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Application of Active Soil Gas Screening for the Identification of Groundwater Contamination with Chlorinated Hydrocarbons at an Industrial Area—A Case Study of the Former Refrigerator Manufacturer Calex (City of Zlaté Moravce, Western Slovakia)

Roman Tóth [1,2], Edgar Hiller [1,*], Veronika Špirová [1], Ľubomír Jurkovič [1], Ľubica Ševčíková [3], Juraj Macek [1,2], Claudia Čičáková [1], Tibor Kovács [4] and Anton Auxt [5]

[1] Department of Geochemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia; roman.toth@uniba.sk (R.T.); veronika.spirova@uniba.sk (V.Š.); lubomir.jurkovic@uniba.sk (Ľ.J.); juraj.macek@uniba.sk (J.M.); claudia.cicakova@uniba.sk (C.Č.)
[2] The Centre of Environmental Services, Ltd. (CENVIS), Kutlíkova 17, 852 50 Bratislava, Slovakia
[3] MM Revital, Inc., Šustekova 10, 851 04 Bratislava, Slovakia; sevcikova@mmrevital.sk
[4] NuSi, Ltd., Hattalova 3409/12B, 831 03 Bratislava, Slovakia; nusitk@gmail.com
[5] HES-COMGEO, Inc., Medený Hámor 25, 974 01 Banská Bystrica, Slovakia; hes-comgeo@hes-comgeo.sk
* Correspondence: edgar.hiller@uniba.sk; Tel.: +421-2-9014-9218

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Featured Application: A semi-quantitative method based on the determination of volatile organic compounds and other chemical parameters in soil gas using portable instruments with photo-ionisation and infrared detectors is well known for searching for hydrocarbon structures below the Earth's surface and subsurface contamination with organic contaminants. Here, in a case study from an industrial area, we have shown and confirmed that soil gas measurements are a very effective method for identifying the spatial extent and magnitude of groundwater contamination with volatile chlorinated hydrocarbons, such as tetrachloroethylene, trichloroethylene, etc. The application of soil gas screening contributes to a significant reduction in costs related to monitoring the extent of subsurface contamination.

Abstract: Background: Groundwater contamination with chlorinated hydrocarbons (CLHCs), particularly with tetrachloroethylene (PCE) and trichloroethylene (TCE), which are used in industry for degreasing and cleaning, can be considered a serious problem concerning the entire world. In addition to conventional groundwater monitoring from a network of wells, several screening methods have been proposed to identify and delineate groundwater contamination with volatile organic compounds (VOCs), such as soil gas measurement, bioindicators, direct-push technologies or geophysical techniques. The main objectives of this study were to confirm the feasibility of active soil gas screening for the characterisation of groundwater contamination with CLHCs under the wider area of the former refrigerator manufacturer (city of Zlaté Moravce, western Slovakia) and to evaluate the human health risks through exposure to CLHCs present in groundwater. Methods: a conventional site investigation based on concentration measurements using gas chromatography-mass spectrometry from monitoring wells and soil gas measurements using a portable photo-ionisation detector device were applied. Results: The chemical analyses showed the persistent contamination of groundwater, with PCE, TCE and other CLHCs, such as *cis*-1,2-dichloroethylene (*cis*-DCE) or 1,1,2-trichloroethane (TCA), being most severe in the zone of the former factory (up to 2690, 83,900, 6020 and 156 μg/L for PCE, TCE, *cis*-DCE and TCA, respectively), but also extended into the residential zone located 600 m along the groundwater flow line. Soil gas measurements of VOCs and other chemical parameters (methane (CH_4), total petroleum (TP), carbon dioxide (CO_2) and oxygen (O_2)) from a densely designed network of sampling points (n = 300) helped trace the current state of groundwater contamination. Spatial distribution maps of VOCs concentrations in soil gas clearly marked the areas of the highest CLHCs concentrations in groundwater. Principal component analysis (PCA) confirmed a significant correlation of VOCs and CLHCs with the first principal component, PC1, explaining up to 84% of the total variability of the concentration data, suggesting that VOCs in soil gas were a suitable marker of the extent of groundwater contamination with CLHCs. Despite severe groundwater contamination with CLHCs reaching residential areas, local residents were not exposed to non-carcinogenic risks, but a potential carcinogenic risk was present. Conclusions: based on the results, it could be confirmed that soil gas screening is an efficient and quick tool for identifying the sources of groundwater contamination with CLHCs as well as the level of this contamination.

Keywords: contamination; groundwater; chlorinated hydrocarbons; soil gas; human health risk

1. Introduction

Groundwater in urbanised and industrial areas is highly vulnerable to contamination with a wide range of volatile organic compounds (VOCs). An important position among VOCs is occupied by chlorinated ethenes, which are used in industrial processes as dry-cleaning and degreasing agents [1,2]. Tetrachloroethylene (PCE) and trichloroethylene (TCE) belong to the best-known and historically most studied chlorinated solvents. The long-term interest in the study of these compounds results from their high toxicity, mobility, persistence and the fact that they often accumulate in aquifers to a state of saturation as dense non-aqueous-phase liquids (DNAPLs), representing a challenge for the development of effective groundwater remediation methods [3–5]. The highest concentrations of PCE, TCE and their main anaerobic degradation products, *cis*-1,2-dichloroethylene (*cis*-DCE) and vinyl chloride (VC), in groundwater are usually associated with point sources. Groundwater in the close vicinity of a point source, e.g., the landfill of chemical waste and various industrial facilities, contained up to thousands of ug/L PCE and TCE with significant concentrations of *cis*-DCE and VC [6–8]. However, CLHCs concentrations of environmental concern may reach further from the source as a result of their transport under favourable conditions, limiting natural attenuation [9,10].

Tetrachloroethylene is classified as probably carcinogenic to humans (Group 2A), while TCE and VC belong to the carcinogens to humans group (Group 1) [11], highlighting the need for studies of groundwater contamination with CLHCs, especially in residential areas adjacent to industrial sites. In addition, several epidemiological studies have shown that the long-term environmental exposure of humans to PCE, TCE and VC causes an increase in the incidence of cancer and other serious diseases [5,12–14]. The harmfulness of chlorinated ethenes is reflected, for example, in their strict limits in waters intended for drinking purposes [15–17].

Human exposure to CLHCs in groundwater occurs through several routes such as oral ingestion, dermal contact with water during irrigation and hygiene or the inhalation of CLHCs vapours indoors and outdoors [8,18]. A human health risk assessment is an important tool for quantifying the contaminant intake of the exposed population from a particular medium through one or more exposure routes. A risk assessment characterises specific health risks, i.e., the existence of an incremental excess lifetime risk of developing cancer or the probability of an adverse effect in the exposed population [19]. It thus helps to decide the need for groundwater remediation and to implement effective remediation measures in the context of their technical complexity, cost and implementation time [20]. According to [18,19,21,22], a risk assessment of organic contaminants to human health is also important for ensuring the safety of groundwater, which is used as a source of drinking water.

For the investigation and delineation of VOCs in groundwater and soil, conventional methods are performed, including an analysis of groundwater and/or soil samples from soil borings and monitoring wells. Samples from these investigations provide reliable information about VOCs in groundwater and/or soil, both qualitatively and quantitatively [23,24]. However, these methods have some limitations—they are expensive, invasive, time-consuming, labour-intensive, one-dimensional and characterised by serious issues of spatial under-sampling in the space [25–28], especially in the densely built-up, still active industrial facilities, with buried installations or hazards such as cables. This entails an enhanced risk of overlooking single contamination sources or even high-risk areas, which, in consequence, can dramatically hinder the risk assessment and effective remediation [29–31]. Therefore, characterisation with sufficient spatial resolution is one of the main concerns and is still an open area of research. Today, there are multiple cost-effective, reliable and fast screening methods, e.g., phytoscreening [32–34], geophysical methods [31,35,36], direct-push with a membrane interface probe (MIP) and laser-induced fluorescence (LIF) sensors [37–39], as well as soil gas measurements and sampling [40–43]. These, if applied correctly, minimise the risk of missing single contamination sources or high-risk areas without increasing the financial burden by directing and focusing the subsequent, more precise, but also more expensive methods [44–47].

Volatile organic compounds, besides having a high vapour pressure, tend to be slightly soluble in water, in the order of tens to thousands mg/L. The high vapour pressures of most VOCs result in their strong partitioning from water into the gas phase [48]. Thus, almost all VOCs in soils and groundwater are also present in soil gas [49]. Over time, VOCs migrate from groundwater contaminant plumes into the overlying soil gas, which in turn may become a source of vapour intrusion [50]. Concentrations of VOCs in soil gas depend on their concentrations in groundwater, solubility in water, vapour pressure and soil/subsurface properties [40]. Particularly, chlorinated ethenes have low solubility in water, a high vapour pressure and diffusion coefficients and are relatively resistant to degradation in most soils. These properties make them suitable for detection using soil gas sampling [51]. In order to minimise the risk of missing a single groundwater contamination source and avoid the inaccurate reconstruction of the spatial contamination extent, a more thorough pre-screening of the site at a reduced cost with rapid analytical results was carried out using soil gas measurements and sampling, whose effective use, also in combination with phytoscreening or geophysical methods, has already been confirmed [26,33,43]. Moreover, results of soil gas measurements can be much more sensitive in some cases than those of soil and water sampling outputs [42]. On the other hand, screening techniques cannot replace conventional in situ sampling. Soil and/or groundwater sampling with chemical analysis should be applied as the last step to confirm and interpret identified contamination and to quantify the contaminant levels to avoid the potential misinterpretation of the findings [31,52].

