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**BOUNDARY FIELD PROBLEMS AND  
COMPUTER SIMULATION**

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**DATORMODELĒŠANA UN  
ROBEŽPROBLĒMAS**

**STUDY ABOUT POSSIBILITIES TO MODEL TRANSPORT OF MANGANESE IN  
COURSE OF GROUNDWATER ARTIFICIAL RECHARGE**

**PĒTĪJUMS PAR IESPĒJĀM MODELĒT MANGĀNA TRANSPORTU GRUNTSŪDENS  
MĀKSLĪGĀS PAPILDINĀŠANAS PROCESĀ**

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**Introduction**

Manganese (Mn) is often naturally present in the groundwater. If the groundwater is used for the drinking water production, the Mn concentration should be below 50 µg/l [1] otherwise Mn may cause some health, but mostly aesthetic and engineering concerns. When Mn ions enter the drinking water distribution system, they gradually are oxidized to insoluble Mn dioxide (MnO<sub>2</sub>) causing water discoloration, metallic taste, odor, turbidity, biofouling and corrosion, staining of laundry and plumbing fixture. The speciation of Mn depends on the pH, environment Redox conditions and on the chemical composition of water. Mn can be found in natural waters both in its most reduced and soluble form, as divalent (Mn<sup>2+</sup>) or quadrivalent (Mn<sup>4+</sup>) ions, or in the form of MnO<sub>2</sub>. In surface water Mn occurs in colloidal form (MnO<sub>2</sub> attached to inorganic or organic particles) or as a complex with the humic substances.

The removal of Mn from groundwater is often accomplished by a chemical oxidation or biological filtration [2]. Artificial groundwater recharge (AGR) is frequently used for the drinking water production [3], as it enables to replenish the groundwater with the surface water, thus, maintaining the desirable yields of groundwater abstraction. However, infiltration of aerobic surface water into the mostly anaerobic aquifer influences the fate in groundwater of many chemical compounds, including

Mn. As the result, the Mn concentration at the abstraction wells may be highly variable depending on infiltrated water amount and quality. Due to high complexity of physicochemical and biological processes occurring in the recharged aquifer, the previous attempts to develop deterministic mathematic models [4] for describing transport of Mn for AGR were not very successful.

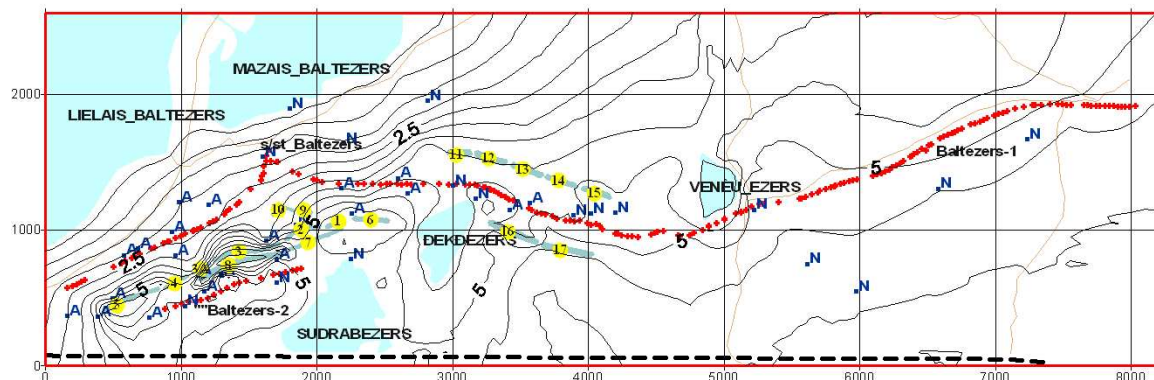
The aim of this study was to investigate the possibilities to develop a semi-empirical model for the prediction of Mn concentrations at abstraction wells of AGR plants.

The approach was based on the collection of sufficient number of samples and by using multivariate data analyses for investigating the correlation between the Mn concentration and the environmental factors. The task of the present study was to integrate the acquired correlation into the hydrogeological model which had been previously developed for this site [5].

