Phytoscreening for Volatile Organic Compounds in a Clay-based Glacial Till at the Niagara Falls Storage Site, New York - 17372

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ABSTRACT

The Niagara Falls Storage Site (NFSS) and associated vicinity properties (VPs) occupy approximately 607 hectares (1,500 acres) of the original 3,035-hectare (7,500-acre) Lake Ontario Ordnance Works (LOOW). The NFSS was used to store radioactive materials, residues and waste from uranium ore processing between 1944 and 1952. The waste-handling practices produced an array of groundwater impacts throughout the site. Although the groundwater at the NFSS is naturally high in total dissolved solids that preclude untreated consumption, the groundwater contaminant levels in some areas of the site are very high and may pose risk to a Construction Worker receptor, as well as limit the options for future site re-use.

Volatile organic compound (VOC) impacted soil in the northern portion of the site has produced a groundwater plume with significant concentrations of tetrachloroethene (PCE) and associated daughter compounds. Active groundwater remediation is impractical due to the clayey soils, as evident from adjacent property owners who have unsuccessfully attempted active remediation of their VOC plumes. Consequently, the Buffalo District may evaluate excavation options, with secondary phytoremediative approaches as passive alternatives to lessen the groundwater impacts during the project’s life cycle.

A preliminary field-study in the VOC plume area sampled the interior of a Black Locust (*Robinia pseudoacacia*) tree using a Haglof tree corer. Detectable levels of tetrachloroethene (PCE), trichloroethene (TCE), and cis-1,2,-dichloroethene (cis-DCE) were found in the woody interior of the tree. Subsequent sampling and analyses were performed on proximal trees of varying species in and around the currently delineated VOC plume. The results indicate that poplar and native cottonwood variants preferentially contain the VOCs, whereas collocated hardwood trees produced non-detectable results. Additional sampling of Cottonwoods in the VOC-impacted area promoted further delineations of the impacts.

The tree-sampling data can be considered a broad surrogate for soil sampling to optimally delineate the VOC plume without performing additional invasive sampling of the subsurface (e.g., drilling) [5,7,8]. The results also will be used to determine which native tree species preferentially uptake the VOCs from soil and groundwater. These species, and possibly other hybrid species known for VOC uptake and transpiration, would be propagated to promote interim phytoextraction of the VOCs during the maintenance period between decision-document completion and likely remedial action under the Formerly Utilized Sites Remedial Action Program (FUSRAP).

INTRODUCTION

The U.S. Army Corps of Engineers (USACE) Buffalo District is evaluating dendroremediative techniques as a phytomanagement strategy to control contaminants in soil and groundwater at the NFSS. This interim site-management effort has relevance to the FUSRAP goal of risk mitigation [1,2,3,4] and site maintenance [5]. A set of tree species were sampled on the NFSS to evaluate the potential for 1) hydrologic control in areas of higher VOC concentrations in groundwater, 2) scavenging of VOC mass from the clayey soils, and 3) the use of specific tree species to limit the migration of VOCs between soils and groundwater [5,7,8]. The characterization of metals and radionuclides in soils and native flora within the NFSS was also assessed, but data do not indicate the uptake of radium, thorium, or uranium in the sampled trees and shrubs (i.e., these elements are not nutrients). This effort aligns with the Corps' Engineering with Nature Initiative, which encourages the use of aesthetic vegetation that can 1) create a new habitat for wildlife while phytomanaging soil and groundwater contaminants and 2) provide site maintenance tools to lessen project lifecycle costs. Figure 1 shows the VOC impacts in groundwater and areas of phytomanagement evaluation [1,2].

