# ASSESSMENT OF PAHS AND SELECTED PESTICIDES IN SHALLOW GROUNDWATER IN THE HIGHEST PROTECTED AREAS IN THE OPOLE REGION, POLAND

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**Abstract**

The ground water quality was determined after the analyses of water samples from 18 wells. The wells were in the Groundwater Area with the Highest Protection (Triassic water, Opole region, Poland), rural build up. The water table level was low: 0.5 – 18.0 m below the ground surface level (except for one artesian well). The following parameters were determined: pH, EC, colour, ammonium, nitrite, nitrate, dissolved orthophosphate, total phosphorus, dissolved oxygen, BOD, COD-Mn, COD-Cr, humic substances, chloride, sulphate, total hardness, alkalinity, dry residue PAHs (16 compounds), pesticides (6 compounds), however, only selected data were presented in this paper. In all the analysed water samples chloro-organic pesticides were observed. The analysed water contained heptachlor in the highest concentrations of 15.97 mg/dm$^3$. Good quality water must not include concentrations higher than 0.5 mg/dm$^3$ of heptachlor. However, the concentration was circa 32 times higher than this value. The second pesticide determining poor water quality is dieldrin. This compound in the investigated groundwater was 1.94 mg/dm$^3$ – 4 times higher than the limit for acceptable quality ground water. The concentration of pesticides also changed over the course of the research; the concentration in the analysed groundwater in the same well changed quite dramatically over a period of 1 year. Although PAHs and pesticides are potentially toxic for biological organisms they do exist in the environment as a product of the natural biological transformation of organic matter. The noted concentrations and compositions of PAH compounds were different to natural PAHs. It confirms the fact that agricultural activity influences groundwater quality.

**Keywords:** reservoir, groundwater, PAH, pesticides.

## INTRODUCTION

Not only is waste disposal considered a critical factor in environmental degradation. Agricultural activities can adversely affect the environmental quality as a result of the emissions of nutrients and organic compounds [Fianko et al. 2009, Jayasekera et al. 2011]. It is also known as a non-point-source pollution [Ritter et al. 2002]. Persistent organic pollutants in a form of PAHs are present in all natural environmental components [Ake et al. 2003, Owabor et al. 2010, Pranagal and Oleszczuk 2007]. They may be of anthropogenic (mainly combustion processes) or natural (volcano eruptions, organic matter decomposition) origin [Lazzari et al. 1999, Thiele and Brummer 2002, Wilcke et al. 1999]. The highest amount can be traced in soil (about 80%) and bottom sediments [Oleszczuk et al. 2007]. PAHs are bad solvents in water but they can translocate in this environment because other organic compounds, existing as effluents, can take a role of a solvent [Włodarczyk-Makuła et al. 2003]. Pesticides used in agricultural areas can also be present in ground water and soil [Geyikci and Büyükgüngör 2011, Swarcewicz and Gregorczyk 2011]. This is a result of high stability, low microbial degradation and the sorption of these com-

pounds in soil. Migration of PAHs and pesticides with humic substances in vertical water streams of the soil profile is a fundamental process. This could be a primary source of groundwater contamination by organic compounds [Pisarek and Głowacki 2005]. The compounds contained in groundwater, sometimes used as drinking water, are dangerous to human health because of the possibility of a mutagenic and carcinogenic reaction [Owabor et al. 2010, Ritter et al. 2002].

The aim of this paper is to determine the concentration of PAHs and pesticides in groundwater as a result of co-transport with humic substances contained in soil solutions.

## MATERIALS AND METHODS

The research area was localized to the biggest ground water reservoir in the Opole region (south-west part of Poland) – The Main Groundwater Reservoir No. 333 (MRGW No 333) [Stasko and Wcislo 2006]. This region is situated in the western part of the Silesian Upland with post-volcanic rocks. An erupting volcano went through Triassic limestone sediments and formed a basaltic cone on towering limestone. Nowadays, this area is protected and known as "St. Anna Mountain" Landscape-Protection Park. The towering of limestone layers and their penetration by non-porous, little eroding basaltic rocks created good

conditions for the karst phenomena [Flaczyk 1987]. The main water level of the reservoir is in the Triassic limestone [Kryza and Stasko 2000]. Total water capacity MRGW No. 333 was calculated at about 250 000 m$^3$/d, the reservoir being about 40 km long [Szczygieł et al. 2006]. The bottom of the mountain and the adjacent areas are used for agricultural purposes - the farmers grow various plants and breed stock animals.

The research from wells situated on the Main Groundwater Reservoir is presented in Figure 1.

Polycyclic aromatic hydrocarbons (PAHs) were examined in groundwater samples taken from wells localized on the main groundwater reservoir MRGW No 333 (Main Reservoir of Groundwater No 333) lower Silesia region (Poland). Wells 7 and 13 were removed from calculations due to incomplete results.

