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MONITORING OF TRICHLOROETHENE  
AND TETRACHLOROETHENE CONTENT IN SOIL-WATER  
ENVIRONMENT IN THIRD PHASE OF ECOLOGICAL AUDIT  
OF LAND

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**Keywords:** Trichloroethene, tetrachloroethene, monitoring, soil-water environment, pollution.

**Abstract:** Trichloroethene (TCE) and tetrachloroethene (PCE) are chemical compounds which pose a serious threat for human health. Their specific properties make it possible that these substances may linger in soil and water for many years. These are the reasons why wells with water designed for drinking purposes have been subject of monitoring since 2006. This paper presents the results of monitoring research conducted in the soil-water environment within the framework in third phase of an ecological audit of land. The ecological audit of land made it possible to identify the cause and degree of the degradation, and helped formulate rationale for remedy decisions pertaining to the land (remediation/reclamation). The objective of the paper was to determine the pollution status of the soil-water environment and, subsequently, monitor (in years 2008–2010) the contents of the hazardous substances, namely trichloroethene and tetrachloroethene, within the area of the potential impact of metallurgical plant located in borders of the Main Underground Water Reservoir Wierzbica-Ostrowiec (GZWP 420) in in voivodeship Świętokrzyskie.

## INTRODUCTION

The Directive on the protection of groundwater against pollution and deterioration adopted in 2006, the so-called *Groundwater Directive*, [4] is a part of the legislation applicable to monitoring and assessment of the environmental quality. The Directive introduced a list of pollutants and indicators of pollution in the case of which the Member States were obliged to consider the necessity of setting the ‘threshold values’. The list included i.a. trichloroethene (TCE) and tetrachloroethene (PCE), synthetic substances produced by man. In Poland in the period from 2007 to 2010 two delegate legislation acts were issued as regards those pollutants. In 2007 the Minister of Health issued Regulation

on the quality of water to be used for human consumption [17] (Official Journal No 61 Item 417 and its novelty in year 2010 in Official Journal No 72 Item 466) and in 2008 the Minister of the Environment issued Regulation on groundwater condition assessment criteria and method [16] (Official Journal No 143 Item 896). Those regulations set the permissible threshold value of  $10 \mu\text{g}\cdot\text{dm}^{-3}$  for the total content of trichloroethene and tetrachloroethene in water to be used for human consumption.

In connection with the aforementioned legislation in 2008 Polish Sanitary and Epidemiological Stations included the two compounds discussed above into the scope of their routine control tests. All over Poland numerous cases of exceeded content of both compounds in the water to be used for human consumption purposes have been identified (e.g. water intakes in Gryfino, Ząbkowice Śląskie, Stoszowice, Kraśnik, Poniatowa, Tarnowskie Góry [19] etc.). In most cases no one to be blamed for the pollution has been discovered. In the international arena the pollution of soil and water environment by trichloroethene has been found, among other places, at least at half of the hazardous waste dumps in the USA. In the literature [5, 6, 8] one can find that together with tetrachloroethene and trichloroethane it is the mostly discovered volatile organic compound in groundwater in USA. The scale of phenomenon relates to amount of trichloroethene production, which in the 1990s in the European Union was estimated at 138 000 t per year [7]. According to the findings of the US Environmental Protection Agency (EPA) people drinking, for a relatively short period of time, water with trichloroethene concentrations exceeding the permissible levels can suffer from vomiting or stomach ache [5]. Drinking water containing those compounds in concentrations exceeding the permissible levels for a prolonged period of time may result in liver damage. International Agency for Research on Cancer (IARC) has classified trichloroethene with the category of factors which are *probably carcinogenic for humans*. Chlorinated aliphatic hydrocarbons have become widely used as non-polar substance solvents, e.g. in metallurgical or electronic industry, or dry cleaners [2, 11, 12, 18]. Apart from trichloroethene, other examples of such substances include carbon tetrachloride, vinyl chloride or chloroform. It is important to point out that all those compounds are indicators of general environmental pollution with organic compounds [3, 9] but at present, out of the aforementioned compounds, trichloroethene is considered to be one of the priority pollutants of the soil-water environment.

This paper focuses on a monitoring research conducted in the soil-water environment within the framework of an ecological audit of land, using four phases of the review. The ecological audit of land is a kind of environmental review, carried out for a clearly specified area, which makes it possible to identify the cause and degree of the degradation, and may help formulate rationale for sound remedy decisions pertaining to the land (remediation/reclamation) [13]. It consists of 4 phases:

- Phase I → (preliminary) land classification;
- Phase II → analysis of documentation (archived data) and detailed site inspection;
- Phase III → field research;
- Phase IV → activities aimed at remediation – land reclamation.

The objective of the paper was to determine the pollution status of the soil-water environment and, subsequently, monitor the contents of the hazardous substances, namely trichloroethene and tetrachloroethene, within the area of the potential impact of metallurgical

plant. The plant is situated in borders of the Main Underground Water Reservoir Wierzbica Ostrowiec (GZWP 420) in voivodeship Świętokrzyskie. The objective was achieved by carrying out the third phase of the ecological audit of land and examining trichloroethene and tetrachloroethene contents in groundwater and soil at identified research points.

## MATERIAL AND METHODS

### *Collection of groundwater samples*

Groundwater samples were taken for research purposes in the period from 2008 to 2010. The samples were collected, first and foremost, from drilled wells but also from piezometers. In the case of the drilled wells the samples were collected directly from test valves fitted on pressure conduits in pits except for S-3 well where water was taken as it was done from piezometers but, for technical reasons, without pumping out. Sample collection from piezometers involved the use of a special small bucket put down the pipe below the water level: for technical reasons (mainly due to the level of the water table) water was not fully pumped out from the piezometer hole nor replaced. Locations of particular points where groundwater samples were collected for research purposes can be found in Figure 1.

