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INTRINSIC BIODEGRADATION POTENTIALS IN GROUNDWATER CONTAMINATED WITH TRI- AND TETRACHLOROETHENE IN THE VICINITY OF NOWA DEBA WATERWORKS

OCENA MOŻLIWOŚCI SAMOISTNEJ BIODEGRADACJI TRI- I TETRACHLOROETENU W WODACH PODZIEMNYCH W REJONIE UJĘCIA NOWA DĘBA

Abstract: *Natural Attenuation* (NA) in the case of groundwater contaminated with organic compounds relies mainly on intrinsic biodegradation processes. The aim of reliance on natural processes is to achieve site-specific cleanup objectives within reasonable time frames and costs. Such approach may be considered as a risk reduction/remedial option for groundwater contaminated with *trichloroethene* (TCE) and *tetrachloroethene* (PCE) in the vicinity of Nowa Deba waterworks. This case study presents implementation of the USEPA's guideline „Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water" to asses intrinsic biodegradation potentials in contaminated groundwater in the case of Nowa Deba. Literature and field data collected from wells and piezometers were used to develop a conceptual model of contaminants' fate and transport from a source to a receptor. The intrinsic biodegradation was investigated basing on available analytical parameters (*eg* concentrations of oxygen, nitrates, chlorides, and pH, TOC and temperature) that are considered as indicators of TCE and PCE transformation. Preliminary screening was done by giving certain points for these parameters, and interpreted in order to asses intrinsic biodegradation potentials. The results indicate inadequate evidence for intrinsic biodegradation (reductive dehalogenation) of TCE and PCE, thus a limited potential for NA as a remedial/risk reduction option in the studied case, unless some measures for enhancement of TCE and PCE intrinsic biodegradation are applied.

Keywords: intrinsic biodegradation, TCE, PCE, risk reduction, remediation

Introduction

The term *Natural Attenuation* (NA) refers to the reliance on natural processes to achieve site-specific cleanup objectives within a reasonable time frame and costs [1]. The NA includes a variety of destructive and non-destructive physical, chemical, and biological processes like: dispersion, dilution, adsorption, volatilization, chemical or biological stabilization, biodegradation (biotransformation) or destruction of contaminants [2]. In the case of groundwater contaminated with organic compounds NA relies mainly on intrinsic biodegradation processes. Such approach may be considered as a risk reduction/remedial option for groundwater contaminated with *trichloroethene* (TCE) and *tetrachloroethene* (PCE) in the vicinity of Nowa Deba waterworks (south-east Poland).

TCE and PCE are halogenated alkenes used commonly as industrial solvents. Generally, they are present both, as: DNAPLs (*denser than water non-aqueous phase liquids*) and dissolved in groundwater [3]. Biodegradation is usually the most important destructive process leading to reduction of the contaminant loads in groundwater, therefore it is an important factor to consider [4]. The biodegradation of TCE and PCE may occur

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firstly by reductive dehalogenation in anaerobic conditions or secondly by cometabolism in aerobic conditions. Reductive TCE and PCE is associated with the accumulation of daughter products (DCE and VC) and an increase in chloride [4].

To estimate the intrinsic TCE and PCE biodegradation rates different lines of evidence can be used [5]. Microcosm studies can physically demonstrate that NA is occurring but they are time consuming and expensive [4]. An effective alternative is to base the estimation on data about groundwater and soil chemistry (biogeochemistry and hydrogeochemistry), as well as on hydrogeological conditions.

To evaluate whether NA by itself, or in conjunction with other remedial technologies is sufficient to achieve site-specific remedial objectives as concerns TCE and PCE contaminated groundwater in the vicinity of Nowa Deba, the USEPA's guideline „Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water" [4] was implemented.

Methodology

The protocol is designed to evaluate the fate of chlorinated aliphatic hydrocarbons in groundwater [4]. It is aimed at improving the characterization process for sites at which a remedy involving *monitored natural attenuation* (MNA) is being considered, and contains methods and recommended strategies for completing the remedial investigation process. Emphasis is placed on developing a more complete understanding of the site through the conceptual site model process, early pathways analysis, and evaluation of remedial processes. Understanding the contaminant transport in the subsurface is essential for a technically justified evaluation of a MNA-based remedial option.

According to the protocol, firstly available data about site (groundwater and soil chemistry, hydrogeological conditions, site history) and contamination must be collected. Basing on that the conceptual model can be developed. Next the MNA assessment process, which involves a six-step screening method (Fig. 1) [4, 6] can be performed.

