Use of Compound Specific Isotope Analysis (CSIA) for Assessing Degradation

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Resumo

Análise Isotópica de Compostos Específicos (CSIA) é uma tecnologia analítica estabelecida que consta com mais de 20 anos de pesquisa focadas em aplicações para a avaliação e remediação de áreas contaminadas. Avanços analíticos forneceram a transição desta tecnologia de uma ferramenta de pesquisa para um método aplicado de availação do destino e comportamento de contaminantes prioritários, incluindo solventes clorados, hidrocarbonetos de petróleo, clorobenzenos, aditivos de gasolina e vários outros. A CSIA é usada principalmente em: a) análises forensicas ambientais para diferenciar fontes de contaminação em um site/s; b) avaliação do local como uma linha de evidência para atenuação natural monitorada (MNA) de compostos clorados e hidrocarbonetos de petróleo e contaminantes relacionados; c) avaliação de desempenho de remediação para bioaugumentação, tratamentos de oxidação química in-situ, e tratamentos com ferro de zero valência. Esta apresentação irá discutir o estado atual da prática para CSIA e encorajar as partes interessadas a considerá-la como uma ferramenta valiosa para avaliar a extensão do tratamento e da atenuação natural em locais impactados.

Abstract

Compound Specific Isotope Analysis (CSIA) is an analytical technology that has been established through over 20 years of research for applications in contaminated site assessment and remediation. Analytical advances in CSIA have provided the transition of this technology from a research tool to an applied method for assessing the fate and behavior of priority contaminants including chlorinated solvents, petroleum hydrocarbons, chlorobenzenes, gasoline additives and various others. CSIA is primarily used in: a) environmental forensics to differentiate between sources of contamination at a site/s; b) site assessment as a line of evidence for monitored natural attenuation (MNA) of chlorinated compounds and petroleum hydrocarbons and related contaminants; c) remediation performance evaluation for bioaugmentation, in-situ chemical oxidation treatments, and zero-valent iron treatments. This presentation will discuss the current state of the practice for CSIA and encourage stakeholders to consider it as a valuable tool for assessing the extent of treatment and natural attenuation at impacted sites.

Keywords

Biodegradation, isotopes, natural attenuation

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1 - WHAT IS CSIA?

CSIA measures the ratio of naturally abundant stable isotopes in an environmental sample for a contaminant of interest (i.e., chlorinated solvents, petroleum hydrocarbons) relative to an international standard. Each contaminant is made up of different elements (e.g. C, H, Cl) and each element has a distinct isotopic ratio. Isotopic compositions of a specific contaminant are reported in delta (e.g., $\delta^{13}C$, $\delta^{2}H$) notation in units of parts per thousand (‰) relative to an international standard of known isotopic composition where: δ (‰) = $(R_s/R_r - 1) \times 1000$ and R_s is the ratio of heavy to light isotopes in the sample, R_r is the ratio of heavy to light isotopes in the standard.

2 - CSIA TO ASSESS BIODEGRADATION

Biodegradation processes can cause systematic and reproducible shifts in the relative abundance of the stable isotopes of the contaminant within a plume and such changes in isotopic ratio or "isotopic fractionation" can be measured within environmental samples using CSIA. Therefore, CSIA can be used to assess biodegradation processes at contaminated sites. Dilution, sorption and volatilization are a few of the physical processes which can affect contaminants in groundwater but these processes exhibit little to no isotopic effect on the contaminant in most groundwater systems. In contrast, biotic degradation processes can impart significant isotopic fractionation on contaminants. In this way, the impact of biotic transformation can be identified and distinguished from physical processes using CSIA (Figure 1). In many case studies, CSIA has provided conclusive evidence of actual contaminant clean-up rather than just dilution or other non-degradative physical processes. While further field evaluation is warranted, case studies demonstrate enhanced interpretation with the use of CSIA and/or a multi-element isotope approach including carbon, chlorine and hydrogen isotope analyses. Isotopic fractionation patterns have been established for many biodegradation systems, isotopes and priority contaminants and as such, CSIA is increasingly more versatile for contaminant site assessment.

3 - BEYOND BIODEGRADATION

CSIA can also be extended to abiotic degradation systems such as during in-situ chemical oxidation and zero valent iron (ZVI) reduction of contaminants such as chlorinated hydrocarbons. Significant isotopic fractionation is documented in the literature for abiotic systems during the degradation of chlorinated hydrocarbons and petroleum hydrocarbons. In the case of degradation of TCE by ZVI, carbon isotopic fractionation