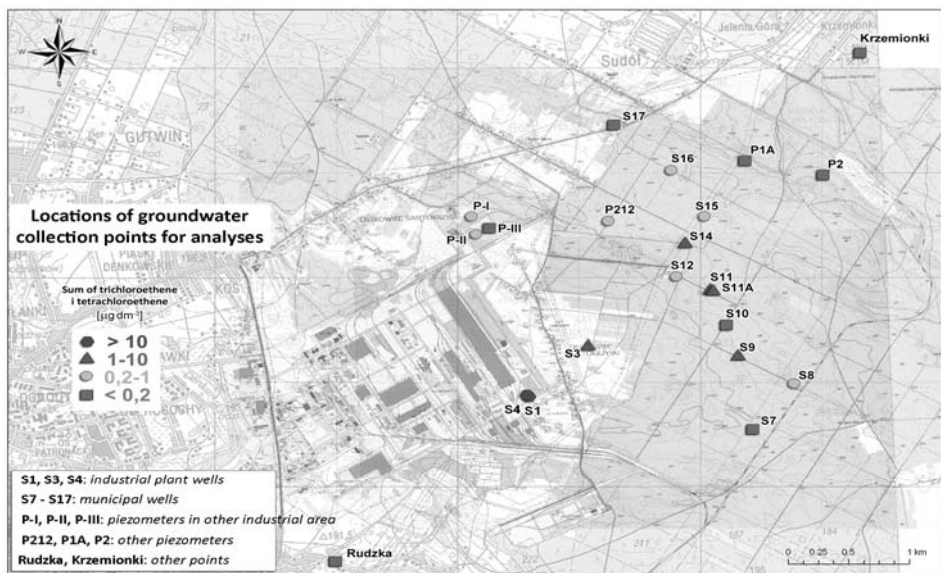


Fig. 1. Locations of groundwater collection points for analyses and characteristics of groundwater in terms of trichloroethene and tetrachloroethene contamination levels in particular testing points

The following wells: S-1, S-3, S-7, S-8, S-9 and S-12 had their filtering parts placed in the Upper and Middle Jurassic layer, S-4, S-10, S-11, S-11A, S-14, S-15, S-16 and the piezometers: P-I, P-II and P-III had their filtering parts placed in the Upper Jurassic layer. The sample from S-17 well was collected in the process of new well construction.

In 2008 the initial round of research covered 15 groundwater sample collection points. In 2009 six regular series of groundwater tests were carried out. In each series 8 samples were collected (a total of 48 samples). The samples were collected at 15 different points with varying frequency: six times from wells S-1, S-4, S-3 and S-15 each; five times from S-11 and S-14 each; three times from S-9; twice from S-11A, P-I and P-II each; and once from S-12, P-212 and P-III.

In 2010 six series of groundwater tests were carried out. In each of the first three series 8 samples were collected and in each of the following three series 4 samples were collected (a total of 36 samples). The samples were collected at 15 different points with varying frequency: six times from wells S-1 and S-4 each; five times from S-11; three times from S-3 and S-9 each; twice from S-8, S-10 and S-14 each; and once from S-12, S-16, S-17, Krzemionki, P-2 and P-I. Moreover, a water sample was collected once from a well drilled on a private property "Rudzka".

### ***Collection of soil samples***

Selection of soil sampling locations have been related to locations of individual departments of metallurgical plant with potential impact on land contamination. In order to collect soil samples seven research points were selected on the premises of the investigated industrial plant. The drilling operation was done at those points using a mobile mechanical drilling rig. The bore-holes penetrated the ground down to the depth of 1.5 m to 7.7 m below the ground surface. One or two soil samples were collected from different depths at each research point, altogether 12 soil samples were collected for research purposes (Table 4).

### ***Chemical analyses***

The reaction of the water samples was determined using potentiometric method according to PN-90/C-04540.01, and the electrolytic specific conductance was determined according to PN-EN 27888:1999. Concentrations of trichloroethene and tetrachloroethene in the water and soil samples were determined according to PN-EN ISO 10301:2002. '*Method using capillary gas chromatography with mass spectrometric detection after extraction by means of a solvent*'. Laboratory tests were conducted in cooperation with an accredited Laboratory of Environmental Chemistry in Warsaw approved by State Poviast Sanitary Inspection in Warsaw '*for testing of water to be used for human consumption*'. Additional determinations of sodium concentrations were done using the flame photometry method [15].

## RESULTS AND DISCUSSION

### ***Phase one***

It is clear from related publications that trichloroethene was a component used for production of some pesticides, resins, paints and varnishes [2, 12]. For dozens of years its application in industry as a cleaner used mainly as a solvent for metal degreasing resulted in its widespread migration into the soil and water environment [11]. Therefore in the first phase of the research work the historic data about the examined industrial area were reviewed along with the existing data about the land use in the past and activities carried out in the vicinity of the investigated industrial plant. Moreover, this phase included also a preliminary round of research conducted in 2008. The research showed that the sum of

trichloroethene and tetrachloroethene concentrations was exceeded almost threefold as compared with the permissible levels (as shown in Tables 1 and 2).

### *Phase two*

The next phase (phase two) of the ecological land review included gathering and analysis of archived materials: geological and hydrogeological data, information about the land use (development), finding and analysis of documentation about the history of the plant covered by the research and activities carried out in individual departments of the plant [13]. Moreover, in this phase the area was illustrated in detail during a site visit, assessing the ongoing activities and trying to identify potential sources of pollution. Interviews with the employees turned out to be quite a valuable source of information at that stage, and that information was used for identifying potential pollution spots and sources.

Taking into consideration no documented information, in particular related to location and time of movement of pollution into the soil, as well as its amount, results of this phase were not included in the report.

### *Phase three – groundwater samples*

Phase three involved preparation for and actual monitoring research, including determination of the scope of the research and design of a monitoring network. The key element of the phase was to collect groundwater and soil samples and analyse the samples in a laboratory environment.

The wells S-1 and S-4 situated on the premises of the discussed plant were the first measurement points used in the research. The results of trichloroethene and tetrachloroethene concentration tests and the total concentration of the two substances found in the water taken from the deep wells: S-1 and S-4 in the period from July 30, 2008 to December 10, 2010 can be found in Figure 2.