## Materials and methods

The study was carried out in the AGR plant Baltezers which supplies Riga city (Latvia) with about 25 000 m<sup>3</sup>/day of drinking water [8]. During the AGR process, the surface water from humic rich lake (Mazais Baltezers) is pumped into the infiltration basins where it percolates down to the groundwater. After underground transport (retention time 30-180 days), the recharged groundwater is abstracted by a siphon system (the production wells are connected to vacuumed siphon-pipes) using about 200 production wells, disinfected by adding 1 mg of Cl<sub>2</sub> per litre, and then pumped into the city water distribution system.

During the study, water was sampled from 40 observation wells which were located in the vicinity of the production wells. The wells were sampled during a three months period from May to July 2008. The well consisted of a PVC tube of 63 cm of diameter (external) and its depth was about 10 m. The water was extracted with a centrifugal pump applying a flow rate of 2 m<sup>3</sup>/h. Each well was flushed before analysis in order to remove the fine sand accumulated in it during the non-working period. To avoid bias, due to contamination from well itself, the samples were taken only after stabilization of the pH, temperature, electro conductivity (EcoScan Con5, Eutech instrument) and Redox potential (ORP) measured by (WTW Multiline P4).



**Fig. 1.** Study site at Baltezers AGR plant. Water is pumped from Lake Mazais Baltezers and infiltrated through 17 basins (yellow). After the passage through aquifer the water is abstracted by wells (red) and collected in the water reservoir (s/st Baltezers). Measured groundwater levels are shown as gray lines

ORP was related to the standard hydrogen electrode (SHE) and measured in millivolts (mV). The stabilization of these parameters was performed between 30 to 60 minutes. The total organic carbon (TOC) was detected using a TOC 5000A Analyzer of Total Organic Carbon (Shimadzu, Japan).

The Mn concentration was analyzed with a spectrophotometer (Hach DR2000, country), following the 1-(Pyridylazo)-2-Naphthol (PAN) method, which was highly sensitive and rapid for detecting low

levels of Mn. An ascorbic acid reagent was used to reduce all oxidized forms of manganese to Mn(II). An alkaline-cyanide reagent was added to mask any potential interference. The PAN indicator was then added to combine it with the Mn(II) to form an orange-colored complex. Its absorbance was measured with a UV/Visible spectrometer. For each well at least three samples were taken in order to obtain accurate results of the Mn concentration.

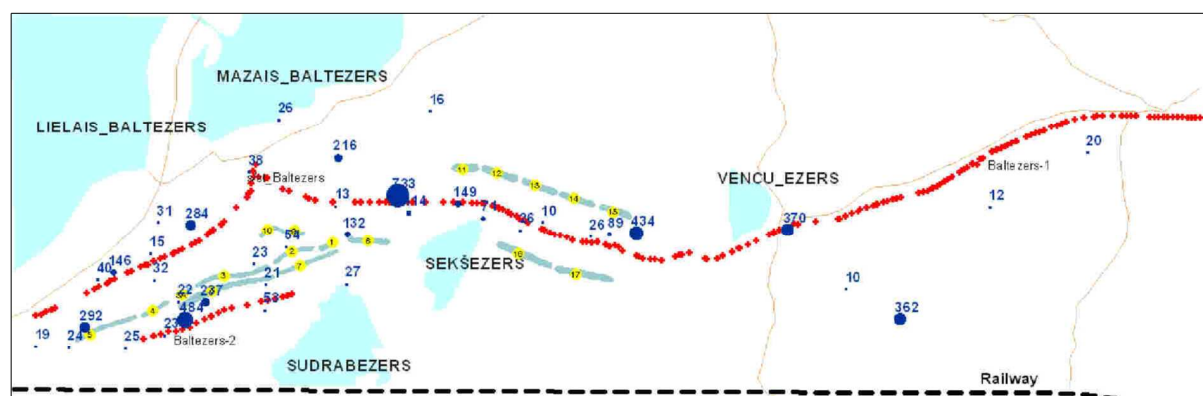
To check the PAN method accuracy, its results were compared with the ones obtained by the Flame Atomic Absorption Spectrometry (FAAS) method (SIA “Vides audits” laboratory, Riga, Latvia, Standard Method 3111B). The correlation between the both methods was 0.8635 ( $R_2 = 0.9997$ ,  $n=10$ ) and the PAN method provided 14% higher concentrations than the FAAS method.

