

Subsurface Transport of Sulfidated Nano Zero Valent Iron and In Situ Biogeochemical Transformation of Chlorinated Solvents: A Field Study

Jingzhi Liang[‡], Hardiljeet Boparai[‡], Line Lomheim[‡], Ariel Nunez Garcia[§], Elizabeth Edwards[‡], Denis O'Carroll[‡], Brent Sleep[‡]

[‡] University of Toronto, Toronto, Canada

[§] Queen's University, Kingston, Canada

[|] University of New South Wales, Sydney, Australia

Corresponding author: Jingzhi Liang (amanda.liang@mail.utoronto.ca)

Abstract

In situ chemical reduction of chlorinated volatile organic compounds (cVOCs) by nano zero-valent iron (nZVI) has been widely applied in the past 20 years, but with limited effectiveness for bare nZVI due to rapid particle settling, short lifespan, and low reactivity. Stabilization and sulfidation of nZVI have improved its mobility and longevity, increased reactivity towards cVOCs, and reduced toxicity to microbes (Nunez Garcia et al. 2021).

In the first-ever CMC-S-nZVI field trial, nZVI sulfidated by dithionite (S-nZVI) and stabilized by carboxymethyl cellulose (CMC) was injected into the subsurface of a site contaminated with a wide range of cVOCs. Multi-level wells were installed to monitor the transport of the CMC-S-nZVI suspension and its remedial performance for two years. Short-term (0-17 days) monitoring demonstrated a good transport of the suspension in the down- and up-gradient wells, in terms of total iron, boron, and sulfides which were major constituents of CMC-S-nZVI. Changes in concentrations of parent compounds, intermediates, and ethene showed effective dechlorination of high-chlorinated VOCs such as tetrachloroethene (PCE) and carbon tetrachloride (Nunez Garcia et al. 2020a, Nunez Garcia et al. 2020b).

Long-term (157-729 days) performance was evaluated through temporal analyses of microbial communities, total iron, boron, and cVOCs in groundwater samples. Microbial populations, including organohalide-respiring bacteria, increased by >1 order of magnitude; with *Geobacter* being the most abundant. This long-term enrichment can be attributed to the low toxicity of CMC-S-nZVI and biostimulation by CMC and perhaps Fe³⁺. Non-metric multidimensional scaling analysis was carried out on microbial data grouped by depth range and proximity to the injection well. At locations that clearly received CMC-

S-nZVI, there was a significant shift in microbial communities that was sustained for the long term.

Iron concentrations increased substantially in long-term samples while boron concentrations decreased, suggesting that this iron did not come from CMC-S-nZVI. Microbial dissolution of iron minerals might have contributed to the increased iron content (Jones et al. 2006). Excess dithionite in CMC-S-nZVI would also have reductively dissolved native iron from the soil, as successfully demonstrated in the *in situ* redox manipulation (ISRM) technology wherein subsurface Fe^{3+} in soil was reduced to Fe^{2+} for long-term remedial purposes (Vermeul et al. 2000).

Long-term changes in concentrations of lesser-chlorinated VOCs and hydrocarbons suggest that PCE was degraded via both the microbially-mediated sequential hydrogenolysis as well as the abiotic β -elimination. The intermediate vinyl chloride (VC) surprisingly did not accumulate in the current study, in contrast to the significant VC accumulation in a previous un-sulfidated CMC-nZVI trial at the same location (Kocur et al. 2016). Excess dithionite injected in this study might have avoided VC accumulation, as previously reported for ISRM treatment of a cVOCs-contaminated site (Vermeul et al. 2000). Additionally, the identified bacterial populations might have utilized sulfur species (from dithionite decomposition) and iron to form iron sulfides, which could dechlorinate cVOCs via *in situ* biogeochemical transformation (Kennedy et al. 2006).

In summary, this study has demonstrated the long-term efficiency of CMC-S-nZVI for cVOCs removal through a combination of abiotic, biotic, and biostimulatory processes in the subsurface.

Keywords

dithionite sulfidation, reductive dechlorination, microbial analysis, nZVI, ISBGT

Presenting author

Jingzhi Liang

Presented at

ISEB-ISSM 2023; Theme 2; Oral

Conflicts of interest

The authors have declared that no competing interests exist.

References

- Jones EJP, Nadeau T, Voytek MA, Landa ER (2006) Role of microbial iron reduction in the dissolution of iron hydroxysulfate minerals. *J. Geophys. Res.-Biogeo.* 111.
- Kennedy LG, Everett JW, Becvar E, DeFeo D (2006) Field-scale demonstration of induced biogeochemical reductive dechlorination at Dover Air Force Base, Dover, Delaware. *J. Contam. Hydrol.* 88.
- Kocur CMD, Lomheim L, Molenda O, Weber KP, Austrins LM, Sleep BE, Boparai HK, Edwards EA, O'Carroll DM (2016) Long-Term Field Study of Microbial Community and Dechlorinating Activity Following Carboxymethyl Cellulose-Stabilized Nanoscale Zero-Valent Iron Injection. *Environ. Sci. Technol.* 50.
- Nunez Garcia A, Boparai HK, de Boer CV, Chowdhury AIA, Kocur CMD, Austrins LM, Herrera J, O'Carroll DM (2020a) Fate and transport of sulfidated nano zerovalent iron (S-nZVI): A field study. *Water Res.* 170.
- Nunez Garcia A, Boparai HK, Chowdhury AIA, de Boer CV, Kocur CMD, Passeur E, Sherwood Lollar B, Austrins LM, Herrera J, O'Carroll DM (2020b) Sulfidated nano zerovalent iron (S-nZVI) for in situ treatment of chlorinated solvents: A field study. *Water Res.* 174.
- Nunez Garcia A, Zhang Y, Ghoshal S, He F, O'Carroll DM (2021) Recent Advances in Sulfidated Zerovalent Iron for Contaminant Transformation. *Environ. Sci. Technol.* 55.
- Vermeul VR, Williams MD, Evans JC, Szecsody JE, Bjornstad BN, Liikala TL (2000) In Situ Redox Manipulation Proof-of-principle Test at the Fort Lewis Logistics Center: Final Report. PNNL. <https://doi.org/10.2172/781433>