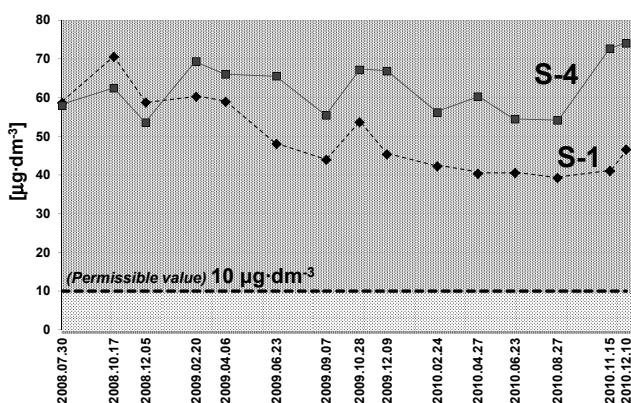


Fig. 2. Sum of trichloroethene and tetrachloroethene content in S-1 and S-4 wells situated in the examined industrial area (in the period of 2008 to 2010)

In the water samples collected from deep wells S-1 and S-4 the total concentration of both compounds varied from around 40 to 74  $\mu\text{g}\cdot\text{dm}^{-3}$  which is equivalent to 4÷7 times

Table 1. Trichloroethene (TCE) contents in water samples collected on the premises and in the vicinity of the investigated industrial plant (in the period of 2008 to 2010)

| Points of water samples collection | Date of water samples collection (trichloroethene content [ $\mu\text{g}\cdot\text{dm}^{-3}$ ]) |               |               |               |              |               |              |               |              |               |               |               |               |               |               |
|------------------------------------|---|---------------|---------------|---------------|--------------|---------------|--------------|---------------|--------------|---------------|---------------|---------------|---------------|---------------|---------------|
|                                    | 30.07<br>2008   | 17.10<br>2008 | 12.12<br>2008 | 20.02<br>2009 | 6.04<br>2009 | 23.06<br>2009 | 7.09<br>2009 | 28.10<br>2009 | 9.12<br>2009 | 24.02<br>2010 | 27.04<br>2010 | 23.06<br>2010 | 27.08<br>2010 | 15.11<br>2010 | 10.12<br>2010 |
| S-1                                | 34.7  | 44.0          | 37.7          | 39.5          | 38.1         | 30.9          | 28.8         | 35.4          | 29.5         | 28.6          | 26.8          | 27.3          | 26.2          | 27.7          | 31.5          |
| S-4                                | 34.0  | 38.4          | 33.8          | 44.8          | 42.9         | 42.4          | 36.3         | 44.4          | 43.6         | 38.1          | 40.3          | 36.5          | 36.2          | 49.2          | 50.7          |
| S-3                                | 4.4   | 3.2           | 1.7           | 0.67          | 0.24         | 0.38          | 0.49         | 1.01          | 1.20         | 1.37          | 1.02          |               |               |               |               |
| S-7                                | <0.05   |               |               |               |              |               |              |               |              |               |               |               |               |               |               |
| S-8                                |   |               |               |               |              |               |              |               | 0.64         | 0.55          |               |               |               |               |               |
| S-9                                |   |               |               |               |              | 1.56          | 1.97         | 2.15          | 1.92         | 2.40          | 2.12          |               |               |               |               |
| S-10                               |   |               |               |               |              |               |              |               | <0.20        | <0.05         |               |               |               |               |               |
| S-II                               | 2.7   | 2.6           | 3.3           | 3.4           | 2.63         | 2.43          | 2.46         | 2.35          | 1.87         | 0.84          | 2.02          | 2.02          | 2.02          | 2.02          | 2.02          |
| S-IIA                              |   |               |               |               |              | 3.1           | 3.07         |               |              |               |               |               |               |               |               |
| S-12                               | 0.11  |               |               |               | <0.06        |               |              |               |              |               |               |               |               |               | 0.14          |
| S-14                               |   | 0.88          | 1.49          | 1.5           | 1.8          | 1.85          | 1.7          | 1.73          |              |               | 1.21          |               |               |               |               |
| S-15                               |   | 0.2           | 0.29          | 0.25          | 0.42         | 0.09          | 0.2          | 0.26          |              |               |               |               |               |               |               |
| S-16                               |   | 0.09          |               |               |              |               |              |               |              |               | 0.047         |               |               |               |               |
| S-17                               |   |               |               |               |              |               |              |               |              |               | <0.1          |               |               |               |               |
| R-zb.                              |   | 0.28          | 0.57          |               |              |               |              |               |              |               |               |               |               |               |               |
| Krzemionki                         |   |               |               |               |              |               |              |               |              |               |               |               |               |               |               |
| P-1A                               | <0.05   | <0.05         |               |               |              |               |              |               |              |               | <0.1          |               |               |               |               |
| P-2                                |   |               |               |               |              |               |              |               |              |               | <0.1          |               |               |               |               |
| P-212                              |   | <0.05         | 0.05          |               | <0.06        |               |              |               |              |               |               |               |               |               |               |
| P-I                                |   | 0.12          | 0.16          |               |              | 0.085         |              |               |              |               |               |               |               | 0.15          |               |
| P-II                               |   | 0.06          | 0.17          |               |              | 0.092         |              |               |              |               |               |               |               |               |               |
| P-III                              |   | <0.05         |               |               |              | <0.06         |              |               |              |               |               |               |               |               |               |
| Rudzka                             |   |               |               |               |              |               |              |               |              |               |               |               |               |               | <0.1          |

