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NATURAL ATTENUATION OF BTEX CONTAMINATED GROUNDWATER: THE TOMASZÓW MAZOWIECKI CASE STUDY

SAMOOCZYSZCZANIE WÓD PODZIEMNYCH ZANIECZYSZCZONYCH BTEX W REJONIE TOMASZOWA MAZOWIECKIEGO

Zanieczyszczenie wód podziemnych substancjami ropopochodnymi, takimi jak: benzen, toluen, etylbenzen i ksyleny (określanymi wspólną nazwą BTEX) stanowi powszechny problem. W sprzyjających warunkach procesy samooczyszczania (odpowiednik angielskiego wyrażenia – natural attenuation) zachodzące w wodach podziemnych mogą spowodować istotną redukcję masy (ładunku), mobilności, biodostępności i/lub toksyczności BTEX w wodach podziemnych, likwidując lub ograniczając tym samym zagrożenie dla człowieka i ekosystemów. W artykule przedstawiono efekty samooczyszczania wód podziemnych zanieczyszczonych BTEX w rejonie Tomaszowa Mazowieckiego. Na wstępie krótko scharakteryzowano mechanizmy i procesy odpowiedzialne za samooczyszczanie wód podziemnych. Następnie przeprowadzono ocenę możliwości samooczyszczania wód podziemnych na badanym terenie przy pomocy analizy graficznej oraz analizy statystycznej „chmury” zanieczyszczeń z wykorzystaniem testu Mann-Kendalla. Dane z ponad 12 letnich obserwacji wskazują na redukcję stężeń BTEX w wodach podziemnych poniżej wartości dopuszczalnych przy jednoczesnym braku widocznych oznak odradzania się „plamy” zanieczyszczeń, potwierdzając tym samym efekty samooczyszczania. Wyniki wskazują także, że cele remediacji wód podziemnych w rozpatrywanym rejonie zostały już osiągnięte. Wykonane analizy statystyczne dostępnych danych wskazujących na istotny spadek stężeń BTEX w wodach podziemnych potwierdzają to stwierdzenie. Szybkości samooczyszczania obliczone dla poszczególnych węglowodorów jednopierścieniowych z grupy BTEX wahały się w granicach od 0.00027/d (benzen) do 0.00055/d (ksylen). Stwierdzono również wpływ niejednorodności materiału warstwy wodonośnej na szybkość samooczyszczania wód podziemnych zanieczyszczonych BTEX.

1. Introduction

Monoaromatic hydrocarbons (benzene, toluene, ethyl benzene and xylenes), commonly referred to as BTEX, are among the well-known and extensively studied environmental contaminants in the world, and due to the threat they pose to humans and the environment, their presence in soil and groundwater resources often raises a lot of concern [1-3]. As a result of the slow rates of groundwater flow, the effects of these contaminants can persist even long after the source of contamination has been removed. Literature abounds on studies involving the use of engineered approaches to sever the linkage between the source of these harmful substances and their transport in the environment. However, there is a wealth of information available in the literature which gives unambiguous evidence that under favourable conditions, some natural processes occurring *in-situ* can result in significant reduction of mass, mobility, bioavailability and toxicity of BTEX in groundwater, thereby eliminating their debilitating effects on humans and other life forms. These natural processes/mechanisms are collectively referred to as natural attenuation (NA) [4,5]. NA is now considered as an alternative to the traditional soil and groundwater remediation methods. It is therefore important to consider the potential of these natural processes to attenuate contaminants when planning to remediate contaminated sites. Where it is obvious that NA alone is inefficient, human interventions can be employed to help achieve site remediation goals. This can be done by providing suitable conditions that enhance the NA, or use of a different remedial technology.

In order to prove that NA is occurring at a site of concern, at least one of the following lines of evidence must be provided. These lines of evidence have been divided into three main categories, namely: primary, secondary, and tertiary lines of evidence [6-9]:

- the primary line of evidence is obtained from historical groundwater data indicating the stabilization or loss of contaminant mass over time. This can be evaluated using visual or statistical techniques such as the Mann-Kendal trend test,
- the secondary line of evidence is obtained from hydrogeologic and geochemical data, including depletion of electron acceptor concentrations, attenuation rates, and/or increase of by-products in groundwater; statistical analysis could be used to buttress the secondary line of evidence,
- the tertiary line of evidence can be obtained from microbiological laboratory data, such as the results of microcosm studies; results from modelling the transport of contaminants in groundwater can also be used as evidence of NA.

Recent analysis of data from a site in Tomaszów Mazowiecki, which was previously contaminated with BTEX compounds via an accidental spill, revealed that contaminant concentrations were declining naturally without any human intervention, and this was attributed to NA [10]. Therefore, the aims of the presented study were to provide substantial evidence that NA was indeed occurring; determine the attenuation rates for each BTEX compound, and evaluate the order of attenuation of the BTEX constituents.

2. Physical-chemical properties, toxicity, and general behaviour of BTEX in soil and groundwater

BTEX belong to the group of monoaromatic hydrocarbons because they contain mainly hydrogen and carbon atoms and one benzene ring. They make up a significant proportion of gasoline, and they occur as clear, colourless, non-corrosive and volatile compounds with a sweet odour. BTEX are used mostly in the industrial production of synthetic materials and consumer products such as: synthetic rubber, paints, coating, leathers, and glues. Despite their usefulness to humans, they are also known to represent some of the most hazardous components of petroleum products. They impact the quality of drinking water when they come in contact with fresh water resources. When ingested or inhaled into the human system, they can be harmful to the liver, kidneys, heart, lungs, nervous system, and the bone marrow [11]. Water bodies with concentrations of BTEX exceeding threshold limits can be inimical to aquatic organisms such as algae and fish. Like other hazardous chemical compound, BTEX have threshold limits, and there are regulations in every country that ensure such limits are not exceeded. In Poland, threshold limits are: 0.01 mg/L for benzene and 0.1 mg/L for toluene, ethylbenzene and xylene [12]. Normal environmental concentrations of BTEX are unlikely to damage the environment, however, when they exceed the threshold limits their toxicity effects begin to manifest.

