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8 **Title: Inferential monitoring of chlorinated solvents through Raman spectroscopic**
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10 **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 cm^{-1} (δ skeletal), 840 cm^{-1} (νCCl) and 1242 cm^{-1} (δCH)) 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 cm^{-1} TCE line, whereas observation of the OH stretching line of water (3393 cm^{-1}) provides an indirect indication of TCE presence with nearly a 9x 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.

Keywords: chlorinated solvents; trichloroethylene; Raman spectroscopy; inferential monitoring;
water vibrational modes

1.0 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

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4 pockets of contaminants in soil pore spaces (source zones), the release of vapors in soil pore
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6 space, dissolution in groundwater (to the extent possible) in the capillary fringe and below the
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8 groundwater table, and pooling above an aquitard, as well as continued infiltration into fractures
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10 in boundary rock layers. The tendency for these compounds to partition makes them an
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12 exceptionally menacing pollutant. While the fate and transport of the dissolved fractions are
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14 influenced by phenomenon such as groundwater advection, mechanical dispersion, molecular
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16 diffusion, and groundwater-porous media chemical partitioning, movement of the compounds
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18 can be significantly influenced by gravity and capillary effects that make it difficult to
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20 adequately characterize and track their presence in the subsurface [5]. The sporadic and localized
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22 concentration of chlorinated solvents in soil pores and retarded pools also serves as a recalcitrant
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24 contaminant source which can often frustrate remediation attempts.
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34 The unique challenges posed by chlorinated solvent DNAPLs in the geoenvironment have led
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36 both the U.S. EPA and the National Academy of Sciences to conclude that “DNAPL sources
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38 may be contained, but remediation to typical cleanup levels for most DNAPL sites is often
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40 ‘technically impracticable’” at justifiable costs [2]. This realization has increased attention to the
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42 potential to pursue “monitored natural attenuation” (MNA) rather than or in combination with
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44 proactive remediation at sites contaminated with chlorinated solvents [6]. This site management
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46 approach relies upon natural physical, chemical and biological processes to reduce contaminant
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48 concentrations [3]. Successful application of MNA typically requires extensive site analyses for
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50 initial screening for MNA potential, modeling and verification of attenuation processes,
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52 confirmation of effective MNA, and long term monitoring for any changes to the natural system
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54 that could alter the potential to achieve remediation goals [7] [8]. While initially conceived as a
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4 cost effective alternative to proactive remedial intervention it is becoming clear that the costs of
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6 site characterization and long term monitoring may be prohibitive, and so significant effort has
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8 been focused on developing more cost-effective approaches to carry out these tasks [8].
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11 12 13 14 15 **1.1 Current Characterization and Monitoring Solutions** 16 17

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19 Currently, the technology used in common practice to assess contaminated site chlorinated
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21 solvent levels with actionable reliability involves either very costly and/or sophisticated
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23 laboratory instrumentation or expensive field instruments that can assess only a short-list of
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25 compounds, provide information over a limited spatial extent, and/or are too costly or complex to
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27 leave behind in long-term monitoring scenarios. Attempts to measure the effects of remediation
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29 efforts or the availability of attenuation mechanisms, for example to support mass balance
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31 evaluations of monitored natural attenuation, are even more challenging.
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39 In the realm of laboratory measurements of chlorinated solvents and their daughter compounds, a
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41 host of wet chemistry techniques are applied. Chief amongst which are variants of gas
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43 chromatography–mass spectrometry (GC–MS) that have been adapted to perform stable isotope
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45 analysis of carbon and chlorine to assess levels of chlorinated aliphatic hydrocarbons while
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47 mitigating alteration of sample components resulting from pre-processing (e.g., Helium
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49 Microwave Induced Plasma MS to GC [9]; carrier gas extraction to GC [10]; multiple collector
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51 inductively coupled plasma-source mass spectrometry (MC-ICPMS) [11]. These techniques
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53 require field acquisition of samples (e.g., with devices such as the Waterloo profiler or precision
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55 injection/extraction probes [12]) and subsequent laboratory preparation and analysis – a time
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4 consuming and expensive process – yet yield highly chemical-specific results with great
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6 sensitivity (ppb or better).
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11 In the field, remote sensing techniques (primarily satellite based) provide general information on
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13 field conditions or inferential indications of contaminant presence (such as foliage discoloration
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15 or depletion), yet offer limited resolution (typically several m²), and provide virtually no insight
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17 into subsurface conditions [13] [14]. Geophysical methods, such as reflectivity profiling (e.g.,
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19 [15]), electrical resistivity imaging [16], and non-linear complex-resistivity cross-hole imaging
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21 [17], can successfully indicate the presence of chlorinated solvents in-situ, but typically at
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23 limited depths, spatial resolution, and sensitivity. Others have put forward concepts that involve
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25 the introduction of foreign materials, such as graphite, Zeolite, or Samms particles, into the
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27 subsurface to enhance geophysical signatures [18]. Portable GC/MS units have also emerged
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29 commercially [19] [20], but again require considerable sample handling. Other novel field
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31 approaches to chlorinated solvent evaluation include single point sensors that use replenishable
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33 reagents [21], or biosensors (e.g., [22] [23]), but any one sensor of this type tends to have limited
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35 versatility. Beyond these techniques, an array of indirect methods are employed to indicate the
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37 presence of DNAPLs such as chlorinated solvents including use of reactive inter-well tracers,
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39 radon flux sensors, soil vapor probes, and membrane interface probes that monitor related
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41 volatiles [24] [12]. However, these in-situ techniques tend to provide only directional input on
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43 the presence of contaminants or information over a very limited spatial extent.
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56 In other cases, sensors are incorporated into cone penetrometer-type devices, and used to make
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58 direct field measurements. These instruments provide flexibility by enabling the investigator to
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4 rapidly examine multiple points in the field, both spatially and at depth, while limiting the errors
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6 that can often accompany sample extraction techniques, and thus their use has become
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8 increasingly common in practice. The majority of these penetrometer-based systems make use
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10 of optical spectroscopic phenomenon. Near-infrared (NIR) probes have been explored [25] [26],
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12 as well as optical fiber sensors that rely on evanescent field phenomenon. However, these
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14 devices apply only to compounds which absorb at the frequency of the excitation source [27]
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16 [28] [29] [30] [26] [31]. Ultra-violet (UV) Laser Induced Fluorescence (e.g., [32] [33] [34]) has
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18 also been explored, but has difficulty yielding chemical specific or quantitative insights due to
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20 the overlap of fluorescence signatures of similar compounds. Some of the most promising
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22 results in this arena stem from work done with continuous wave (CW) Raman spectroscopy
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24 which has been shown to yield highly specific chemical signatures even in complex in-situ
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26 settings (e.g., [35] [36] [37]). Effectiveness of Raman systems, however, has traditionally been
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28 adversely affected by fluorescence interference in natural environments [38] [39] [37]. More
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30 recently, Sinfield et al. [40] demonstrated the ability to significantly suppress the impact of
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32 fluorescence on Raman observations by employing pulsed-laser technology to perform Time
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34 Resolved Raman Spectroscopy and effectively gate Raman from fluorescence phenomenon in
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36 the time-domain, with a closed-path fiber optic system that could be incorporated in a
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38 penetrometer or field monitoring station.
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51 **1.2 Challenges of Obtaining Actionable In-situ Measurements**