### Preparation of Groundwater

Water samples were taken from wells and collected in amber glass bottles. Preservation was achieved by an addition of methanol. All samples were stored in a dark place without access to sunlight before analysis. The PAH extraction from the samples was performed with dichlomethane (GC grade) by 4-hour shaking. Dichlomethane – water sample ratio was 1:10 (v/v). Pesticide extraction from the samples was performed with hexane (GC grade) by 4-hour shaking. Hexane
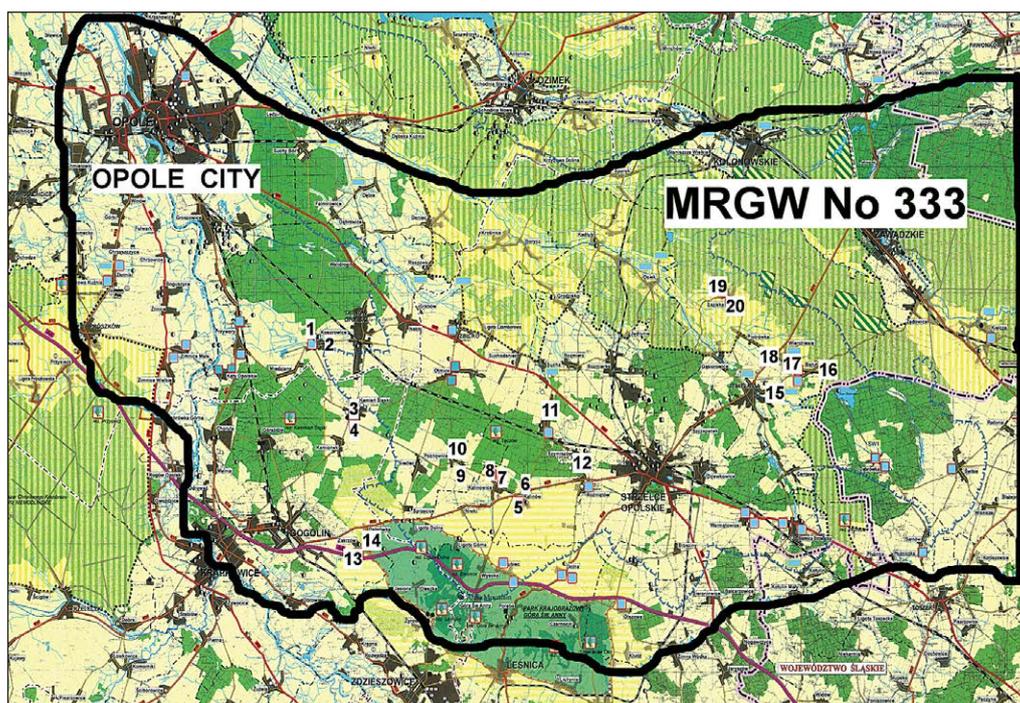


**Figure 1.** Sampling points on the investigated area of MRGW No 333

– water sample ratio was 1:10 (v/v). After that, the shaken organic layers were separated in separatory funnels, dried by anhydrous $Na_2SO_4$ and evaporated to about 0.5ml volume. All samples were determined in two replicates.

## Samples analysis

In each sample 16 single compounds were determined which are recommended to be monitored by the U.S. Environmental Protection Agency (US-EPA). They include: naphthalene (NAPH), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenantrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (B[a]ANT), chrysene (CHR), benzo[b,k]fluoranthene (B[b,k]FLA), benzo[a]pyrene (B[a]PYR), dibenzo[a,h]anthracene (D[a,h]ANT), indeno[1,2,3-c,d]pyrene (Ind[1,2,3-c,d]P), benzo[g,h,i]perylene (B[g,h,i] PER). PAHs were determined in unpurified extracts by the GC-FID method using a ZB-5 (5% diphenyl–95% dimethylsiloxane) capillary column with constant carrier (He) flow through the column in the quantity of 1 ml/min. The temperature of the chromatograph (Varian CP 3800) injector was 300 °C while the FID detector was 320 °C. The temperature program of the stove began at 100 °C which lasted for 2 minutes, and then with a stable increase of 5 °C/min the temperature reached 300 °C which lasted for 10 minutes. Certified PAHs standards (2000 mg/$cm^3$ of each compound; LGC Promochem Corporation, Teddington, UK) were used in order to determine the calibration curve [Rosik-Dulewska et al. 2008a]. Recovery levels for this procedure were low for naphthalene (62–74%), and higher (83–94%) for the rest of the individual PAHs. The detection limit was 0.005 mg/$dm^3$ for each compound of PAHs group. The uncertainty of the results was calculated as a standard deviation value. Moreover, particular compound concentration ratios: ANT/(ANT+PHE), BaA/(BaA+CHR), FLT/(FLT+PYR) were calculated for estimation: petrogenic and pyrogenic compounds – from burning solid fuels.