The principal source of BTEX in groundwater is the leakage of petroleum products from underground storage tanks (UST). Other important sources include accidental spills, leaks from pipelines and improper disposal of wastes. Once released to the environment, BTEX will have to migrate through the vadose zone before reaching the groundwater. In the subsurface, BTEX undergo several physical, chemical, and biological processes including sorption, volatilization and dissolution that result in their quantitative distribution into different phases, and their degradation or transformation to other chemical compounds. Some of these processes have been treated further in the ensuing chapter. Sorption of BTEX is mainly onto mineral particles and organic matter, and is dependent on the fraction of organic carbon (f_{oc}) and the organic carbon partition coefficient (K_{oc}). A portion of BTEX can volatilize into soil pore spaces or out of the medium. The Henry's law constant (K_H) gives an indication of this tendency and is dependent on the solubility and vapour pressure of the constituent. Depending on the solubility of the constituent, some of the BTEX will dissolve in the water occupying the pore spaces in the vadose and/or saturated zones. The selective affinity of the constituent for organic solvents and water is indicated by the octanol-water partition coefficient (K_{ow}). In general, the fate and transport mechanisms, and the risk of BTEX to humans are dependent on the physical-chemical properties of each BTEX compound, as well as the local hydro-geological conditions [13]. Figure 1 is a schematic diagramme showing the behaviour of light non-aqueous phase liquid (LNAPL), including BTEX in the vadose zone and groundwater following a release of petroleum hydrocarbons. In Table 1 some of the physical and chemical properties of BTEX are presented.

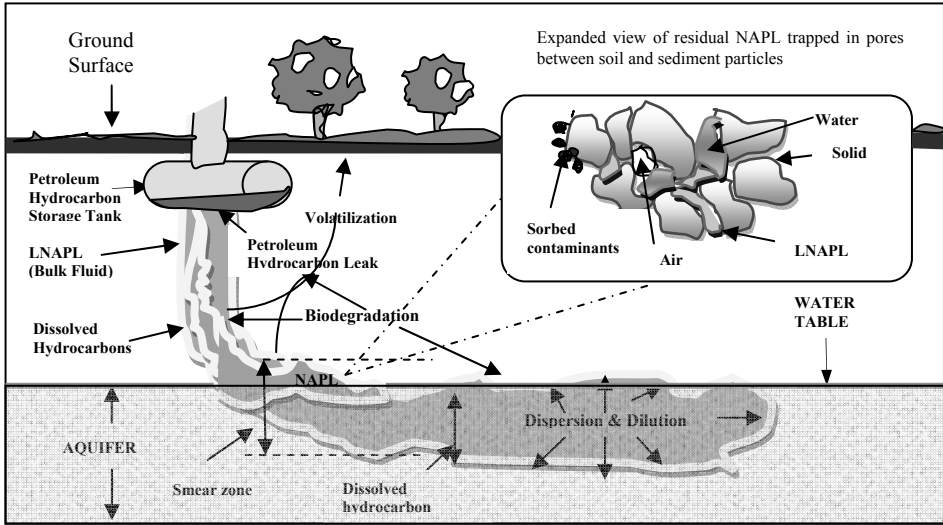


Fig. 1. Behaviour of LNAPL (including BTEX) in the vadose zone and groundwater following a release of petroleum hydrocarbons [14]

Rys. 1. Zachowanie się LNAPL (w tym BTEX) w strefie aeracji i warstwie wodonośnej po wycieku substancji ropopochodnych [14]

Tab. 1. Some physical-chemical properties of BTEX

Tab. 1. Niektóre właściwości fizyko-chemiczne BTEX

Contaminants	S ^[15] [mg/L]	log K _{ow} ^[16]	log K _{oc} ^[16]	M _i ^[15] [g/mol]	P _i ^[17] [mmHg]	K _H ^[15] [atm m ³ /mol]
Benzene	1750	2.17	1.77	78.1	95	0.00555
Toluene	526	2.69	2.26	92.2	28	0.00664
Ethylbenzene	169	3.20	2.56	106.2	9.5	0.00788
o-Xylene	178	3.16	2.56	106.2	6.8	0.00519
m- Xylene	161	3.30	2.61	106.2	8.3	0.00734
p-Xylene	185	3.27	2.59	106.2	8.8	0.00766

Notation: K_{ow} - octanol-water partition constant; K_{oc} - organic carbon partition coefficient; K_H - Henry's law constant; P_i - vapour pressure; M_i - molar mass; S - solubility of pure compound

3. Mechanisms of natural attenuation of BTEX contaminated groundwater

While the contamination plume is moving in the groundwater from a source towards a receptor different biogeochemical factors may influence the contaminants behaviour. The term NA is usually used to refer to the fate of contaminants during their transport within groundwater. NA includes physical, chemical and/or biological destructive and/or non-destructive processes that under favourable conditions may lead to the reduction of mass, mobility, volume or concentration and toxicity of contaminants in soil and/or groundwater [7]. The efficiency of these processes depends on the type and the concentration of the contaminants, as well as the physical-chemical and biological characteristics of the matrix [18]. Information on biogeochemistry is, therefore crucial for the evaluation of the spreading of oil hydrocarbons in the groundwater. Geochemical data may provide important information on the occurrence of NA processes. If the efficiency of the NA processes at a particular location is known, they can be taken into account when the risk to the specific receptors (e.g. extraction wells) is to be evaluated. The process of attenuating contaminants by natural means can be somewhat complex; however, a quantum of work has been done to expound the fundamentals of these processes to aid in their understanding [19-21]. Below in this section, a succinct description of the major NA processes/mechanisms is given to help explicate the results obtained in this study. Figure 2 shows the effects of the different NA mechanisms on contaminant behaviour in groundwater.