Determinability level varies depending on the analytical procedure

Table 2. Tetrachloroethene (PCE) contents in water samples collected on the premises and in the vicinity of the investigated industrial plant covered by the research (in the period of 2008 to 2010)

| Points of water samples collection | Date of water samples collection (tetrachloroethene content [ $\mu\text{g}\cdot\text{dm}^{-3}$ ]) |               |               |               |              |               |              |               |              |               |               |               |               |               |               |
|------------------------------------|---|---------------|---------------|---------------|--------------|---------------|--------------|---------------|--------------|---------------|---------------|---------------|---------------|---------------|---------------|
|                                    | 30.07<br>2008   | 17.10<br>2008 | 12.12<br>2008 | 20.02<br>2009 | 6.04<br>2009 | 23.06<br>2009 | 7.09<br>2009 | 28.10<br>2009 | 9.12<br>2009 | 24.02<br>2010 | 27.04<br>2010 | 23.06<br>2010 | 27.08<br>2010 | 15.11<br>2010 | 10.12<br>2010 |
| S-1                                | 23.9  | 26.5          | 21.0          | 20.7          | 20.8         | 17.1          | 15.1         | 18.2          | 15.8         | 13.6          | 13.5          | 13.2          | 13.0          | 13.3          | 15.02         |
| S-4                                | 23.9  | 24.0          | 19.7          | 24.5          | 23.1         | 23.1          | 19.1         | 22.7          | 23.2         | 18.0          | 19.9          | 17.9          | 17.9          | 23.4          | 23.3          |
| S-3                                | 3.4   | 3.2           | 1.4           | 0.73          | 0.33         | 0.32          | 0.42         | 0.64          | 0.72         | 0.88          | 0.63          |               |               |               |               |
| S-7                                | <0.05   |               |               |               |              |               |              |               |              |               |               |               |               |               |               |
| S-8                                |   |               |               |               |              |               |              |               | 0.35         | 0.41          |               |               |               |               |               |
| S-9                                |   |               |               |               |              |               | 1.05         | 1.3           | 1.34         | 1.11          | 1.48          |               |               | 1.33          |               |
| S-10                               |   |               |               |               |              |               |              |               | <0.20        |               |               |               |               |               |               |
| S-11                               | 1.8   | 1.5           | 1.9           | 2.0           | 1.72         |               | 1.63         | 1.62          | 1.46         | 1.29          | 0.51          | 1.35          | 1.29          |               |               |
| S-11A                              |   |               |               |               |              |               | 1.94         | 1.99          |              |               |               |               |               |               |               |
| S-12                               | 0.095   |               |               | <0.06         |              |               |              |               |              |               |               |               |               |               | 0.09          |
| S-14                               |   | 0.61          | 0.97          | 0.91          | 1.24         |               | 1.21         | 1.08          | 1.07         |               |               |               | 0.85          |               |               |
| S-15                               |   | 0.2           | 0.25          | 0.24          | 0.36         | 0.14          | 0.25         | 0.25          |              |               |               |               |               |               |               |
| S-16                               |   | 0.13          |               |               |              |               |              |               |              |               |               | 0.19          |               |               |               |
| S-17                               |   |               |               |               |              |               |              |               |              |               |               | <0.1          |               |               |               |
| R-zb.                              |   | 0.26          | 0.4           |               |              |               |              |               |              |               |               |               |               |               |               |
| <b>Krzemionki</b>                  |   |               |               |               |              |               |              |               |              |               |               |               |               |               |               |
| P-1A                               | <0.05   | <0.05         |               |               |              |               |              |               |              |               |               |               | <0.1          |               |               |
| P-2                                |   |               |               |               |              |               |              |               |              |               |               |               | <0.1          |               |               |
| P-2I2                              |   | 0.1           | 0.12          | 0.15          |              |               |              |               |              |               |               |               |               |               |               |
| P-1                                |   | 0.13          | 0.12          |               |              | 0.122         |              |               |              |               |               |               |               | 0.11          |               |
| P-II                               |   | 0.04          | 0.076         |               |              | <0.06         |              |               |              |               |               |               |               |               |               |
| P-III                              |   | <0.05         |               |               |              | <0.06         |              |               |              |               |               |               |               |               |               |
| <b>Rudzka</b>                      |   |               |               |               |              |               |              |               |              |               |               |               |               |               | <0.1          |

Determinability level varies depending on the analytical procedure



more than the maximum permissible concentration set in the Regulation on the quality of water to be used for human consumption. The sum of total trichloroethene and tetrachloroethene concentrations in S-1 well differs from the concentration found in S-4 well. Comparing year 2009 to year 2010, it is important to point out that the results of the trichloroethene and tetrachloroethene concentration tests carried out with samples collected in 2010 from S-1 well situated on the premises of the industrial plant are lower than those obtained in 2009 and show a clear downward trend. The total concentration levels of both compounds recorded in S-4 well in the period from 2009 to 2010 remained quite stable and did not show any significant changes.

After determination of the direction of the groundwater flow (to the east, towards the municipal water intake well situated at a distance of around 2 kilometres from the investigated industrial plant) the very important task was to examine the municipal water intake well. The research confirmed the presence of trichloroethene and tetrachloroethene in most of the wells discussed in this paper, especially in wells: S-9, S-11, S-14 and S-15 (Figure 3). Although the values recorded there have not exceeded the permissible levels in any well, they pointed to the movement of both examined compounds.

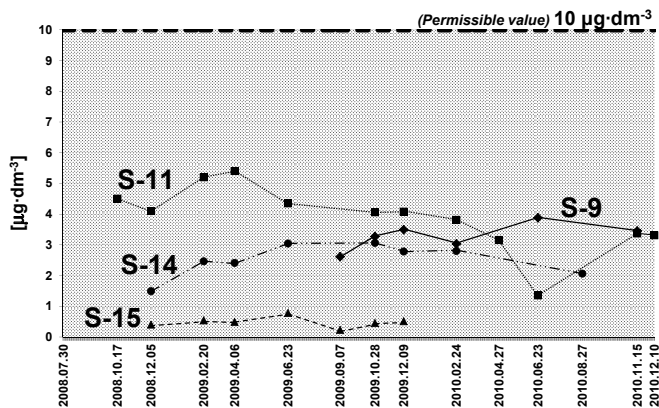


Fig. 3. Sum of trichloroethene and tetrachloroethene content in S-9, S-11, S-14 and S-15 wells situated at a municipal water intake (in the period of 2008 to 2010)

In general, it can be concluded that trichloroethene and tetrachloroethene concentrations show diverse changes, clearly depending on the location of a given measurement point. One can see that the total concentration of trichloroethene and tetrachloroethene in the municipal water intake well (S-9) did not exceed  $4 \mu\text{g}\cdot\text{dm}^{-3}$  and its maximum value for 2010 was  $3.88 \mu\text{g}\cdot\text{dm}^{-3}$ .