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54 Despite these advances, in-situ analyses, which are necessary for cost effective site management,
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56 inevitably involve tradeoffs between the time and cost associated with the analysis, and the
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58 degree to which the results represent actual field conditions and provide information of
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4 actionable quality. In particular, one of the biggest challenges with arguably the most versatile of
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6 the optical techniques, Raman spectroscopy, is its overall sensitivity.
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12 In early work by Bilodeau et al. [35], direct Raman analysis was performed on samples of
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14 Ottawa sand and two NIST soils, saturated with neat TCE, using the 488 nm line of a 100 mW
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16 Argon laser. In these studies the researchers reported clear evidence of the C-Cl vibrational
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18 mode at 628 cm^{-1} , but the intensity of the Raman line did not correlate well to the soil mass
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20 fraction of the compound, indicating presence but providing little ability to quantify in-situ
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22 concentrations. In 1999, the USDOE [36] reported on the second generation of a cone-
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24 penetrometer equipped with a 785 nm CW Raman system (originally a 415 nm system) which
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26 was employed in two distinct in-situ settings to a) evaluate DNAPL contaminated radioactive
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28 waste in large containment vessels and b) assess DNAPL contamination directly in soils. For the
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30 in-tank tests, “the Raman probe demonstration resulted in more than 99 percent accuracy for
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32 compound identification and greater than 93 percent accuracy in identifying both the compounds
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34 and the concentration” for organic constituents above 20% by weight ([36], p. 6 and 13). For
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36 the direct push soil tests, the Raman probe was reported to be effective at detecting PCE at the
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38 “highest levels of contamination” in saturated zones ($\sim 1,500\text{ ppm}$ by mass), and was less
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40 reliable in the vadose zone [36]). Later work by Rossabi et al. [37] [41], made use of a 300 mW
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42 785 nm CW laser and demonstrated detection of TCE in-situ in proximity to a solvent storage
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44 tank at locations with depth that were later verified in the laboratory to contain concentrations of
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46 200-750 ppm by mass TCE, but failed to detect TCE in other zones with concentrations on the
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48 order of 50 ppm by mass. No major advances in in-situ Raman analysis of chlorinated solvents
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50 have been reported for the last decade.
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4 These initial studies helped define the value of even coarse in-situ Raman analysis and several
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6 commercially available cone-penetrometer Raman probe systems now exist. However, to date,
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8 these probes are generally used for rapid detect – non-detect profiling as detection limits have
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10 been high relative to chlorinated solvent concentrations typically present in the field (due to an
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12 inability to manage interference in the field) and the fact that the systems have traditionally used
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14 low resolution CCD detectors (limiting a system's ability to differentiate varying analyte
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16 concentrations).
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25 Sites contaminated with chlorinated solvents frequently contain the pollutant at levels ranging
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27 from a neat state (e.g., [42]) to low ppb concentrations that exceed Maximum Contaminant Level
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29 (MCL) drinking water standards (e.g., TCE MCL = 5 ppb), with aqueous concentrations of 3 to
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31 500 ppm commonly encountered in groundwater [43] [44] [45]. By comparison, the detection
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33 levels reported in the historical studies noted above, which are on a mass of soil basis, are
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35 equivalent to ~ 300 to 9000 ppm on a volume to volume basis in the pore fluid of a soil
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37 (assuming a typical range of soil void ratios from 0.3 to 1.2 for the soils studied). To this end,
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39 any improvements to the sensitivity and resolution of a monitoring technology can be very
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41 valuable to facilitate enhanced plume delineation, earlier warnings of contaminant release from a
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43 containment zone, and/or the design of more tailored monitoring approaches.
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53 With this context in mind, herein, the authors put forward an approach to improve the overall
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55 sensitivity of Raman observations of chlorinated solvents through indirect measurements that
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57 take advantage of the influence of chlorine on the vibrational modes of water to indicate the
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59 presence of chlorinated compounds in solution. The technique is contrasted to direct observation
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of select Raman frequencies of TCE in simple aqueous solutions, and demonstrated in more complex samples which simulate a natural field condition.