The Principal Component Analysis (PCA) (Statgraph 21) was used to determine if there was a multivariate relationship between the parameters measured. This method generates new variables which explain as much of the information in the data set as possible. These new variables, known as the principal components, are linear combinations of the original ones. The first principal component is chosen to explain the largest possible amount of information in the data; the second principal component is designed to be as different from the first one as possible and to explain the second largest amount of information and so on. The plot of the two parameter system represents a circle of a radius one. The variable which is close to the circle has the most importance; the second one closer to the center is less significant. On the other hand, two variables (points) close to each other indicate a good correlation between them. Two opposite points show an opposite evolution of the variables.

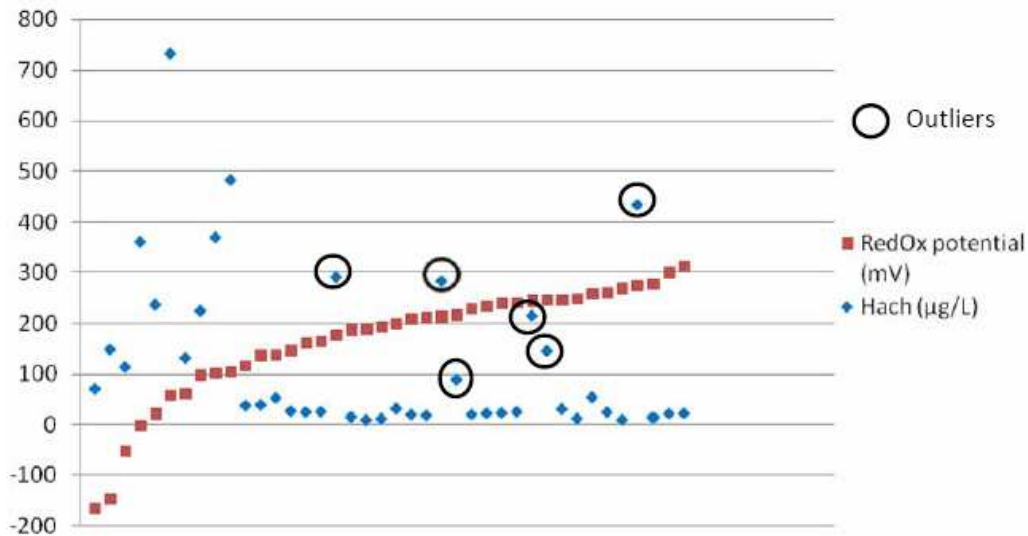
## Results and discussion

Over the period of three months, 42 samples were taken from 40 wells. The samples were analyzed for Mn, TOC, ORP, electro conductivity, temperature and pH. In addition, water levels in the wells were recorded. Results showed that the Mn concentrations were in the range from 10 to 740  $\mu\text{g/L}$  (see Fig. 2).

The Mn concentration was locally considerably variable. Between the wells located just a few meters apart, the observed Mn concentration difference was more than tenfold. Thus, the location of a well (more influenced by lake water, closer to a basin infiltration, etc.) was not the most important factor determining the Mn concentrations in the samples.