The pollutant concentrations found at S-11 point are characterised by a slight downward trend recorded in the second half of 2009 and variable changes in 2010. In the next well (S-14) slightly increased and, at the same time, rather stable concentrations of trichloroethene and tetrachloroethene were found.

Recapitulating the data shown in Figure 3, one can conclude that the water samples collected from wells: S-9, S-11 and S-14 are clearly contaminated and the sum of trichloroethene and tetrachloroethene concentrations amount to: up to  $3.88 \mu\text{g}\cdot\text{dm}^{-3}$  for



S-9;  $5.40 \mu\text{g}\cdot\text{dm}^{-3}$  for S-11; and  $3.06 \mu\text{g}\cdot\text{dm}^{-3}$  for S-14 respectively. Those values have not exceeded the permissible level yet but they point to a clear influence exercised by an unidentified (existing) source of pollution. In S-15 well stable levels of pollutant concentrations were found, below  $1.0 \mu\text{g}\cdot\text{dm}^{-3}$ .

The conducted research indicates that in other intakes (S-7, S-8, S-10, S-12 and S-16) the total concentrations of trichloroethene and tetrachloroethene are below  $1 \mu\text{g}\cdot\text{dm}^{-3}$  and amount to the maximum of  $0.99 \mu\text{g}\cdot\text{dm}^{-3}$  recorded in S-8 well; except for S-11A well which behaves exactly as S-11 well does. Tests of the water samples collected from the water-main pipe (R-zb.) confirm the presence of trichloroethene and tetrachloroethene in the monitored wells of the municipal water intake.

Another important stage was to find a well between the investigated industrial plant and municipal water intakes. Such a well has been successfully identified (S-3) although it has been out of operation and disused for many years. Changes in concentrations of trichloroethene and tetrachloroethene and the total concentrations of those substances in the water collected from S-3 deep well in the period from October 17, 2008 to June 23, 2010 can be found in Figure 4. The diagram shows a downward trend in concentrations of both examined compounds in late 2008 and early 2009, and a slight increase of the concentrations in late 2009. The well had not been used as a water intake point for quite a long time therefore the first and the second opening of the well was probably followed by evaporation of both examined compounds [1].

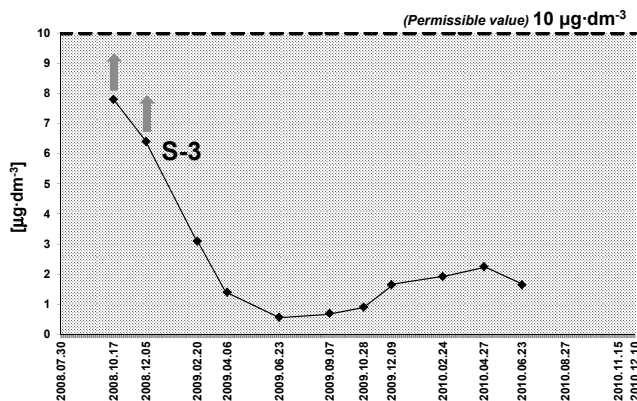


Fig. 4. Sum of trichloroethene and tetrachloroethene content in S-3 well situated in the vicinity of the industrial plant covered by the research (in the period of 2008 to 2010)

In a few interviews with the employees of the plant covered by the research another industrial plant was frequently mentioned as a potential source of pollution. On the premises of that plant where different hazardous substances were stored in barrels three piezometers were identified: P-I, P-II and P-III. Examination of the water collected from the piezometers showed minute quantities of trichloroethene and tetrachloroethene ( $\Sigma$  from  $< 0.12$  to  $0.28 \mu\text{g}\cdot\text{dm}^{-3}$ ). Other monitored points are piezometers (P-212, P-1A, P-2) in Figure 1. The research showed that the total concentrations of trichloroethene and tetrachloroethene in the water samples collected at piezometers: P-1A and P-2 were below  $0.1 \mu\text{g}\cdot\text{dm}^{-3}$ ; and minute

quantities of tetrachloroethene were found in P-212 piezometer. Other points identified as suitable for collection of water samples for research purposes included a well situated on a private property (Rudzka), another well situated in a geological reserve (Krzemionki), and S-17 water intake, the last currently under construction. The research showed that the total concentrations of trichloroethene and tetrachloroethene in the water collected at those points were below  $0.1 \mu\text{g}\cdot\text{dm}^{-3}$ . A total of 106 samples collected at 23 measurement points were analysed. Collectively the points form a network (as shown in Tables 1 and 2) used for monitoring of the area covered by the research.

Summarised results of the determination of trichloroethene and tetrachloroethene contents are shown in Figure 1 where research points have been classified with correct ranges of total concentrations of both examined compounds. The following figures have been assigned to particular ranges: the range  $< 0.2 \mu\text{g}\cdot\text{dm}^{-3}$  points marked with squares; the range from  $0.2$  to  $1.0 \mu\text{g}\cdot\text{dm}^{-3}$  points marked with circles; the range from  $1.0$  to  $10 \mu\text{g}\cdot\text{dm}^{-3}$  points marked with triangles and the range  $> 10 \mu\text{g}\cdot\text{dm}^{-3}$  points marked with hexagons. One can see in the figure that the highest levels of total concentrations of trichloroethene and tetrachloroethene (in excess of  $10 \mu\text{g}\cdot\text{dm}^{-3}$ ) were found in wells S-1 and S-4. The following wells: S-3, S-9, S-11, S-11A and S-14 have been classified within the range from  $1.0$  to  $10 \mu\text{g}\cdot\text{dm}^{-3}$ . The range from  $0.2$  to  $1.0 \mu\text{g}\cdot\text{dm}^{-3}$  included 4 wells of the municipal water intake (S-8, S-12, S-15 and S-16) as well as 3 piezometers. Two piezometers are situated on the premises of a different than the industrial plant covered by the research (P-I and P-II) and P-212 piezometer. The last range  $< 0.2 \mu\text{g}\cdot\text{dm}^{-3}$  included three wells of the municipal water intake (S-7, S-10, S-17 – under construction), 3 piezometers, including one (P-III) situated on the premises of a different industrial plant and two (P-1A and P-2) situated near the former industrial waste dump, as well as the water samples collected in the reserve and from the well drilled on a private property.

