project included the development of specific sampling tools, field measurements and modeling of the NA-interface processes.

During the project, NA-interface gradients were measured on site. Based on model scenario's flux decrease is estimated between 5-70%. In a follow-up project, more detailed measurements will take place to determine the quantitative contribution of NA-interface processes to the contaminant flux decrease.

### Introduction

The policy in soil remediation in the Netherlands concerning mobile contaminants consists of cost effective removal strategies. This results often in active removal of the source of the contamination and treatment of the plume. In this approach, natural processes play an increasing role. Important aspects are objects of risk, which are often surface water systems like rivers, canals and harbours. In many situations, especially in river delta regions, the source area is situated close to the surface water, to which the plume moves and the groundwater is being discharged. The current situation is that in these situations relatively intensive and long lasting clean-up methods are used (e.g. pump and treat), to prevent any contamination from reaching the surface water.

There are strong indications that the interface between groundwater and surface water can play an important role in the natural degradation of organic contaminants (NA-interface see figure 1). This is especially the case for mobile contaminants or degradation products that are persistent in anaerobic (subsurface) environments, but can be degraded more easily under oxidized environmental conditions (e.g. monochlorobenzene, vinyl chloride, MTBE, light mineral oil fraction; see figure 2).

Previous investigations have indicated indirectly that NA-interface processes contribute to a reduction of contaminant flux into surface water systems. Until now, no straightforward assessment and quantification of these processes have been performed.

In the Netherlands, present water policy is oriented at zero emission towards surface water systems. Regulation based on maximum allowable contaminant influx into water systems is not yet available.

This project was carried out by TNO-MEP, TNO-NITG, WL|Delft Hydraulics and Delft Geotechnics. The aim was to gain more understanding of the occurrence of NA-interface processes and to quantify their contribution to emission reduction towards the surface water system. In case of a substantial contribution an additional aim was to promote application of NA-interface as part of a cost-effective integrated environmental management system for contaminated sites and surrounding water bodies.

Figure 1: Cross-section of the pollutant plume, the reactive interface and the surface water

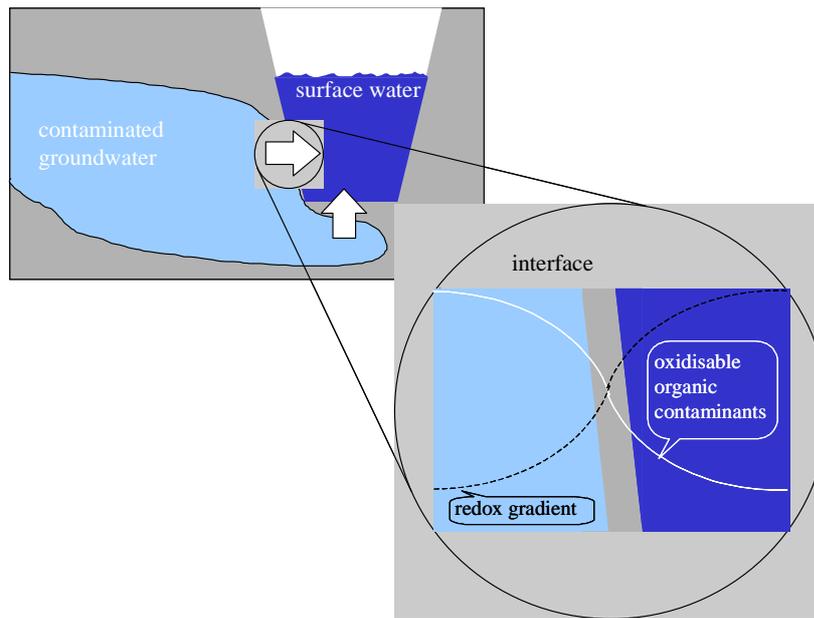
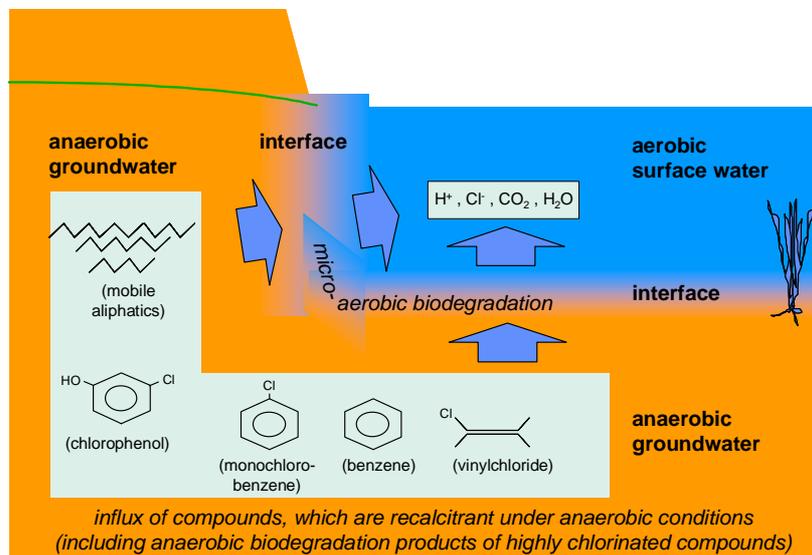


Figure 2: Schematic view of the NA-interface, in which the anaerobic degradation products (e.g. chlorobenzene, benzene, chlorophenol, vinyl chloride) are mineralised in the (micro-)aerobic interface. This principle of micro-aerobic degradation is also applicable to non-chlorinated contaminants, such as aniline, oil compounds, MTBE, etc.