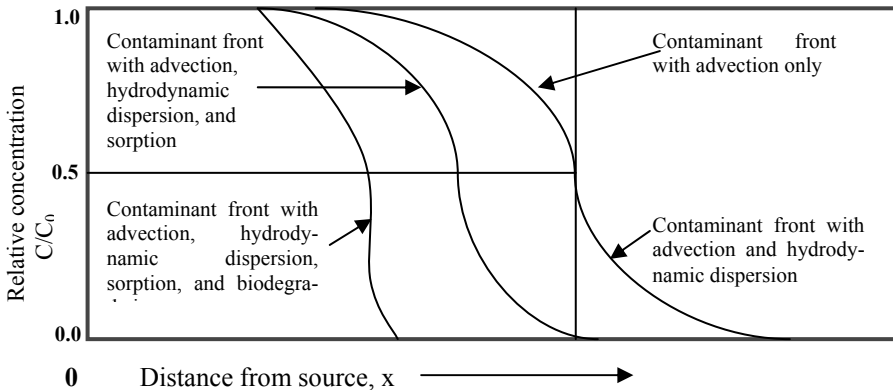


Fig. 2. Breakthrough curves showing plug flow in groundwater with a continuous source and the combined NA processes [22]

Rys. 2. Krzywe przejścia dla przepływu tłokowego w wodach podziemnych z ciągłym dopływem zanieczyszczenia z ogniska w zależności od procesów samooczyszczania

3.1. Volatilization

Volatilization is one of the processes involved in the NA of soil and groundwater contaminated with BTEX. When dissolved solutes are transported from the liquid phase to the gaseous phase, the process is referred to as volatilization. This process is controlled by temperature, depth of the water table, contaminant concentrations and the Henry's Law Constant (K_H) of the specific compound [22]. Volatilization may permanently remove contaminants from groundwater; however, its effects on mass loss of petroleum hydrocarbons are generally not so significant, as it accounts for less than 5% of the total mass loss [4,23]. The work of Rivette [24] also indicated that a plume located one meter below the groundwater table may be insignificantly affected by volatilization. However, where groundwater temperatures are high and biodegradation rates are slow, the contribution of volatilization to the contaminant mass loss cannot be ignored [25].

3.2. Dispersion, diffusion, advection and recharge

These are processes which directly decrease contaminant concentrations; however, they do not have any direct effect on the contaminant mass loss. Contaminant migration in the subsurface is mainly due to advection, which is mostly dependent on aquifer properties such as the effective porosity, hydraulic conductivity and hydraulic gradient. Without any delay, the effective velocity and travel distance of contaminants between points will be the same as that of the groundwater. Heterogeneities in an aquifer matrix, however, can lead to contaminants being transported with different velocities and in different directions (longitudinal, transverse, and vertical) along the water flow path. This phenomenon is referred to as dispersion. Diffusion is the movement of a contaminant from a higher to a lower concentration resulting in its spreading and dilution. This process is dependent on the diffusion coefficient of the contaminant and the concentration gradient. Contaminant spreading by diffusion can be described by Fick's laws [26]. In most geological settings, diffusion of contaminant is almost insignificant compared to dispersion. Recharge is the movement of water through the capillary fringe into the saturated zone. Both recharge and dispersion can indirectly enhance biodegradation of contaminants in that, processes of former can lead to replenishment of the electron acceptor pool, with the processes of the latter resulting in increased contact between contaminants and the electron acceptors [27]. Where these processes are very effective, their direct effects alone can result in reduction of contaminant concentrations to innocuous levels.

3.3. Sorption

Sorption is a general process whereby contaminants become associated with solid phases either by being taken up from the liquid or air phases onto (adsorption) or into (absorption) organic or mineral matter, and held by different attractive forces [16,19,28]. The amount that is sorbed is a function of the distribution coefficient K_d , which is equal to the product of the fraction of organic carbon (f_{oc}) in the soil and aquifer material, and the K_{oc} . Therefore, sorption generally will depend on the amounts of organic matter and clay mineral contents in the soil and aquifer material, as well as contaminant properties such as solubility and hydrophobicity [23]. Typical values for f_{oc} are between 10^{-3} and 10^{-4} [15]. Though BTEX can sorb to inorganic surfaces [29], their attenuation via sorption is largely controlled by the f_{oc} [30,31]. Sorption generally results in contaminant retardation with

respect to average groundwater velocities according to the formula: $R = 1 + \rho_s K_d / n_e$ [32]. The retardation coefficient (R) can be determined based on parameters of the sorption isotherm and soil/aquifer material, such as K_d , effective porosity (n_e) and density of soil/aquifer material (ρ_s). However, due to the relatively low K_{oc} of BTEX, their mobility is generally moderately affected, particularly for benzene [33], making them relatively mobile and, thus potentially dangerous to the environment. Due to the likelihood of contaminant to desorb through, for example, the effects of recharge and temperature, sorption only temporarily or semi-permanently removes contaminants from groundwater [19,27], and retards their transport with groundwater from a source towards a receptor.

