

# Chlorine isotope fractionation during catalytic reductive dechlorination of Trichloromethane ( $\text{CHCl}_3$ ) over palladium-on-alumina in hydrogen-saturated water: implication to managed aquifer recharge as sustainable storage solution for desalinated water (MAR-DSW) in Menashe recharge basin, Israel.

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## INTRODUCTION

During the storage of excess desalinated water in a managed coastal aquifer in Israel, chlorine in the desalinated water may react with natural organic matter, forming toxic disinfection by-products (DBPs), like Trihalomethanes (THMs). In order to facilitate managed aquifer recharge as storage solution for desalinated water (MAR-DSW), it is important to understand the mechanisms of the formation and degradation of such DBPs. In this work, after a CI-CSIA method development and optimization, degradation of chloroform ( $\text{CHCl}_3$ ), a main pollutant of interest at the Menashe recharge basin in Israel, was investigated to derive its chlorine isotope enrichment factor as a part of the Israel-German joint research "Aquifer recharge as sustainable storage solution for desalinated water (MAR-DSW)".

### Objectives of this study

- To optimize an experimental setting to reductively degrade chloroform ( $\text{CHCl}_3$ ) and derive the reaction rate constant
- To investigate the stable chlorine isotope fractionation during the reductive degradation process and derive the corresponding isotope enrichment factor using an optimized CI-CSIA method for chloroform, developed at TU-Darmstadt

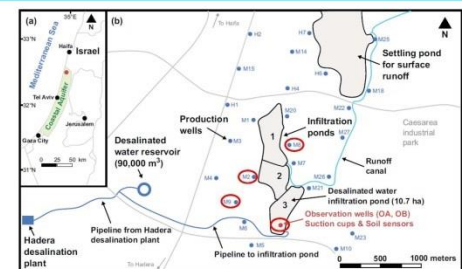


Figure 1 : Regional (a) and local (b) map of the study area. Water samples from wells encircled in red are found to have THMs. (Map modified after Ganot et al., 2018).

## METHODS

- A 100ml of deionized water spiked with 30mg/l chloroform (251 $\mu\text{M}$ ) was saturated with hydrogen (app. 0.8mM), which serves as an electron donor. Further, 0.25g/l palladium was added as palladium-on-alumina (10% wt.) to catalyse the reaction.
- Samples were taken at specified intervals from a sampling port designed near the bottom of the reactor, which is closed with a plunger from the top so that no headspace was created as samples were taken out or during the entire experimental period.



Figure 2: (a) Hydrogen generator (Schmidlin, NMH2 160, Germany) used to saturate the deionized water with hydrogen (b) Reactor with a sampling port near the bottom (c) Close up view of the reactor as the reaction proceeds (d) samples taken



Figure 3: P&T-GC-QMS system was used for the CI-CSIA: Agilent 6890N GC coupled to an Agilent 5973N QMS (Santa Clara, USA) and a P&T system PTA 3000 by IMT (Vohenstrauß, Germany).

## DISCUSSION

- Almost 50 % of the chloroform was hydrodechlorinated in the first 10 minutes of the experiment. Chloroform was directly degraded mainly into methane with very small DCM and CM intermediates.
- The data until the first 60 minutes of the degradation, which represents almost 88% of chloroform degradation, were considered to determine the reaction rate constant ( $k=0.033 \pm 0.002$  per minute).
- The simple online method for  $\delta^{37}\text{Cl}-\text{CHCl}_3$ , applied in this study was developed and optimized to a precision of 0.37‰, at TU Darmstadt, based on Sakaguchi-Söder et al., 2007.
- During the degradation of chloroform, the change in chlorine isotope ratios of  $\text{CHCl}_3$  was determined, with peak areas of masses 85 and 83 using the following equation:

$$R_{\text{CHCl}_3} = \frac{85/2}{83/1} = \frac{37\text{Cl}}{35\text{Cl}}$$

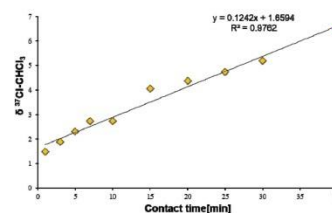


Figure 6: Chlorine isotope fractionation during dechlorination of  $\text{CHCl}_3$  on  $\text{Pd}/\text{Al}_2\text{O}_3$  (10%wt)

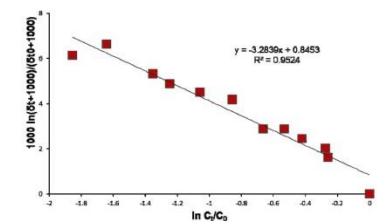


Figure 7: The slope, based on Rayleigh model, is the enrichment factor of Chlorine ( $\epsilon_{\text{Cl}}$ ) during dechlorination of  $\text{CHCl}_3$  on  $\text{Pd}/\text{Al}_2\text{O}_3$  (10%wt).

## RESULTS

- Degradation followed first order process (s. Figure 4). Reproducibility was also confirmed.
- A first-order rate constant ( $k$ ) was determined:  $0.033 \pm 0.002$  (1/min,  $r^2 = 0.964$ ) (s. Figure 5).
- Chlorine isotope composition ( $\delta^{37}\text{Cl}$ ) has changed from 1.62 to 6.14 ‰ during the first 40 minutes of the degradation (s. Figure 6).
- An enrichment factor of  $-3.28 \pm 0.23$  ‰ ( $r^2 = 0.952$ ) was determined (s. Figure 7).

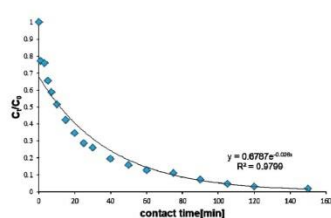


Figure 4: Chloroform Hydrodechlorination kinetics

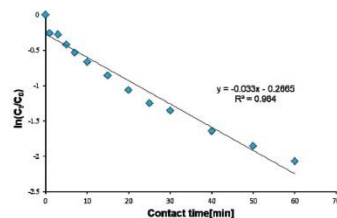


Figure 5: Experimental data fitted to 1<sup>st</sup> order reaction.

## CONCLUSIONS

- It is demonstrated that stable chlorine isotope ratios, isotope fractionation and enrichment factors during catalytic reductive dehalogenation of chloroform on palladium can be measured with good precision using a simple online CI-CSIA method that is developed and optimized for a MAR-DSW project at TU-Darmstadt, Germany.
- During dechlorination of  $\text{CHCl}_3$  on  $\text{Pd}/\text{Al}_2\text{O}_3$  (10%wt), the reaction rate constant,  $k=0.033 \pm 0.002$  per min and chlorine isotope enrichment factor ( $\epsilon_{\text{Cl}}$ ) of  $-3.28 \pm 0.23$  ‰ were determined.
- The results and the method can potentially be used as a tool to discriminate the source, pathway and fate of chloroform to foresee the feasibility of medium and long term use of managed aquifer recharge as a storage solution in the study area and elsewhere.
- However, site specific fractionation factors need to be determined.

References: Ganot, Y., Holtzman, R., Weisbrod, N., Russak, A., Katz, Y., & Kurtzman, D. (2018). Geochemical Processes During Managed Aquifer Recharge With Desalinated Seawater. *Water Resour. Res.*, 54(2), 978–994.  
Sakaguchi-Söder, K., Jäger, J., Grund, H., Matthäus, F., Schüth, C. (2007) Monitoring and evaluation of dechlorination processes using compound-specific chlorine isotope analysis. *RCM*, 21:3077-3084

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