The application of soil gas measurements to delineate subsurface organic contamination is well-known and has been used extensively since the 1980s [53–58]. Soil gas measurements were used as a tool to assess VOCs-containing hazardous waste landfills [59,60] or to monitor the non-aqueous-phase liquids and hydrocarbon accumulation by measuring radon concentrations and other gaseous compounds [61–63].

Soil gas measurements (active and passive), defined as the collection, analysis and interpretation of soil gas data, are typically used in site investigation and remediation projects where VOCs are the primary constituents of concern [64]. Measurements of vapours in the soil pore space can help to determine the occurrence, composition, source and type of release and distribution of contaminants in the subsurface. In addition, they can be used to delineate VOCs vapour plumes as a screening tool to refine soil and groundwater sampling and to monitor soil remediation progress. Active soil gas measurement is conducted by analysing soil gas from specific depths, which is pumped from the ground through probe holes. Volatile organic compounds can be detected directly by soil gas sampling methods, while semi-volatile organic compounds (SVOCs) and nonvolatile organic compounds can be detected indirectly by measuring gases (e.g., O_2, CO_2, H_2S, and CH_4) [65]. Soil gas measurement is a rapid, non-invasive screening method, but limited only to VOCs in the unsaturated zone with medium-to-high permeability, i.e., it is not feasible in a low permeable rock environment. The disadvantage is the fact that soil gas sampling captures a limited area, but this can be overcome by thickening the sampling grid [26,38]. Soil gas measurement and analysis are a constantly evolving method. Considerable research is focused on the determination of greenhouse gases [66,67] and the latest technological developments in soil gas screening, such as the development of modern spectrometry methods, the soil gas sampling technique, involving AI approaches, the application of mathematical statistics and regression analysis or the influence of design features on the accuracy of measurements over time, were attentively summarised in a recent extensive review [68].

More than 1800 environmental burdens of different industrial and agricultural origins were identified in Slovakia. It was estimated that around 1200 of these contaminated areas pose a serious risk to human health and the environment and more than 100 areas are at high risk, requiring immediate remediation [69]. One of these contaminated areas is located in the city of Zlaté Moravce (western Slovakia)—the former refrigerator manufacturer, Calex company. The improper handling of chemicals during ~50 years of refrigerator manufacturing led to extensive groundwater contamination with CLHCs, mostly with PCE, TCE, *cis*- and *trans*-DCE and VC [70]. Compared to drinking water standards applicable in the European Union (EU) [15], the maximum concentrations of PCE, TCE and VC in groundwater for 2015 (6482, 85,200 and 5186 μg/L for PCE, TCE and VC, respectively) exceeded the limit values by more than 8500 and 10,000 times, respectively. Despite some minor remedial pump-and-treat interventions in the restricted area of the northern part of the industrial area [71,72], severe groundwater contamination persists to this day. It is likely that not all sources of groundwater contamination were identified and remediated. To identify these potentially "hidden" and persistent contamination sources, an extensive active soil gas measurement was carried out. It should be noted that the soil gas measurement was not a substitute for a conventional methodology, but served as a screening tool, allowing for the more effective use of conventional methods. Based on the soil gas screening, new groundwater sampling sites were selected for further exploration work to confirm these sources and identify sites intended for remediation. Although many studies and academic reports used soil gas screening to determine subsurface contamination by CLHCs and other VOCs, and to identify its main sources, they were mostly limited to pre-characterised source locations with the significant accumulation of contaminants (so-called hot spots) that were identified by a conventional groundwater sampling methodology. In this study, soil gas screening was used over a large area and at sites hundreds of meters away from the contamination source. Taking into account the advantages and disadvantages of soil gas screening, this method seems to be suitable for the studied area as the existing data showed that the groundwater contained contrasting concentrations of CLHCs spanning several orders of magnitude and, at the same time, the area has a relatively uniform rock environment with high permeability. In addition, the elucidation of the extent of groundwater contamination and its sources is of public interest due to permanent settlement in the south-western part of the study area, where residents are exposed to vapour intrusions from contaminated groundwater. In addition, the results of this study could be verified in other industrial areas with a similar type of contamination and geological settings. Therefore, the main objectives of this study could be summarised as follows: (i) to determine the extent of groundwater contamination with CLHCs using a conventional methodology and existing historical data at an industrial area (the former refrigerator manufacturer—Calex company, city of Zlaté Moravce in western Slovakia); (ii) to apply soil gas screening to further refine the delineation of groundwater contamination and source identification, and to verify the suitability of its application by combining the results of soil gas screening with the results of a conventional methodology through spatial distribution map outputs and multivariate statistics; and last but not least,

(iii) to assess human health risks from the exposure of residents to CLHCs in groundwater. This last objective is important because groundwater contamination with CLHCs has extended to the surrounding residential zones.

2. Materials and Methods

2.1. Area Description

The area of the former refrigerator manufacturer is situated in the western part of Slovakia, in the north of Zlaté Moravce city (Figure 1). Refrigerators and related components have been produced since the 1950s; production ended in 2002 [70,71]. The study area included the former factory (source area, area A), agricultural land (area B) and residential zone (area C). The former factory is located in the north of the area, residential zone is in the southern part of the area and the central part is an agricultural land (Figure 1). Smaller engineering and repair companies are still in operation in the area of former refrigerator production.

The aquifer is formed by Quaternary fluvial sediments, mainly clayey and silty gravels with inter-granular permeability. The aquifer has a thickness ranging from 2 m to 5 m within the entire area, and the mean depth of the water table is 4.0 m below ground surface (b.g.s.). The direction of groundwater flow is from northeast to southwest. A layer of silts and sandy silts with a mean thickness of 2.4 m is above the aquifer, and the source area is covered by a 0.5 to 1.0 m-thick layer of anthropogenic sediments. Below the aquifer, at a depth of approximately 6.0 to 8.0 m b.g.s., Neogene sediments consisting of diverse clays of firm consistency are deposited, representing an impermeable layer, i.e., aquitard (Figure S1 in Supplementary Material (SM)).

Previous hydro-geochemical monitoring confirmed a serious contamination of groundwater with CLHCs. According to [70], groundwater in the source area (area A in Figure 1) contained 21.7–6482 μg/L PCE, 53–85,200 μg/L TCE, 32–34,190 μg/L *cis*-DCE and 11–5186 μg/L VC. However, VC was below the detection limit at most monitoring sites. Concentrations of CLHCs above the EU drinking water limit were also confirmed in the residential area C (15–186 μg/L PCE and up to 80 μg/L *cis*-DCE). Free-floating oil product (0.14 to 0.29 m thick) was found at the groundwater table in two wells located in source area A [30]. Soil analyses found high concentrations of total petroleum (TP; 1040–17,900 mg/kg) and benzene, toluene, ethylbenzene and xylenes (BTEX; 190 mg/kg); however, contaminated soils were excavated and removed [70]. Due to the persistent and extensive groundwater contamination in the area, remediation is necessary.