3.4. Intrinsic biodegradation

Intrinsic biodegradation relies on indigenous microorganisms at the site to degrade contaminants, and a variety of microorganisms are known to be involved in this process. This is the only NA process that results in the destruction or transformation of BTEX compounds, thus reduction of the contaminant mass (load) in the environment. The biodegradation of BTEX compounds is probably the best documented of all known NA processes [4,34]. Biodegradation of BTEX is a metabolic or enzymatic process, which results in BTEX being transformed to CO_2 , H_2O , inorganic compounds or other organic substances. The main driving force for this mechanism is the transfer of electrons from the electron donor (BTEX) to terminal electron acceptors (TEA) which could be oxygen under aerobic conditions, or a “substitute” for oxygen such as nitrate, ferric iron, and sulphate under anoxic conditions [35-39]. Such a process is crucial for microbial growth, protein synthesis, and reproduction. If oxygen is present, it will be used first before other electron acceptors present in the system are used. Even though BTEX degradation occurs faster under aerobic conditions, the core of the plume usually rests under anaerobic conditions; therefore, anaerobic processes dominate in most cases. Biodegradation mostly occurs in the dissolved part and periphery of the plume. Apart from the availability of electron acceptors, other requirements must also be fulfilled to enhance biodegradation. These include availability of suitable degrading organisms; conducive environmental conditions such as optimum pH, salinity, temperature, oxidation-reduction potential (ORP) and nutrients (N, P, K, Ca, Mg) [15]. Spatial and temporal changes in concentrations of BTEX compounds, electron acceptors, metabolic by-products, pH, etc., can be indicative of intrinsic biodegradation, and for that matter of NA [25].

The ability of microorganisms to biodegrade BTEX has been extensively studied at both lab and field scales. Laboratory experiments were conducted by Mazzeo et al. [40] to investigate the ability to reduce BTEX genotoxic and mutagenic effects by bacteria obtained from effluents of petroleum refinery. Results of the study indicated the potential of the bacterial strains to transform BTEX to environmentally amiable products. A survey of up to 7167 water supply wells for evidence of chemical contamination after 50 years showed very little amount of BTEX contamination. Based on further studies, the decline in contaminant concentration was attributed to microbial degradation [41]. In another field studies conducted by Barker et al. [42], in which groundwater was spiked with 0.24 mg/L of benzene, 1.8 mg/L of toluene, and 1.1 mg/L of xylenes, a substantial decline of BTEX concentration was observed after 108 days. Toluene had almost completely disappeared by this time. By analysing the physical and biogeochemical processes of the system, it was concluded that biodegradation was the main processes leading to the contaminant mass loss. Kłonowski et al. [43] investigated the effect of intrinsic biodegradation of contaminated sandy aquifer due to a jet fuel spill. By observing the

spatial and temporal changes in the contaminated aquifer, they found that changes between intrinsic remediation indicators such as the hydrocarbons concentration and electron acceptors were highly correlated, and concluded the occurrence of intrinsic bio-attenuation of contaminants. An evaluation of BTEX remediation by NA at a coastal facility in the USA previously contaminated with about 300,000 gallons of BTEX showed that within 17 years, 92% of the total mass of BTEX was removed from the site through microbial degradation [44]. Through these and many other studies, intrinsic bioremediation has been clearly demonstrated as an active part of NA, and understanding of processes involved has also been increased.

4. Materials and methods

4.1. Study site description

The site used in this study is in Tomaszów Mazowiecki, a city situated in central Poland. This area is characterized mainly by deposits of the Quaternary age. The aquifer is shallow, unconfined and heterogeneous, consisting of varying amounts of post-glacial sands, gravels and Quaternary river-terrace deposits. The upper layer of the aquifer is made up of a mixture of coarse sands and gravels. The underlying layer is mainly filled with fine sands. The lower portion is characterized by layers of fine to medium sands, with glacial till covering the base of the shallow aquifer. The average hydraulic conductivity, effective porosity and saturated thickness of the aquifer are of: 1.57×10^{-4} m/s, 0.25 and 1 m, respectively. Since work started on this site groundwater levels have varied seasonally. Measured groundwater tables are generally between 1.2 and 5 m b.s.l. Recharge of groundwater in this area is mainly by precipitation of 640 mm/yr. The groundwater flows through the shallow aquifer from south-west to north-east with an effective velocity of 0.54 m/day, and feeds the Czarna River, which flows with a velocity of 0.63 m/s from north-west to south-east.

4.2. Groundwater contamination, sampling and analysis

In March 1999, the groundwater at the study site was contaminated with petroleum hydrocarbon through an accidental spill. A train which was transporting 10 tanks of diesel derailed and about 133 tonnes of fuel spilled into the ground. Since the spill, several activities have taken place, including the installation of a barrier made of high density polyethylene (HDPE), and a network of piezometers and wells to intercept the contaminant plume and to monitor contaminants behaviour. Recovery of free products, sampling of groundwater and analysis of samples for dissolved hydrocarbons (BTEX) have been carried out as well. By the end of 2010, about 16,000 L of free products was recovered [45]. Recently, an installation of a permeable reactive multi barrier (PRmB) has been considered to aid the removal of BTEX from groundwater. However, screening the potential for using PRmB showed that groundwater concentration of BTEX was already reduced below the standard values, thus remediation goals have been achieved that was attributed to NA [10].

In order to provide evidence that NA was indeed occurring, and to determine the attenuation rates for BTEX compounds all existing data were collected and analysed. In addition, in January 2012 a sampling campaign was carried out. Previous work at the test site focused on 27 piezometers and 3 monitoring wells in the barrier. However, in this study, the measurements were performed specifically in some selected piezometers (P-5, P-7, P-8, P-9, P-10, P-27), as well as in the central monitoring well (CW) in the hydro-physical barrier, where the PRMB was intended to be installed. The global positional system (GPS) was used to locate the positions of the piezometers and barrier wells. The groundwater level was measured with a water level meter. A solinst bladder pump and a bailer were used to pump groundwater samples. Water samples were collected in 250 ml airtight labelled bottles and sent in a cool-box to the laboratory for analysis. The analyses were done in the licensed laboratory of Przedsiębiorstwo Geologiczne in Kielce. Groundwater analysis for BTEX and total petroleum hydrocarbons (TPH) using gas chromatography was done according to the Polish standard (PN-89/C-04641/03). Figure 3 shows the nature of the plume and the location of the piezometers from which the groundwater sampling data were used.

