INTRODUCTION

It is believed that groundwater is the most important natural resource and requires constant monitoring of intakes and changes in its composition. Groundwater is typically well isolated from the ground surface by a layer of soil, eluvium formations and rocks in comparison with surface water and is thus protected against contamination. However, with excessive extraction, the quality of groundwater may deteriorate [Wen et al. 2005] affecting such parameters as water reaction (pH) which is one of the most important indices of water quality, even though its potential changes are not directly felt by consumers. Reaction of water may change due to, for instance, saturation with carbon dioxide. In the case of natural water, higher reaction changes may indicate water contamination. It is important for untreated water, as it impacts water treatment and natural processes occurring in water.

Water reaction requires careful control at all stages of water treatment to ensure a sufficient degree of decontamination and disinfection. The control of pH is also important at the stage of driving water into pipelines and internal installations. Hence, the highest permissible value of water reaction should range between 6.5 and 8.5. Non-compliance with these requirements may cause secondary contamination of drinking water and negatively influence its taste, smell and appearance.

Ammonium ions in groundwater originate mainly from the reduction of nitrates and nitrites in the presence of hydrogen sulphide or other reductive compounds. From a sanitary point of view, both the content of ammonium ions and their origin are important. They are often generated by decomposition of animal waste products, which pose a serious risk, especially if water is used for consumption. Non-organic origin of ammonium ions in water does not present a
direct health risk, as its toxic effects are seen when its intake exceeds 200 mg/kg BW. However, ammonium ions may reduce the efficacy of water disinfection, cause nitrite formation, hinder manganese elimination and cause changes in water smell and taste [WHO, 2004]. Nevertheless, from 2007 the recommended permissible limit for ammonium ion in drinking water is 0.50 mg·dm⁻³ NH₄⁺.

Chlorides may be an indicator of potential water contamination, but the risk of their presence in drinking water depends on natural conditions to a large extent [Kabata-Pendias, Pendias 1999]. In shallow groundwater layers, contamination with chlorides often cause water salinity by inversion, especially in urbanized areas and within rural infrastructure [Macioszczyk, Jeż, 1995].

Liquid inclusions in the minerals of igneous rocks may be an additional source of small amounts of chlorides [Prince Edward Island, 2000]. Substantial amounts of Cl⁻ ions may originate from easily-soluble minerals of sedimentary rocks, mainly from halite (NaCl). The origin of chlorides is varied and a fraction of their amount may be supplied with precipitation, especially on coastal marine areas and on saline soil. The presence of chlorides in drinking water gives it a salty taste in the case of NaCl and salty-bitter taste with Ca²⁺, Mg²⁺ or NH₄⁺ cations co-present with chlorides. Taste perception is important as it determines common implementation of the regulations that limit the amount of Cl⁻ in water intended for consumption. Although the highest permissible limit of chlorides in drinking water is 250 mg·dm⁻³ [The Regulation by the Minister of Health] the World Health Organization [Wen et al. 2005] has not proposed any recommended permissible limit of chlorides in water intended for consumption based on health premises. The presence of chlorides in water at 100 mg·dm⁻³ causes its aggressive effects on iron and concrete.

Considering the aforementioned, the objective of the paper was to determine the impact of utilization of wells on the utility value of water on the background of reaction variability and changes in ammonium ion and chloride concentrations.

Table 1. Compilation of the existing well holes on the “Motława” intake located in Tczew [Legal documentation on water utilization, 2005]

<table>
<thead>
<tr>
<th>The number of well</th>
<th>Depth of well [m]</th>
<th>Production capacity [m³·h⁻¹]</th>
<th>Aquifer stages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.0</td>
<td>90.2</td>
<td>Tertiary</td>
</tr>
<tr>
<td>2</td>
<td>95.0</td>
<td>60.4</td>
<td>Tertiary</td>
</tr>
<tr>
<td>3</td>
<td>100.0</td>
<td>110.7</td>
<td>Tertiary</td>
</tr>
<tr>
<td>4</td>
<td>97.5</td>
<td>110.7</td>
<td>Tertiary</td>
</tr>
<tr>
<td>5</td>
<td>101.5</td>
<td>90.2</td>
<td>Tertiary</td>
</tr>
<tr>
<td>6</td>
<td>95.3</td>
<td>91.4</td>
<td>Tertiary</td>
</tr>
<tr>
<td>7</td>
<td>150.0</td>
<td>85.8</td>
<td>Cretaceous</td>
</tr>
<tr>
<td>8</td>
<td>99.0</td>
<td>39.1</td>
<td>Tertiary</td>
</tr>
<tr>
<td>9</td>
<td>93.0</td>
<td>69.3</td>
<td>Tertiary</td>
</tr>
<tr>
<td>10</td>
<td>96.0</td>
<td>60.0</td>
<td>Tertiary</td>
</tr>
<tr>
<td>11</td>
<td>96.0</td>
<td>102.0</td>
<td>Tertiary</td>
</tr>
</tbody>
</table>