## Pesticides determination

In each sample 6 single compounds (Heptachlor, Aldrine, Dieldrine, DDE, DDD, DDT) were determined. Pesticides were determined in unpurified extracts by GC-ECD method using DB-1701 capillary column with constant carrier (He) flow through the column in quantity of 1ml/min. The temperature of the chromatograph injector was 250 °C while the ECD detector was 310 °C. The temperature program of the stove began at 150 °C which lasted for 1 minute, and then with a stable increase of 5 °C/min the temperature reached 305 °C that lasted for 10 minutes. Certified pesticides standards (500 mg/$cm^3$ of each compound; LGC Promochem Corporation, Teddington, UK) were used in order to determine calibration curve.

## Basis analysis

The conductivity and pH was determined with the use of electronic instruments: pH-meter and conductivity-meter immediately after sampling. Temperature and deep horizon groundwater was determined in the well with a thermometer and a specialized meter with a water table detector on the end.

## RESULTS AND DISCUSSION

In autumn, the water table was situated at 0.99 m under ground level (ugl) (well 9) to 9.0 m ugl (well 15). The mean depth of the water table during autumn was 3.48 m ugl. In winter the water table was measured from 0.7 m ugl (well 18) to 8.78 m ugl (well 15). The mean depth of the water table during autumn was 3.35 m ugl. Well 8 is particularly noteworthy. This is an artesian spring with an outflow of 0.7 m above ground. It is a rare phenomenon in the Lower Silesia Region. The temperature of the investigated water was high during autumn 10.3–19.0 °C and low during winter 3.5–10.0 °C. Values of pH and EC were typical for unpolluted ground waters (Table 1).

The investigated waters initially created a shallow water layer. It was mostly located from 1.0 to 3.5 meters under ground level. Additionally, the character of the soil and rocks – full of caverns – made it possible for effective transmission of rainwater (also with pollutants) directly and quickly to the water layer [Aghazadeh and Mogaddam 2011]. Only three wells (no. 14 to 16) were deeper – the water table being under 6 meters ugl. The pH values were typical for well-buffered waters and these values were close to existing data from the Opole region [Rosik-Dulewska et al. 2008b]. In this area, it manifests itself in rocks rich in calcium and magnesium carbonates, so pH data from other areas are lower

**Table 1.** Main water samples' parameters

| Nr of well | Deep to horizon water [m ugl] | | pH | | EC [μS*cm$^{-1}$] | | Temperature [°C] | |
|---|---|---|---|---|---|---|---|---|
| | Min–max | average | Min–max | median | Min–max | average | Min–max | average |
| 1 | 1.10–1.12 | 1.05 | 7.02–7.10 | 7.05 | 760–872 | 806 | 5.5–17.0 | 9.9 |
| 2 | 0.81–1.15 | 0.99 | 7.42–7.68 | 7.59 | 103–415 | 287 | 4.5–17.0 | 10.2 |
| 3 | 0.83–1.59 | 1.23 | 7.07–7.68 | 7.11 | 524–726 | 606 | 3.1–16.0 | 5.3 |
| 4 | 2.08–2.48 | 2.30 | 6.90–7.21 | 6.95 | 609–951 | 833 | 6.4–16.0 | 10.7 |
| 5 | 2.10–2.76 | 2.35 | 7.17–7.95 | 7.36 | 462–836 | 643 | 5.7–16.0 | 10.0 |
| 6 | 1.80–2.28 | 2.06 | 7.00–7.34 | 7.22 | 695–1145 | 867 | 7.5–16.0 | 12.0 |
| 8 | dnp | dnp | 7.04–7.40 | 7.25 | 649–774 | 702 | 9.4–11.0 | 10.2 |
| 9 | 0.76–1.12 | 0.92 | 7.00–7.33 | 7.16 | 580–764 | 656 | 6.6–19.0 | 12.0 |
| 10 | 2.03–2.12 | 2.07 | 7.04–7.30 | 7.23 | 695–857 | 767 | 8.2–14.8 | 11.0 |
| 11 | 3.85–4–64 | 4.04 | 7.85–8.33 | 8.16 | 372–490 | 420 | 7.0–13.2 | 9.9 |
| 12 | 1.09–1.70 | 1.38 | 7.31–8.11 | 7.88 | 363–420 | 382 | 5.5–13.2 | 9.0 |
| 14 | 7.12–7.85 | 7.49 | 7.08–7.68 | 7.41 | 709–895 | 786 | 8.9–11.3 | 10.2 |
| 15 | 8.78–9.46 | 9.07 | 6.89–7.49 | 7.27 | 816–895 | 872 | 9.1–10.3 | 9.6 |
| 16 | 6.60–6.85 | 6.73 | 6.68–7.71 | 7.21 | 460–535 | 506 | 7.6–11.3 | 9.5 |
| 17 | 0.98–1.63 | 1.32 | 6.68–7.86 | 7.47 | 502–620 | 561 | 2.6–13.0 | 8.1 |
| 18 | 0.51–1.15 | 0.85 | 6.26–7.62 | 7.35 | 424–619 | 547 | 2.1–13.1 | 7.4 |
| 19 | 2.74–3.04 | 2.89 | 6.24–7.02 | 6.67 | 439–524 | 502 | 7.5–13.4 | 10.3 |
| 20 | 2.25–2.30 | 2.27 | 6.88–7.30 | 7.09 | 292–528 | 410 | 6.5–12.5 | 9.7 |

