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# Credibility criteria of results for underground water analysis

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**Motivatioon**

The wells data base compiled by the LVGMC includes results of several thousands groundwater sample analysis made as early as 60$^{th}$ of the previous century. As the data is accumulated during the period of more than 50 years including progress in analytical technologies and turmoil in political system the credibility of data need to be evaluated before it can be used for scientific research.

**Formation of groundwater composition**

Infiltration of precipitation water is the force moving groundwater flow while the shape of the flow is determined by geological structures and earth surface elevation. As none of these factors has changed significantly during the last 10 thousand years since the end of the ice age [1], it can be concluded that configuration of groundwater flow has not substantially changed and dynamic equilibrium of water composition is maintained. The steady groundwater flow means that any systematic changes of the composition will happen gradually in a long period of time determined by gradual disarrangement of flow patterns smoothed out by flow dispersion and diffusion [2]. The measured variations of the groundwater composition will have a character of an unintentional fluctuation which could be even induced by perturbations created during water sample collection. Exception is regions with an intensive water extraction such as surroundings of Riga and Jelgava where during 60$^{th}$, 70ties and 80ties huge depressions of groundwater level developed [3]. But even here gradual rather than abrupt groundwater composition changes will take place.

**Identification of analytical errors References**

In order to identify analytical mistakes we suggest using total validation criterion (TVC) that is calculated by dividing concentration of $Ca^{2+}$ ion (mgekv/l) with the sum of the concentration of anions (mgekv/l). The TVC is calculated from the only chemical components that even in the early days of systematic groundwater composition exploration were determined directly, that is $HCO_3^-$, $SO_4^{2-}$, $Cl^-$ and $Ca^{2+}$. The rest of the major components – $Na^+$, $K^+$, $Mg^{2+}$ – according to GOST standards were calculated from the ion balance ($Na^+$ and $K^+$) or from the indirect measurements ($Mg^{2+}$).

The TVC can be used to validate long time series of groundwater monitoring data in observation points were short term variations caused by climatic and meteorological or human factors can be excluded. Outlays from the general trend at each monitoring spot shall be considered bad measurements and dismissed (Fig. 1.).

In order to identify sample spoiling during the storage due to freezing or aeration that can result in calcium carbonate precipitation the results need to be checked for consistency of concentration of $Ca^{2+}$ and $HCO_3^-$ ion concentrations in (mgekv/l). If changes are severe and correlate for both ions then results should be considered as a bad mistake. It is possible that TVC does not spot this deviation (Fig. 2. and 3.).

**Conclusions**

In the Table 1 proportion of the individual analyses for several monitoring posts that are outside the confidence interval of 95% is shown, ranging from 0% to 12%. In total 3% to 6% of analyses of individual ions seem to be erroneous. The likely sources of errors are analytical mistakes or poor sample handling. For example sample freezing during the storage results in precipitation of calcium carbonate. The proportion of suspected mistakes is rather similar for different monitoring posts. We speculate that this value can be upscale to the full data base of groundwater chemical composition compiled by the LVGMC.

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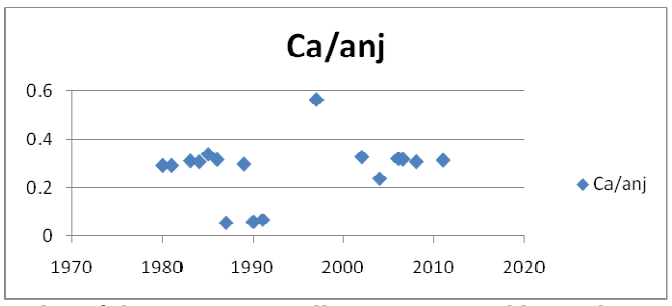


**Fig. 1.** TVC value of the monitoring well No. 1508 at Baldone. There is no feasible geological explanation for the four outliers from the general trend and these analyses should be regarded as wrong.

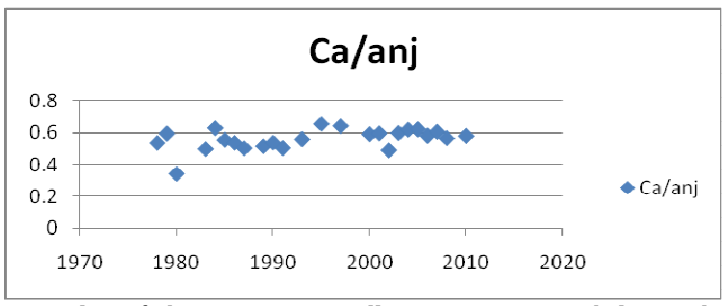


**Fig. 2.** TVC value of the monitoring well No. 1492 at Inčukalns. Only one bad measurement can be identified using TVC.

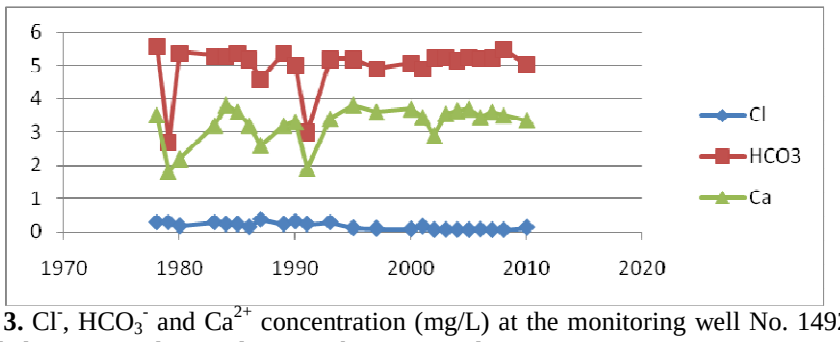


**Fig. 3.** $Cl^-$, $HCO_3^-$ and $Ca^{2+}$ concentration (mg/L) at the monitoring well No. 1492 at Inčukalns. Two coherent drops in the Ca2+ and HCO3- concentrations suggest that CaCO3 precipitated from the sample during the storage possibly due to sample freezing or lose of the $CO_2$ gas.