Table 2. Compilation of the existing well holes on the “Park” intake situated in Tczew [Legal documentation on water utilization, 2005]

<table>
<thead>
<tr>
<th>The number of well</th>
<th>Depth of well [m]</th>
<th>Production capacity [m³·h⁻¹]</th>
<th>Aquifer stages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>97.6</td>
<td>60.0</td>
<td>Quaternary-tertiary</td>
</tr>
<tr>
<td>5</td>
<td>96.0</td>
<td>74.3</td>
<td>Quaternary-tertiary</td>
</tr>
<tr>
<td>2a</td>
<td>101.0</td>
<td>72.0</td>
<td>Quaternary-tertiary</td>
</tr>
<tr>
<td>4</td>
<td>92.0</td>
<td>60.0</td>
<td>Quaternary-tertiary</td>
</tr>
<tr>
<td>6</td>
<td>96.3</td>
<td>63.7</td>
<td>Quaternary-tertiary</td>
</tr>
<tr>
<td>K-1</td>
<td>180.0</td>
<td>74.0</td>
<td>Cretaceous</td>
</tr>
<tr>
<td>K-2</td>
<td>150.0</td>
<td>138.4</td>
<td>Cretaceous</td>
</tr>
<tr>
<td>K-3</td>
<td>160.0</td>
<td>88.0</td>
<td>Cretaceous</td>
</tr>
</tbody>
</table>
MATERIALS AND METHODS

The studies were carried out on the intakes located in Tczew (E 18º46'57.4" N 54º05'23.2") which supply water to approx. 60 000 inhabitants. Two intakes are the main source of drinking water (Tables 1 and 2) and they utilize groundwater from the tertiary and cretaceous stages (the “Motława” intake, Figure 1) and tertiary-quaternary and cretaceous stages (the “Park Miejski” intake, Figure 2).

The wells on the “Motława” intake (Fig. 1) derive groundwater from the cretaceous and tertiary aquifer layers. The quaternary aquifer stages are supplied mainly by a lateral influx from the upland and to a minor extent by filtration from the tertiary stage and direct infiltration of precipitation and melting water and surface water. The tertiary layer is supplied with a lateral influx and filtration.

The oldest formations identified on the “Motława” intake are marls and limestone reaching depths of 150 m, whereas the oldest quaternary formations are aqua-glacial sands of mid-Polish glaciations, linked to tertiary sands located underneath. The “Motława” intake meets approx. 65% of the requirements of the town and the approved utility resources are set at $Q_{\text{max}} = 16 872 \text{ m}^3\cdot\text{d}^{-1}$, including the volume from the tertiary formations at $Q_{\text{max}} = 14712 \text{ m}^3\cdot\text{d}^{-1}$ (with the wells No 1, 2, 3, 4, 5, 6, 8, 9, 10, 11) and from the cretaceous formations at $Q_{\text{max}} = 2160 \text{ m}^3\cdot\text{d}^{-1}$ (with the well No 7). The wells are used alternately, usually three to five of them at the same time. Additional wells are mobilized occasionally in the case of a high intensity of distribution.

Although the “Park” intake (Fig. 2) from eight wells supplies approx. 35% of the water to the municipal water pipeline, the intake of water cannot exceed the utilization limits specified in the legal documentation on water utilization set at $Q_{\text{max}} = 12 200 \text{ m}^3\cdot\text{d}^{-1}$, of which $Q_{\text{max}} = 14 660 \text{ m}^3\cdot\text{d}^{-1}$ for quaternary-tertiary formations (with the wells No 1b, 2a, 4, 5, 6) and $Q_{\text{max}} = 7540 \text{ m}^3\cdot\text{d}^{-1}$ for cretaceous formations (with the wells No K-1, K-2, K-3).