## Methods

The project's starting point is that the surface water is regarded as an object of risk. Thus, the interface should eliminate contaminants by natural occurring processes, thereby protecting the aquatic ecosystem.

Three industrial sites in The Netherlands were selected for site investigations and for the development and application of high-resolution monitoring instruments and modelling procedures. The groundwater - surface water interfaces at these sites can be divided into two tidal systems and one steady state system.

A new tool was developed and applied for sampling groundwater with high resolution in the interface between groundwater and surface water together with existing tools (monitoring wells, environfilters) for measuring NA-interface gradients in the field. Using these tools, the NA-interface gradients for contaminants and macrochemical parameters were identified in the steady state interface system.

Due to the low resolution of the sampling at the tidal interface system, the results of the measurements were considered not sufficiently reliable and suitable for drawing conclusions concerning the occurrence of NA-interface processes. Therefore, the measured values were only used for boundary values to be introduced in the models.

On the basis of a previously developed conceptual model of the NA-interface processes, quantitative models describing these processes and the processes in the adjoining subsoil and surface water was performed using the model codes CHARON, DELWAQ and RT3D.

## Results and discussion

From the modelling it appeared that diffusion/dispersion alone gave a relatively large contribution to the decrease of the upwelling pollutant concentration at the sediment-water interface. The data obtained in the field on pollutant concentration profiles cannot yet be used to determine the biodegradation. Therefore, the degradation rate constants were determined in laboratory experiments. This was performed in batch tests for monochlorobenzene with sediment from the steady state system.

Modelling several scenarios for oxygen consumption of the sediment, dispersivity and biodegradation rate constants showed that the additional concentration decrease due to biodegradation is small compared to the concentrations in the upwelling groundwater at the lower boundary of the active sediment layer.

Quite a different picture arises for the flux of micropollutants that enter the surface water through the sediment-water interface. Dispersion alone does not reduce the pollutant flux that is conveyed to the top sediment by groundwater. The models showed that the flux entering the surface water could be substantially reduced by biodegradation. Depending on the presence of favourable biodegradation conditions, the flux reduction percentage might be more than 95%.

However, such optimal conditions are probably not met at most contaminated sites. The reduction percentage may be virtually equal to nil at very unfavourable conditions (e.g. high outflux rate) or when the maximal degradation rate is small.

A crucial factor is the penetration depth of dissolved oxygen, since the degradation of the relevant pollutants requires oxygen. The penetration depth is maximal for sediments with low oxygen consumption, high dispersion and low upwelling groundwater velocity. The magnitude of the sediment oxygen consumption depends on several parameters, which vary over the seasons.

A high upwelling velocity of groundwater is negative with respect to the degradation potential of the sediment-water interface, because this causes small residence times in the oxygen containing top layer. Moreover, the oxygen consumption may be raised by the presence of reduced substances such as ammonium, sulphide, iron(II) and methane in the groundwater.

The presence of tidal movement of water enhances degradation when combined with a low net groundwater upwelling velocity and with adsorption.

The interface between surface water and groundwater for non-tidal *steady state flow systems* is relatively thin. The estimates of the thickness of the interface vary between 1 mm and 1.5 cm for oxygen penetration depth. The decrease of the contaminant concentration when approaching the surface water is mainly due to dispersion.

In *tidal systems*, a relatively thick interface may exist. It strongly depends on the amount of water that infiltrates during high tide. In the pilot study, the modelled thickness of the interfaces was approximately 2 - 6 cm. In such systems, biodegradation of micropollutants can be substantial if the pollutant strongly adsorbs to the soil material.

## Conclusions

It has been possible to measure NA-interface gradients on site. Contaminant concentrations are mainly determined by diffusion and dispersion processes, whereas flux decrease is determined by biodegradation. Based on model scenario's flux decrease is estimated between 5-70%.

More detailed measurements are needed to determine the quantitative contribution of NA-interface processes to the contaminant flux decrease.

A next step in future research will focus on the quantification of biological degradation of contaminants in the interface, either in the laboratory or, preferentially, under field conditions. This will form the basis

for determining a possible position of NA-interface processes within the framework of management systems for contaminated sites and for more cost-effective and sustainable remedial actions.

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