2.0 Equipment, Materials, and Methods

2.1 Equipment

Experiments performed for the work reported herein were carried out using a research-oriented open-path variation of a closed-path fiber optically coupled time-resolved Raman spectroscopy system specifically designed for application in field settings. The system trades-off lower power and longer sampling times for reduced cost, simple reconfigurability, and the ability to manage multiple environmental interferences (e.g., fluorescence, turbidity, soil-solution interface). Open- and closed-path system configurations have been previously reported in detail (e.g., [40] [46] [47]) and the system design has received a U.S. Patent [48]. The system employs a 532 nm Q-switched microchip laser (~ 20 μ J /pulse; ~600 ps pulse duration; ~2 kHz repetition rate (Teem Photonics)) for excitation. Light scattered by the test sample is collected in a 180° back scattered geometry and focused on the entrance slit of a monochromator (Oriel 130 1/8 m, with flat-ruled 1200 lines/mm grating blazed at 500 nm) and observed using a photomultiplier tube (PMT) (Hamamatsu H7422-40P) operated in photon counting mode, in conjunction with a pre-amplifier (Ortec 9326, gain of 20x) and a 100-ps binned comparator (Ortec 9353).

2.2 Materials

Spectrometric grade trichloroethylene (TCE) (purity > 99.5%) obtained from Alfa Aesar was used as received for all experiments. Trichloroethylene (C₂HCl₃) is denser than water, slightly

soluble and volatile. Its properties are as follows: density of 1.465 g/mol; a relative solubility of 1.2g/L at 25°C; $K_{oc} = 2.03-2.70$; a vapor pressure of 74 mm Hg and a Henry's law constant of 0.011 atm-m³/mol. All non-neat test solutions were prepared using TCE and distilled, deionized water.

2.3 Methods

2.3.1 Aqueous sample preparation - Aqueous samples were prepared at room temperature 24.5-26.7°C in a 40-ml amber colored glass vial with a Teflon-coated silicone rubber septa that was sealed in place with a screw cap. The 40 ml bottles were filled with deionized water to a capacity of 30mL and then neat TCE was injected at the base of the water filled vial with the use of a disposable pipette to help ensure that no bubbles were introduced in the process. The injection was stopped when the supernatant water reached the brim of the vial. The vials were then sealed immediately to avoid headspace and prevent loss due to vaporization. These vials were then gently manually shaken and allowed to settle to equilibrium for at least three days.

The aqueous equilibrium trichloroethylene concentration served as a stock solution for further dilution to lower aqueous concentrations and these diluted samples were tested immediately to minimize losses due to volatilization and degradation. To prepare dilute concentrations, the aqueous equilibrium solution of TCE was extracted with a syringe and injected into a closed vial containing an appropriate volume of deionized water to make that particular concentration based on a molarity mass balance ratio (see Equation 1).

$$C_i V_i = C_f V_f \quad \text{(Equation 1)}$$

The concentration and volume are represented by C and V , while the subscripts i and f represent the initial and final target solution respectively, with consistent volumetric units.

2.3.2 Simulated biodegraded field samples - Test samples designed to simulate biodegradation in a field environment were prepared by first cultivating an anaerobic microbial population within a natural saturated soil sample. Soil for the experiment was obtained from a forested area near the intersection of Cherry Lane and McCormick Road in West Lafayette, IN and was characterized as a silty clay that plots in the CL-ML region of a soil plasticity chart. It has a brownish gray color and a plastic and liquid limit of 8% and 26%, respectively. The soil was used as obtained from the site without any modifications.

The soil was placed in a flask, saturated with a buffered solution and fed a solution consisting of glucose ($C_6H_{12}O_6$), methanol (CH_3OH), and ethanol (C_2H_5OH). It was incubated in a foil covered (opaque to light) sealed vessel and monitored for microbial activity as evidenced by steady production of CO_2 and CH_4 gases. Glucose is easily and rapidly degradable by a diverse array of microbes, while ethanol and methanol are easily catabolized by acetogenic and methanogenic bacteria respectively, thus ensuring a rapid onset of anaerobic and methanogenic conditions needed to simulate groundwater conditions found at many contaminated sites. A steady pH of 7.2 was maintained daily and when needed the pH was adjusted with small additions of a concentrated buffer stock (per 100ml; ammonium chloride (NH_4Cl) 100mg, potassium dihydrogen phosphate (KH_2PO_4) 500mg, and potassium hydrogen phosphate (K_2HPO_4) 2000mg). The microbial bioassay created (supernatant liquid and slurry soil composition) was extracted using a pipette and combined with aqueous solutions of TCE on a