Assessing the intrinsic biodegradation potentials is based on assigning a specified number of "points" depending on the concentration or value of the geochemical indicators of TCE and PCE transformation (oxygen, nitrates, chlorides, pH, TOC, temperature) observed in the wells. The "points" can be awarded only if the concentration of a geochemical indicator is within the range specified in the screening criteria, and if the indicator is not a constituent of the original contaminant source. The "points" are added and interpreted based on the guideline to determine whether biodegradation is occurring at the selected location [6]. Table 1 presents the interpretation of given "points".

Table 1

The interpretation of "points" for MNA (*via reductive dehalogenation - RD*) assessment process [4]

Score	Interpretation
0 to 5	Inadequate evidence for anaerobic biodegradation (RD) of chlorinated organics
6 to 14	Limited evidence for anaerobic biodegradation (RD) of chlorinated organics
15 to 20	Adequate evidence for anaerobic biodegradation (RD) of chlorinated organics
>20	Strong evidence for anaerobic biodegradation (RD) of chlorinated organics

Three points were selected to characterize the Nowa Deba site: a piezometer M-5 located about 1100 m from source area, and two wells: S-2tr (about 900 m from source area) and S-6b (about 2400 from source area). Preliminary screening was done by giving certain points for certain parameters, and interpreted in order to asses intrinsic biodegradation potentials according to the scoring scheme provided by Wiedemeier et al. [4].

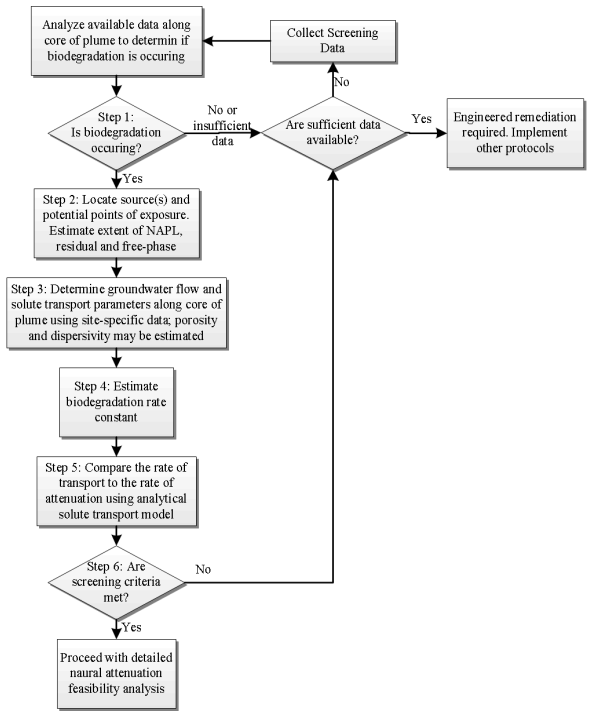

Fig. 1. Screening process flow chart for evaluating NA of chlorinated solvents in groundwater (after [4, 6])

Characteristics of biogeochemistry involve description of range of geochemical indicators, shortly discussed below. *Dissolved oxygen* (DO) levels inform about aerobic/anaerobic conditions in the aquifer. Nitrates and sulfates concentrations below background values in areas with high organic carbon concentrations are indicative of denitrification and sulphate reduction, respectively [4]. Iron(II) is being produced at a site, where reductive dechlorination of alkenes is ongoing. Optimal pH range for reductive biodegradation pathway is 5-9. *Oxidation-reduction potential* (ORP) may indicate if reductive processes are likely to occur. *Total organic carbon* (TOC) informs about the carbon content that is an energy source and drives dechlorination. Temperature ($T > 20$ºC) is also important, because at higher temperature biochemical processes are accelerated. *Dichloroethene* (DCE) or *vinyl chlorides* (VC) are metabolites of TCE and PCE biotransformation, and their presence (if not released at a site) indicates that reductive dehalogenation may take place.

Results and discussion

Site and contamination characteristics

In Nowa Deba (S-E Poland) the metal works "DEZAMET" established in 1939, firstly as an ammunition factory, have been operating until now in a restructured form. TCE and PCE were used there for degreasing the metal parts.

Hydrogeological conditions. Groundwater is connected with the Quaternary river deposits. The most permeable deposits occur in the bottom part of the aquifer. The Quaternary deposits attain thickness of over 30 m and are underlain by impermeable Miocene clay [7]. The aquifer is unconfined and depths to groundwater vary from 1.0 to 9.0 m. This aquifer is the main source of potable water in the Nowa Deba region, and the groundwater flow is predominately from south-east towards the waterworks.

