INTEGRATIVE APPROACH FOR CHARACTERIZATION OF CHLORINATED BENZENES AT CONTAMINATED SITES: LABORATORY AND FIELD STUDY

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Introduction

Chlorinated benzenes (CBs) are commonly found as groundwater contaminants at chemical production sites. Oxygen is usually depleted at contaminated sites so reductive dechlorination could represent the main process for CBs biodegradation. However, dechlorination processes become less favorable with a decreasing number of chlorine substituents, hence monochlorobenzene (MCB) is believed to be highly recalcitrant in anaerobic aquifers. (Kaschl et al., 2005) Still, recent studies have shown that MCB can be degraded in anaerobic conditions to Benzene (Liang et al., 2011) or sequentially transformed to CO_2 and CH_4 (Liang et al., 2013). Whereas CO_2 and CH_4 are non-toxic compounds, benzene is more toxic than MCB, having a lower EPA Maximum Contaminant Level (MCL, 5 µg/L) compared to MCB (100 µg/L). Because of this adverse effect a comprehensive site characterization and natural attenuation assessment is required, especially at MCB contaminated sites where also benzene is detected. Compound Specific Isotope (CSIA) and biological tools are commonly used in groundwater studies but very few have focused on MCB. This study investigates the combined application of CSIA with biological molecular techniques for fingerprinting, site characterization and natural attenuation assessment at MCB contaminated sites. The project involves Politecnico di Milano, ENI E&P laboratories, ENI Corporate Laboratories (TEAMB), Syndial and Università degli Studi Milano-Bicocca aiming to create a center of excellence able to integrate standard hydrogeological approach with isotopic and microbiology tools for contaminated site characterization.

Methods

The laboratory activities included a series of aerobic and anaerobic microcosms under different conditions: incubated with pure cultures and with in-situ microbial populations, amended with nutrients and under natural conditions. The main goal is to investigate the ^{13}C fractionation and the kinetic of MCB and Benzene biodegradation under aerobic and anaerobic conditions. The isotopic enrichment factors (ε) obtained in the laboratory will be used to better (i) distinguish between aerobic and anaerobic processes, (ii) asses and quantify natural attenuation, (iii) to understand the fate of MCB and Benzene when present as co-contaminant or degradation product and, overall, to refine the CSIA application for (iv) fingerprinting purposes at MCB contaminated sites.
Laboratory results will complement data collected at a large-scale MCB and benzene (among others organic contaminants) contaminated site, located in Italy. The contaminated site presents evidences of multiple sources and biodegradation processes. Biodegradation kinetic rates and enrichment factors obtained from the microcosms will be incorporated in a reactive transport model to simulate the contaminated site's contaminant $\delta^{13}C$ and concentrations (for MCB and benzene) to assess natural attenuation, potential mixing processes, and finally to link the multiple plumes to their original sources.

Preliminary results

LABORATORY: 8 control wells were sampled to collect water for the incubation of microcosms with site-specific microbial population. Preliminary laboratory results obtained indicate conditions suitable for aerobic and anaerobic biodegradation of MCB. Under aerobic

conditions all the microcosms have shown a rapid decrease in MCB concentration even after several MCB spikes of 90 mg/L.

In case of the anaerobic microcosms, they showed a significant MCB reduction only for 3 microcosms, obtained by incubating the water collected in some wells. Furthermore, under anaerobic conditions MCB degradation was much slower (only one microcosm showed a 90 % decrease in 20 days), while in all the aerobic microcosms amended with nutrients MCB disappeared in 10-15 days. No benzene was produced in the anaerobic process and most likely the MCB degraded to CO_2 and CH_4.

FIELD STUDY: $\delta^{13}C$ and concentration data for MCB and benzene showed no significant differences for the 2010, 2011 and 2013 sampling events (except for wells P-32, P-33 and P-37). These data allowed distinguishing two distinct sources and plumes for MCB: the area A with $\delta^{13}C$ values ranging between -25 ‰ to -26 ‰ and a second area, B characterized by more depleted values between -36 ‰ and -40 ‰.

