

# **New Data on Seawater Intrusion in Liepāja (Latvia) and Methodology for Establishing Background Levels and Threshold Values in Groundwater Body at Risk F5**

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## **ABSTRACT**

Intensive water consumption in former decades caused formation of large depression cone near city Liepāja and resulted with seawater intrusion into Upper Devonian Mūru-Žagaru confined freshwater aquifer. Area affected by seawater intrusion is delineated as separate groundwater body at risk (F5) and according to Groundwater Directive threshold values for groundwater bodies at risk must be established to assess the status of a body and identify possible trends. Correct estimation of background levels is significant for determination of threshold values. This study shows an updated so called “BRIDGE” methodology for determination of background levels. A two-step approach how to establish background levels in much stricter manner is presented. Also, data on major ion chemistry, biogenic and trace elements in groundwater and seawater from sampling campaign in 2017 are displayed. Dataset include unique seawater sample taken from Baltic Sea. Finally, the calculated seawater fraction results in groundwater samples shows up to 50 % presence of seawater which decrease with increasing distance from the coast and increasing screen interval.

## **INTRODUCTION**

Groundwater body is a management unit established by Water Framework Directive (WFD 2000). Good chemical status of groundwater body shall be based on compliance to existing Community quality standards and on threshold values (TV) to be established by Member States at the most appropriate level (local, regional or national) (Marandi and Karro 2008).

TV must be established for all pollutants and indicators of pollution which characterized groundwater bodies as being at risk of failing to achieve good groundwater chemical status in accordance with WFD (2000). Regarding saline concentrations resulting from human activities, Member States may decide to establish TV values either for sulphate and chloride or for conductivity (GWD 2006).

The determination of TV should be based on several aspects including hydrogeological characteristics and information on background levels (BL) (GDW 2000). Normally BL are estimated following so called “BRIDGE methodology” (Müller et al. 2006). Methodology proposes approach for derivation of TV which includes application of both natural BL and environmental quality standards (Urresti-Estala et al. 2013).

The aim of this study was to develop and present updated methodological approach for determination of BL and TV for groundwater body at risk F5- seawater intrusion in Liepāja (Latvia). As well the results from sampling campaign (year 2017) are presented demonstrating data on major ion chemistry, biogenic and trace elements taken from

monitoring wells and Baltic Sea. Finally, the results from survey were used to calculate the proportion of seawater fraction (%) in groundwater.

## METHODS

### *Materials and data preprocessing*

Information about monitoring and abstraction wells and springs was gathered from the largest Latvian hydrogeological database “Wells” (limited access) (Urbumi 2017). Data about major ion chemistry (Ca, Mg, Na, K, Cl, SO<sub>4</sub>, HCO<sub>3</sub>) and nitrates (NO<sub>3</sub>) were extracted and limited to: (1) the area of groundwater body F1 part of which is the area affected by seawater intrusion (F5) and (2) to aquifers of interest - Upper Devonian Mūru-Žagaru (D<sub>3</sub>mr-žg).

BRIDGE methodology (Müller et al. 2006) suggests a list of minimum criteria which should be used to avoid usage of anthropogenically influenced samples (Marandi and Karro 2008). Data preprocessing included: (1) removal of historical samples which reported sodium and potassium as a sum (NaK) (an additional criterion); (2) removal of samples with ionic balances error greater than ± 10% as suggested by Müller et al. (2006) and (3) where such information was available samples with nitrate content exceeding 4 mg/l were removed as potentially affected by human activities. Much stricter criterion than suggested 10 mg/l by Müller et al. 2006 was chosen based on most recent study about geochemical composition of groundwater in Latvia (Retike et al. 2016).

### *Determination of background levels*

BL for chloride ion was calculated in two steps to minimize the error of visual identification of the inflection point. Firstly, freshwater samples were separated from seawater affected samples - the value of the inflection point on groundwater samples was detected by applying probability plots (Panno et al. 2006). According to BRIDGE methodology samples with NaCl > 1000 mg/l should be removed. Much stricter criteria were used, and value of the inflection point for chloride was set 18 mg/l. Results were compared with values obtained by Retike et al. (2016). Next, BL for chloride ion was determined as 90<sup>th</sup> percentile of all freshwater samples below the inflection point value according to BRIDGE methodology (Müller et al. 2006). This step was accomplished for two reasons: (1) the validation results from previous study suggested that 18 mg/l for chloride might be too high (Retike et al. 2016) and (2) visual observation of the inflection point is subjective and may hold some uncertainty. Similarly, BL were set for sulphate and sodium.