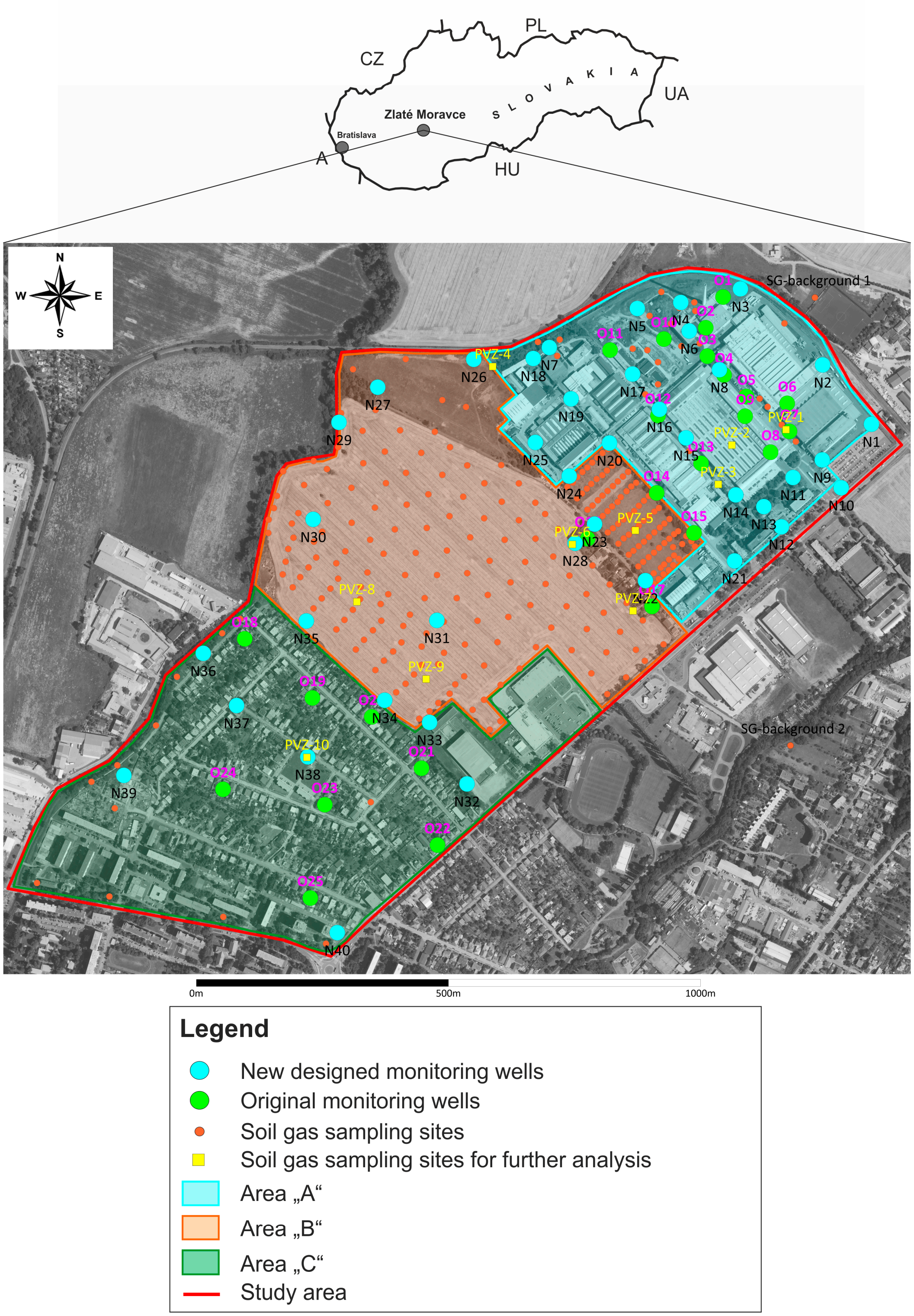

Figure 1. Location of the study area within Slovakia and investigated zones: area A = source area (the former refrigerator manufacturer, Calex Company, City of Zlaté Moravce, Slovakia), area B = agricultural land and area C = residential zone, including also sampling sites for semi-quantitative measurements of chemical parameters in soil gas (orange circles) and existing and newly installed wells (green and light-blue circles, respectively) for groundwater sampling. Yellow square shows sampling sites of soil gas for GC-MS analyses.

2.2. Soil Gas and Groundwater Sampling and Analysis

For the purposes of this study, i.e., identification of groundwater contamination sources and gas plume delineation, active soil gas screening, including semi-quantitative measurements of VOCs and other parameters (CH_4, TP, CO_2 and O_2) in soil gas, was carried out with a portable instrument equipped with photo-ionisation detector (PID) within temporary soil probes and uniform sampling and chemical analyses of soil gases.

Temporary soil probes with a diameter of 8 cm were deepened with a hand auger and slam bar to a depth of 0.8 m below the ground in the entire studied area. After removing the auger or slam bar, the sampling device (hollow steel probe) was inserted into the opening and the atmospheric gases were purged. The space between the soil probe and the device was sealed with a sealing cone at the ground surface. The soil gas quality was analysed with a portable photo-ionisation detector (PID) device (Ecoprobe 5 Infrared, RS Dynamics, Zug, Switzerland). This device enables real-time chemical monitoring (contaminant detection) by measuring total VOCs concentration with PID calibrated using isobutylene and separate measurements of CH_4, TP and CO_2 with an infrared (IR) analyser calibrated using methane. In addition, temperature, pressure and O_2 are also measured. The device uses a small pump to draw gases through access tubes into the ionisation chamber. Simultaneous with determining the optimal depth of soil gas measurements and sampling (0.8 m), the pump flow rate (1.0 L/min), soil gas volume (0.4 L) and measurement duration (25 s) were adjusted to the level of soil contamination and soil air permeability tests in vertical profiles at selected sites prior to soil gas screening. The depth of 0.8 m below the surface for soil gas measurement and sampling was selected to minimise the effect of changes in barometric pressure, temperature, break-through of ambient air from the surface, high saturation, clay, organic matter and presence of anthropogenic sediments, which could limit soil gas transfer at the near-surface horizon. Carrying out soil gas measurements in this depth should avoid water-table depth variations, depending on the season and the rainfalls, that may also have an impact on the soil gas transfer. The PID detector was calibrated daily with 100 ppm isobutylene standard to provide fast in situ correction of instrument’s response that might be changed due to internal dusting or depositing of various particles, etc. Before each measurement, the soil gas installation was purged by extracting three system volumes and measurement and sampling started only after the stabilisation of the physicochemical parameters monitored by the PID. In total, soil gas measurements were performed at 300 sampling sites across the study area (Figure 1). Soil gas measurements were also carried out at two sites outside the study area (marked as SG background 1 (above the industrial area) and SG background 2 (left bank of the local stream of Žitava) in Figure 1), i.e., at sites that are not in contact with source area A. Concentrations of chemical indicators in soil gas at these sites were considered as local background because groundwater contamination with CLHCs was not confirmed after repeated sampling [70].

As already known [13,38,49,64,65,73–78], there are limitations of soil gas measurement and sampling methods, such as meteorological conditions (rainfall, low barometric pressure, wind), depth of groundwater, lithology and properties of the overlaying soils (very-low-permeable or saturated soils, high soil moisture, preferential pathways), microbial activity and biodegradation (resistance of contaminants to biodegradation), etc. To overcome these limitations, prior to soil gas measurements, a detailed historical study of the geology, hydrogeology and operational activity of the industrial area, as well as continuously cored borings in individual parts of the studied area, was carried out to collect information about lithology and depth of groundwater. Subsequently, all soil gas measurements were carried out following the same procedure, sampling sites spacing and frequency was thickened and, where possible, the measurements were carried out in a regular grid, decontamination procedures were practiced to prevent contaminant gain or loss that results from adsorption onto sampling equipment, blank samples were tested regularly and pressure, temperature, wind speed, depth of groundwater and rainfall were monitored during the whole soil gas measurement campaign. To limit the effect of soil moisture and seasonal variations on the results of the soil gas measurements to the greatest possible extent, soil gas measurements were realised during longer dry periods without precipitation and in the shortest possible time, while season, moisture content and water-table depth variations among others also affect the biodegradation of VOCs in soil gas available for measurements and sampling [65].

For qualitative/quantitative chemical analyses, ten soil gas samples were taken from probes evenly distributed throughout the study area (Figure 1). A volume of soil gas equal to three system volumes was vented from each soil probe before the soil gas samples were collected in a glass tube with sorbent (activated carbon). The sorbent tube was connected to a pump inserted into the soil probe. Soil gas samples were taken at a pump flow rate of 200 mL/min and a sampling duration of 10 min. After the end of the sampling, the test tubes were stored in the cold (<4 °C) and dark environment until the analysis. Soil gas samples were analysed for BTEX, CLHCs and TP using gas chromatography-mass spectrometry (GC-MS). Soil gas sampling was carried out according to the European standard ISO 18400-204:2017 Soil quality–Sampling–Part 204: Guidance on sampling of soil gas [79].

Before the screening, groundwater samples were taken from 25 existing monitoring wells (marked as O1–O25 in Figure 1). Based on the results of the soil gas screening, at sites with anomalously high concentrations of VOCs or other gases (CH_4, CO_2 and O_2) in contrast to their mean concentrations in the study area as a whole, further conventional works were optimised, specifically where new monitoring wells for groundwater sampling were situated. A total of additional 40 monitoring wells (diameter = 110 mm) were drilled to a depth of 6 to 9 m b.g.s. (marked as N1–N40 in Figure 1), depending on the depth of the aquitard, at sites of potential sources of groundwater contamination identified by the soil gas screening. Concentrations of targeted chemicals (PCE, TCE, *cis*-, *trans*-DCE, VC and TCA) in groundwater were determined using GC-MS according to the USEPA method 8260D [80]. All determinations of targeted compounds in soil gas and groundwater samples were performed by the accredited laboratories of ALS Slovakia (a member of the ALS Group).

2.3. Data Analysis and Human Health Risk Assessment (HHRA)

Data were processed by several statistical methods. The Kolmogorov–Smirnov test was used to test the null hypothesis that the data set comes from a normal distribution. Since there were many repeated values in some variables and also some outliers, the data were identified as non-normally distributed. The non-parametric Spearman rank correlation coefficient was used for the primary inspection of the relationships among the determined parameters in the soil gas. The effect of VOCs and TP, which are indicators of soil gas contamination, on parameters indicating possible VOCs degradation, and thus tracking groundwater contamination, was investigated by Spearman correlation and principal component analysis (PCA). Principal component analysis was used to simplify the data set, to identify outliers and to reveal hidden relationships among the variables and samples. Kruskal–Wallis and Dunn's post hoc tests were used to determine significant differences in the values of the variables among the designated zones within the study area. Results were considered statistically significant at $p < 0.05$ or lower. Since the raw data were measured in different units, standardisation of the original data was necessary. Data transformation was carried out according to the following equation:

$$Y = (X - b)/a, \tag{1}$$

where Y is the standardised value, X is the original value, b is the sample mean and a is the sample standard deviation. The contoured isopleth maps were constructed using the Surfer® program, version 17 (Golden Software, LLC, Golden, CO, USA) and STATISTICA 12.0 and GraphPad Prism 8.0.1 software were used for statistical data processing.