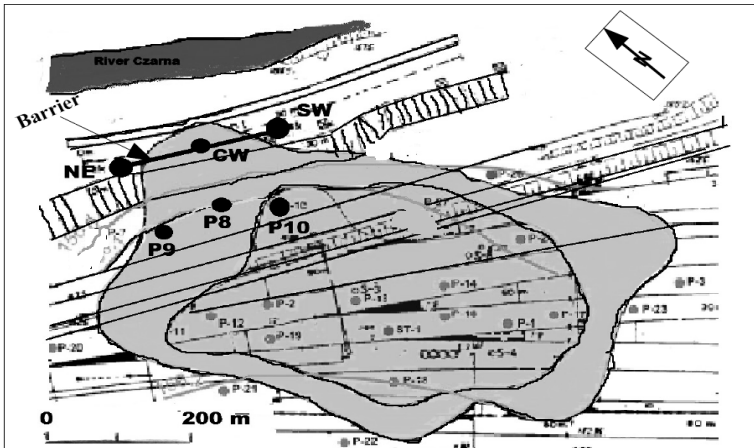


Fig. 3. Nature of the plume and location of the piezometers from which groundwater sampling data were used

Rys. 3. Charakter "chmury" BTEX i lokalizacja piezometrów do opróbowania wód podziemnych

4.3. Evaluation of natural attenuation

In this study, primary and secondary indicators based on availability of data, were used to evaluate the occurrence of NA at the site. This was based on graphical presentation of plume characteristics indicating loss of a contaminant with time, statistical analysis of the plume, and computation of attenuation rates.

4.3.1. Graphical analysis of plume

The simplest way of evaluating plume dynamics is to plot contaminant concentrations at a well versus time. The analysis can be performed for one or more wells. This plot allows for visual analysis of trends in contaminant concentrations as to whether they are stable, increasing or declining over time. A decrease in contaminant concentration at one point may not necessarily imply the occurrence of NA, due to the possibility of contaminants migrating to new locations. To overcome this problem, more than one well at different locations is required [4,6,25]. In this study, data on concentrations of the BTEX constituents in three piezometers: P-8, P-9, and P-10 (see Fig. 3) were selected for the assessment. Data obtained from these piezometers previously indicated that the quality of groundwater had been impacted, as high BTEX concentrations above permissible limits were detected. The concentrations were plotted against time, followed by fitting a trend line to the data. The trend line was to enable clear visualization of a trend, if any. This analysis was accomplished using Microsoft Excel.

4.3.2. Statistical analysis of BTEX concentration in groundwater

The statistical package used to evaluate the trend in the data was XLSTAT. It is a suite of statistical modules that run in Microsoft Excel. The XLSTAT can perform functions including preparing, describing, analyzing, modelling data and testing a hypothesis (parametric, nonparametric and correlation/association tests). Also included in the functions of this package is the ability to perform a trend test as suggested in [46,47]. Statistical analyses were, therefore performed on the data using the Mann-Kendall test to ascertain if plume trend (decreasing or stable) is significant or not. The Mann-Kendall test is a non-parametric test used for the detection of a trend in time series. It does not require consistent sampling data, and it is also insensitive to outliers [21]. The output of this test is the S statistic. The initial value of the Mann-Kendall statistic, S , is assumed to be 0 (e.g., no trend). If subsequent data values are higher or lower than the initial and every subsequent value, S is incremented or decremented by 1 for that additional value. The net result yields the final value of S . A negative or positive S indicates a decreasing or increasing trend, respectively. When the S statistic is zero, the implication is that there is no trend in the time series. The significance of the trend at a certain confidence interval (95%) can be tested, which is usually based on two hypotheses:

- H_0 = the null hypothesis: it states that there is no significant trend in the data,
- H_A = the alternative hypothesis: it states that there is a significant trend in the data.

When the trend test is performed using XLSTAT, a p -value which indicates how much evidence there is against the null hypothesis is generated. If the p -value is lower than $\alpha = 0.05$, H_0 will be rejected, and the alternative hypothesis H_A accepted. On the other hand, if the p -value is greater than $\alpha = 0.05$, the null hypothesis will not be rejected. With this test data (Σ BTEX) obtained from three piezometers were used.

4.3.3. BTEX attenuation rates and half-lives

The attenuation rate constants and half-lives were calculated for the different BTEX compounds. Methods of deriving different first order rate constants (point decay rates, bulk attenuation rates, and biodegradation rates) have been described by Newell et al. [48]. In this study, point decay rates were calculated using equation (1), which is trans-

formed into equation (2) to obtain a straight line by plotting the natural logarithm of the concentration of BTEX against time.

$$C_t = C_o e^{-kt} \quad (1)$$

$$\ln C_t = -kt \times \ln C_o \quad (2)$$

where: C_t - is concentration of contaminants at some time t after time zero (mg/L), C_o - is concentration of contaminants of concern at time zero (mg/L), t - is time (days) after time zero; k - is total attenuation rate (day^{-1}), which includes advection, dispersion, biodegradation, sorption, dilution from recharge, and volatilization of contaminants.

The half-life, $t_{1/2}$ (days) defined as the time required to reduce the initial concentration of the contaminant by 50% was derived using the equation below:

$$t_{1/2} = \ln(2)/k \quad (3)$$

By estimating the half-life, it will be possible to estimate the time to reach the remediation goal. Using 0.03 mg/L; 0.148 mg/L; 0.2 mg/L; and 0.187 mg/L as C_{start} for benzene, toluene, ethylbenzene and xylene, respectively, the time required to reach the maximum permissible concentrations in groundwater which are: 0.01 mg/L for benzene, and 0.1 mg/L for toluene, ethylbenzene and xylene were computed using the equation below:

$$t_{\text{goal}} = [-\ln(C_{\text{goal}}/C_{\text{start}})]/k \quad (4)$$

where: t_{goal} - is time (days) required to reach goal concentrations C_{goal} (mg/L), C_{start} - is initial concentration of a compound of concern (mg/L).