**Fig. 2.** Concentration of manganese [mg/L] (shown in blue with numbers proportional to size of the node) in observation wells over the study site

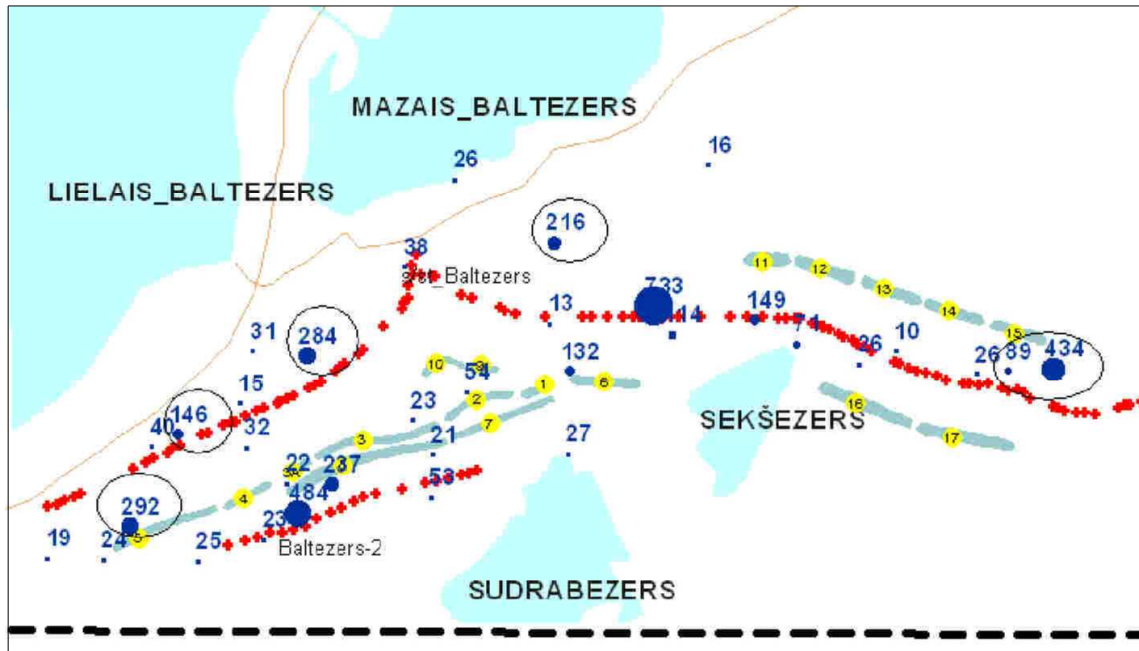


**Fig. 3.** Correlation between ORP [mV] and manganese concentrations [ $\mu\text{g/L}$ ] for sampled wells. The parameters have been classified with regard to ascending ORP values

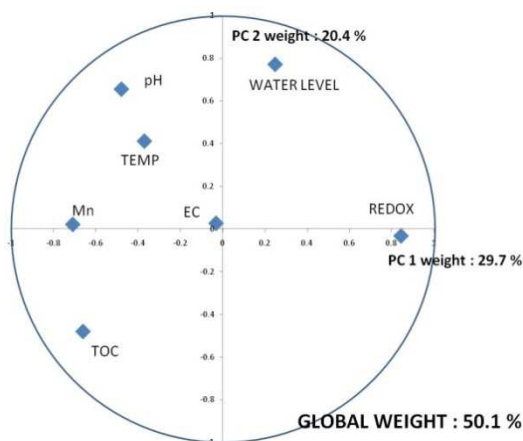
Fig. 3 presents ORP and the Mn concentration for each well. These parameters have been classified according to the ascending ORP values. The results confirmed that in the samples with ORP value less than 120 mV, the Mn concentration was always higher than 50  $\mu\text{g/L}$ . In samples with ORP values above this threshold, the Mn concentration was less than 50  $\mu\text{g/L}$ . However, there were 6 outliers which had high concentrations of the Mn even if the Redox potential was high. The wells with outliers were located close to the lakes Mazais and Lielais Baltezers. Probably these wells were influenced by humic rich water infiltration from these lakes (Fig. 4).

To identify the relation between environmental parameters and the Mn concentration, the (PCA) method was performed for all the collected data. When the variable TOC was included in the analysis, PCA was made for 33 wells (available data for TOC). In other cases, the entire data set was used.