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4 volumetric basis, shaken, and allowed to equilibrate evenly in a Teflon sealed screw cap vial.
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7 Extracts of the supernatant liquid were then used for testing instrument performance in a
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9 simulated biologically active and complex environment.
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15 *2.3.3 Sample validation* - Trichloroethylene concentrations were validated by USEPA Method
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17 8010 using a Stanford Research Instruments (SRI) Environmental Gas Chromatograph (GC
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19 8610C chassis) equipped with a Photo Ionization Detector (PID) in series with a combination
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21 Flame Ionization Detector (FID) and a Dry Electrolytic Conductivity Detector (DELCD). The
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23 PID detector responds to compounds, whose ionization potential is below 10.6eV, including
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25 aromatics and chlorinated molecules with double carbon bonds (TCE has an ionization potential
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27 of 9.45eV). The FID detector responds to the hydrocarbons in the sample while the DELCD
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29 selectively detects the chlorinated compounds in the FID exhaust.
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39 *2.3.4 Time Resolved Raman Spectroscopy (TRRS) testing* – Unless stated otherwise, all spectra
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41 were collected with a 25 μm slit size and an optical resolution of 4 cm^{-1} ($\sim 0.1\text{nm}$ step size) with a
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43 sampling time of 120 sec per wavelength. For simple aqueous solutions, a five point analysis
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45 procedure was applied for all studied frequencies, which included observation of Raman returns
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47 at the line of interest, two additional points immediately adjacent to the line, and two more points
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49 on either side of the peak within the baseline noise. These observations represent a single
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51 complete sampling process, and provide a robust assessment of the Raman contribution relative
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53 to background noise.
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The information obtained from the TRRS analysis can be portrayed in an x-y plot of the Raman intensity (counts) vs. Raman shift (cm^{-1}). Total counts were obtained by the progressive summation of returned Raman photon counts from the output of the photomultiplier tube (PMT) as observed by the time digitizer in one thousand 100 pico-second time bins that collect counts following incidence of the laser pulse at the sample [40]. The Signal-to-Noise Ratio (SNR) is defined as the average of the counts at the Raman peak (i.e. counts at a given Raman vibrational mode) minus the baseline divided by the standard deviation of the peak counts (after McCreery [49]). Spectral processing (e.g., to account for variations in PMT spectral response, signal normalization, and/or baseline removal), peak identification and smoothing were performed using GRAMS suite 9.0 software (Thermo Fischer).

3.0 Time-Resolved Raman Spectroscopy

3.1 Overview of the Raman Phenomenon

Raman spectroscopy is an analytical technique in which a monochromatic light source (typically a laser) is directed toward a target and inelastic photon-molecule collisions are observed. The inelastically scattered photons display a change in energy from their initial state that is equivalent to the energy transferred between the incident photon and the sample, and corresponds to the vibrational and rotational energy states of the target molecule bonds. Conventionally these changes in energy, or shifts, are reported in units of wavenumber (cm^{-1}) relative to the wavelength of the incident light. The spectrum of observed scattered frequencies, known as the Raman spectrum, thus relates to the bonds in a molecule, and the relative intensity of lines in the spectrum is consistent with molecule stoichiometry. In time-resolved Raman spectroscopy, a

pulsed, rather than a continuous wave, laser is employed to interrogate a sample and scattered photons are collected only during a brief period of time from the onset of the incident pulse ($\sim 10^{-9}$ sec or less). Observations are then typically accumulated via photon counting techniques over repeated laser pulse cycles to enhance SNR and develop a robust Raman spectrum.

3.2 Chlorinated Solvent Raman Functional Groups

Chlorinated solvents are fundamentally composed of single, double or triple carbon-carbon bonds, carbon-chlorine bonds (C-Cl) and carbon-hydrogen bonds (CH). Bonds are associated with characteristic molecular vibrations and hence Raman frequencies. Previous studies [50] [51] [52] have shown that C=C bonds give rise to characteristic shifts in the $1580\text{-}1664\text{ cm}^{-1}$ region. Vibrations involving CH bonds are characterized by shifts in the $2840\text{-}3000\text{ cm}^{-1}$ region. Shifts in groups at $730\text{-}840\text{ cm}^{-1}$ and $1240\text{-}1360\text{ cm}^{-1}$ are attributed to wagging and stretching of CH bonds, respectively. The presence of halogens such as chlorine atoms are identified by shifts in the frequency region of $550\text{-}760\text{ cm}^{-1}$. In addition, skeletal deformations associated with the C-Cl bonds relate to frequencies at 381 cm^{-1} and 274 cm^{-1} .

These characteristic groups for C=C, CCl and CH were clearly observed in the Raman spectra of six neat chlorinated compounds (trichloroethylene (TCE), tetra-chloroethene (PCE), 1,1,2,2 tetrachloroethane (PCA), 1,1,1 trichloroethane (1,1,1 TCA), dichloromethane (DCM), and Cis 1,2 dichloroethene (cis 1,2 DCE)) tested using the TRRS system, confirming system performance that is consistent with literature (not shown). Although there are a wide range of chlorinated solvent DNAPLs encountered in the field, research in this effort was focused on

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4 trichloroethylene (TCE). This was primarily due to the limited availability of substantial
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6 quantities of other chlorinated solvents, which can be traced to the move by regulatory bodies
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8 like the United States Environmental Protection Agency (USEPA) to gradually limit or eradicate
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10 use of these carcinogenic chemicals. Thus work here focused on a more detailed analysis of the
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12 Raman spectrum of trichloroethylene to highlight “fingerprint” frequencies which are unique to
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14 TCE. Overall, the characteristics of the trichloroethylene Raman spectra obtained using the 20μJ
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16 system (and only a 10s sampling time per wavelength) are consistent with standard assigned
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18 vibrational modes presented in literature [53] [54] (Figure 1a).
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30 **[Figure 1: Representative Raman Spectra of a) Neat TCE, b) Water, and c) 600 ppm TCE**
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32 aqueous solution.]
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43 **3.3 Water Raman Functional Groups**