**Table 2.** Content of PAHs in water samples taken in autumn (A) and winter (W) [mg/dm$^3$]

| Well / Compound | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | W | A | W | A | W | A | W | A | W | A | W |
| NAPH | 0.294 | 0.693 | 0.671 | 1.106 | 0.764 | 2.045 | 0.011 | 1.042 | 0.705 | 1.957 | 0.341 | 1.187 |
| ACY | 0.023 | 0.013 | 0.019 | 0.228 | 0.025 | 0.128 | <0.005 | 0.017 | 0.028 | 0.045 | 0.024 | 0.019 |
| ACE | 0.050 | 0.093 | 0.030 | <0.005 | 0.043 | 2.212 | 0.016 | <0.005 | 0.041 | 0.158 | 0.035 | 0.056 |
| FLU | 0.019 | 0.090 | 0.032 | 0.487 | 0.015 | 1.013 | 0.009 | 0.047 | 0.075 | 0.377 | 0.122 | 0.546 |
| FEN | 0.106 | 0.060 | 0.032 | 0.322 | 0.116 | 1.238 | 0.038 | 0.139 | 0.095 | 0.474 | 0.140 | 0.632 |
| ANT | 0.178 | 0.052 | 0.103 | 0.473 | 0.150 | 0.100 | 0.058 | 0.132 | 0.169 | 0.026 | 0.160 | 0.037 |
| FLA | 0.330 | 0.117 | 0.223 | 0.128 | 0.353 | 0.718 | 0.129 | 0.044 | 0.559 | 0.084 | 0.392 | 0.032 |
| PYR | 0.129 | 0.135 | 0.427 | 0.402 | 0.022 | 0.065 | 0.010 | <0.005 | 0.022 | 0.022 | <0.005 | 0.027 |
| B(a)ANT | 0.124 | 0.044 | 0.081 | 0.019 | 0.111 | 0.104 | 0.105 | 0.120 | 0.197 | 0.034 | 0.117 | 0.059 |
| CHR | 0.071 | <0.005 | 0.191 | 0.145 | 0.064 | <0.005 | 0.033 | <0.005 | 0.097 | <0.005 | 0.069 | <0.005 |
| B(b)FLU | 0.602 | 0.385 | 0.111 | <0.005 | 0.599 | <0.005 | 0.185 | <0.005 | 0.712 | 0.035 | 0.544 | 0.058 |
| B(k)FLU | 0.753 | 0.028 | 1.278 | <0.005 | 0.659 | 0.055 | 0.253 | 0.281 | 0.667 | 0.104 | 0.188 | 0.166 |
| B(a)PYR | <0.005 | 0.050 | 0.809 | 0.032 | <0.005 | <0.005 | <0.005 | <0.005 | 0.037 | 0.040 | 0.018 | <0.005 |
| Ind(1,2,3-cd)P | 0.026 | 0.180 | <0.005 | 0.121 | 0.113 | 0.254 | 0.016 | <0.005 | 0.034 | 0.096 | 0.022 | 0.114 |
| D(a,h)ANT | <0.005 | <0.005 | 0.022 | 0.310 | 0.160 | <0.005 | 0.049 | <0.005 | 0.073 | <0.005 | 0.220 | <0.005 |
| B(g,h,i)PER | <0.005 | <0.005 | 0.032 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 |
| Mean value | 0.169 | 0.121 | 0.254 | 0.236 | 0.199 | 0.496 | 0.057 | 0.114 | 0.219 | 0.216 | 0.149 | 0.183 |