The human health risk assessment (HHRA) was oriented around areas B and C with permanent settlement. The carcinogenic risk (expressed as individual excess lifetime cancer risk, IELCR) and non-carcinogenic risk (expressed as hazard quotient, HQ) from multiple exposure routes of the population to the main CLHCs were calculated. The following exposure routes were considered: (i) dermal contact with contaminated groundwater during irrigation, (ii) inhalation of irrigation water spray, (iii) ingestion of groundwater during irrigation period, (iv) inhalation of indoor or outdoor air and (v) ingestion of home-grown vegetables irrigated with contaminated groundwater. Equations for calculating exposure doses, HQs and IELCRs, and other details on HHRA are given in Supplementary Text 1. The values of chemical toxicity values for PCE, TCE and *cis*-DCE and of the parameters in the equations are shown in Tables S1 and S2, respectively. The RISC5 software, version 5.0, was used for human health risk assessment. To identify the contamination of groundwater with CLHCs, their concentrations were compared to drinking water standards of the European Union [15], the United States Environmental Protection Agency (USEPA) [17], the World Health Organisation (WHO) [16] and the indication and intervention criteria (ID and IT, respectively). Exceeding the ID value of a particular compound means that contamination is confirmed, while exceeding the IT indicates the need for remediation due to a serious environmental and health risk arising from the presence of the toxic compound [81]. The drinking water standards and ID/IT criteria values of CLHCs are shown in Table S3.

3. Results and Discussion

3.1. Occurrence of Chlorinated Hydrocarbons and Their Spatial Distribution in Groundwater

The concentrations of studied CLHCs in groundwater from original and newly designed wells are listed in Table S4 and illustrated in the form of Tukey box plots in Figure 2. Many of the CLHCs, e.g., VC, most of the chlorinated ethanes, chloroform, BTEX, etc., were below the detection limit of GC-MS in most wells; therefore, the discussion was limited to the major CLHCs like PCE, TCE, *cis*- and *trans*-DCE and TCA. Comparing the median values of CLHCs concentrations in groundwater, PCE showed the highest median concentration, followed by TCE, *cis*-DCE, TCA and *trans*-DCE; however, the concentration difference was statistically significant only for PCE vs. *trans*-DCE, PCE vs. TCA, TCE vs. *trans*-DCE and *cis*-DCE vs. *trans*-DCE. This order reflects the fact that TCE was the primary chlorinated solvent used in production, while PCE was used as a substitute for TCE. In addition, part of TCE is an intermediate product of the microbial degradation of PCE, which is further degraded to form *cis*- and rarely *trans*-DCE [82,83]. This fact was also indicated by highly positive correlations between PCE and TCE ($r_S = 0.41$; $p < 0.01$; Spearman rank-order correlation), PCE and the sum of *cis*- + *trans*-DCE ($r_S = 0.74$; $p < 0.0001$), PCE and TCA ($r_S = 0.64$; $p < 0.001$) and TCE and *cis*- + *trans*-DCE ($r_S = 0.60$; $p < 0.0001$). However, the broad absence of VC, being present only in three wells from source area A, suggests the incomplete dechlorination of PCE/TCE in this area [4], possibly due to a low population of suitable bacteria or the rapid conversion of VC through oxidation reactions [84]. A large part of the area has oxygen-saturated groundwater (Figure 3), in which VC is unstable and rapidly oxidises aerobically [10,84]. This could be the reason for the low frequency of its occurrence in groundwater. It was found that *cis*-DCE is also degraded by aerobic oxidation but to a lesser extent [85], which finally coincides with the higher frequency of occurrence of *cis*-DCE compared to that of VC (Figures 3 and 4). From the point of view of groundwater contamination and its impact on the environment and human health, this is a favourable situation, since VC is more toxic compared to *cis*-DCE, PCE and TCE.

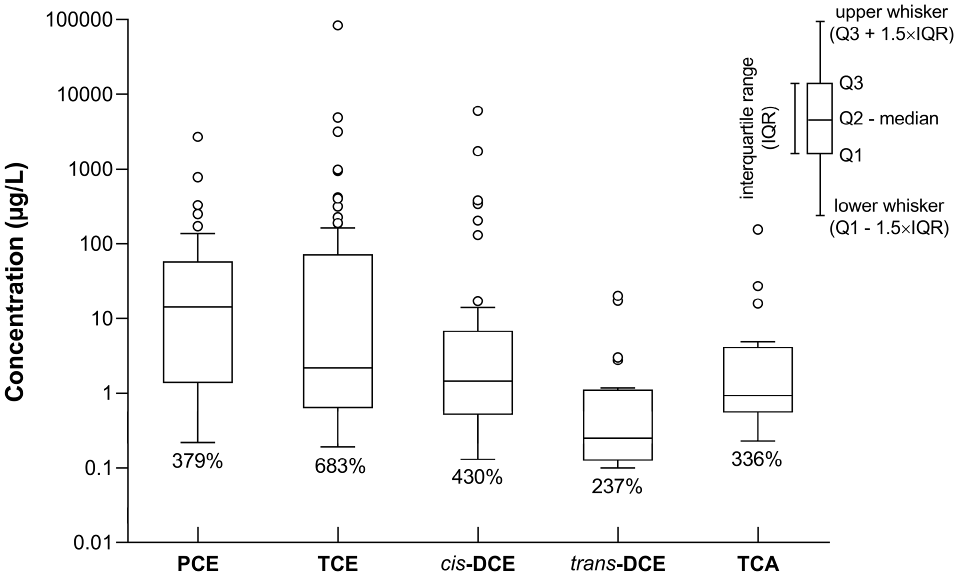

Figure 2. Statistical summary of concentrations of the most frequently detected chlorinated hydrocarbons in groundwater in the form of Tukey box-plot. Vinyl chloride (VC) is not shown due to the small number of samples above the relevant detection limit (<1.0 µg/L). White circles represent outliers. The percentage numbers below the lower whisker are the coefficient of variation (CV).

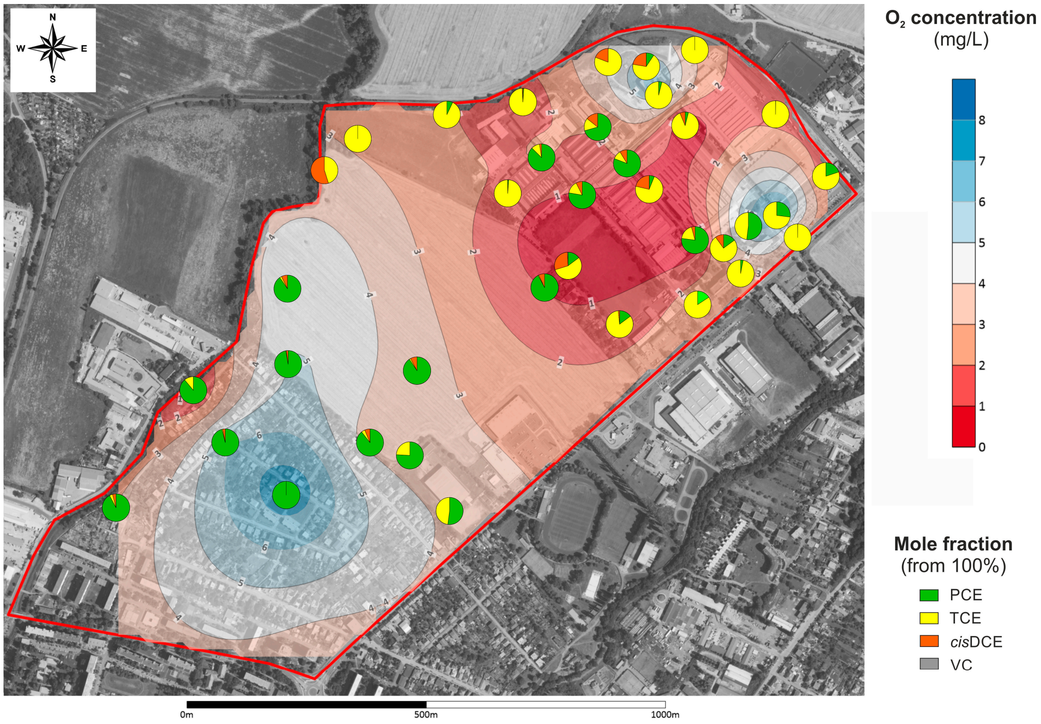

Figure 3. Evolution of PCE mole fraction relative to other less chlorinated ethenes (calculated as the ratio of PCE mole concentrations to the sum of mole concentrations of PCE, TCE, *cis*-DCE and VC) in groundwater with increasing distance from the source area A and its relation to the spatial distribution of dissolved oxygen concentrations (mg/L). Generally, PCE mole fraction in groundwater increased towards higher dissolved oxygen. Note that groundwater flows from northeast to southwest. The red frame indicates the studied area.

The first systematic data on the concentrations of PCE, TCE, *cis*-, *trans*-DCE and VC in the groundwater of this industrial area come from 2005 and 2015. One of the possibilities of demonstrating the natural attenuation of CLHCs is to compare existing historical concentration data with the current data obtained in this study. The median PCE concentration from the sampling campaign in 2020 was significantly lower than that of 2005, while the median concentrations of TCE and the sum of DCEs from the most current sampling campaign were lower than those of 2015 and 2005 (Figure 4). Vinyl chloride also showed lower concentrations in the groundwater sampled in 2020, but the statistical comparison was meaningless due to the limited number of groundwater samples above the detection limit. This decrease over the last 15 years averaged 72% for PCE, 80% for TCE and 85% for the sum of *cis*- and *trans*-DCE. Two reasons could be behind the gradual decrease in CLHCs concentrations: (i) slow natural attenuation through microbial, physical and chemical processes [86] and (ii) small-scale remedial intervention using the pump-and-treat method targeting identified dense non-aqueous-phase liquids (DNAPLs) carried out in the study area [71,72]. On the other hand, high CLHCs concentrations in source area A (Figure 5) and PCE, TCE and *cis*-DCE concentrations in several wells above the 1:1 concentration line (that is, a straight line expressing the same concentration in an individual well between the two evaluated sampling years), i.e., higher in the last groundwater sample than in previous years (Figure S2), were observed. This is evidence of the persistent contamination of the aquifer. These compounds accumulate in the deepest aquifer parts as DNAPLs. The fate of DNAPLs is complicated; they can be divided into smaller units that are trapped in low-permeability zones, releasing contaminants for a long time [87,88]. It has been estimated that DNAPLs can persist for hundreds of years [89]. Also, the seepage of chlorinated solvents from still-operating smaller manufacturers in source area A and slow diffusional dissolution from the sorbed state into the pore spaces of the aquifer, a process that may take years [90], cannot be ruled out.