5. Results and discussion

The plots presented in Figures 4-6 evidently show a declining trend of BTEX concentrations with time in P-9 and P-10. However, in P-8, the trend is not very obvious as it appears to have stabilized after some years. By visual observation of trends and comparing contaminant concentrations to their acceptable limits (which is 10 $\mu\text{g/L}$ for benzene and 100 $\mu\text{g/L}$ for toluene, ethylbenzene, and xylene), it could be inferred that without any human intervention natural processes occurring *in situ* have been able to reduce concentrations of BTEX to below acceptable limits.

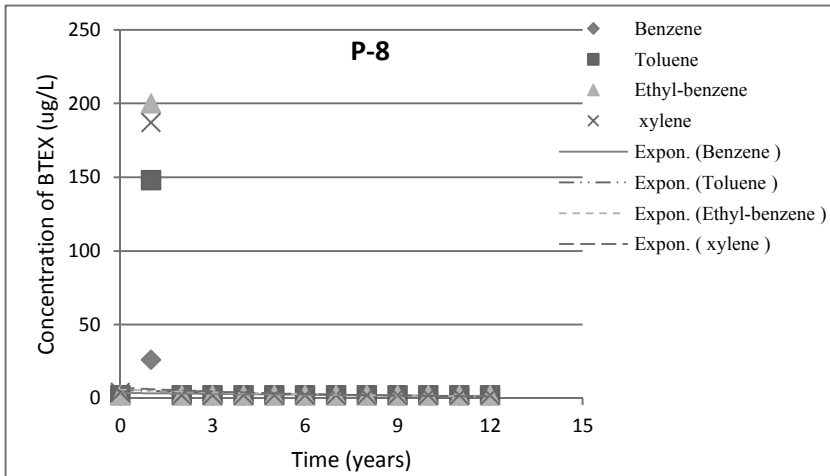


Fig. 4. Changes of BTEX concentration in time in P-8

Rys. 4. Zmiany stężenia BTEX w wodach podziemnych w czasie (piezometr P-8)

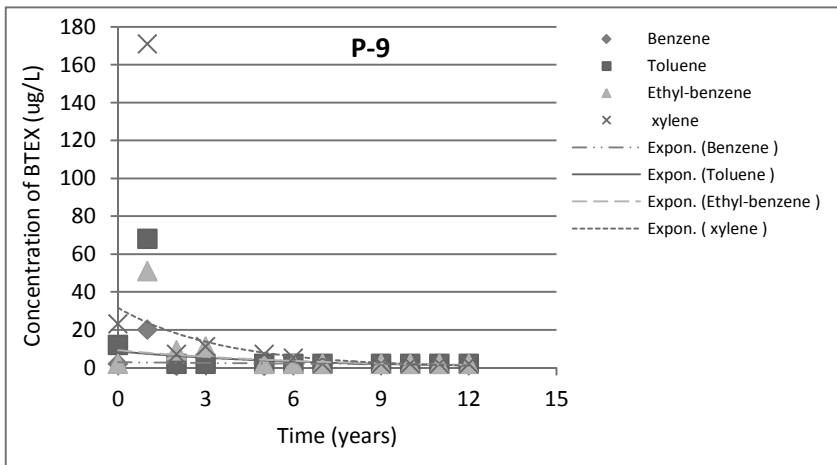


Fig. 5. Changes of BTEX concentration in time in P-9

Rys. 5. Zmiany stężenia BTEX w wodach podziemnych w czasie (piezometr P-9)

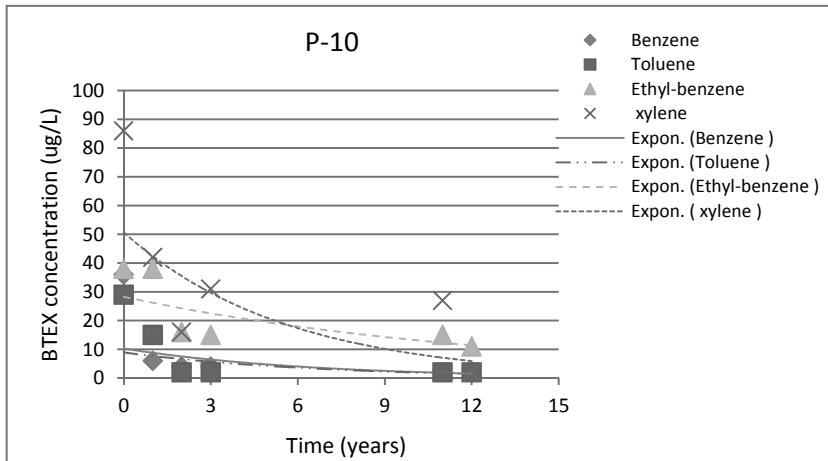


Fig. 6. Changes of BTEX concentration in time in P-10

Rys. 6. Zmiany stężenia BTEX w wodach podziemnych w czasie (piezometr P-10)

Being able to identify trends visually from graphs is useful, and probably, the simplest way of evaluating the occurrence of NA; however, information obtained from such analysis is often insufficient to demonstrate its effectiveness. The plots in Figures 5 and 6, which represent P-9 and P-10, respectively, can be indicative of a decreasing trend of BTEX concentrations since the beginning of sampling. However, in P-8, it is not very clear whether or not the concentrations are decreasing with time. It is also not known whether the trends observed in these figures, including Fig 4 are significant or not.