### *Calculation of threshold values*

TV for chloride, sulphate and sodium were calculated according to BRIDGE methodology (Müller et al. 2006) which suggests deriving TV on the basis of the ratio between the estimated BL and relevant reference value (REF). In this case BL < REF, therefore Equation 1 was used.

$$TV=(REF+BL)/2 \tag{1}$$

Drinking water standard from Latvian legislation (CR No-671 2017) was chosen as REF, respectively 250 mg/l for chloride and sulphate, and 200 mg/l for sodium.

### ***Sampling campaign***

Groundwater samples were collected from 9 monitoring wells during sampling campaign accomplished from 08.06.2017 till 19.06.2017. Samples were taken by the staff of Latvian Environment, Geology and Meteorology Centre (LEGMC) responsible for national groundwater monitoring. Groundwater samples were taken according to LVS ISO 5667-11:2011 standard. Sample from Baltic Sea aquatory was taken in 11.05.2017 by the stuff of Latvian Institute of Aquatic Ecology. The seawater sampling area and depth (9 m) was chosen based on existing knowledge about possible area where seawater intrudes freshwater aquifers. All samples were analyzed in LEGMC laboratory which is accredited according to the standard LVS EN ISO/IEC 17025.

Concentrations of Ca, Na, K and Mg were determined by inductively coupled plasma optical emission spectrometry; SO<sub>4</sub>, Cl and Br by ion chromatography; NO<sub>3</sub> and NH<sub>4</sub> by segmented flow analysis; As by atomic absorption spectroscopy; HCO<sub>3</sub> by titration; TOC by catalytic oxidation; P<sub>tot</sub> by persulphate digestion, molybdenum blue colorimetry. Sampling methods are in accordance with the procedure laid down in Article 21 of WFD (2000) and meet the requirements of the European Commission “Guidance on Groundwater Monitoring” (European Commission 2007).

### ***Calculations of seawater fraction***

Seawater fractions  $f_{sea}$  in groundwater samples were calculated based on both chloride and bromide ions as conservative tracers (Appelo and Postma 2005) by Equation 1:

$$f_{sea} = \frac{m_{X(sample)} - m_{X(freshwater)}}{m_{X(seawater)} - m_{X(freshwater)}} \times 100\% \quad (1)$$

where  $m_x$  – concentration of either chloride or bromide concentration in either freshwater, seawater or groundwater sample. Chloride concentration for freshwater sample (3.4 mg/l) was calculated as average chloride value from samples taken from wells No.9322 and No.2254. These wells are inland background monitoring stations for D<sub>3</sub>mr-žg aquifer (samples not affected by seawater intrusion). Sample taken from Baltic Sea represented overall seawater chemical composition.

## **RESULTS**

### ***Background levels and threshold values***

Final BL for chloride was set as 13.2 mg/l, for sulphate 42.5 mg/l and for sodium 22.3 mg/l. Calculated TV for chloride, sulphate and sodium was respectively 131.6 mg/l, 146.3 mg/l and 111.2 mg/l. TV values are officially introduced in national level by an order of the Minister (Order-257 2016).

### ***New data on seawater intrusion***

Results from sapling campaign are presented in Table 1. Ionic balance for 6 samples (5 groundwater and 1 seawater) was in range from -0.3% till 6.9%. For three samples sodium was removed due to erroneous values derived from laboratory. All nitrates were under detection limit (0.091 mg/l).

**Table 1. Results for major ion chemistry of groundwater samples taken from Upper Devonian Mūru-Žagaru aquifer and Baltic Sea.**

Sample No	Coordinates (LKS-92)		Screen interval m	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>
	X	Y								
862	316954	270095	40-50	186	77	45.7	17.3	151	87	534
2642	316749	267688	47-57	221	107	-	41	224	1270	186.3
2645	316398	268166	72-77	57.4	31.2	24.8	11.8	267	8.6	63
2647	316425	268173	45-58	240	129	-	47	213	1800	203
9322	379051	279726	38-52	74	24.3	5.1	5.2	340	3.08	10
2254	405437	302631	40-47	101	22.8	4.65	1.59	420	3.71	0.03
8849	318470	266461	54-67	63	32.8	21	12.3	370	9.1	16
8850	317574	267496	51-66	134	67.8	-	24.7	276	435	78
8851	318105	267105	51-65	68	35.4	30.8	14.2	310	62.1	31
Baltic Sea sample	310789	270506	9	94	286	2400	70	107	4100	537