**Table 1.** Number of **o**bvious mistakes sum in measurements of each ion and TVC

| Nr. | Object identification | Observation period (years) | Number of samples | Number of individual analyses | Number of suspected mistakes | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | TVC | Cl | $HCO_3$ | $SO_4$ | Ca | sum without TVC | in % |
| 1 | 24552-Dāvida | 2004-2011 | 7 | 28 | 0 | 0 | 0 | 0 | 0 | 0 | **0.0** |
| 2 | 24551-Briņķu | 2006-2011 | 5 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | **0.0** |
| 3 | 24550-Bānūžu | 2006-2011 | 6 | 24 | 0 | 0 | 0 | 0 | 0 | 0 | **0.0** |
| 4 | 24560-Saltavots | 2004-2011 | 7 | 28 | 0 | 0 | 0 | 0 | 0 | 0 | **0.0** |
| 5 | 1596-Tīreļi | 1973-1978 | 20 | 80 | 0 | 0 | 1 | 2 | 1 | 4 | **5.0** |
| 6 | 1511-Baldone | 1980-2011 | 19 | 76 | 1 | 0 | 0 | 0 | 2 | 2 | **2.6** |
| 7 | 1508-Baldone | 1980-2011 | 17 | 68 | 0 | 0 | 0 | 1 | 0 | 1 | **1.5** |
| 8 | 1507-Baldone | 1997-2011 | 5 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | **0.0** |
| 9 | 1-Piukas | 1978-2010 | 12 | 48 | 1 | 0 | 1 | 1 | 0 | 2 | **4.2** |
| 10 | 3-Piukas | 1978-2010 | 12 | 48 | 2 | 1 | 1 | 1 | 1 | 4 | **8.3** |
| 11 | 4-Piukas | 1978-2010 | 20 | 80 | 1 | 1 | 0 | 0 | 0 | 1 | **1.3** |
| 12 | 6- Baltezers | 1977-2008 | 25 | 100 | 2 | 0 | 0 | 2 | 0 | 2 | **2.0** |
| 13 | 7-Baltezers | 1977-2010 | 27 | 108 | 1 | 2 | 1 | 1 | 1 | 5 | **4.6** |
| 14 | 135-Baltezers | 1980-2010 | 25 | 100 | 0 | 1 | 1 | 2 | 1 | 5 | **5.0** |
| 15 | 136-Baltezers | 1977-2010 | 25 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | **0.0** |
| 16 | 683-Imanta | 1973-2010 | 31 | 124 | 2 | 2 | 1 | 3 | 3 | 9 | **7.3** |
| 17 | 685-Imanta | 1972-2010 | 32 | 128 | 1 | 1 | 2 | 2 | 1 | 6 | **4.7** |
| 18 | 686-Imanta | 1972-2010 | 36 | 144 | 1 | 0 | 1 | 2 | 1 | 4 | **2.8** |
| 19 | 693-Jaundubulti | 1973-2010 | 38 | 152 | 2 | 1 | 2 | 1 | 1 | 5 | **3.3** |
| 20 | 862-Lauma | 1985-2011 | 18 | 72 | 1 | 0 | 0 | 0 | 0 | 0 | **0.0** |
| 21 | 1243-Baltezers | 1975-2010 | 2 | 8 | 0 | 0 | 0 | 0 | 0 | 0 | **0.0** |
| 22 | 1483-Kalngale | 1980-2010 | 21 | 84 | 2 | 1 | 2 | 2 | 2 | 7 | **8.3** |
| 23 | 1484-Kalngale | 1980-2010 | 21 | 84 | 2 | 2 | 0 | 1 | 2 | 5 | **6.0** |
| 24 | 1488-Carnikava | 1979-2010 | 24 | 96 | 2 | 1 | 1 | 2 | 2 | 6 | **6.3** |
| 25 | 1489-Inčukalns | 1985-2003 | 10 | 40 | 1 | 1 | 2 | 2 | 0 | 5 | **12.5** |
| 26 | 1491-Inčukalns | 1978-2010 | 22 | 88 | 0 | 2 | 3 | 3 | 2 | 10 | **11.4** |
| 27 | 1492-Inčukalns | 1978-2010 | 24 | 96 | 1 | 1 | 2 | 3 | 2 | 8 | **8.3** |
| 28 | 1493-Inčukalns | 1978-2010 | 23 | 92 | 2 | 2 | 1 | 2 | 1 | 6 | **6.5** |
| 29 | 2647-Liepāja | 1961-2011 | 26 | 104 | 1 | 1 | 1 | 1 | 1 | 4 | **3.8** |
| | **All sites** | | 560 | 2240 | 26 | 20 | 23 | 34 | 24 | | |
| | Relative quantity of mistakes % | | | | **4.6** | **3.6** | **4.1** | **6.1** | **4.3** | | |

**References**

1. Mokrik R, Mazeika J., 2002. Palaeohydrogeological reconstruction of groundwater recharge during Late Weichselian in the Baltic basin. *Geologija 39*, p. 49-57
2. Ingebritsen, S.E., Sanford, W.E., Neuzil C.E., 2008. *Groundwater in geologic processes*, 2nd ed. Cambridge Cambridge University Press, p. 536
3. Levina N., Levins I., 2005. *Pazemes ūdeņu pamatmonitorings 2004.gads.* Rīga, Latvijas Vides, ģeoloģijas un meteoroloģijas aģentūra, p. 345