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48 The Raman spectrum of water is characterized by the intramolecular O-H stretching modes from
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50 2700-3800 cm^{-1} . This broad response can be deconvolved into five peaks, 3051, 3233, 3393,
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52 3511, 3628 cm^{-1} [55]. Further characteristic vibrations have been identified at the 1581 and 1640
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54 cm^{-1} Raman shift, which are associated with the bending modes of O-H bonds. A third set of
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56 peaks can be observed at the 65 and 162 cm^{-1} frequencies. The former is linked to O-O-O
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4 bending, while the latter is attributed to the O-O stretching along the O-H---O or hydrogen bond
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6 direction [56] [57] [58] [59] [60]. Figure 1b displays a TRRS scan of water obtained using the
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8 open path 20 μ J laser configuration, with similar experimental settings to the TCE spectrum,
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10 which reflects the vibration modes outlined above.
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18 **4.0 Discussion of Results**

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21 Experiments were performed to directly and indirectly assess TCE levels in aqueous solution.
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24 Observations from each approach are described in detail below.
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30 **4.1 Direct Observations**

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33 In the early seventies when it was first illustrated that Raman spectroscopy could be used for the
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35 detection of pollutants in water [61], there was a surge in the application of Raman spectroscopy
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37 for environmental analyses. This is because, unlike other spectroscopic techniques which are
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39 limited because water absorbs mid-IR (such as infrared spectroscopy) [49], water is generally a
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41 weak Raman scatterer and even water's stronger vibrational modes are notably displaced in the
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43 frequency domain from those of most target analytes [62].
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53 When a single compound is analyzed in water, the observed spectrum is made up of signals
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55 arising from Raman scatter from the analyte, water, and various forms of background (for
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57 example elastic scattering, signatures from impurities, and, of course, electrical noise). Under
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59 consistent test conditions (e.g., power of excitation source, optical configuration, sample
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position), the magnitude of the analyte signal is generally linearly proportional to the analyte concentration in the water based on the classic equation:

$$I_R = I_{\text{vib}} \sigma C dz K \quad (\text{Equation 2})$$

Where I_R = measured Raman intensity, in photons per second;

I_{vib} = laser intensity, in photons per second;

σ = absolute Raman cross section, in cm^2 per molecule

dz = sample path length, in cm;

C = concentration, in molecules per cm^3

K = measurement parameter (to account for experimental parameters such as optical collection efficiency and transmission of the Raman spectrometer which is unitless, instrument specific, and determined from the optical configuration).

When performing quantitative analyses, researchers often employ internal [63] or external [64], [65] standards to identify and correct for system performance variations during and/or between tests (e.g., fluctuations in excitation power). For the work performed herein, two steps were taken to address this issue. First, the system was designed to minimize system performance variability. The laser employed in the system is a solid state device with power stability of $\pm 1\%$. All tests were also run with a standard laser warm up time and laser pulse energy and average power were monitored routinely between tests over the course of the testing program using a laser power meter, with insignificant observed fluctuations in energy. In addition, the optical train and thus alignment of the system is fixed. Further, the sample cuvette was positioned in a spring-loaded holder against a fixed stop-block to ensure reproducible positioning in the optical path. Beyond these physical measures to ensure consistent testing conditions and system

performance, an external standard – in this case a sealed cuvette of neat benzene [64], [66] – was also employed in an asynchronous manner between target analyte tests to routinely assess system performance via observation of the intensity of Raman return at 992 cm^{-1} ($\nu(\text{CC})$ ring stretch) at standard sampling times.

With these experimental measures in place, tests in this effort were initiated with direct observation of the Raman features of TCE in aqueous solution at levels below solubility (i.e., approximately 1200 ppm) to obtain a baseline of the TCE Raman frequencies observable in the aqueous system and to determine their relative intensities. As illustrated in Figure 1, which compares representative Raman signatures (again acquired with a sampling time of 10s per wavelength) of (a) neat TCE, (b) water, and (c) TCE in aqueous solution at 600 ppm, TCE Raman lines at 381 (δ skeletal), 628 (νCCl), 780 (δCH), 840, 930 (CCl), 1242 (CH), 1589 ($\text{C}=\text{C}$) and 3080 cm^{-1} (νCH) were observed in neat solution. The Raman signature for TCE in aqueous solution, however, is notably different, with clear suppression of C-Cl vibrational modes in the mid-frequencies, reflecting a signature that is consistent with those reported by others that have explored aqueous chlorinated solvent systems (e.g., [67] [68] [69] [37]). These changes in Raman scatter in the aqueous system can most likely be attributed to intermolecular interaction between H atoms in water and the C-Cl groups of the TCE molecules, which, by creating regions of hydrophobic hydration around the Cl atoms, weaken the C-Cl vibrations, as first put forward by Kato et al. [70]. In addition, the intensity of C-H group frequencies are likely impacted by the formation of hydrogen bonds with proximal water molecules as discussed in more detail below.

