



# Inferential monitoring of chlorinated solvents through Raman spectroscopic observation of the vibrational modes of water



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## ABSTRACT

Recent improvements in diode laser, fiber optic, and data acquisition technology have rejuvenated interest in field applications of Raman spectroscopy in a wide range of settings. One such application involves the observation of chlorinated solvents to facilitate the practice of "monitored natural attenuation." In this context, this manuscript focuses on means to improve the sensitivity of in-situ Raman analysis of chlorinated solvents. In particular, the work explores the performance limits of a Time-Resolved Raman Spectroscopy (TRRS) system employed to observe chlorinated solvents in aqueous samples via laboratory tests conducted on both liquid standards of trichloroethylene (TCE) and simulated biodegraded field samples. Quantitative assessment of TCE in solution is carried out through both direct observation of TCE Raman functional groups ( $381\text{ cm}^{-1}$  ( $\delta$  skeletal),  $840\text{ cm}^{-1}$  ( $\nu\text{CCl}$ ) and  $1242\text{ cm}^{-1}$  ( $\delta\text{CH}$ )) and indirect observation of the broad OH stretching ( $2700\text{--}3800\text{ cm}^{-1}$ ) Raman modes of water. Results from tests on simple solutions show that the TRRS system can detect TCE at aqueous concentrations as low as 70ppm by directly monitoring the  $381\text{ cm}^{-1}$  TCE line, whereas observation of the OH stretching line of water ( $3393\text{ cm}^{-1}$ ) provides an indirect indication of TCE presence with nearly a  $9\times$  improvement in detection level. This unique and counterintuitive mechanism to detect the presence of chlorinated compounds in solution takes advantage of the influence of chlorine on the vibrational modes of water. This influence, which is believed to be attributed to the formation of hydrogen bonds and their resultant interactions with the solvation shell, may serve as a more sensitive and robust indication of the presence of aggregate chlorinated solvent contamination in aqueous systems. Tests performed on simulated biodegraded field samples demonstrate that the indirect detection mechanism is apparent even in complex samples representative of typical field conditions.

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## 1. Introduction

Production and environmental release of chlorinated aliphatic hydrocarbons peaked between the late eighties and early nineties. Due to their widespread use in the production of household products, degreasing operations, and petroleum refining, chlorinated solvents have become ubiquitous pollutants. According to the Environmental Protection Agency's (EPA) Toxic Chemical Release Inventory, between 1987 and 1993, releases to water and land of trichloroethylene (TCE), 1,2-Dichloroethane (1,2-DCA), Dichloromethane (DCM), and 1,1,1-Trichloroethane (1,1,1-TCA)

totaled over 1.7 million kg, representing only a subset of all chlorinated solvents. These contaminants are still known to persist in the environment and it has been reported that up to 34% of the drinking water supply sources in the U.S. likely contain TCE contamination [1]. Compounds such as trichloroethylene (TCE) and tetrachloroethene (PCE) are found at approximately 80% of all Superfund sites with groundwater contamination (852 facilities) and more than 3000 Department of Defense (DoD) sites in the U.S. [2]. The net result is that these solvents pose a considerable threat as groundwater contaminants and account for a significant proportion of the 90+ drinking water contaminants listed by the EPA [3,4].

Chlorinated solvents are Dense Non-Aqueous Phase Liquids (DNAPLs) and by definition are denser than water and thus when spilled or released into the environment tend to migrate downward in the subsurface. Their migration through the vadose zone can lead to residual pockets of contaminants in soil pore spaces (source zones), the release of vapors in soil pore space, dissolution

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in groundwater (to the extent possible) in the capillary fringe and below the groundwater table, and pooling above an aquitard, as well as continued infiltration into fractures in boundary rock layers. The tendency for these compounds to partition makes them an exceptionally menacing pollutant. While the fate and transport of the dissolved fractions are influenced by phenomenon such as groundwater advection, mechanical dispersion, molecular diffusion, and groundwater-porous media chemical partitioning, movement of the compounds can be significantly influenced by gravity and capillary effects that make it difficult to adequately characterize and track their presence in the subsurface [5]. The sporadic and localized concentration of chlorinated solvents in soil pores and retarded pools also serves as a recalcitrant contaminant source which can often frustrate remediation attempts.

The unique challenges posed by chlorinated solvent DNAPLs in the geoenvironment have led both the U.S. EPA and the National Academy of Sciences to conclude that “DNAPL sources may be contained, but remediation to typical cleanup levels for most DNAPL sites is often ‘technically impracticable’” at justifiable costs [2]. This realization has increased attention to the potential to pursue “monitored natural attenuation” (MNA) rather than or in combination with proactive remediation at sites contaminated with chlorinated solvents [6]. This site management approach relies upon natural physical, chemical and biological processes to reduce contaminant concentrations [3]. Successful application of MNA typically requires extensive site analyses for initial screening for MNA potential, modeling and verification of attenuation processes, confirmation of effective MNA, and long term monitoring for any changes to the natural system that could alter the potential to achieve remediation goals [7,8]. While initially conceived as a cost effective alternative to proactive remedial intervention it is becoming clear that the costs of site characterization and long term monitoring may be prohibitive, and so significant effort has been focused on developing more cost-effective approaches to carry out these tasks [8].