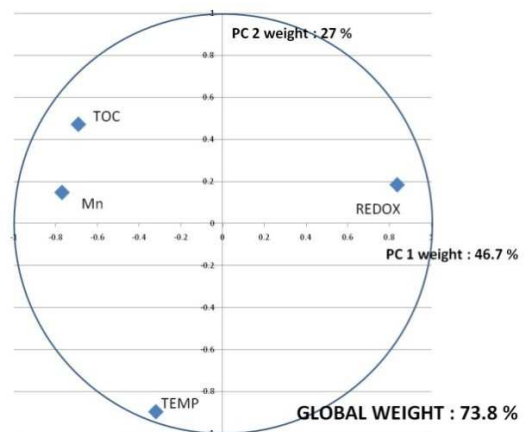
The RCA results for all seven parameters (Fig. 5) had not a very good inertia, because only 50.1% of the information was explained by the two principal components. Nevertheless, the graph shows an opposite behavior between ORP and the Mn concentration. This correlation was confirmed when only four parameters (Fig. 6) were taken into account, the inertia being higher, 73.8%. Another two important parameters which correlated positively and negatively with the Mn concentrations were TOC and temperature, respectively.



**Fig. 4.** Location of outliers from the relation between Mn concentrations and the Redox potential



**Fig. 5.** PCA diagram for the seven parameters: water level; pH; temperature; Redox potential; electro conductivity (EC); manganese concentration (Mn); TOC

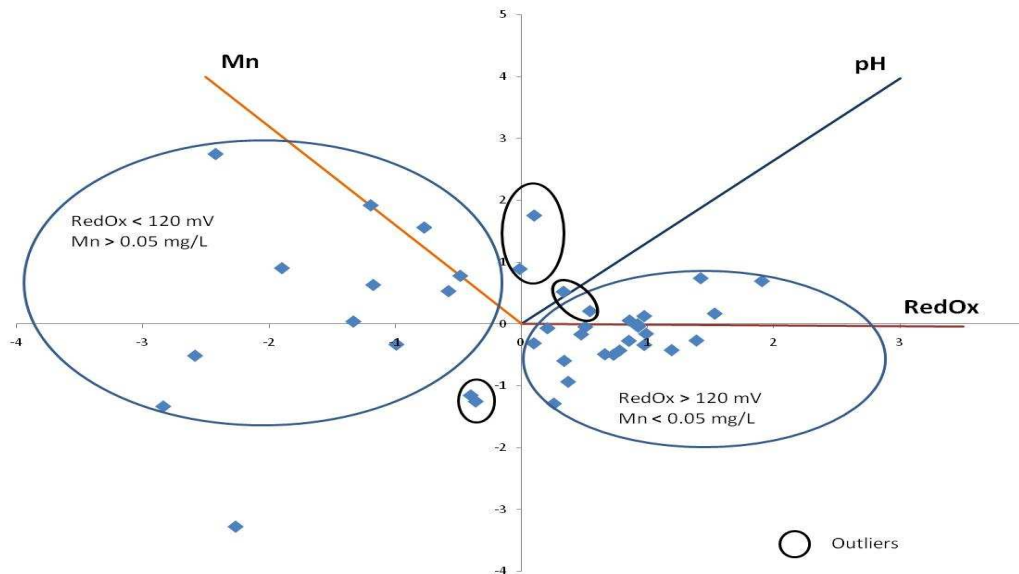


**Fig. 6.** PCA diagram for 4 variables: temperature; Redox potential; TOC; manganese concentration (Mn)

Fig. 7 shows the PCA result when the principal components merge into two main clusters, excluding the outliers. The first cluster was formed for ORP values below 120 mV and the Mn concentration above 0.05 mg/L. The second cluster was formed for ORP values above 120 mV and the Mn concentration below 0.05 mg/L.