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4 In order to assess direct detection limits for TCE with the TRRS system in a simple aqueous
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6 solution laboratory setting (noting that detection limits are inevitably a function of the system
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8 excitation power, transfer function, and noise signature), a subset of the observable TCE Raman
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10 vibrations were selected for further analysis that are both present in aqueous solution and do not
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12 overlap with primary water functional group vibration modes, namely 381, 840, and 1242 cm^{-1} .
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20 The relationship between the intensity of the Raman return (in counts) at each of these lines to
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22 the concentration of TCE in solution was then studied over a range of concentrations.
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24 Verification of analyte concentration for all tests was performed using a GC-FID-DELCD in
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26 series combination. For all tests, scans were performed using a step size of 0.1 nm with a
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28 sampling time of 120 sec per wavelength. At least three scans were performed at each line of
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30 interest, for each concentration studied. Raman peak heights were determined utilizing the
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32 classic Gaussian-Lorentzian (G-L) fitting method in GRAMS suite 9.0 [71] [72] [73] [74]. The
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34 results of these analyses are depicted in Figure 2 for vibrations at 381, 840, and 1242 cm^{-1} ,
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37 respectively.
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47 **[Figure 2: Raman intensity as a function of TCE concentration in aqueous solution at 381, 840,**
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49 **and 1242 cm^{-1} .]**
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56 Detection limits, defined as the concentration observable at an SNR of 3, are approximately 70
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58 ppm, 110 ppm, and 135 ppm, for the vibrations at 381, 840, and 1242 cm^{-1} , respectively. While
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not representative of drinking water maximum contaminant levels, these detection limits are well within a range that can be valuable for directional mapping of contaminant plumes, site characterization, and long term monitoring, even at the modest laser power of the employed system, indicating significant potential for use in environmental applications, especially given the typical contaminated site groundwater and plume TCE concentrations noted earlier.

4.2 Indirect TCE Observations via Water Raman Line Monitoring

While performing direct observations of TCE, Raman scans were carried out over an extended range of frequencies to facilitate comparison with literature. As a result, it was observed that as the concentration of TCE in solution increased, the Raman signature of water decreased in intensity, particularly in the OH stretching region ($2700\text{-}3800\text{ cm}^{-1}$). This observation highlighted the potential to employ Raman measurements of water to indirectly infer the presence of the target analyte, or at least compounds within a similar family. This approach is elaborated below.

The Raman signature of water undergoes significant changes as the concentration of TCE in aqueous solution increases. Most notably, increases in TCE concentration drive marked reductions in the intensity of the water vibrational modes at the smaller shifts (65 and 162 cm^{-1}) associated with O-O-O bending, and O-O stretching along the O-H---O or hydrogen bond direction, as well as the OH stretching region ($2700\text{-}3800\text{ cm}^{-1}$). Figure 3, which presents average Raman spectra from three scans of aqueous TCE solutions at each of a range of TCE

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4 concentrations, highlights this effect in the OH stretching region, which is particularly helpful
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6 because this region has little overlap with the Raman modes of chlorinated solvents.
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13 **[Figure 3: Relationship of TCE concentration in aqueous solution to the intensity of Raman**
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15 **vibrational modes in the OH stretching region of water.]**
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21 The inverse relationship between the concentration of TCE in aqueous solution and the intensity
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23 of the OH stretching region water Raman lines is likely the result of intermolecular interaction
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25 between the TCE and surrounding water molecules. The fundamental mechanisms underlying
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27 the effect and its impact on the Raman vibrations of water molecules (rather than those of the
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29 TCE), however, are subject to debate.
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33 While no prior investigation could be identified that explored specifically the nature of
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35 trichloroethylene-water interaction, research that has explored the influences of various solutes
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37 on water in aqueous solutions indicates that a reduction in the intensity of Raman vibrations of
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39 water can result from either of two phenomena.
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47 First, it has been shown that when water is used as a solvent with small organic halogen
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49 molecules and halide salts, the hydrogen bonded tetrahedral structure of water can be weakened
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51 [70] [75] [76] [77] as the hydrogen atoms of some water molecules develop hydrogen bonds
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53 preferentially with the halogen. This interaction has been termed a “structure breaking” effect
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55 and, in early studies, was reported to increase with increasing ionic radius of the halides [78].
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4 The impact of this effect has been documented by several researchers [79] [58] [80] [81], and is
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6 characterized by a moderate decrease in the Raman intensity of water vibrational lines at 65 and
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8 170 cm^{-1} , corresponding to O-O-O bending, and O-O stretching along the O-H---O direction, as
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10 well as a more pronounced reduction in the intensity of the O-H stretching vibrational modes of
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12 water from 2700-3800 cm^{-1} .
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21 A second potential mechanism driving the observed changes in the water Raman return stems
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23 from more recent experimental and computer simulation work that has called into question the
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25 bulk “structure breaking” phenomenon and instead links water Raman intensity reductions to
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27 electric field effects resulting from O-H ...X (here X = Cl) interactions in the first solvation shell
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29 surrounding the solute which drive strong orientation of hydrogen atoms in the water toward the
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31 solute (and potentially reduced rotational mobility of the local water molecules [82]), rather than
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33 formation of hydrogen bonds with other water molecules [83].
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42 Beyond these influences which likely contribute to a reduction in water Raman intensities, for
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44 every TCE molecule, there is one hydrogen atom within the C-H group that could offer a counter
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46 effect by driving the creation of hydrogen bonds with neighboring water molecules [58].
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48 However, the 3:1 ratio of Cl to H in TCE suggests that the former effects dominate the observed
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50 trends, resulting in a net decrease in the intensity of water Raman vibrations with increasing TCE
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52 concentration.
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On this basis it is possible to develop a “calibration curve” for analysis of aqueous TCE samples, in this case, relating changes in TCE concentration to changes in the intensity of the most affected vibrational modes of water. As discussed earlier, the water Raman spectrum is distinguished by broad intermolecular OH stretching modes from 2700-3800 cm^{-1} , which can be deconvoluted into five peaks [55]. Here, the 3393 cm^{-1} peak (which was deconvoluted using GRAMS) was employed to develop a calibration curve used for the indirect monitoring of TCE concentration as it consistently yielded the highest SNR during TRRS measurements of TCE concentrations. The resulting calibration curve is shown in Figure 4. The curve specifically highlights the relationship between counts observed at the 3393 cm^{-1} Raman line of water and the concentration of TCE in solution.