### 1.1. Current characterization and monitoring solutions

Currently, the technology used in common practice to assess contaminated site chlorinated solvent levels with actionable reliability involves either very costly and/or sophisticated laboratory instrumentation or expensive field instruments that can assess only a short-list of compounds, provide information over a limited spatial extent, and/or are too costly or complex to leave behind in long-term monitoring scenarios. Attempts to measure the effects of remediation efforts or the availability of attenuation mechanisms, for example to support mass balance evaluations of monitored natural attenuation, are even more challenging.

In the realm of laboratory measurements of chlorinated solvents and their daughter compounds, a host of wet chemistry techniques are applied. Chief amongst which are variants of gas chromatography–mass spectrometry (GC–MS) that have been adapted to perform stable isotope analysis of carbon and chlorine to assess levels of chlorinated aliphatic hydrocarbons while mitigating alteration of sample components resulting from pre-processing (e.g., Helium Microwave Induced Plasma MS to GC [9]; carrier gas extraction to GC [10]; multiple collector inductively coupled plasma-source mass spectrometry (MC-ICPMS) [11]. These techniques require field acquisition of samples (e.g., with devices such as the Waterloo profiler or precision injection/extraction probes [12]) and subsequent laboratory preparation and analysis – a time consuming and expensive process – yet yield highly chemical-specific results with great sensitivity (ppb or better).

In the field, remote sensing techniques (primarily satellite based) provide general information on field conditions or inferential indications of contaminant presence (such as foliage

discoloration or depletion), yet offer limited resolution (typically several  $m^2$ ), and provide virtually no insight into subsurface conditions [13,14]. Geophysical methods, such as reflectivity profiling (e.g., [15]), electrical resistivity imaging [16], and non-linear complex-resistivity cross-hole imaging [17], can successfully indicate the presence of chlorinated solvents in-situ, but typically at limited depths, spatial resolution, and sensitivity. Others have put forward concepts that involve the introduction of foreign materials, such as graphite, Zeolite, or Samms particles, into the subsurface to enhance geophysical signatures [18]. Portable GC/MS units have also emerged commercially [19,20], but again require considerable sample handling. Other novel field approaches to chlorinated solvent evaluation include single point sensors that use replenishable reagents [21], or biosensors (e.g., [22,23]), but any one sensor of this type tends to have limited versatility. Beyond these techniques, an array of indirect methods are employed to indicate the presence of DNAPLs such as chlorinated solvents including use of reactive inter-well tracers, radon flux sensors, soil vapor probes, and membrane interface probes that monitor related volatiles [24,12]. However, these in-situ techniques tend to provide only directional input on the presence of contaminants or information over a very limited spatial extent.

In other cases, sensors are incorporated into cone penetrometer-type devices, and used to make direct field measurements. These instruments provide flexibility by enabling the investigator to rapidly examine multiple points in the field, both spatially and at depth, while limiting the errors that can often accompany sample extraction techniques, and thus their use has become increasingly common in practice. The majority of these penetrometer-based systems make use of optical spectroscopic phenomenon. Near-infrared (NIR) probes have been explored [25,26], as well as optical fiber sensors that rely on evanescent field phenomenon. However, these devices apply only to compounds which absorb at the frequency of the excitation source [26–31]. Ultra-violet (UV) Laser Induced Fluorescence (e.g., [32–34]) has also been explored, but has difficulty yielding chemical specific or quantitative insights due to the overlap of fluorescence signatures of similar compounds. Some of the most promising results in this arena stem from work done with continuous wave (CW) Raman spectroscopy which has been shown to yield highly specific chemical signatures even in complex in-situ settings (e.g., [35–37]). Effectiveness of Raman systems, however, has traditionally been adversely affected by fluorescence interference in natural environments [37–39]. More recently, Sinfield et al. [40] demonstrated the ability to significantly suppress the impact of fluorescence on Raman observations by employing pulsed-laser technology to perform Time Resolved Raman Spectroscopy and effectively gate Raman from fluorescence phenomenon in the time-domain, with a closed-path fiber optic system that could be incorporated in a penetrometer or field monitoring station.

### 1.2. Challenges of obtaining actionable in-situ measurements

Despite these advances, in-situ analyses, which are necessary for cost effective site management, inevitably involve tradeoffs between the time and cost associated with the analysis, and the degree to which the results represent actual field conditions and provide information of actionable quality. In particular, one of the biggest challenges with arguably the most versatile of the optical techniques, Raman spectroscopy, is its overall sensitivity.

In early work by Bilodeau et al. [35], direct Raman analysis was performed on samples of Ottawa sand and two NIST soils, saturated with neat TCE, using the 488 nm line of a 100 mW Argon laser. In these studies the researchers reported clear evidence of the C–Cl vibrational mode at  $628\text{ cm}^{-1}$ , but the intensity of the Raman line did not correlate well to the soil mass fraction of the

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