**Table 2. Results for *in situ* measurements, biogenic and trace elements of groundwater samples taken from Upper Devonian Mūru-Žagaru aquifer and Baltic Sea.**

Sample No	pH	EC	T	Fe <sub>tot</sub>	Br	As	P <sub>tot</sub>	NH <sub>4</sub>	TOC
		μS/cm (20°C)	°C	mg/l					
862	7.65	685	10.4	1.45	0.31	1.19	0.006*	0.24	0.19
2642	7.6	3747	9.6	1.06	0.38	0.2*	0.011	0.6	1.27
2645	7.95	587	9.8	0.85	0.05*	3.4	0.098	0.3	0.71
2647	7.57	6971	10.4	1.12	6.1	0.2*	0.013	0.73	1.6
9322	7.67	234	7.9	1.66	0.05*	1.69	0.027	0.22	1.19
2254	7.52	360	7.4	2.13	0.05*	0.2*	0.037	0.13	7.7
8849	7.63	367	10.2	0.44	0.05*	0.2*	0.004*	0.27	1.38
8850	7.64	1593	10.1	0.83	1.33	0.2*	0.006	0.44	1.37
8851	7.75	495	10	0.86	0.19	0.2*	0.007	0.3	0.95
Baltic Sea sample	-	13300	5.86	0.02	12.2	0.92	0.024	0.042	4.4

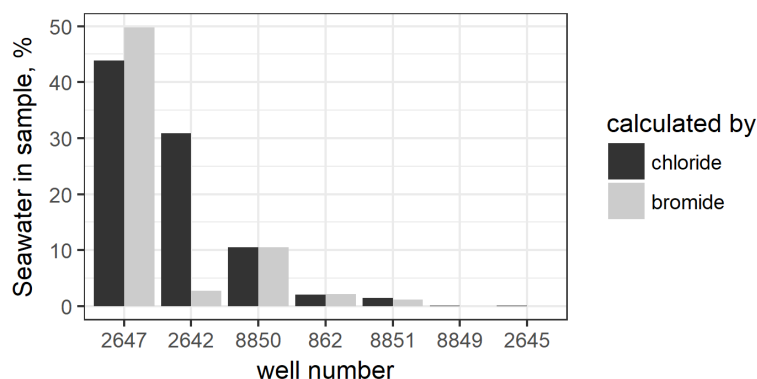
\*under detection limit

### ***Seawater fraction in groundwater samples***

Seawater fraction in groundwater samples from D<sub>3</sub>mr-žg aquifer was calculated based on chloride and bromide ions as conservative tracers. Calculation by both tracers yield comparable results for less mineralized groundwater, however, more saline groundwater samples from wells No.2647 and No.2642 yield different results (Figure 1).

Seawater fraction reaches 50% in groundwater sample at the central part of seawater affected zone (distance from coastline about 1.3 km). The seawater fraction significantly decreases with increasing distance from coastline- at 3.4 km from the coastline the fraction is only 1% (well No.8851). Wells No.2647 and 2645 are both representing the same aquifer and located in the same area (one station), about 1.3 km from the coastline- but they have different screen intervals (Table 1). Well No.2647 with shallower screen interval shows seawater fraction up to 50%, but the well No.2645 with deeper screen interval reflects no seawater

presence. The cause for such difference is more than 6 m thick clay layer separating  $D_3mr$ -žg upper part from lower part of the aquifer.



**Figure 1. Seawater fractions in groundwater samples from  $D_3mr$ -žg aquifer.**

## DISCUSSION AND CONCLUSIONS

Up to 50% of groundwater in study area consists of seawater. Such high seawater fraction was promoted by continuous groundwater abstraction from the  $D_3mr$ -žg aquifer. Seawater fraction decreases with increasing distance from coastline as well as with increasing depth.

Background levels established by two-step approach are strict and accounts for worst case scenario. Such approach yields lower threshold values therefore it is more sensitive to water quality changes and it takes more time to reach good chemical status. However, this leads to more sustainable water management in coastal areas where groundwater resources are limited.

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