[Figure 4: Relationship between water line Raman counts at 3393 cm^{-1} and TCE concentration in aqueous solution.]

Although clearly non-linear, the calibration curve has a negative slope and is steeper than those obtained from direct observation of TCE lines, thus providing a larger “calibration factor” as in the classic characterization of a sensor. This implies that observations of the OH stretching region of water could offer greater sensitivity to changes in TCE concentration than observation of TCE-specific lines, and thus enable improved detection limits, depending on the complexity of the solution being examined. In this simple case of a single compound solution, a detection limit of ~8 ppm is achievable, again on the basis of maintaining an $\text{SNR} \geq 3$. The ratio of the

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4 direct to indirect calibration factors is $70/8 = 8.7$, which implies 8.7x greater sensitivity to
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6 changes in TCE concentration.
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12 While the phenomena described above which likely account for the inverse relationship between
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14 water line Raman intensities and TCE concentration have been known for quite some time, the
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16 authors believe that the work presented herein highlights a potentially unique use of the effect as
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18 a sensing mechanism for chlorinated contaminants, particularly in environmental applications.
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20 Although halogens other than chlorine are known to cause a similar effect to a lesser or greater
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22 extent (i.e, F, Br, I), and a broad array of “structure breaking and making” compounds have been
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24 observed (e.g., alcohols, surfactants, urea) [84], few of these alternate drivers of the water Raman
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26 intensity are likely to be encountered in most natural settings, particularly at the depths where
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28 DNAPLs are often found. Further, work by Li et al. [85], demonstrated that chlorine has the
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30 greatest adverse effect on water Raman intensities among Group VII elements. Thus, even if
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32 other influences were present but as part of the natural “background” signature, a reduction in the
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34 intensity of the water signature at a given site location relative to the water signature from a
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36 related but uncontaminated location would be indicative of water contamination with high
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38 likelihood. With this in mind, careful observation of water Raman signatures in site exploration
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40 and monitoring efforts may offer a valuable and more sensitive indication of aggregate
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42 chlorinated solvent contamination than direct observation of the target compounds.
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57 **4.3 Indirect TCE Observations in Simulated Biodegraded Field Samples**

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4 Recognizing that successful field application of a TRRS monitoring system will require the
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6 capability to make effective Raman observations in the field in an environment much more
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8 complex than simple aqueous solutions, tests were also performed on samples that simulated an
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10 environment representative of a field scenario. These samples, which contained water, TCE in
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12 aqueous solution, soil particles, and microbes capable of biodegradation, were derived from the
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14 supernatant turbid liquid separated from a natural soil slurry and were prepared as discussed in
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25 To initiate the study of simulated degradation samples, TRRS scans (20 μ J open path
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27 configuration, 120 s per wavelength, 0.1 nm step interval) were run over a broad Raman shift
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29 range for turbid supernatant doped to contain 150, 500, and 1000 ppm TCE by volume. The
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31 results of these scans are shown in Figure 5.
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39 **[Figure 5: Raman spectra of TCE doped turbid supernatant bioassay.]**
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45 It is apparent from the figure that the observed Raman signature is quite complex. While it is not
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47 the intent of this analysis to study the full breadth of constituents in these samples, contributions
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49 to the Raman spectrum of this complex sample can be anticipated from an array of sources. The
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51 elevated spectral range between 900-2000 cm^{-1} may be attributed to group frequencies usually
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53 found in soil constituents, with spectral ranges between 950-1170 cm^{-1} typically pertaining to C-
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55 O stretching of polysaccharides; 1450-1650 cm^{-1} to COO-stretching, and 1630-1750 cm^{-1} to C=O
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57 stretching [86]. Glucose, which is known to be in the sample, can be anticipated to provide
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4 Raman returns appearing in the 400-550 cm^{-1} range (most notably 397, 424, and 543 cm^{-1})
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6 which have been attributed to the skeletal vibrations $\delta(\text{C-C-C})$, $\delta(\text{C-C-O})$, and $\delta(\text{C-O})$,
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8 respectively, [87] and in the 850-950 cm^{-1} range (notably 868 and 916 cm^{-1}) due to the $\nu(\text{C-C})$
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10 and $\delta(\text{C1-H1})$ vibrations [88]. Vibrational bands between 1000-2000 cm^{-1} are generally related to
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12 contributions from $\nu(\text{C-C})$ and $\nu(\text{C-O})$ stretching vibrations in soil functional groups and the
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14 microbe feed. The Raman spectrum of the supernatant liquid clearly showed the distinctive
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16 intramolecular O-H stretching modes of water from regions 2700-3800 cm^{-1} . Contributions from
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18 the Raman vibrational modes of TCE are not obviously discerned upon visual examination. In
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20 addition, a non time-gated analysis of the photon returns also confirmed that there is some
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22 contribution of fluorescence in the baseline of the signature, likely from fulvic and/or humic
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24 compounds present in the natural soil.
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35 Beyond these contributions, spectral analysis was undertaken on the turbid supernatant spectra
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37 using GRAMS suite 9.0. A spectral background subtraction was performed, after which a peak
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39 fit utilizing the Gaussian-Lorentzian (G-L) fitting method was explored to locate TCE peaks at
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41 381, 840 and 1242 cm^{-1} . While peak intensity and concentration were observed to be generally
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43 correlated, these trends were not as robust as those associated with indirect monitoring.
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51 Hence subsequent analysis was focused on the indirect measurement of the 3393 cm^{-1} mode of
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53 water which displayed a distinct peak and change in intensity due to the presence of chlorinated
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55 solvents (see Figure 5). Tests were performed to obtain these indirect measurements of TCE at
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57 seven aqueous TCE concentrations (150, 250, 400, 500, 600, 800, 1000 ppm) in the turbid
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supernatant bioassay. The turbidity value for each sample was also measured before TRRS analysis using a turbidimeter, and ranged from 20 to 150 NTU.