The oldest formations that were drilled during intake construction are cretaceous fine sands, with a roof approx. 200 m below the sea level and a depth of horizon of over 55 m. They are covered with a complex of marls, often with clefts. Crevice water of the cretaceous stage is fed exclusively with filtration, mainly from the tertiary aquifer layer. The degree of mixing is variable, which is indicated by unsteady salinity. The quaternary-tertiary aquifer stage is composed of sands with a complete range of grain size composition and
at roof-adjacent zones they may be fed with carbonaceous substances, although near the bottom they may be muddy and contain glauconite.

The thickness of the aquifer layer ranges from 12 to 19 m and the water mirror oscillates around 2.0 m below sea level (Fig. 3). Under natural conditions, water in the quaternary-tertiary aquifer stage flowed from the upland towards the east and the Vistula River Valley.

The water parameters were tested with the following methods: reaction (pH) with potentiometric method, ammonium with colorimetric method using Nessler’s reagent at 410 nm wavelength and the thickness of cuvette at 5 mm and chlorides with titration with silver nitrate in relation to potassium chromate as an indicator [PN-75/C-04617.02, PN-75/C-04540.02, PN-75/C0-04576.01].

The results of the measurement of water operational capacity from the intakes (wells) and the legal documentation on water utilization were submitted by the manufacturer of water [Legal documentation on water utilization, 2005].

![Map of the intake “Park” located in Tczew](Legal documentation on water utilization, 2005)

**Fig. 2.** Map at 1: 25000 of the intake “Park” located in Tczew [Legal documentation on water utilization, 2005]

![Diagram of water-bearing horizons](Diagram of water-bearing horizons)

**Fig. 3.** Depth of the wells (m) taking water from the aquifer layers QT, K, and T. 

![Diagram of water-bearing horizons](Diagram of water-bearing horizons)
analysis of hydro-geological conditions was performed based on the documentation of the disposable groundwater resources [Kreczko et al. 2000].

The data included several environmental factors which were used in the statistical analysis for calculating correlations and in the one-way analysis of variance (ANOVA) with Duncan’s parametric test at $p \leq 0.05$. The impact of environmental factors on the concentration of parameters in the analysed water samples was determined using principal component analysis (PCA).

RESULTS

The results of the studies conducted in 1994–2009 on the water intakes located in Tczew demonstrated that the water reaction and concentrations of chlorides and ammonium varied across a wide range of values and were differentiated depending on the water intake and well depths as well as operational capacity (Table 3).

The reaction of tested water ranged from 7.10 to 7.80 on the intake “Park” and from 7.20 to 8.40 on the “Motława” intake. The average values indicate a comparable reaction of tested water regardless of the intake. Higher diversification was found in water from different aquifer layers. The statistical data shows that the reaction values of QT and T water stages were insignificant, which is indicated by the same homogenous group in relation to significant differences recorded for water samples from the cretaceous stage expressed with a homogenous group.

The presence of ammonia in water at higher concentrations may suggest an effect of anthropogenic factors, as it is important in a technological context.

In the tested water samples, the content of ammonia was diversified in the extreme ranges for the examined intakes from 0.74 to 1.76 mg · dm$^{-3}$ NH$_4$ for the “Park” intake and from 0.45 to 1.67 mg · dm$^{-3}$ NH$_4$ for the “Motława” intake (Table 3). However, the values of this parameter were similar for both intakes (1.07 mg · dm$^{-3}$ NH$_4$), what indicates comparable chemism conditions of this chemical group in the water samples collected from both intakes (Fig. 5).

The diversification of this parameter was demonstrated for the aquifer stages (Fig. 5). Similar to the reaction of water originating from QT and T layers, the differences in the content of ammonia were statistically insignificant, which is indicated by the same homogenous group. The K water stages which were statistically included in the homogenous group had a significantly lower content of ammonia than the QT and T water layers.

Chlorides are another parameter which impact the quality of water and their presence is thus very important for humans. The results (Table 3) show that the content of chlorides in groundwater at both intakes varied across a wide range of values. It is interesting to note that at comparable fluctuation ranges in the concentration of this element, its average content was highly diversified between the intakes. In the case of the “Park” intake, the content was 52.7 mg · dm$^{-3}$ Cl and for the “Motława” intake it was 14.1 mg · dm$^{-3}$ Cl.