Thus, the above results clearly showed that the most important parameter related with the Mn concentration in artificially recharged groundwater was ORP, followed by temperature and TOC. ORP shows the tendency of chemical species to acquire electrons and be reduced. Redox processes are generally microbially catalyzed. It may be suggested that the Mn transport is governed largely by the bacteria occurring in a groundwater aquifer. Importance of biological processes is confirmed by the influence of temperature and TOC. It is known that the temperature influences the microbial activity [6] where degradation of organic matters play important role in denitrification, iron, sulphate and

manganese reduction and oxidation. A metabolically diverse population of heterotrophic bacteria couples the process of organic carbon oxidation to the reduction of terminal electron acceptors, primarily,  $O_2$ ,  $NO_3^-$ ,  $Fe(III)$ ,  $Mn(IV)$ ,  $SO_4^{2-}$ , [4,7].



**Fig. 7.** The PCA diagram. Data plotted in the two principal component system

This study shows in the reducing conditions ( $ORP < 120$  mV) there is a high probability that in artificially recharged groundwater Mn would be present in large concentrations. A strict mathematical relationship between the Mn concentration and environmental factors, however, was not found. It was thus not possible to create an exact manganese transport model.

## Conclusions

The major conclusions from the study are as follows:

- the Mn concentration in artificially recharged groundwater depends on the Redox potential, on temperature and on the natural organic carbon concentration;
- biological processes strongly govern transport of Mn from the infiltration pools to the groundwater abstraction sites.
- the Redox potential measurements may be used to develop a semi-empirical model for predicting Mn concentrations in ARG plant abstraction wells.

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**Salicis Y., Juhna T., Spalviņš A. Pētījums par iespējām modelēt mangāna transportu gruntsūdens mākslīgās papildināšanas procesā**

*Lai noskaidrotu iespēju modelēt mangāna koncentrācijas izmaiņas ūdens ņemšanas akās, kuras tiek papildinātas no ezera, trīs mēnešu laikā ievākti ūdens paraugi no 40 akām ūdensgūtvē „Baltezers”, Latvija. Paraugiem noteikta ūdens temperatūra, pH, oksidēšanās-reducēšanās potenciāls, elektrovadāmība, kopējā organiskā oglekļa koncentrācija un mangāna koncentrācija. Mangāna koncentrācija bija robežās no 0.01 līdz 0.75 mg/L. Apstrādājot datus ar principiālo komponentu analīzes metodi, konstatēts, ka mangāna koncentrācija ir atkarīga galvenokārt no ūdens oksidēšanās un reducēšanās potenciāla. Šo novērojumu var izmantot semi-empīriskā empīriskā transporta modeļa izstrādē mākslīgās infiltrācijas ūdensgūtvei.*

**Y. Salicis, T. Juhna, A. Spalvins. Study about possibilities to model transport of manganese in course of groundwater artificial recharge**

*To study possibilities of modelling the transport of manganese during artificial groundwater recharge (AGR), water samples were taken from 40 wells of Baltezers water supply site, Latvia. The samples were analyzed for temperature, pH, Redox potential, electro conductivity, total organic carbon and manganese concentration. The manganese concentration has been found to be in the range of 0.01 to 0.75 mg/L. The principal Component Analyze method showed that the manganese concentration was mainly dependent on the Redox potential. This observation could be used for development of a semi-empirical model for prediction of manganese concentrations in AGR plant abstraction wells.*

**Салицис И., Юхна Т., Спалвиньш А. Исследование возможностей моделирования транспорта марганца для процессов искусственного пополнения запасов подземной воды**

*Для выяснения возможности моделирования изменений концентрации марганца в эксплуатационных скважинах водосборов с искусственным пополнением запасов подземных вод, в течении трех месяцев были собраны образцы воды из 40 скважин водозабора Балтээерс, Латвия. Для образцов изучены следующие параметры: температура, pH, Redox потенциал, электропроводимость, общая концентрация органического углерода, концентрация марганца. Концентрация марганца была в пределах (0.01 – 0.75) мг/л. Обработывая полученные данные методом анализа принципиальных компонент, был сделан вывод, что концентрация марганца зависит от Redox потенциала. Это наблюдение можно использовать для построения семи-эмпирической модели транспорта марганца для водосборов с искусственным пополнением запасов подземной воды.*