The Mann-Kendall test was therefore used to verify, if the plume was decreasing or stable, and whether or not the observed trend is significant. The test results presented in Table 2 show the Mann-Kendall S statistic, number of missing data, maximum and minimum concentrations, and number of observations, p -value and significance level α . The S statistic was negative for all three piezometers. These values confirm the results of the graphical analysis, which revealed that BTEX concentrations were decreasing in P-9 and P-10, and also clarify the situation in P-8. The p -values obtained for P-9 and P-10 were lower than $\alpha = 0.05$. This led to the rejection of the null hypothesis which stated that there is no significant trend in the data. On the other hand, the null hypothesis was accepted for the data obtained from P-8, implying that the decreasing trend was not significant. The results could imply that significant NA of BTEX compounds is occurring in the area of the piezometers 9 and 10, which could also be an indication that conditions that enhance rapid degradation of BTEX are favourable in these vicinities. The trend observed in the vicinity of P-8 may suggest the opposite.

Tab. 2. Results of the Mann-Kendall Test

Tab. 2. Wyniki testu Mann-Kendalla

Piezometer	Mann-Kendall S	Missing data	Min.	Max.	Observations	p-value	α	Trend
P-8	-13.00	0	0.002	0.56	13	0.239	0.05	Decreasing
P-9	-39.00	2	0.002	0.31	13	0.003	0.05	Decreasing
P-10	-12.00	7	0.01	0.2	13	0.027	0.05	Decreasing

Table 3 presents the results of the attenuation rates and half-lives for each of the BTEX compounds. The attenuation rates were derived from the slope of the plots of natural log of concentration versus time for the contaminants in each piezometer (Fig. 7-9). Generally, results show that attenuation rates were higher in P-9 and P-10 than in P-8. This observation confirms or could be used to explain the results obtained from the Mann-Kendall trend analysis, which indicated that the decreasing BTEX concentration in the vicinity of P-8 was not significant as it was in the P-9 and P-10.

The average degradation rates for the BTEX constituents ranged from 0.00027-0.00055/day. These results are in perfect consonance with what was reported by Rifai et al. [49] whose work showed that attenuation rates for BTEX ranged between 0.0002 and 0.21/day. From the attenuation rates, it was revealed that xylene degraded at the fastest rate while benzene degradation occurred at the slowest rate, intimating that benzene is more recalcitrant to degrade at this site. This observation is also in accord with the results obtained by [43,44,50-53] who found benzene to be more recalcitrant to degrade than other BTEX compounds at the studied sites. However, the work of Bruce et al. [54] showed a contrary result. Benzene was found to degrade faster than the other constituents. The results of the attenuation rates in this study and those cited in this work show that the order and rate of degradation of BTEX are site specific.

Relative attenuation rates were also computed for the different BTEX compounds. With this, the attenuation rate of each compound was compared to the fastest attenuating compound. In this study, the fastest degrading contaminant was xylene. This was followed by toluene which was attenuating at an average rate of 72% of that of xylene. Ethylbenzene and benzene were also found to be attenuating at average rates of 60% and 48%, respectively, to that of xylene.

Tab. 3. Natural attenuation (NA) rate constants and half-lives for BTEX constituents at Tomaszów Mazowiecki

Tab. 3. Stałe szybkości samooczyszczania i czasy półrozpadu BTEX w wodach podziemnych w rejonie Tomaszowa Mazowieckiego

Contaminants	P-8	P-9	P-10	Average	Relative attenuation rate	Half-life	Time to reach remediation goal
	k (day ⁻¹)	k (day ⁻¹)	k (day ⁻¹)	k (day ⁻¹)	kC_o/k_x (day ⁻¹)	days(yrs.)	(yrs.)
benzene	1.9×10^{-4}	1.8×10^{-4}	4.2×10^{-4}	2.7×10^{-4}	0.48	2615(7.2)	11
toluene	3.2×10^{-4}	4.5×10^{-4}	4.1×10^{-4}	3.9×10^{-4}	0.72	1764(4.8)	2.73
ethylbenzene	3.5×10^{-4}	4.3×10^{-4}	2.1×10^{-5}	3.3×10^{-4}	0.60	2107(5.78)	5.77
xylene	4.0×10^{-4}	7.6×10^{-4}	4.9×10^{-4}	5.5×10^{-4}	1.00	1260(3.45)	3.1

Note: kC_o = attenuation rates of contaminants (BTEX); k_x = attenuation rate of xylene

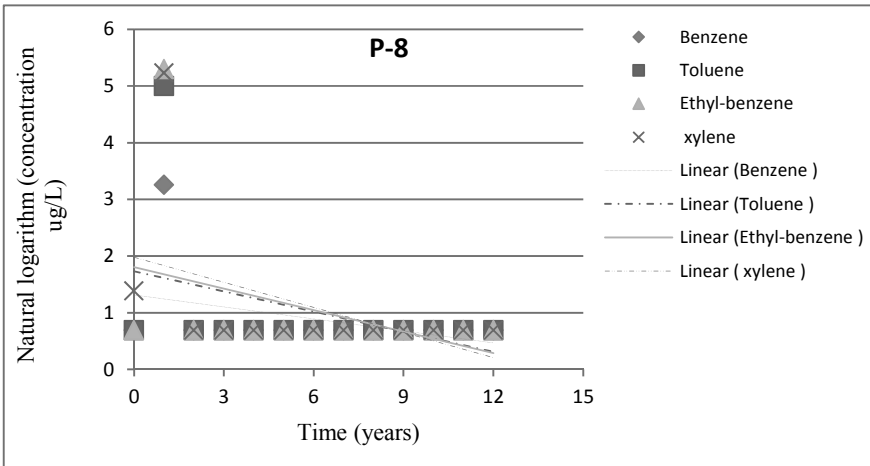


Fig. 7. Natural logarithm of BTEX concentration vs. time (P-8)