**Table 3.** Content of PAHs in water samples taken in autumn (A) and winter (W) [mg/dm³]

| Well | 8 | | 9 | | 10 | | 11 | | 12 | | 14 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | A | W | A | W | A | W | A | W | A | W | A | W |
| NAPH | 0.639 | 1.151 | 1.103 | 0.812 | 0.926 | 0.832 | 0.391 | 0.627 | 0.634 | 0.863 | 0.113 | 0.651 |
| ACY | <0.005 | 0.022 | 0.031 | 0.043 | 0.021 | 0.050 | 0.012 | 0.168 | 0.013 | <0.005 | 0.004 | <0.005 |
| ACE | 0.008 | 0.123 | 0.059 | 0.068 | 0.033 | <0.005 | 0.010 | 0.005 | 0.018 | <0.005 | 0.012 | <0.005 |
| FLU | 0.047 | 0.796 | 0.030 | 0.025 | 0.081 | 0.016 | 0.059 | 0.659 | 0.039 | 0.182 | 0.003 | 0.337 |
| FEN | 0.104 | 0.825 | 0.124 | 0.038 | 0.084 | 0.035 | 0.047 | 0.124 | 0.035 | 1.722 | 0.015 | 0.194 |
| ANT | 0.115 | 0.030 | 0.242 | 0.055 | 0.205 | 0.070 | 0.080 | 0.183 | 0.281 | 0.340 | <0.005 | 0.024 |
| FLA | 0.393 | 0.021 | 0.393 | 0.092 | 0.313 | 0.107 | 0.183 | 0.122 | 0.097 | 0.005 | 0.010 | 0.027 |
| PYR | 0.220 | 0.036 | <0.005 | 0.007 | <0.005 | 0.041 | 0.025 | 0.018 | 0.016 | 0.106 | 0.007 | 0.006 |
| B(a)ANT | 0.524 | 0.097 | 0.231 | 0.139 | 0.128 | 0.178 | 0.023 | 0.017 | 0.047 | 0.039 | <0.005 | 0.013 |
| CHR | 0.447 | <0.005 | 0.010 | 0.036 | 0.040 | 0.020 | 0.005 | <0.005 | 0.289 | 0.044 | <0.005 | 0.015 |
| B(b)FLU | 0.026 | 0.038 | 0.199 | 0.063 | 0.595 | 0.069 | 0.128 | 0.230 | 0.748 | 0.026 | 0.423 | 0.042 |
| B(k)FLU | 0.876 | 0.177 | 0.318 | 0.153 | 0.152 | 0.188 | 0.193 | 0.551 | 0.633 | 0.119 | 0.586 | 0.068 |
| B(a)PYR | 1.067 | 0.069 | 0.085 | 0.056 | 0.063 | 0.055 | 0.065 | <0.005 | 0.151 | 0.029 | <0.005 | <0.005 |
| Ind(1,2,3-cd)P | 0.779 | 0.184 | 0.028 | 0.148 | 0.014 | 0.207 | 0.034 | <0.005 | 0.168 | 0.080 | <0.005 | <0.005 |
| D(a,h)ANT | 0.126 | 0.133 | 0.192 | 0.086 | 0.090 | 0.116 | 0.035 | <0.005 | 1.190 | <0.005 | <0.005 | 0.074 |
| B(g,h,i)PER | 0.460 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | 0.231 | <0.005 | <0.005 |
| Mean value | 0.364 | 0.231 | 0.190 | 0.114 | 0.172 | 0.124 | 0.081 | 0.169 | 0.272 | 0.237 | 0.073 | 0.091 |