The concentrations of the supernatant TCE-bioassay solutions were verified using the GC-FID-DELCD and it was noticed that TCE concentrations in the supernatant were 12-26% lower than planned volumetric concentrations. This reduction can likely be attributed to the partitioning (K_d) of the TCE on to the organic carbon fractions (f_{oc}) of the soil. An f_{oc} for the investigated soil was determined to be 2.21%, leading to a K_d value of 3.67 for TCE, which is consistent with values of the distribution coefficient of TCE in the field [89], and, based on the mass of soil in the supernatant, could readily account for the discrepancy between intended prepared concentrations and those evident in the supernatant liquid fraction.

Given this variation, the TCE concentration in the supernatant liquid as verified by GC-FID-DELCD analyses was then compared to the Raman intensity of the OH stretching water vibration at 3393 cm^{-1} , also obtained on tests of the supernatant, as shown in Figure 6. Although the absolute magnitudes of these observations differ relative to those presented in Figure 5, which can be attributed to the highly turbid nature of the studied samples, the results uphold the form of inverse relationship discussed earlier relating chlorinated solvent concentration to observable changes in the OH stretching vibrational modes of water, even in complex samples representative of field conditions, highlighting the potential to calibrate a sensing system for application in these environments.

[Figure 6: Relationship of water line Raman counts at 3393 cm^{-1} to the TCE-concentration in simulated field samples consisting of doped turbid supernatant bioassay.]

5.0 Concluding remarks

The work presented in this paper contrasted direct and indirect means to assess TCE levels in aqueous solution using time-resolved Raman spectroscopy. The TRRS system employed herein was able to directly detect TCE at aqueous concentrations as low as 70 ppm in simple aqueous solution by monitoring the 381 cm^{-1} Raman line corresponding to the δCCl vibrational mode. This level of sensitivity, while notably above drinking water maximum contaminant limits, has value in certain field monitoring applications such as plume delineation, warning of contaminant release, or the design of tailored monitoring approaches, and certainly could be enhanced through use of a higher power laser system and/or combination with technologies such as Surface-Enhanced Raman Spectroscopy (SERs). Additional observations highlighted that the intensity of water Raman vibrations in the OH stretching region are inversely related to TCE concentration in aqueous solutions following a negative exponential relationship. At comparable laser power and test parameters, observation of the OH stretching water Raman line provided nearly a 9x improvement in detection level relative to direct observation of the strongest observable TCE Raman line in simple aqueous systems (here 381 cm^{-1}), with observation of the 3393 cm^{-1} OH stretch providing evidence of the presence of the chlorinated solvent TCE in water at aqueous concentrations as low as ~ 8 ppm. Additional tests performed on simulated biodegraded field samples reaffirmed the potential to employ monitoring of the OH stretch

Raman vibrational modes for indirect monitoring of TCE even in complex samples containing TCE, water, natural suspended soil particles, and microbes.

The interrelationship between chlorinated solvent presence and the vibrational modes of water suggests that Raman monitoring of the OH stretching band of water may serve as a valuable indication of the presence of aggregate chlorinated solvent contamination in aqueous systems, which could be more sensitive and robust than direct monitoring of chlorinated solvent Raman peaks. Although the observations reported herein are promising, it is important to note several limitations to application of the findings. First, the monitoring method put forward does not, as of yet, offer an opportunity to differentiate different chlorinated compounds or their daughter products that might be encountered in the field (e.g., vinyl chloride, or ethylene chloride in the case of TCE). Further, a number of chemicals are also known to influence the OH stretching band of water, such as surfactants and urea, which could potentially introduce errors in some field settings. However, these compounds are not likely to be encountered at ground depths associated with chlorinated solvent contamination. Overall, the results presented herein offer promising support for continued exploration of Raman analysis as a means to facilitate chlorinated solvent monitoring.

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Figure 5: Raman spectra of TCE doped turbid supernatant bioassay.

Figure 6: Relationship of water line Raman counts at 3393 cm^{-1} to the TCE-concentration in simulated field samples consisting of doped turbid supernatant bioassay.

Figureg

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Direct Observation of TCE Raman Returns

Indirect Observation of TCE via Water Raman Returns

Graphical Abstract