In order to identify differences in terms of the groundwater properties and its homogeneity, and to answer the question whether the water taken in the wells on the premises of the investigated industrial plant and in the wells of the municipal water intake come from the same aquiferous layer and are fed from the same area, an additional determination of sodium concentration was done. Sodium concentration was determined in the last seven measurement series (2009 to 2010). The results obtained can be found in Table 3.

The analysis of the obtained data indicates that sodium concentration in wells S-1 and S-4 (from  $3.6$  to  $3.8 \text{ mg}\cdot\text{dm}^{-3}$ ) is clearly higher than the concentration recorded in wells: S-3, S-8, S-9, S-10, S-11 and S-11A ( $2.4\div 2.8 \text{ mg}\cdot\text{dm}^{-3}$ ). In the following wells: S-12, S-14, S-15 and S-16 sodium concentration has been determined at the level of  $3.4\div 3.9 \text{ mg}\cdot\text{dm}^{-3}$ . Piezometers P-1A and P-2 show higher variability of sodium concentrations: from  $2.8$  to  $5.0 \text{ mg}\cdot\text{dm}^{-3}$  due to, probably, the impact of a nearby former industrial waste dump which is currently under reclamation. The water in P-I piezometer is characterised by substantially higher sodium contents ( $12 \text{ mg}\cdot\text{dm}^{-3}$ ). The water in the well situated on the private property at Rudzka shows similar characteristics. Sodium concentration levels in the water samples collected from S-17 well and from the reserve amount to  $4.1$  and  $3.1 \text{ mg}\cdot\text{dm}^{-3}$ , respectively. Figure 5 shows a breakdown of distances from the ground elevation level to the lower edge of the filtering part in particular wells, compared with the sodium concentration in water samples collected from the municipal wells and the wells owned by the investigated industrial plant.

Table 3. Sodium content ( $\text{mg} \cdot \text{dm}^{-3}$ ) at individual water sample collection points (in the period of 2009 to 2010)

| Points of water samples collection | 2009  |       |       | 2010  |       |       |       |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|
|                                    | 09.12 | 24.02 | 27.04 | 23.06 | 27.08 | 15.11 | 10.12 |
| S-1                                | 3.7   | 3.8   | 3.6   | 3.8   | 3.8   | 3.6   | 3.6   |
| S-4                                | 3.8   | 3.7   | 3.6   | 3.7   | 3.8   | 3.7   | 3.7   |
| S-3                                | 2.6   | 2.6   | 2.6   | 2.6   |       |       |       |
| S-8                                |       | 2.4   |       | 2.4   |       |       |       |
| S-9                                | 2.4   | 2.5   |       | 2.4   |       | 2.4   |       |
| S-10                               | 2.5   | 2.5   |       | 2.4   |       |       |       |
| S-11                               | 2.7   | 2.7   | 2.6   | 2.7   |       | 2.7   | 2.5   |
| S-11A                              | 2.8   |       |       |       |       |       |       |
| S-12                               |       |       |       |       |       |       | 3.6   |
| S-14                               | 3.4   | 3.5   |       |       | 3.9   |       |       |
| S-15                               | 3.4   |       |       |       |       |       |       |
| S-16                               |       |       |       | 3.6   |       |       |       |
| S-17                               |       |       | 4.1   |       |       |       |       |
| Krzemionki                         |       |       | 3.1   |       |       |       |       |
| P-1A                               | 5.0   |       |       |       |       |       |       |
| P-2                                | 2.9   |       | 2.8   |       |       |       |       |
| P-I                                |       |       |       |       | 12.0  |       |       |
| Rudzka                             |       |       | 11.5  |       |       |       |       |

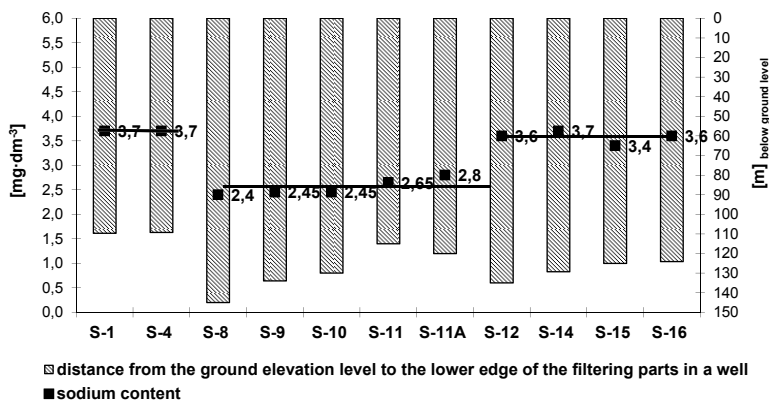


Fig. 5. Sodium content in water samples from selected measurements points

Additionally, control determinations of the reaction and specific conductance were done. The levels of pH at individual measurement points varied between 7.20 (Rudzka) and 8.07 (S-3 point) → averaging at around 7.6 pH; and specific conductance varied between  $170.7 \mu\text{S} \cdot \text{cm}^{-1}$  (P-2 point) and  $754.3 \mu\text{S} \cdot \text{cm}^{-1}$  (Rudzka) → averaging at around

366.9  $\mu\text{S}\cdot\text{cm}^{-1}$  – without Rudzka, P-III and P-I points where specific conductance levels were clearly higher. Results of the research conducted in the period from 2009 to 2010 point to stable levels of both examined parameters and do not provide a basis for presuming that there are other significant pollutant types in place.