Rys. 7. Logarytm naturalny stężenia BTEX w wodach podziemnych w zależności od czasu (piezometr P-8)

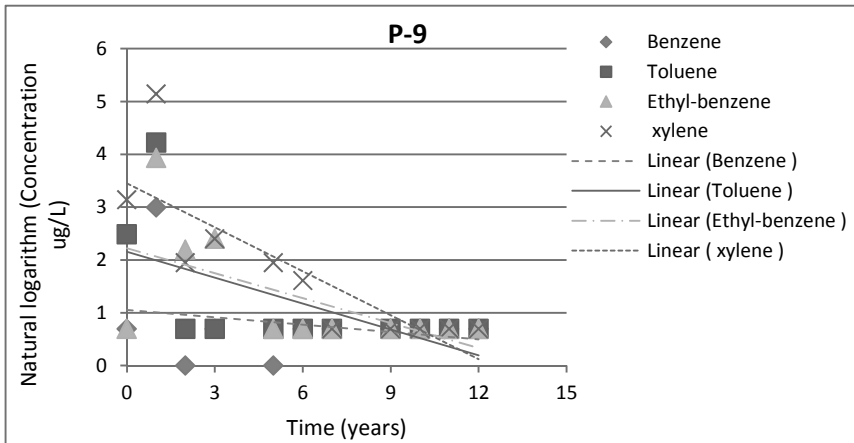


Fig. 8. Natural logarithm of BTEX concentration vs. time (P-9)

Rys. 8. Logarytm naturalny stężenia BTEX w wodach podziemnych w zależności od czasu (piezometr P-9)

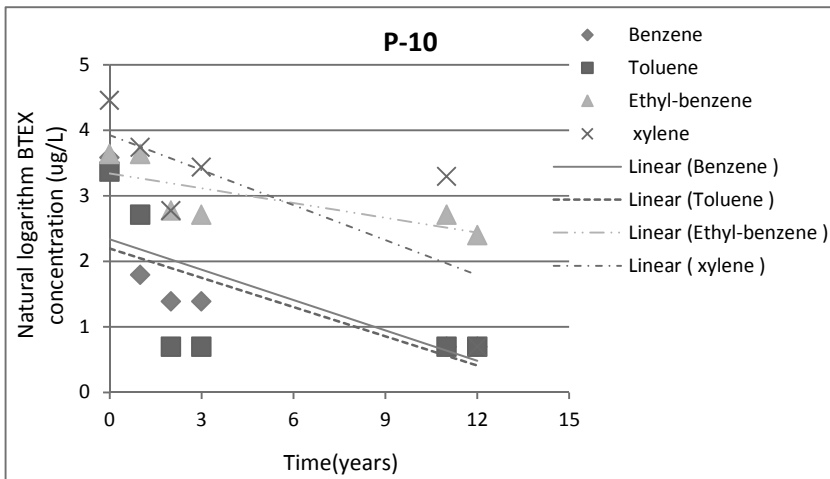


Fig. 9. Natural logarithm of BTEX concentration vs. time (P-10)

Fig. 9. Logarytm naturalny stężenia BTEX w wodach podziemnych w zależności od czasu (piezometr P-10)

The time to reach remediation goals was also computed for each BTEX compound (see Tab. 3). The remediation goals for xylene and toluene were reached almost three years, while for ethylbenzene almost six years after the accidental spill. For benzene, due its recalcitrance, it took 11 years after the spill to achieve the remediation goal.

After reaching the remediation goals, 27 to 50% of the initial contaminant mass (load) remained. If the effect of volatilization alone on the plume mass loss is to be considered, then about 95% of the total mass would have remained after the period of reaching the remediation goal. According to Wiedemeier et al. [3] and Chiang et al. [10], this estimate can even be expected to increase due to limitations imposed on contaminant mass loss by the capillary fringe. The differences in these results evidently show that volatilization is minimally affecting the contaminant loss. Due to lack of data, it was not possible to compute the actual effects of sorption and biodegradation on the contaminant reduction. However, assumptions were made to see the possible effect of sorption on the contaminant mass loss. Using the effective porosity and average groundwater velocity of 0.25 and 0.54 m/day, respectively, for the site, the effective velocity will be 2.16 m/day. Assuming a bulk density of 1.8 g/cm^3 and the fraction of organic carbon (f_{oc}) to be 0.001, and using the K_{oc} given in Table 1, retarded contaminant velocities will be between 2.10 and 2.13 m/day. These velocities are not very different from the effective groundwater velocity. This also shows that the effect of BTEX sorption is minimal. Based on these calculations and the assumptions herein made, it may be concluded that biodegradation is contributing to contaminant mass loss significantly, and therefore cannot be ignored.

6. Conclusion

Without any human intervention, natural processes occurring *in-situ* have been able to reduce BTEX concentrations in groundwater to innocuous levels without any sign of resurgence at the Tomaszów Mazowiecki study site. Primary and secondary lines of evidence were provided to prove this phenomenon. Graphical analysis showed that concentrations of BTEX were declining with time. Statistical trend analysis using the Mann-Kendall trend test also confirmed these results, but indicated that the decreasing trends were significant only in P-9 and P-10 at the 95% confidence level. The calculated BTEX attenuation rates were also in agreement with those obtained in other studies.

Xylenes attenuated at the fastest rate while benzene was recalcitrant to degradation. It was not shown in this study which mechanism was actually contributing to the observed phenomena; however, based on some assumptions, the results show that volatilization and sorption may be negligibly affecting contaminant mass loss in the site of concern. Results also suggest some spatial variations in NA mechanisms at the site, which may probably be due to aquifer heterogeneities. The results of this study, and the other works herein cited for comparison, suggest also that NA patterns and attenuation rates of BTEX are site specific.

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