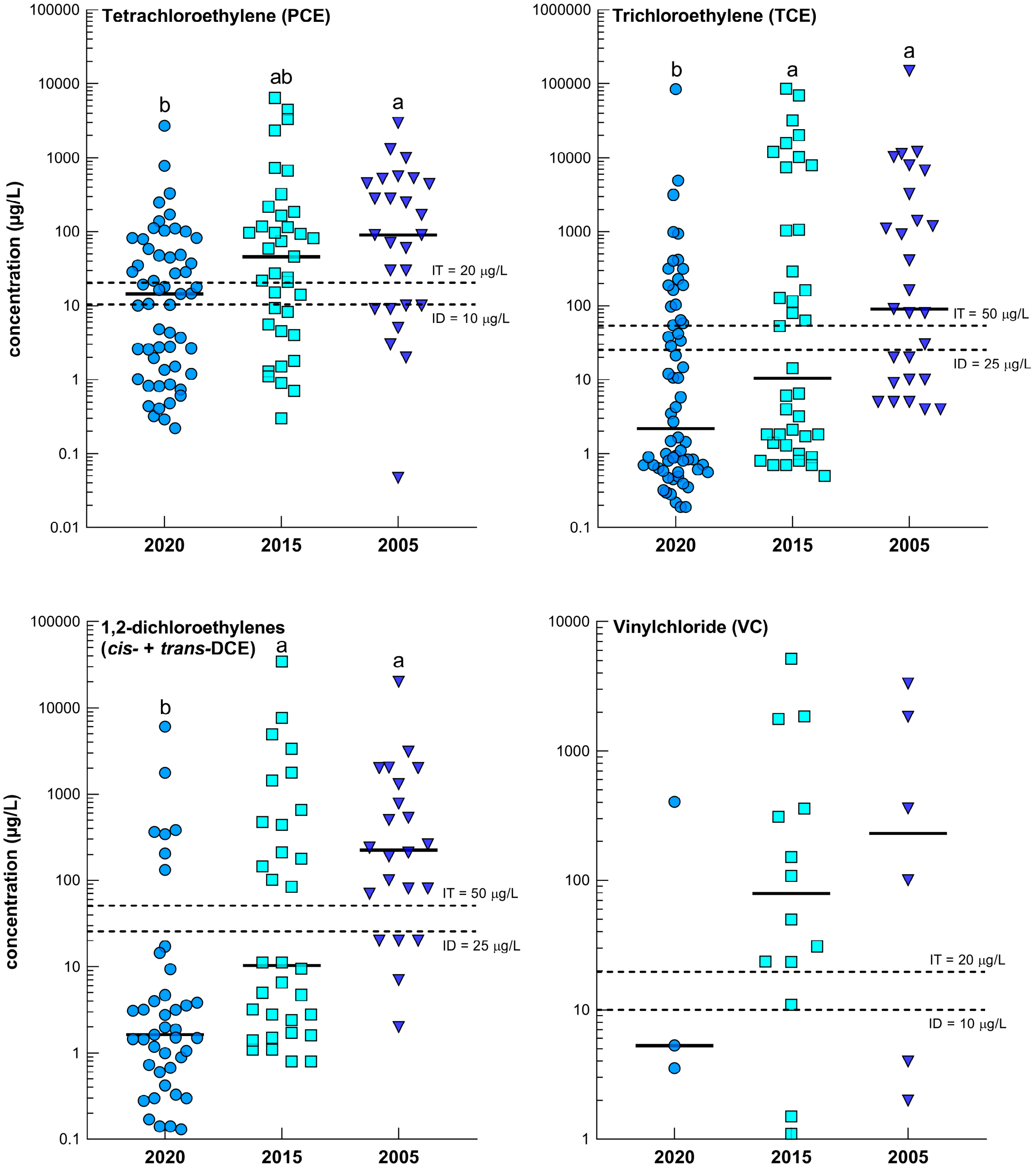

Figure 4. The concentrations of chlorinated hydrocarbons determined in this study (year 2020) compared to older concentration data (years 2005 and 2015) from the study area, taken from the final report of [70]. Different lowercase letters above concentration points indicate a statistically significant difference in concentrations among the sampling campaigns at a significance level of <0.05 (Kruskal–Wallis test with Dunn's post hoc test).

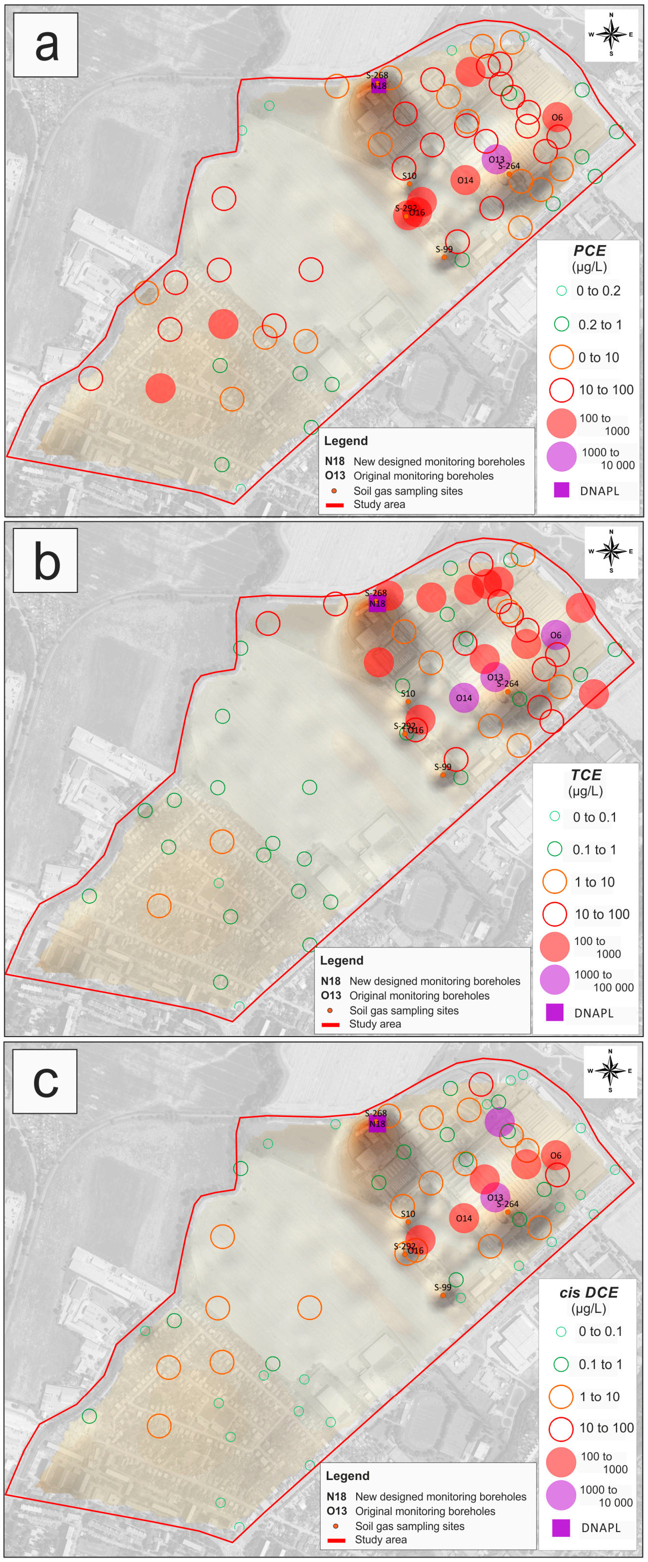

Figure 5. Dot distribution maps: (**a**) PCE, (**b**) TCE and (**c**) *cis*-DCE concentrations in groundwater from the study area on a background showing the spatial distribution of VOCs concentrations in soil gas. Maps for VC and TCA are shown in Figure S3 in Supplementary Material. Specifically mentioned soil gas (symbol S) and groundwater (symbol N and O) sampling sites in the text are numbered. The direction of groundwater flow is from northeast to southwest.