### ***Phase three – soil samples***

Another step within the predefined objective of the research work was to examine the soil samples collected on the premises of the investigated industrial plant. In order to check potential places of origin of the groundwater pollutants, in 2009 – 9 soil sample collection points were identified. A preliminary identification and final selection of the soil testing points was done on the basis of information about the land use methods and potential soil contamination spots, obtained from the employees of the plant, as well as using the data collected during the site visit. Table 4 shows the description of the soil sample collection points and the results of soil samples investigation. Determinations of trichloroethene and tetrachloroethene were done in 12 soil samples. Concentration levels of the examined pollutants below 0.06  $\text{mg}\cdot\text{kg}^{-1}$  of dry matter (determinability level depending on the conditions of the applied analytical procedure) were found in all the analysed samples and that means that no hypothetical place of trichloroethene and tetrachloroethene release into the ground has been confirmed.

### ***Phase four***

The last phase of the ecological review consisted of actions aimed at land remediation/reclamation, if any. There are different reclamation methods for tested compounds in soil and groundwater [14, 10, 20, 21, 22, 23]. Choosing one of them, many factors influencing purification effectiveness should be taken into consideration. It should be stressed that realization of this phase was not the aim of the research, although analysing and comparing particular data it was indicated that there were certain correlations that might influence a decision on a practical solution which would probably protect the municipal water intake wells. Comparing the total concentrations of trichloroethene and tetrachloroethene with the water production of S-1 well (Figure 6) and S-4 well (Figure 7) on a day-by-day basis, one can see that there is no direct relationship between those variables, either in S-1 well or in S-4 well.

The highest concentration levels of trichloroethene and tetrachloroethene were found in S-4 well where the rate of delivery of the pump in the research period was maintained on a stable level of around 38  $\text{m}^3/\text{h}$  for the period of 14 months (June 2009 to August 2010). In the same period of time the well showed variations in the sum of trichloroethene and tetrachloroethene concentrations centred at around 60  $\mu\text{g}\cdot\text{dm}^{-3}$ . An increase in the rate of delivery of the pump at S-4 well in the final period of time (August 2010 to December 2010) up to around 45  $\text{m}^3/\text{h}$  resulted in a significant increase in the sum of trichloroethene and tetrachloroethene concentrations up to the level of 75  $\mu\text{g}\cdot\text{dm}^{-3}$ . Although this final period of time was too short to draw any firm and documented conclusions about an increase in the concentration levels, nevertheless the observed relationship between the concentrations and the water production of the well would confirm the assumption that S-4 well produces groundwater contaminated with trichloroethene and tetrachloroethene released (in a dissolved form and diffusing) by a compact liquid source located on the floor of the Jurassic layer.

Table 4. Physical and chemical properties of soil samples collected on the area of the industrial plant and particular sampling points

| Sample number | Location of soil samples collection points                                 | Depth of sample collection [m ppt]* | Name of deposit     | Smell                    | Trichloroethene [mg·kg-1 d.m.]** | Tetrachloroethene [mg·kg-1 d.m.]** |
|---------------|--|-------------------------------------|---------------------|--------------------------|----------------------------------|------------------------------------|
| 1             | Area of former gas station   | 5,7÷6,0                             | slightly loamy sand | weakly specific chemical | <0.06                            | <0.06                              |
| 2a            | Area of current gas station  | 1,3÷1,5                             | sandy loam          | chemical (petrol)        | <0.06                            | <0.06                              |
| 2b            |  | 2,8÷3,0                             | sandy loam          | chemical (petrol)        | <0.06                            | <0.06                              |
| 3a            | Area of temporary industrial waste site                                    | 1,3÷1,5                             | sandy loam          | earthy weak              | <0.06                            | <0.06                              |
| 3b            |  | 2,8÷3,0                             | heavy loam          | earthy weak              | <0.06                            | <0.06                              |
| 4a            | Area of former grease warehouse, sample taken near oil spot                | 1,3÷1,5                             | loam/sand           | specific chemical        | <0.06                            | <0.06                              |
| 4b            |  | 2,8÷3,0                             | slightly loamy sand | specific chemical        | <0.06                            | <0.06                              |
| 4c            |  | 4,3÷4,5                             | sandy loam          | specific chemical        | <0.06                            | <0.06                              |
| 5a            | Area of former oil warehouse shelters (oils)                               | 2,8÷3,0                             | light loam          | weakly specific chemical | <0.06                            | <0.06                              |
| 5b            |  | 7,70                                | limestone           | earthy                   | <0.06                            | <0.06                              |
| 6             | Area of steelworks – soil taken in the neighborhood of oil and water tanks | 4,3÷4,5                             | light loam          | weakly specific chemical | <0.06                            | <0.06                              |
| 7             | Area of temporary waste site (oils and grease)                             | 2,8÷3,0                             | loose sand          | strong earthy            | <0.06                            | <0.06                              |

\* Depth of soil sampling was determined during drilling based on sample organoleptic characteristics (color, smell)

\*\* Determinability level depending on the analytical procedure

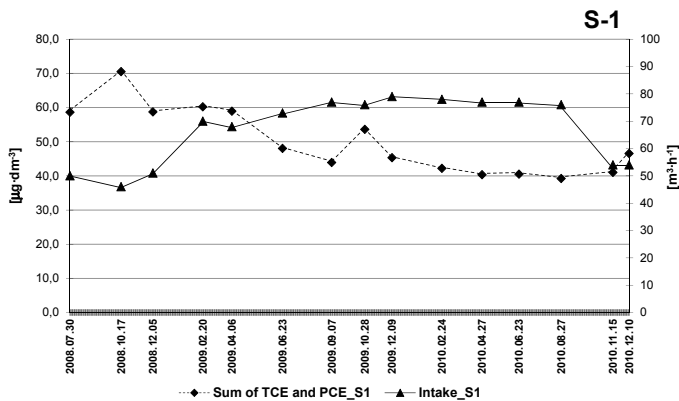


Fig. 6. Comparison of water intake performance for S-1 well with sum of trichloroethene and tetrachloroethene concentrations