Contamination. The contaminants' distribution maps (Fig. 2) show that the source of TCE and PCE is located within the area of the former metal works "DEZAMET". The contaminants have probably been releasing gradually for decades into soil and groundwater because of *eg* improper storage and usage with no or poor environmental concern [7]. TCE has already reached wells of the municipal waterworks while PCE is less widespread.

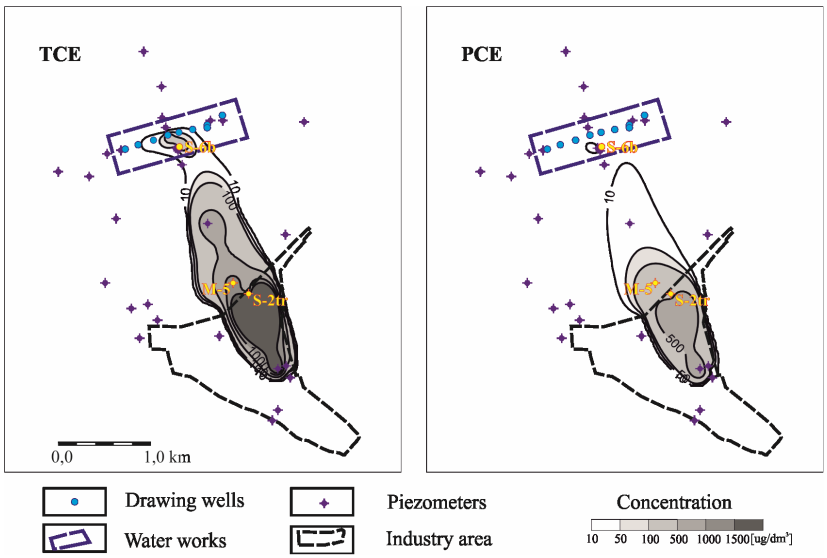

Fig. 2. TCE and PCE concentrations in groundwater at Nowa Deba

High TCE and PCE concentrations of up to 6130 and 694 µg/dm^3, respectively, observed in some wells of the waterworks [8] exceed the limits for potable water [9]. Moreover, they are responsible for the "poor" chemical status of groundwater (class V) in the Nowa Deba region according to [10].

A conceptual model. A conceptual model of TCE and PCE fate and transport in groundwater in the vicinity of Nowa Deba (Fig. 3) was developed based on the "source - pathway - receptor" sequence [7]. The source is within the area of the former metal works

"DEZAMET", while the municipal waterworks in Nowa Deba, supplying about 20 000 inhabitants with potable water, is the receptor affected by the contamination.

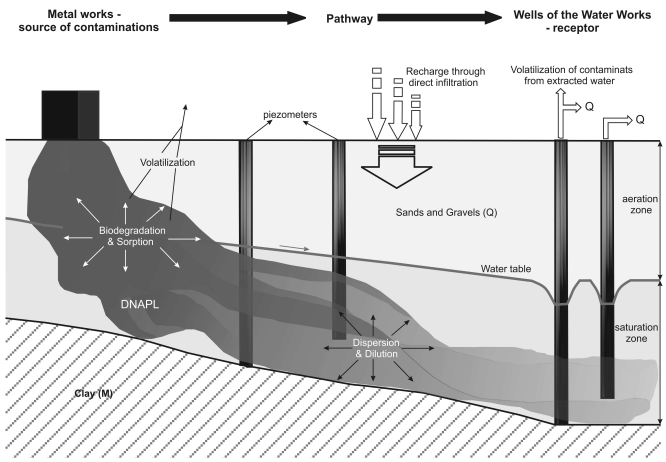

Fig. 3. Conceptual model of contaminants' fate and transport for Nowa Deba [7]

Table 2

Analytical parameters and weighting for preliminary screening for anaerobic biodegradation processes[a/] at the Nowa Deba Region (after [4], changed)