Statistically significant differences in the content of chlorides (Fig. 6) demonstrate that their concentration was influenced by a type of aquifer stages. At QT and T stages that were predominant in the area of “Park” intake, the content of chlorides was at a comparable level. Significantly higher concentrations of this element were detected in water from the cretaceous aquifer stage. This factor may be associated with the type of layer as well as the depth of individual aquifer layer, even though the strength of this relationship was different for the individual water intakes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Tczew “Park”</th>
<th>Tczew “Motława”</th>
</tr>
</thead>
<tbody>
<tr>
<td>The depth of well</td>
<td>m</td>
<td>92 – 180*</td>
<td>93 – 150*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>122**</td>
<td>102</td>
</tr>
<tr>
<td>Operational capacity</td>
<td>m$^3$·rok</td>
<td>10 456 – 682 308</td>
<td>13 135 – 738 370</td>
</tr>
<tr>
<td></td>
<td></td>
<td>191 048</td>
<td>220 118</td>
</tr>
<tr>
<td>Reaction</td>
<td>mg · dm$^{-3}$</td>
<td>7.10 – 7.80</td>
<td>7.20 – 8.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.37</td>
<td>7.54</td>
</tr>
<tr>
<td>Ammonia</td>
<td>mg · dm$^{-3}$</td>
<td>0.74 – 1.76</td>
<td>0.45 – 1.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>Chlorides</td>
<td>mg · dm$^{-3}$</td>
<td>10.0 – 173.5</td>
<td>5.4 – 177.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>52.7</td>
<td>14.1</td>
</tr>
</tbody>
</table>

Explanation: * range of values; ** average value.
(Table 4), being the strongest for “Park” intake both in relation to the aquifer layer (r = 0.84) and to depth (r = 0.83).

In the face of increasing groundwater utilization, it is recommended to wisely use water sources in order to ensure abundant water resources for the next generations. It is therefore important that a water supplier applies specific evaluation systems for all extraction procedures in relation to, for instance, water protection to eliminate different and changing factors while simultaneously monitoring water pollutant concentrations.

The awareness of the general public, as well as representatives of different industries should be involved to ensure the protection of groundwater quality and resources.
Table 4. Pearson’s simple correlation (r) coefficients at p < 0.05 for the intakes of untreated water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water-bearing horizon</th>
<th>Depth of well [m]</th>
<th>Exploitation</th>
<th>Reaction</th>
<th>Ammonia</th>
<th>Chlorides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intake located in Tczew “Park and Motława”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depth of well</td>
<td>0.57*</td>
<td>0.18*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exploitation</td>
<td>0.37*</td>
<td>0.26*</td>
<td>0.28*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>0.64*</td>
<td>-0.24*</td>
<td>-0.25*</td>
<td>-0.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>-0.44*</td>
<td>0.51*</td>
<td>-0.07</td>
<td>-0.09</td>
<td>-0.24*</td>
<td></td>
</tr>
<tr>
<td>Chlorides</td>
<td>0.20*</td>
<td>0.51*</td>
<td>-0.07</td>
<td>-0.09</td>
<td>-0.24*</td>
<td></td>
</tr>
<tr>
<td>Intake located in Tczew “Park”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depth of well</td>
<td>0.85*</td>
<td>0.24*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exploitation</td>
<td>0.43*</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>0.71*</td>
<td>0.66*</td>
<td>0.28*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>-0.58*</td>
<td>-0.39*</td>
<td>-0.39*</td>
<td>-0.43*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorides</td>
<td>0.84*</td>
<td>0.83*</td>
<td>0.25*</td>
<td>0.56*</td>
<td>-0.45*</td>
<td></td>
</tr>
<tr>
<td>Intake located in Tczew “Motława”</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depth of well</td>
<td>0.50*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exploitation</td>
<td>0.15</td>
<td>0.24*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.14</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>-0.50*</td>
<td>-0.13</td>
<td>-0.18*</td>
<td>-0.45*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorides</td>
<td>0.20*</td>
<td>0.17*</td>
<td>-0.03</td>
<td>-0.14</td>
<td>-0.20*</td>
<td></td>
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</tbody>
</table>

Explanation: * essential correlations.

CONCLUSIONS

During water extraction from the intakes, no significant changes in its quality and utility value were detected and it was not necessary to modify the treatment technology.

It was demonstrated that, regardless of intake volume, the concentration of ammonia in water exceeded the permissible sanitary limits, which necessitated implementing a water treatment procedure.

It was found that the type of aquifer cretaceous stage exerted a significant impact on the
increase in water reaction and the content of chloride, although it contributed to a decrease in ammonia concentration.

REFERENCES

5. PN-75/c-04617.02 Badania zawartości chlorków. Oznaczanie chlorków w wodzie i ściekach metodą argentometrycznego miareczkowania: 1-3.