	Concentrations (µg/L)			Isotopic values (‰)	
	Benzene	**MCB**	**CH_4**	**Benzene**	**MCB**
P7	97	1325	1024	-27.2 ± 0.4	-25.5 ± 0.1
P8	11	8	419	-26.4 ± 0.3	-33.2 ± 0.5
P9	6	952	675	-24.8 ± 0.5	-25.8 ± 0.1
P12	39	114	1053	bdl	-36.2 ± 0.5
P15	275	402	41.5	-39.9 ± 0.1	-40.8 ± 1.2
P26	3	54	233	-30.9 ± 0.6	bdl
P29	1221	14020	2296	-28.1 ± 0.1	-25.± 0.1
P32	11	3	66	-26.9 ± 0.5	-29.4 ± 0.5
P33	2	13	2273	-27.4 ± 0.8	-31.9 ± 0.1
P37	196	147	238	-31.6 ± 0.5	-33.9 ± 0.5
P40	196	362	16.6	-39.9 ± 0.6	-40.4 ± 0.3
P41	2	211	2132	-23.7 ± 2.1	-26.0 ± 0.7

Tab. 1: field data (concentrations and isotopic signature) for 2013

The $\delta^{13}C$ data also seem to indicate mixing between the two distinct plumes in some areas. High CH_4 concentrations of 1 to 2 mg/L were detected mostly in the monitoring wells in area A (P-7, P-29, and P-41) accompanied with enriched $\delta^{13}C$ values. Concerning benzene, the $\delta^{13}C$ data showed more depleted values for benzene than MCB at the source areas, which is expected for benzene associated to biodegradation of MCB (Liang et al., 2013) The more enriched $\delta^{13}C$ values for benzene than MCB observed in the groundwater with the lower concentration for both compounds can also be related to biodegradation of benzene which can occurred at field sites (Liang et al., 2013). Further, the microcosm results for site-specific enrichment factor also for benzene will be useful to confirm the most realistic conceptual model at the field site. The isotopic enrichment factors obtained in the microcosms will be used to calculate the degree of biodegradation and hence the original isotopic composition of the source in area A.

Conclusions

The CSIA approach allowed distinguishing two sources and two plumes at the study site. An enrichment of ^{13}C on MCB and benzene together with high concentrations of CH_4 suggested active anaerobic biodegradation for the plume located in the area A. This hypothesis was also confirmed by the anaerobic microcosms results performed with water from Area A. Moreover, the fast response from the aerobic microcosms suggested the suitable conditions for a significant contribution also from aerobic degradation activity, although O_2 and nutrients are probably the limiting factors at the site.
These preliminary results demonstrated the potential of combining CSIA with biological molecular techniques for MCB and benzene characterization at contaminated sites.

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References

Kaschl, A., Vogt, C., Uhlig, S., Nijenhuis, I., Weiss, H., Kästner, M. and Richnow, H.H. (2005). "Isotopic fractionation indicates anaerobic monochlorobenzene biodegradation". Environmental Toxicology and Chemistry, 24, 1315-1324.

Liang X., Howlett M. R., Nelson J.L., Grant G., Dworatzek, S., Lacrampe-Couloume, G., Zinder, S.H., Edwards E, A. and Sherwood Lollar B. (2011). "Pathway-dependent isotope fractionation during aerobic and anaerobic degradation of monochlorobenzene and 1,2,4-trichlorobenzene". Environ Sci Technol, 45, 8321-8327.

Liang, X., Devine, C.E, Nelson, J., Sherwood Lollar, B., Zinder S. and Edwards, E.A. (2013). "Anaerobic conversion of chlorobenzene and benzene to CH_4 and CO_2 in bioaugmented microcosms". Environ Sci Technol, 47, 2378-2385.