The concentrations of CLHCs in the groundwater varied by up to five orders of magnitude with high coefficients of variation (379%, 683%, 430%, 237% and 336% for PCE, TCE, *cis*-DCE, *trans*-DCE and TCA, respectively) (Figure 2), indicating a heterogeneous spatial distribution of their concentrations, common in industrial and urban areas with this type of chemical contamination [2,6,7]. These concentrations represented ~10^{-6} up to 100% of the respective solubility of individual CLHCs. Dot distribution maps of CLHCs concentrations in groundwater showed that groundwater contamination with these compounds decreased with the increasing distance from source area A, i.e., in the direction of the groundwater flow (Figures 5 and S3). The decrease was clearly visible for TCE, *cis*-DCE and TCA, with the highest number of wells where the concentration exceeded 10 μg/L in source area A. Although groundwater from this area is not used for drinking purposes, a comparison to drinking water standards could be taken as an indicator of the level of groundwater contamination with CLHCs. The concentration data were compared to the drinking water standards of the EU, USEPA and WHO (Table S3). The comparative results confirmed that PCE and TCE were of primary interest when more than 60% of sampling sites exceeded the EU limit for the sum of PCE and TCE (10 μg/L). Both WHO and USEPA list drinking water standards separately for PCE and TCE. In any case, 50% of all wells exceeded the USEPA standard for PCE (5.0 μg/L), but with a significant decrease to 14% considering the less stringent WHO limit (100 μg/L). TCE concentrations were higher in 43% of sampling sites compared to the WHO and USEPA criteria of 8.0 μg/L and 5.0 μg/L, respectively. *Cis*- and *trans*-DCE, VC and TCA showed a lower frequency of exceeding the respective drinking water standards: 11%, 5% and 5% of all wells, respectively. The severity of groundwater contamination was also indicated by comparison to the IT criteria (Table S3). Up to 42% of all wells showed PCE above the IT criterion (20 μg/L), TCE exceeded the IT value of 50 μg/L in 28% of the wells, but *cis*- + *trans*-DCE were above the IT (50 μg/L) in 11% of all wells.

Also, a gradual increase in the values of the mole fraction of PCE from the sum of the five studied CLHCs and the ratio of PCE to TCE was observed with the increasing distance from source area A towards area B (agricultural land) and area C (residential zone) (Figure 3). This increase corresponded to the transition of redox conditions in the groundwater from low-oxygen conditions in the source area A (<1 mg/L O_2) to predominantly aerobic conditions in residential area C. These findings could be explained by the fact that the anaerobic environment is favourable for the degradation of PCE, which degrades faster than TCE or *cis*-DCE; in other words, ethenes with a higher number of chlorine atoms are more susceptible to anaerobic dechlorination [91]. On the other hand, in aerobic environments, the decomposition of PCE is significantly limited compared to less chlorinated ethenes [92], leading to an increase in the mole fraction of PCE.

3.2. Spatial Distribution of VOC Concentrations in Soil Gas and Its Relation to Groundwater Contamination with CLHCs

The values of all chemical parameters in soil gas from each sampling site are listed in Table S5. The semi-quantitative analyses of soil gases using a portable PID device showed that compared to the background concentration of VOCs (411 μg/m^3), the study area exhibited higher VOCs concentrations. Considering the area as a whole, the mean VOCs concentration was 3090 μg/m^3, while the highest mean VOCs concentration (4850 μg/m^3) was in source area A (Figure 5 and Table S5). However, these VOCs concentrations in soil gas were lower than those determined in the 1990s [93,94], which is in line with the decrease in the dissolved concentrations of PCE, TCE and DCE in groundwater compared to older concentration data [70] (see also Section 3.1 for details). The highest VOCs concentrations within the source area (from 4530 μg/m^3 up to the upper detection limit of the instrument, >100,000 μg/m^3) were found at the processing and cleaning sites for refrigerator components, at the chemical warehouse and at the pumping station for chlorinated solvents (site S268). The mean VOCs concentration in agricultural land (area B) and residential area C was 1470 and 3750 μg/m^3, respectively. The elevated VOC concentrations in the soil gas of residential area C, located approximately 600 m from source area A, clearly indicated the persistence of groundwater contamination over a large area. On the other hand, higher VOC concentrations could be due to additional sources in the residential area, especially road traffic. This was clearly seen from the semi-quantitative soil gas analysis of sample S286 located at the roundabout, with a VOCs concentration of 7620 μg/m^3 and TP of 2032 mg/m^3. Other soil probes along the busy road (orange circles at the lower boundary of the study area, Figure 1) had also higher concentrations of VOCs (3205–7480 μg/m^3) and TP (13–116 mg/m^3), which might be an obstacle for the success of delineating the lateral extent of the CLHCs contamination plume. Studies confirmed that traffic emissions and spills of motor fuels and oils were a significant source of VOCs to soils and air [95–97]. However, our semi-quantitative analyses, without knowledge of the occurrence of individual VOCs in soil gas, could not confirm contributions to VOCs from other sources.

A more detailed view of the spatial distribution of VOCs concentrations in soil gas in relation to the concentrations of other gases (CH_4, CO_2 and O_2) and CLHCs in groundwater helped to identify sites that can be considered as a source of groundwater contamination and to better understand the natural processes responsible for the observed spatial distribution of CLHCs concentrations in groundwater. Particularly high VOCs concentrations (between 8954 and >100,000 μg/m^3), often associated with high CH_4 concentrations, were found at sampling sites S264, S99, S10, S292 and S268, all from source area A (Table S5). These sampling sites, considered as the contamination sources, corresponded to high CLHCs concentrations in groundwater (Figure 5), as confirmed by chemical analyses from wells O6, O13, O14, O16 and N18 (a concentration range from 111 (PCE), 12 (TCE), 9.24 (*cis*-DCE) and 3.73 (1,1,2-TCA) μg/L up to the limit of aqueous solubility; Table S4). Anomalous VOCs and CH_4 concentrations in soil gas (>100,000 μg/m^3 and 1191 mg/m^3, respectively) were observed at well site N18 with concentrations of all CLHCs in the groundwater at the level of 100% of their respective solubility. At this site, there was a pumping station for organic solvents; therefore, it is clear that the leakage of chlorinated solvents led to their accumulation in the form of DNAPLs due to their higher density than water [98,99]. Dense non-aqueous-phase liquids were found to persist in groundwater for several decades and serve as a persistent source of groundwater contamination [100]. In addition, CLHCs in the form of DNAPLs can spread further along the impermeable geological layer by the groundwater flow and settle in aquitard depressions, thus forming long-term secondary contamination sources [4]. It should be emphasised that high CLHCs concentrations in groundwater were not always reflected by increased VOCs levels in soil gas. An example of this situation was the significant groundwater contamination from well O3 of source area A (PCE = 48.3 μg/L, TCE = 97.2 μg/L, *cis*-DCE = 6020 μg/L and VC = 406 μg/L), but the relatively low VOC concentration from the vicinity of this well (a mean of 3810 μg/m^3 calculated from S246-248 and S255 soil probes), which was closer to the VOCs concentrations determined in soil probes outside the source area with lower median concentrations of CLHCs in groundwater. This could be due to the extensive development of this part of source area A with a high density of underground networks and pipelines, which can significantly affect the transport of soil gas vapours [101]. In addition, the topsoil of this part was removed during the reconstruction works, which in turn may constrain the transport of soil gas vapours [42,102–104]. The opposite, i.e., lower or no groundwater contamination versus a high level of VOCs or TP, was demonstrated in wells N27 (only TCE presence at a concentration of 41.7 μg/L) and N40 (all CLHCs below the detection limit) in areas B and C, respectively, with VOCs concentrations of 14,705 and 7620 μg/m^3 and TP concentrations of 432 and 2032 mg/m^3 (S264-265 and S286), respectively. The explanation for this fact is the high density of road and rail traffic in the immediate vicinity of these sites.

However, the general trend of decreasing VOCs concentrations with the increasing distance from the contamination source remained unchanged and copied the decreasing concentrations of CLHCs detected in the groundwater from source area A towards residential area C (Figures 5 and S3). The above-mentioned soil probes, characterised by an anomalous concentration of at least one parameter, were also evidently distinguishable from other soil probes in the bi-plot of the first two main components of observations (Figure 6a). Most of the observations formed one main cluster, situated in the middle of the bi-plot. Soil probe S268 showed VOCs concentrations above the upper detection limit of the instrument, while soil probes S264-265 and S286 were characterised by high TP levels or increased VOCs concentrations. Other soil probes, correlating negatively with PC1 and representing outliers, had a high CO_2 concentration (>50,000 mg/m^3) compared to the rest.

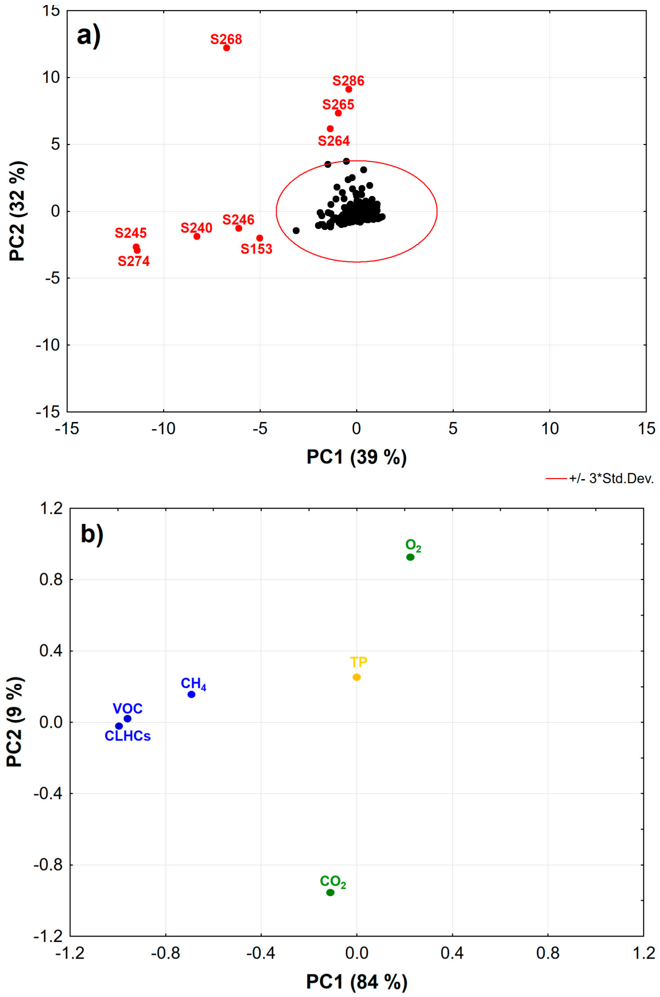

Figure 6. (**a**) Bi-plot of first two principal components for observations (soil gas measurement sites) and (**b**) bi-plot of first two principal components for variables (CLHCs concentrations in groundwater and soil gas chemical indicators). Samples shown in red in (**a**) are outliers. Red ellipse in (**a**) represents the area bounded by three times the standard deviation (±3 × SD) of the principal components PC1 and PC2.