**Table 4.** Content of PAHs in water samples taken in autumn (A) and winter (W) [mg/dm³]

| Well | 15 | | 16 | | 17 | | 18 | | 19 | | 20 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | A | W | A | W | A | W | A | W | A | W | A | W |
| NAPH | 0.064 | 0.648 | 0.274 | 0.586 | 0.527 | 0.685 | 0.603 | 1.479 | 1.034 | 1.657 | 0.551 | 1.157 |
| ACY | <0.005 | 0.019 | 0.006 | 0.004 | 0.020 | 0.004 | 0.014 | 0.019 | 0.026 | 0.018 | 0.039 | 0.007 |
| ACE | 0.048 | 0.112 | 0.021 | 0.022 | 0.033 | 0.021 | 0.035 | 0.157 | 0.020 | 0.126 | 0.034 | 0.207 |
| FLU | 0.039 | 2.026 | 0.002 | 0.392 | 0.010 | 0.324 | 0.014 | 0.611 | 0.016 | 0.031 | 0.034 | 0.056 |
| FEN | 0.060 | 0.238 | 0.004 | 0.564 | 0.063 | 0.413 | <0.005 | 0.489 | 0.051 | 0.209 | 0.042 | 0.107 |
| ANT | <0.005 | 0.039 | 0.020 | 0.122 | 0.093 | 0.043 | <0.005 | 0.719 | 0.093 | 0.049 | 0.068 | 0.041 |
| FLA | 0.007 | 0.027 | 0.057 | 0.023 | 0.223 | 0.007 | 0.040 | 0.023 | 0.200 | 0.017 | 0.227 | 0.013 |
| PYR | 0.084 | 0.007 | 0.008 | 0.008 | <0.005 | 0.008 | 0.094 | 0.015 | <0.005 | 0.043 | <0.005 | 0.032 |
| B(a)ANT | <0.005 | 0.036 | 0.013 | 0.047 | 0.052 | 0.052 | <0.005 | 0.114 | 0.090 | 0.080 | <0.005 | 0.023 |
| CHR | 0.115 | <0.005 | 0.024 | 0.046 | 0.025 | 0.099 | 0.022 | 0.054 | 0.072 | <0.005 | <0.005 | <0.005 |
| B(b)FLU | 0.235 | 0.069 | 0.042 | 0.147 | 0.280 | 0.117 | 0.012 | <0.005 | 0.165 | 0.106 | 0.104 | 0.116 |
| B(k)FLU | 0.840 | 0.091 | 0.135 | 0.208 | 0.315 | 0.266 | 0.149 | 0.298 | 0.366 | 0.163 | 0.212 | 0.143 |
| B(a)PYR | <0.005 | <0.005 | <0.005 | 0.048 | <0.005 | 0.051 | 0.126 | 0.128 | <0.005 | <0.005 | <0.005 | <0.005 |
| Ind(1,2,3-cd)P | 0.264 | <0.005 | 0.037 | 0.058 | <0.005 | 0.201 | <0.005 | <0.005 | 0.081 | 0.151 | <0.005 | <0.005 |
| D(a,h)ANT | 0.177 | <0.005 | 0.026 | 0.543 | <0.005 | 1.009 | <0.005 | <0.005 | <0.005 | <0.005 | 0.145 | <0.005 |
| B(g,h,i)PER | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | 0.071 | <0.005 | <0.005 | <0.005 | <0.005 |
| Mean value | 0.121 | 0.207 | 0.042 | 0.176 | 0.103 | 0.206 | 0.069 | 0.261 | 0.138 | 0.166 | 0.091 | 0.119 |

[Fianko et al. 2009]. The electrically conductivity (EC) is lower than in existing data from the polluted areas and shows that these waters are not polluted with electrolytes [Aghazadeh and Mogaddam 2011, Ciesielczuk et al. 2006a]. The temperature of shallow water is more dependent on atmospheric conditions. Only three samples – wells 14 to 16 were less dependent, particularly during the winter time when the temperature was between 7.6–9.1 °C.

The investigated area is not under industry pressure so organic contaminants mostly come from agricultural activity eg. fertilizing with organic fertilizers and emissions from individual heating systems. Noted concentrations of particular compounds are showed in Tables 2–4.

The sum of 16 PAHs analyzed compounds was high – minimal values of 0.65 mg/dm³ were noted in the sample from well 16 in the autumn and 1.452 mg/dm³ in the winter (well 14). Maximum sum values were noted in sample 8 (autumn) 5.832 mg/dm³ and 7.931 mg/dm³ in well 3 (winter). The Ministry of Environment regulations [Regulation 2008] classify this water as "V" – the poorest quality class. However, this regulation does not state what compounds should be examined in the samples. Naphthalene is easily sol-uble in water – so its concentration was relatively high – and made over 50% of the total content. In general, samples taken during the winter contained lower amounts of PAHs than in the autumn samples. Data from the literature showed that soil eluate may contain 0.3–2.0 mg/dm³ of particular compounds from the PAHs group. However, there were 3–4-ring compounds. The rest of the compounds – 4 and 5 ring – were noted in trace amounts [Goodarzi and Mukhopadhyay 2000]. Especially high concentrations were observed in groundwater polluted by petroleum products [Ciesielczuk et al. 2006b]. Also, elution of PAHs from soil was relatively high [Czop and Wandrasz 2007]. Calculated PAH ratios: ANT/(ANT+PHE), BaA/(BaA+CHR), FLT/(FLT+PYR) showed both sources to be equal: petrogenic and pyrogenic for these compounds. There was no correlation between the sum of 16 and between the sum of 6 PAHs (according to Ministry regulations) and the depth of the water table. High concentrations of investigated PAH compounds was probably an effect of the influence of the well area and water administration. Apart from PAHs, chlorinated pesticides were also observed (Table 5).

Pesticide analyses covered six compounds. In the case of heptachlor, aldrin and dieldrin, high