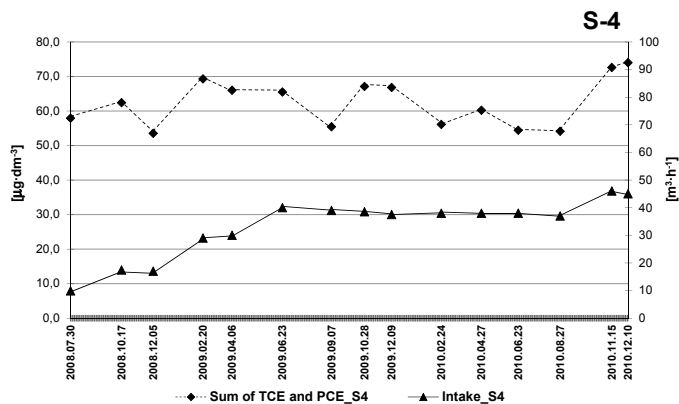


Fig. 7. Comparison of water intake performance for S-4 well with sum of trichloroethene and tetrachloroethene concentrations

Changes of the sum of trichloroethene and tetrachloroethene concentrations in S-1 well differ from the concentration variability observed in S-4 well. The rate of delivery of the pump in the research period was maintained on a high and stable level of around 75 m<sup>3</sup>/h for the period of 14 months (June 2009 to August 2010). In the same period of time a stabilisation of the sum of trichloroethene and tetrachloroethene concentrations at the level of around 40 µg·dm<sup>-3</sup> (i.e. much lower than in S-4 well) was observed in S-1 well (in spite of a higher rate of delivery of the pump). A reduction of the rate of delivery of the pump in S-1 well in the final period of time (August 2010 to December 2010) down to around 50 m<sup>3</sup>/h resulted in an increase in the sum of trichloroethene and tetrachloroethene concentrations up to the level of around 45 µg·dm<sup>-3</sup>. As it was in the case of S-4 well this final period of time was too short to draw any firm and documented conclusions about an increase in the concentration levels.

## CONCLUSIONS

1. The obtained results for S-1 and S-4 point clearly to the presence of trichloroethene and tetrachloroethene in the soil-water environment on and around the area of the investigated industrial plant.
2. Groundwater from other wells are characterised by trichloroethene concentration levels below  $3.4 \mu\text{g}\cdot\text{dm}^{-3}$  and tetrachloroethene concentration levels below  $2.0 \mu\text{g}\cdot\text{dm}^{-3}$  (S-11 point).
3. The water from piezometers P-I, P-II and P-III located in another industrial area situated nearby the investigated industrial plant showed total concentrations of trichloroethene and tetrachloroethene not higher than  $0.28 \mu\text{g}\cdot\text{dm}^{-3}$ .
4. In accordance with *Regulation on Groundwater Condition Assessment Criteria and Method* issued by the Minister of the Environment on July 23, 2008 one can conclude that in terms of the total concentrations of trichloroethene and tetrachloroethene the examined water is in a good chemical condition and can be classified with the following groundwater quality classes: Class I – water in the following wells: S-7, S-12, S-15 and S-16, and in the following piezometers: P-1A, P-212, P-I, P-II and P-III; Class II – water in the following wells: S-3, S-9, S-11, S-11A and S-14; Class III – water in wells: S-1 and S-4.
5. The highest pollutant concentration levels were found in S-4 well situated on the premises of the investigated industrial plant where an increase in the concentrations was recorded as compared with S-1 well where the concentrations showed a downward trend. The dynamics of the total concentrations of trichloroethene and tetrachloroethene recorded in wells: S-1 and S-4 point to a reverse relationship between the pollutant concentration and the rate of delivery of the pump in S-1 well than that observed in S-4 well. Given similar stabilised productivity of both wells and comparable elevation of the filtering parts above the formation floor the aforementioned relationship may be explained by the greater distance between S-1 well and the compact liquid source of trichloroethene and tetrachloroethene than that between S-4 well and the source. Hypothetically it means that drawing groundwater with pollutants from S-4 well ‘shields’ S-1 well from the pollution.

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#### MONITORING ZAWARTOŚCI TRICHLOROETENU I TETRACHLOROETENU W ŚRODOWISKU GRUNTOWO-WODNYM W TRZECIEJ FAZIE PRZEGLĄDU EKOLOGICZNEGO TERENU

Trichloroeten (TCE) oraz tetrachloroeten (PCE) są związkami chemicznymi stanowiącymi poważne zagrożenie dla życia człowieka. Ich specyficzne właściwości powodują, że mogą się utrzymywać w glebie i wodzie przez wiele lat. Z tych powodów studnie z wodą przeznaczoną do spożycia są przedmiotem monitoringu od roku 2006. Praca przedstawia wyniki badania monitoringowego przeprowadzonego w środowisku gruntowo-wodnym w ramach trzeciej fazy przeglądu ekologicznego terenu. Przegląd ekologiczny terenu umożliwia identyfikację przyczyn i stopień degradacji oraz daje podstawy do decyzji remediacyjnych w odniesieniu do terenu (remediacja/rekultywacja). Celem pracy było wyznaczenie poziomu zanieczyszczeń w środowisku gruntowo-wodnym i następnie monitorowanie w latach 2008–2010 zawartości niebezpiecznych substancji tj. trichloroetenu oraz tetrachloroetenu, na obszarze potencjalnego wpływu zakładu metalurgicznego, usytuowanego w granicach Głównego Zbiornika Wód Podziemnych Wierzbica-Ostrowiec (GZWP 420) w województwie świętokrzyskim.