Soil gases from ten sampling sites were further analysed for selected chemical compounds, including PCE, TCE and *cis*-DCE (Table S6). The concentration of most organic compounds in the soil gas was below the detection limit of GC-MS and the most frequently detected were TCE and TP. Tetrachloroethylene and toluene were additionally detected only in sample PVZ3 from source area A. The concentration of TP in soil gas decreased with the increasing distance from industrial source area A, but the TCE concentrations were approximately constant and did not correspond to the decrease in TCE concentrations in the groundwater with distance from source area A (Figure 4). This discrepancy is probably related to the different rate of the sorption and degradation of TCE vapours in the unsaturated zone [105].

The more than fifty-year production of refrigerators, until its termination in 2002, was a source of groundwater contamination. The observed decrease in CLHCs concentrations over time (Section 3.1) suggests that their degradation in groundwater is still occurring [106–108]. The anaerobic degradation of organic compounds is accompanied by CH_4 production [109–111]. The positive correlation between VOCs and CH_4 concentrations (r_S = 0.28; $p < 0.001$) is consistent with this statement. A positive correlation was also found between VOC and CO_2 concentrations (r_S = 0.32; $p < 0.05$) because CO_2 is produced during the aerobic degradation of organic compounds [112–114]. Moreover, CO_2 can also be formed by the oxidation of CH_4 in the unsaturated zone [115,116]. During the aerobic degradation of VOCs, the concentration of O_2 decreases [117]. As expected, lower O_2 concentrations were measured at sites with higher VOCs concentrations (r_S = –0.33; $p < 0.05$). Furthermore, a strong negative correlation between O_2 and CO_2 was statistically demonstrated (r_S = –0.84; $p < 0.001$). An almost constant inverse correlation between CO_2, O_2 and hydrocarbon vapour anomalies was observed by [118]. Organic compounds volatilising from groundwater undergo further degradation in the unsaturated zone with the production of CH_4 and CO_2, as described above. Groundwater sources can, therefore, be traced by analysing gases from progressive degradation, such as CH_4 and CO_2, whose correlations to subsurface organic contamination were confirmed in several studies [26,62,118]. Spatial distribution maps of CH_4 and VOCs concentrations (Figure 7) showed their similarity, but were partially disturbed by higher CH_4 concentrations in the agricultural land (area B), where the decomposition of farmyard manure could be a source of CH_4 [119–121]. These observations were further elaborated using PCA and the bi-plot of the first two principal components is shown in Figure 6b. Three principal components explained most of the variability of the dataset (up to 98%). Chlorinated hydrocarbons in groundwater and VOCs in soil gas corresponded to PC1 with the complete overlap of the component scores, which indicated their close inter-relationship. This supports the use of soil gas sampling as a useful screening tool for identifying contamination in the shallow saturated zone. Both O_2 and CO_2 were correlated to PC2, with the antagonistic position of these two variables pointing to O_2 consumption and CO_2 production during the degradation of organic compounds in groundwater. The third principal component was loaded by TP and partly by CH_4, which also had a close relationship with PC1 and thus with CLHCs in groundwater.

It can be concluded, based on the results of this study and previous findings [26,34,42,51,122], that groundwater contamination with VOCs is strongly related to VOCs concentrations in soil gas under certain conditions. Despite several limitations (source concentration, impermeable horizons above the water table and the presence of pipelines and utility networks) [101,123,124] and the observations of several authors who found no obvious correlation between groundwater contamination and chemical indicators in soil gas [101,125,126], the suitability of active soil gas screening for identifying sources of groundwater contamination with CLHCs, delineating the contamination plume as well as for evaluating the level of current contamination, was confirmed. Soil gas screening clearly delineated areas of the highest concentrations of CLHCs in groundwater and was even able to detect DNAPLs. The success of the application of this screening method for the identification of groundwater contamination could be related to the appropriate timing of field sampling and determination, which was carried out on days of stable weather, limiting the effect of humidity, temperature and pressure on the volatilisation [50]. The permeable unsaturated zone and relatively shallow groundwater of this area increased the feasibility of soil gas screening. The limitation of the application of soil gas measurements was documented in the residential area where engineering networks, built-up zones, road traffic and operations such as car repair shops play a role in VOC readings through changes in the migration pathways of VOCs or their excess sources not related to groundwater. Based on the results of this study, soil gas screening can be recommended as a highly effective methodology for the delineation of groundwater contamination with VOCs for other areas as well, but for its successful application, it is necessary to know the site history, geology and hydrogeological conditions and take into account other local specificities that might affect the migration of VOCs vapours.

Figure 7. Comparison of spatial distribution maps of VOCs and CH_4 concentrations in soil gas from 300 soil probes. The similarity of the spatial concentration distributions of VOCs and CH_4 is evident, with the exception of agricultural land (area B) due to crop plant and animal production. Red frame indicates the study area.

The future research directions should be oriented on coupling the data from conventional monitoring with non- or low-invasive screening methods (soil gas measurements, geophysics, direct-push, etc.) and hydro-geochemical modelling to provide a consistent, realistic and accurate image (conceptual model) integrating the information from different data sources. This could gain the information about the current development and future fate of the extent of contamination, processes of its natural biodegradation and, thus, set the right remediation approaches. Simultaneously, the method should be applied to similar "mega-sites" in order to compare the results and optimise the approach for the future. After obtaining results from other conventional monitoring and screening methods, remediation efforts should focus on identified sources of groundwater contamination using a combination of pump-and-treat methods, the injection of oxidising or reducing agents, electrochemical degradation and bio-augmentation.

The area has been listed for longer in the information system of the environmental burdens of the Ministry of the Environment of the Slovak Republic (MoE SR) as a confirmed environmental burden with a high priority. Exploration works as well as the subsequent remediation are carried out under the supervision of the MoE SR and funded by the Structural Fund of the European Union. Due to the identified extent of contamination, the residents of the affected area were informed by the local government about the state of contamination with the recommendation not to use groundwater for drinking, watering gardens and bathing until the area was remediated.

3.3. Human Health Risk Assessment (HHRA)

Human health risks were assessed in areas B and C. The main reason is that these two areas have permanent settlements. Specifically, area B is designated for industrial use according to the current spatial plan, but it is mainly used for agriculture, while part of the area is residential. The expansion of services and industry is planned in the future. Area C is an exclusively residential zone. The health risk assessment in a specific area included those CLHCs that exceeded the particular IT value in groundwater (Table S3). Groundwater contamination in area B was caused by PCE, TCE and *cis*-DCE with a maximum concentration of 442 μg/L, 1110 μg/L and 500 μg/L, respectively. However, the effect of *cis*-DCE on the carcinogenic health risk could not be evaluated due to missing values of key parameters. According to the selected criterion, the only problematic groundwater contaminant in area C was PCE, with a maximum concentration of 138 μg/L.

The results of the carcinogenic and non-carcinogenic risk assessment due to human contact (adults and children) with CLHCs in groundwater by the five most likely exposure routes (details in Supplementary text 1) are shown in Table 1. Regarding the non-carcinogenic risk in the evaluated areas, B and C, the HI_{total} value for both adults and children was lower than 1.0, so the existence of non-carcinogenic effects on the population was not confirmed. The greatest contribution of the three CLHCs to the total non-carcinogenic risk for both population groups was by TCE (95.3%), followed by PCE (4.0%) and *cis*-DCE with a negligible contribution (0.7%), which is consistent with the toxicological parameters of these CLHCs, while the RfD and RfC values for TCE are one order of magnitude lower than those for PCE and *cis*-DCE. A comparison of several considered exposure routes showed that dermal contact during irrigation (80.4% for adults and 55.6% for children) and indoor breathing (12.7% for adults and 28.6% for children) contributed the most to the non-carcinogenic risk for adults and children. The ingestion of home-grown vegetables and groundwater during the watering period had a less significant effect, 4.5% and 1.8% in adults and 12.4% and 3.5% in children, respectively, while outdoor breathing and the inhalation of water spray were negligible exposure routes to CLHCs. This analysis is consistent with the results of a risk assessment of human exposure to VOCs present in groundwater from Taiwan, which confirmed that water intake, indoor breathing and dermal absorption contributed the most to human health risks [127].

The IELCR values for the individual did not exceed the threshold value of 10^{-4} [128,129], which represents an unacceptable carcinogenic risk (Table 1). However, IELCR values in area B above the threshold of 1×10^{-6} could indicate a potential cancer risk. The main contributor to the $IELCR_{total}$ value was TCE, with almost 100% contribution and the indoor breathing and dermal contact during irrigation were predominant exposure routes accounting for 30.0% and 70.0% in adults and 55.0% and 37.8% in children, respectively. Although the human health risk assessment is limited by uncertainties (e.g., time-varying concentration of organic micro-contaminants in groundwater, other present contaminants not included in the HHRA, default weight of residents instead of their current weight or ambiguity in the consumption of home-grown vegetables), it provides approximate information about the effect of the environmental exposure of the population to these harmful organic compounds. Epidemiological studies have clearly documented a statistically significant association of increased human exposure to PCE, TCE or VC with an increased risk of developing several types of cancer and other non-cancer diseases [130–133].