**Table 5.** Content of pesticides in water samples taken in autumn (A) and winter (W) [mg/dm³]

| Well / Compound | Heptachlor | | Aldrin | | Dieldrin | | DDE | | DDD | | DDT | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | W | A | W | A | W | A | W | A | W | A | W |
| 1 | 0.453 | 1.056 | 0.123 | – | 0.176 | – | 0.054 | – | 0.342 | – | 0.363 | – |
| 2 | 0.701 | 0.411 | 0.600 | – | 0.806 | – | – | – | – | – | – | – |
| 3 | 0.833 | 0.263 | 0.198 | – | 1.160 | – | – | – | – | – | – | – |
| 4 | 1.009 | 0.767 | 0.214 | – | 1.215 | – | – | – | 0.432 | – | 0.746 | – |
| 5 | 15.969 | 0.292 | 6.406 | – | 1.751 | – | 1.038 | – | 1.586 | – | 1.054 | – |
| 6 | 0.870 | 1.346 | 0.415 | – | 1.994 | – | – | – | – | – | – | – |
| 8 | 0.315 | 0.155 | 0.186 | – | 0.954 | – | 0.033 | – | – | – | – | – |
| 9 | 1.152 | 0.878 | 0.452 | – | 0.656 | – | 0.021 | – | 0.025 | – | 0.038 | 0.017 |
| 10 | 0.995 | 0.560 | 0.159 | – | 0.332 | – | – | – | – | – | – | – |
| 11 | 0.735 | 0.338 | 0.385 | – | 0.418 | 0.021 | – | – | – | – | – | – |
| 12 | 0.683 | 0.452 | 0.752 | – | 0.084 | – | 0.009 | – | 0.080 | – | – | – |
| 14 | 0.334 | 0.363 | 0.954 | – | 0.060 | – | 0.058 | 0.008 | 0.007 | – | 0.075 | – |
| 15 | 0.128 | 0.225 | 0.605 | – | 0.175 | – | 0.020 | – | – | 0.009 | 0.043 | – |
| 16 | 0.373 | 0.385 | 0.857 | – | 0.659 | – | – | – | – | – | – | – |
| 17 | 0.485 | 0.452 | 0.907 | – | 0.445 | – | – | – | – | – | – | – |
| 18 | 1.083 | 1.350 | 1.150 | 0.052 | 0.338 | – | 0.064 | – | 0.546 | – | – | 0.023 |
| 19 | 0.787 | 0.681 | 0.858 | – | 0.549 | – | – | – | – | – | – | – |
| 20 | 0.564 | 0.405 | 0.762 | – | 0.587 | – | – | – | – | – | – | – |

concentrations in investigated samples were noted. Other authors found much lower concentrations of these compounds [Geyikci and Büyükgüngör 2011]. Heptachlor was the most noted and the autumn mean concentration reached 1.53 mg/dm³, for aldrin 0.888mg/dm³ and for dieldrin 0.687 mg/dm³. During winter the concentrations of aldrin and dieldrin were low and rarely exceeded the detection limit. Also, the presence of pesticides which had not been in use for around 20 years such as DDT was noted. The pollutants DDT, and metabolites, were observed in lower concentrations and only in some samples. The sample most polluted by these compounds was observed in well 5 – analoguous to high concentrations of heptachlor, aldrin and dieldrin. During winter, the determined amount of DDT and its metabolites (DDE, DDD) were lower and mostly under the detection limit. This confirmed high stability and environmental pollution from this product. There were no observed correlations between pesticides' concentration and the well depth.

## CONCLUSION

The water from the investigated wells was shallow groundwater – 1st level water table, therefore, the pollution risk from external sources is highly possible. The samples contained a wide range of concentrations of PAHs and pesticides. In winter higher amounts of PAHs were observed, however, they were mostly low toxicity 2 and 3 ring compounds, in contrast to autumn with lower summary values but higher amounts of 5 and 6-ring PAHs. The sum of PAHs was high and investigated water samples were in the IV and V – poor quality class (according to Ministry regulations). The pesticides content was also wide ranging and high – showing great pressure from human agricultural activities. The highest noted concentration of heptachlor exceeded the maximum accepted level by 32 times. The most possible source of PAHs and pesticides in investigated water samples was soil eluate which leaks to ground water as an effect of rainfall.

### Acknowledgments

## REFERENCES

1. Aghazadeh N., Mogaddam A.A. 2011. Investigation of hydrochemical characteristics of groundwater in the Harzandat aquifer, Northwest of Iran. Environmental Monitoring and Assessment 176, 183-195.

2. Ake C.L., Wiles M.C., Huebner H.J., McDonald T.J., Cosgriff D., Richardson M.B., Donnelly K.C., Phillips T.D. 2003. Porous organoclay composite for the sorption of polycyclic aromatic hydrocarbons and pentachlorophenol from groundwater. Chemosphere 51, 835-844.

3. Ciesielczuk T., Rosik-Dulewska Cz., Nabzdyjak T. 2006a. Assessment of aliphatic and polycyclic aromatic hydrocarbons in ground water on the fuel storage area of airport (in polish), Ecological Chemistry and Engineering Vol. 13, No S4, 531-538.

4. Ciesielczuk T., Kusza G., Poluszyńska J. 2006b. Assessment of PAHs and total content of organic matter in Landfill Leachate and Groundwater, Ecological Chemistry and Engineering 11(13), 1225-1230.