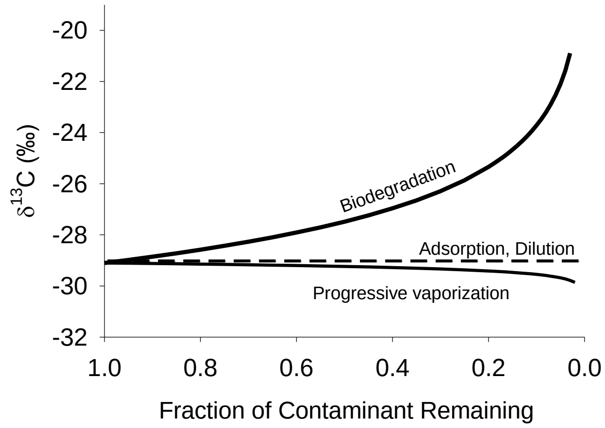

Figure 1. Conceptualization of significant isotopic fractionation during biodegradation of a specific contaminant measured using CSIA. Isotopic fractionation caused by physical processes such as adsorption, dilution and volatilziation are reported to be smaller than the analytical uncertainty associated with CSIA for most natural groundwater systems. CSIA can provide additional insight in the assessment biotic degradation. Adapted from Elsner et al., ES&T, 2008

patterns are documented to be different than what has been observed for biodegradation (Figure 2). As such, CSIA has the ability to be used as a diagnostic tool in distinguishing between abiotic and biotic degradation processes via ZVI for TCE (Elsner et al., 2010; Lojkasek-Lima et al, 2012), providing additional insight to the performance of a remediation program.

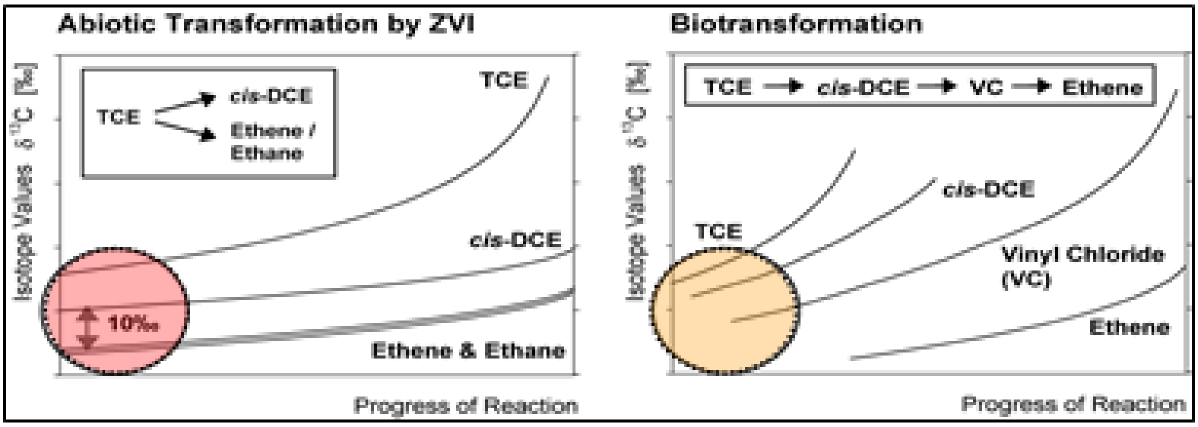

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Figure 2. Distinct carbon isotopic patterns can provide additional insight in the assessment of remediation of TCE via abiotic ZVI degradation and have the unique ability to distinguish between abiotic and biotic degradation. Adapted from Elsner et al., ES&T, 2008

In addition, recent case studies have been published that demonstrate the advantages of this technology to a range of geological environments including vapor intrusion and the unsaturated zone (Hunkeler et al., 2011); at sediment-surface water interfaces (Passeport et al., 2014); and in fractured rock (Pierce et al., 2014) and low permeability aquitards where contaminant transport may be dominated by diffusion and isotopes can provide additional insight into biodegradation processes (Wanner et al., 2014).

4 - ADVANTAGES OF CSIA

The use of CSIA was reviewed and documented in EPA 600/R-08/148. This document provides practical recommendations and information on how to develop sampling plans, analyze and interpret isotopic data. Advantages of this technology are also discussed in this document. Some advantages include:

- CSIA is independent of concentration trends and observation of transient by-products or daughter products
- CSIA can be used to quantify rates and extents of degradation independent of concentrations
- CSIA has the ability to be used as a diagnostic tool in distinguishing between abiotic and biotic degradation processes
- The use of multiple isotopes for a given contaminant can provide additional insight into contaminant sources and process evaluations

Overall, the current state-of-the-science establishes CSIA as a valuable tool for many types of contaminants, environments and applications. On-going research on additional contaminants, analytical applications, and additional field studies will further the accessibility and capabilities of CSIA. The integration of CSIA into Conceptual Site Models (CSM) is encouraged at early stage site investigation in order to provide baseline contaminant source and process evaluation. Information derived from CSIA results in conjunction with the CSMs can provide additional insight and unequivocal data to assess contaminant processes and assist with optimizing contaminated site management plans.

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