In this study, the uncertainty of the human health risk assessment could relate primarily to the concentrations of CLHCs in groundwater and the resulting uncertainties in the model evaluation of their outdoor and indoor air concentrations. Health risks were calculated from the maximum concentrations of CLHCs in the groundwater, determined in one sampling campaign, which corresponded to the worst-case scenario. However, it is known that the concentrations of CLHCs in groundwater fluctuate seasonally, spatially and vertically, making an impact on the exposure concentration [8,134]. As stated above, a significant exposure route was indoor breathing, with a modelled indoor air concentration of individual CLHCs using the Johnson–Ettinger transport model incorporated in the RISC software, version 5.0. Research has documented large spatial variability in soil gas concentrations of VOCs under buildings, which is less observable in indoor air concentrations due to efficient air mixing [50]. However, on the other hand, there are significant temporal fluctuations of the indoor air concentrations of VOCs over time periods of hours to months [135]. These temporal fluctuations are dependent on several factors, e.g., building differential pressure, temporal changes of soil moisture, temperature and groundwater table, building ventilation, meteorological conditions, etc., [136]. Therefore, it is almost impossible to consider a single value of the indoor air concentration of VOCs when assessing their intake via the inhalation route. It should be also emphasised that the values of some toxicity parameters for *cis*-DCE are not available, so its contribution to the overall health risk might be underestimated.

Table 1. Human health risk assessment by six exposure routes for adults and children in areas B and C with permanent settlement and values of individual quantitative risk parameters. Non-carcinogenic risk is expressed by HQ, HI and HI_{total} and carcinogenic risk by IELCR and $IELCR_{total}$.

Receptor		**Adults**							**Children**						
		Exposure Route [a]							**Exposure Route** [a]						
Contaminant		**1**	**2**	**3**	**4**	**5**	**6**		**1**	**2**	**3**	**4**	**5**	**6**	
Area B								**HI = ΣHQ or IELCR = ΣIELCR**							**HI = ΣHQ or IELCR = ΣIELCR**
PCE	HQ	1.2×10^{-2}	9.9×10^{-6}	1.9×10^{-4}	2.1×10^{-3}	2.4×10^{-5}	5.0×10^{-4}	1.5×10^{-2}	4.2×10^{-2}	3.5×10^{-5}	6.0×10^{-4}	2.3×10^{-3}	5.7×10^{-5}	5.0×10^{-4}	4.5×10^{-2}
	IELCR	4.1×10^{-8}	3.4×10^{-11}	8.4×10^{-10}	9.2×10^{-9}	8.5×10^{-11}	2.2×10^{-9}	3.3×10^{-8}	3.6×10^{-8}	3.0×10^{-11}	6.5×10^{-10}	2.5×10^{-9}	4.9×10^{-11}	2.2×10^{-9}	4.1×10^{-8}
TCE	HQ	3.6×10^{-2}	3.9×10^{-5}	5.8×10^{-3}	3.0×10^{-1}	1.3×10^{-3}	1.6×10^{-2}	3.6×10^{-1}	1.3×10^{-1}	1.3×10^{-4}	1.8×10^{-2}	3.3×10^{-1}	3.0×10^{-3}	7.2×10^{-2}	5.5×10^{-1}
	IELCR	1.0×10^{-6}	1.1×10^{-9}	4.6×10^{-8}	2.4×10^{-6}	3.6×10^{-9}	1.3×10^{-7}	3.4×10^{-6}	9.0×10^{-7}	9.5×10^{-10}	3.5×10^{-8}	6.4×10^{-7}	2.0×10^{-9}	1.4×10^{-7}	1.7×10^{-6}
***cis*-DCE**	HQ	NA	NA	7.2×10^{-4}	1.7×10^{-3}	NA	4.8×10^{-4}	2.9×10^{-3}	NA	NA	2.3×10^{-3}	1.8×10^{-3}	NA	2.2×10^{-3}	6.3×10^{-3}
	IELCR	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$\mathbf{HI_{total}}$								$\mathbf{3.8 \times 10^{-1}}$							$\mathbf{6.1 \times 10^{-1}}$
$\mathbf{IELCR_{total}}$								$\mathbf{3.4 \times 10^{-6}}$							$\mathbf{1.7 \times 10^{-6}}$
Area C															
PCE	HQ	2.8×10^{-3}	1.9×10^{-6}	4.6×10^{-3}	1.4×10^{-2}	6.0×10^{-4}	1.1×10^{-2}	$\mathbf{3.3} \times 10^{-2}$	1.3×10^{-2}	1.9×10^{-6}	8.1×10^{-2}	6.8×10^{-1}	7.9×10^{-3}	2.7×10^{-2}	$\mathbf{8.1} \times 10^{-1}$

IELCR	9.7×10^{-9}	6.7×10^{-12}	2.0×10^{-8}	6.2×10^{-8}	2.1×10^{-9}	4.6×10^{-8}	$\mathbf{1.4} \times 10^{-7}$	1.1×10^{-8}	5.6×10^{-11}	8.7×10^{-8}	7.3×10^{-7}	6.8×10^{-9}	2.9×10^{-8}	$\mathbf{8.7} \times 10^{-7}$

[a] Exposure routes: 1 = Inhalation of indoor air; 2 = Inhalation of outdoor air; 3 = Ingestion of groundwater during irrigation period; 4 = Dermal contact with contaminated groundwater during irrigation; 5 = Inhalation of irrigation water spray; 6 = Ingestion of home-grown vegetables irrigated with contaminated groundwater.

4. Conclusions

This work aimed to describe the current state of groundwater contamination with CLHCs used for a long time in a former refrigerator factory and to apply the semi-quantitative screening of selected chemical parameters (VOCs, CH_4, CO_2, O_2 and TP) in soil gas to identify the extent of observed groundwater contamination using a portable PID device. The present study has significant applied information as it tries to verify the suitability of soil gas screening as a substitute for the time-consuming and expensive monitoring of groundwater contamination with CLHCs. Despite the cessation of production more than 20 years ago, chemical analyses have confirmed the continuing contamination of groundwater with PCE, TCE, DCE, VC and TCA, which is widespread even below the residential area. It was shown by comparing current concentration data to the older ones that CLHCs in groundwater were attenuated over time, but the presence of accumulation in the form of DNAPLs and probable use in existing smaller industrial operations limit a further decrease in their concentrations. The similarity of the spatial distribution maps of VOCs and CH_4 concentrations in soil gas to the dot distribution maps of CLHCs concentrations in groundwater and their statistically significant correlation confirmed by multivariate statistics (PCA method) suggested that soil gas screening was a fast, cheap and relatively reliable method for the identification and spatial delineation of groundwater contamination with these types of industrial organic compounds. Specifically, both CLHCs and VOCs concentrations are highly correlated with the first principal component (PC1) with high values of the component scores (>0.96) and their almost complete overlap.

There are some limitations and uncertainties in this study which result mainly from the size of the study area. They can be reduced by the methodology and optimisation only to a certain extent and can bias the results and conclusions. Such uncertainties are the possible presence of preferential pathways (i.e., soil cracks, utilities or conductive zones) in a densely built-up area with still-active industrial facilities, ambient air intrusion, the possible distortion of the concentration gradient between the groundwater table and ground surface in soil gas by hydrologic and geologic variables, such as a varying moisture content, perched water or impermeable layers, heterogeneity in microbial activity and the content of organic matter and clay that affects the adsorption of hydrocarbons in soils and limits the partitioning of contaminants into the vapour phase and other factors. Despite this, the application of soil gas screening led to the identification of before undetected groundwater contamination sources, confirmed by subsequent groundwater sampling by newly designed monitoring wells. Without the application of screening soil gas measurements, these contamination sources would remain undetected, leading to a difficult and risky decision about site management. This emphasises the advantage of applying soil gas measurements and sampling as one of the inexpensive screening methods that are able to cover wide areas with reasonable efforts.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app142310842/s1, Figure S1: Relief of the Neogene sediment formation; Supplementary text 1: Human health risk assessment; Table S1: Chemical toxicity values of chlorinated hydrocarbons used in the human health risk assessment; Table S2: Exposure parameters used to calculate chronic average daily doses (CADD) and lifetime averaged daily dose (LADD) and their explanation; Table S3: Drinking water standards according to the European Union (EU), the United States Environmental Protection Agency (USEPA) and the World Health Organisation (WHO) and indication and intervention criteria (ID and IT, respectively) for chlorinated hydrocarbons in groundwater. The values are in μg/L. Percentage of monitoring wells (industrial area in the city of Zlaté Moravce, western Slovakia) above drinking water standards is also shown; Table S4: Concentrations of selected chlorinated hydrocarbons in groundwater samples (in units of μg/L) in the area of the former refrigerator manufacturer in the city of Zlaté Moravce (western Slovakia); Figure S2: Comparison of the concentrations of CLHCs among different years in groundwater sampled from the same wells; Figure S3: Dot distribution maps: (a) VC and (b) TCA concentrations in groundwater from the study area on a background showing the spatial distribution of VOC concentrations in soil gas; Table S5: Chemical parameter values measured in 300 soil gas probes using a portable PID device; Table S6: Concentrations of selected organic compounds (in mg/m^3), including chlorinated hydrocarbons in soil gas samples.

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