5. Czop M., Wandrasz J.W. 2007. Analysis of mobility Polycyclic Aromatic Hydrocarbons in soils (in polish). Environmental Protection and Natural Resources, IEP, Warsaw 31, 144-148.

6. Fianko J.R, Osae S., Adomako D., Achel D.G. 2009. Relationship between land use and groundwater quality in six districts in the eastern region of Ghana. Environmental Monitoring and Assessment 153, 139-146.

7. Flaczyk Z. 1987. The environmental conditions of agricultural activity (in Polish), IUNG, Pulawy, pp. 82.

8. Geyikci F., Büyükgüngör H. 2011. Monitoring of organochlorine pesticides in the surface waters from Mid-Black Sea Region, Turkey Environmental Monitoring and Assessment 173, 127-137.

9. Goodarzi F., Mukhopadhyay (Muki) P.K. 2000. Metals and polyaromatic hydrocarbons in the drinking water of the Sydney Basin, Nova Scotia, Canada: a preliminary assessment of their source, International Journal of Coal Geology 43, 357-372.

10. Jayasekera D.L., Kaluarachchi J.J., Villholth K.G. 2011. Groundwater stress and vulnerability in rural coastal aquifers under competing demands: a case study from Sri Lanka. Environmental Monitoring and Assessment 176, 13-30.

11. Kryza J., Stasko S. 2000. Groundwater Flow Rate and Contaminant Migration in Fissure-Karstic Aquifer of Opole Triassic System Due to Man Activity. Environmental Geology 39, 3/4, 384-389.

12. Lazzari L., Sperni L., Salizzato M., Pavoni B. 1999. Gas chromatographic determination of organic micropollutants in samples of sewage sludge and compost: behavior of PCB and PAH during composting, Chemosphere 38, 1925-1935.

13. Oleszczuk P., Baran S., Baranowska E., Pranagal J. 2007. Content of Polycyclic Aromatic Hydrocarbons in long-term flooded soil. Ecological Chemistry and Engineering 14(S1), 109-116.

14. Owabor Ch.N., Ogbeide S.E., Susu A.A. 2010. Estimation of transport and degradation parameters for naphthalene and anthracene: influence of mass transfer on kinetics. Environmental Monitoring and Assessment 169, 607-617.

15. Pisarek I., Glowacki M. (2005) Some properties of aquatic humic substances from underground water of Opole region. Polish Journal of Environmental Studies 14, V: 29-32.

16. Pranagal J., Oleszczuk P. 2007. Content and migration of Polycyclic Aromatic Hydrocarbons in different soils used. Ecological Chemistry and Engineering 14(S2), 233-244.

17. Regulation of Polish Ministry of Environment from 23 of July 2008 No 143 pos. 896 (in Polish)

18. Ritter L., Solomon K., Sibley P. 2002. Sources, pathways, and relative risks of contaminants in surface water and groundwater: a perspective prepared for the walkerton inquiry. Journal of Toxicology and Environmental Health, Part A, 65, 1-142.

19. Rosik-Dulewska Cz., Ciesielczuk T., Ramus K. (2008a) Changes in the Polycyclic Aromatic Hydrocarbons (PAHs) content in an urban waste composting process. (In) Management of Pollutant Emission from Landfills and Sludge; Pawłowski, Dudzińska & Pawłowski (eds) Taylor&Francis Group London, 85-89.

20. Rosik-Dulewska Cz., Karwaczyńska U., Ciesielczuk T. 2008b. The impact of municipal landfill on the concentration of heavy metals in genetic soil horizons. (In) Management of Pollutant Emission from Landfills and Sludge; Pawłowski, Dudzińska & Pawłowski (eds) Taylor&Francis Group London, 117-124.

21. Stasko S., Wcislo M. 2006. Finite-difference method limitation in case of groundwater resource evaluation by modelingin karstic-fracture system, Geologos 10, 241-251.

22. Swarcewicz M.K., Gregorczyk A. 2011. The effects of pesticide mixtures on degradation of pendimethalin in soils. Environmental Monitoring and Assessment.

23. Szczygiel I., Kryza J., Fic A. 2006. Aquitard conductivity calibration of the Triassic aquifer numerical model of the Strzelce Opolskie area, Geologos 10, 272-283.

24. Thiele S., Brummer G.W. 2002. Bioformation of polycyclic aromatic hydrocarbons in soil under oxygen deficient conditions. Soil Biology & Biochemistry 34, 733-735.

25. Wilcke W., Muller S., Kanchanakool N., Niamskul Ch., Zech W. 1999. Polycyclic aromatic hydrocarbons in hydromorphic soils of the tropical metropolis Bangkok. Geoderma 91, 297-309.

26. Włodarczyk-Makuła M., Wiśniowska E., Janosz-Rajczyk M. 2003. Carcinogenic PAHs content in over-sludge water. Ecological Chemistry and Engineering 10(5), 467-476.