Analysis	Concentration/ Value in the Most Contaminated Zone	Value	M-5		S-2tr		S-6b	
			Concent./ Value	Score	Concent./ Value	Score	Concent./ Value	Score
Oxygen	< 0.5 mg/dm^3	3	0.42	3	4.60	0	0.23	3
	> 5 mg/dm^3	–3						
Nitrate	< 1 mg/dm^3	2	8.58	0	4.75	0	14.8	0
Iron II	> 1 mg/dm^3	3	0.03	0	0.48	0	2.11	3
Sulfate	< 20 mg/dm^3	2	76.5	0	113.0	0	88.8	0
Oxidation Reduction Potential (ORP) against Ag/AgCl electrode	< 50 mV	1	111	0	124	0	–5	1
	< –100 mV	2						
pH	5 < pH < 9	0	6.5	0	6.2	0	6.4	0
	5 > pH > 9	–2						
TOC	> 20 mg/dm^3	2	3.7	0	2	0	1.1	0
Temperature	> 20ºC	1	11.7	0	11.9	0	9.8	0
Alkalinity	> 2x background	1	147.3	1	51.2	1	0.0	0
Chloride	> 2x background	2	53.6	2	31.9	0	18.5	0
BTEX	> 0.1 mg/dm^3	2	NA	0	ND	0	NA	0
PCE [µg/ dm^3]		0	147	0	243	0	ND	0
TCE [µg/ dm^3]		0	721	0	631	0	149	0
		2 [a/]						
VC [µg/ dm^3]		0	NA	0	ND	0	NA	0
		2 [a/]						
Total points awarded				6		1		7

[a/] Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL). NA - not analyzed, ND - not detected

Intrinsic biodegradation assessment

Characteristics of biogeochemistry. Basing on DO levels it can be suspected that there are some anaerobic areas within the studied site. Concentrations of additional terminal electron acceptors (nitrates, sulfates) are out of the range specified in screening criteria. Ph is in optimal range for reductive dehalogenation, while ORP indicates that reductive dehalogenation pathway is not possible. Temperature criterion (> 20°C) can not be fulfilled normally under climate conditions in Poland for Quaternary groundwater that is also the case at described site. Non metabolites (daughter products) of TCE and PCE dehalogenation like DCE or VC are detected.

Assessment. The results of the intrinsic biodegradation assessment are summarized in Table 2. In selected locations the score is between 1 and 7 points, what indicates: "Inadequate/limited evidence for anaerobic biodegradation of chlorinated organics" (see Table 1).

Conclusions

Intrinsic biodegradation of TCE and PCE via reductive dehalogenation was shown not to be enough efficient for risk reduction in the case of Nowa Deba. Therefore, the remedial option to achieve site-specific objectives can not be based exclusively on MNA. Natural processes have to be enhanced using *in situ remediation* (ISR) methods, like *eg permeable reactive barriers* (PRB) or *in situ chemical oxidation* (ISCO). Detailed description of site biogeochemistry and hydrogeochemistry along with the developed conceptual contaminants' fate and transport model were proved to be a valuable tool in assisting to select effective remediation measures for the studied case.

Acknowledgement

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Abstrakt: Samooczyszczenie (ang. *natural attenuation* - NA) w przypadku wód podziemnych zanieczyszczonych substancjami organicznymi polega głównie na samoistnej biodegradacji zanieczyszczeń. Oparcie remediacji na naturalnych procesach zakłada osiągnięcie wymaganych efektów oczyszczania specyficznych dla danego terenu przy zachowaniu rozsądnych ram czasowych i kosztów. Takie podejście może być zastosowane jako jedna z opcji likwidacji zagrożenia/remediacji wody podziemnej zanieczyszczonej *trichloroetenem* (TCE) i *tetrachloroetenem* (PCE) w rejonie ujęcia Nowa Dęba (południowo-wschodnia Polska). Do oceny możliwości samoistnej biodegradacji TCE i PCE w rejonie Nowej Dęby wykorzystano procedurę opisaną w dokumencie US EPA „Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water". Dane archiwalne oraz wyniki badań terenowych zostały użyte do opracowania modelu koncepcyjnego transportu zanieczyszczeń od ogniska do receptora. Samoistna biodegradacja była oceniana na podstawie dostępnych parametrów analitycznych (np. stężenia tlenu, azotanów, chlorków oraz pH, TOC i temperatury wody), które uważane są jako wskaźniki rozkładu TCE i PCE. Ocena polegała na przypisaniu odpowiedniej liczby punktów i wag dla poszczególnych parametrów oraz interpretacji uzyskanych wyników w celu sprawdzenia możliwości samoistnej biodegradacji badanych zanieczyszczeń. Stwierdzono brak jednoznacznych dowodów na samoistną biodegradację (dehalogenację redukcyjną) TCE i PCE w wodach podziemnych w rejonie ujęcia Nowa Dęba. Wynika z tego, że w opisywanym przypadku oparcie remediacji wód podziemnych (i likwidacji zagrożenia dla ujęcia wody) na NA jest możliwe pod warunkiem zastosowania metod wspomagających biodegradację TCE i PCE.

Słowa kluczowe: samoistna biodegradacja, TCE, PCE, likwidacja zagrożenia, remediacja