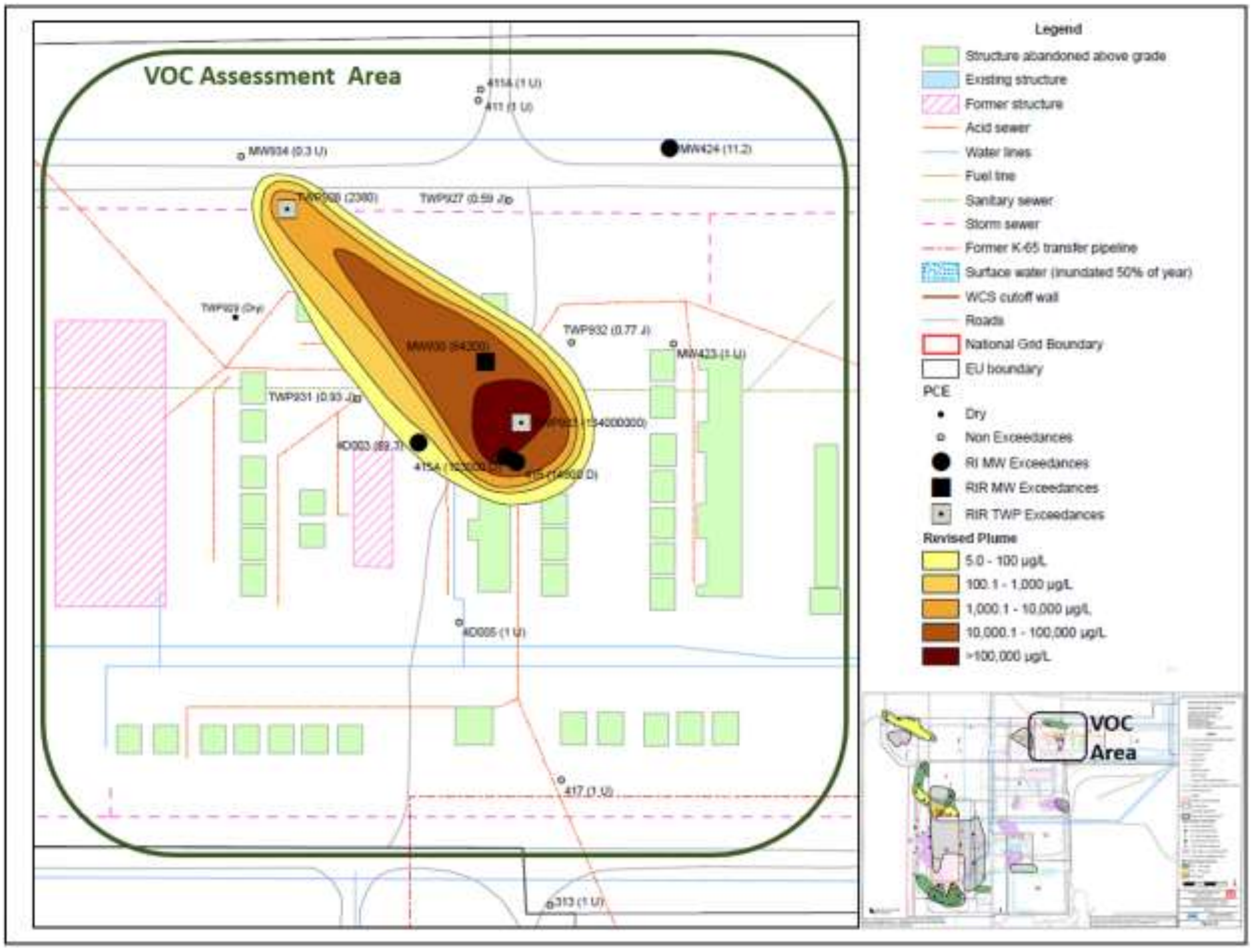


Figure 1. VOC Contamination in the Upper Water-bearing Zone

METHOD

Site hydrogeology

The surficial geology throughout the NFSS starts with a Brown Clay Till that consists of a clayey silt and silty clay groundmass containing non-contiguous sand and gravel lenses, which together comprise the upper water-bearing zone (UWBZ) at the site. A geostatistical analysis of these coarse grained lenses show a vertically and horizontally discontinuous distribution that varies considerably in thickness, color, texture, extent, and saturation. The lenses are not horizontally continuous over distances greater than 4.6 to 6.1 meters (m) (15 to 20 feet [ft]) and vertical distances of 1.2 to 1.8 m (4 to 6 ft) [1]. As a result, the occurrence of groundwater in the

UWBZ varies across the site, with some proximate wells having noticeably different water levels depending on the presence of sand-lenses and evapotranspirative stress (or seasonality) [1,4].

The UWBZ overlies a Gray Lacustrine Clay aquitard that hydraulically separates the UWBZ from the underlying lower water bearing zone (LWBZ), which is a more permeable sequence of an Alluvial Sand and Gravel, Red Lodgment Till, and Queenston Shale bedrock (Figure 2) [2]. The contact between the UWBZ and gray clay aquitard exhibits topographic variations that can provide depressions in the gray clay. These low areas may provide zones where dense non-aqueous phase liquids (DNAPLs), such as volatile organic compounds like tetrachloroethylene (PCE) and its degradation products, can pool along the geologic contact. Figure 3 exemplifies the topography of this subsurface contact in an area of the NFSS impacted by VOCs in the UWBZ [1].

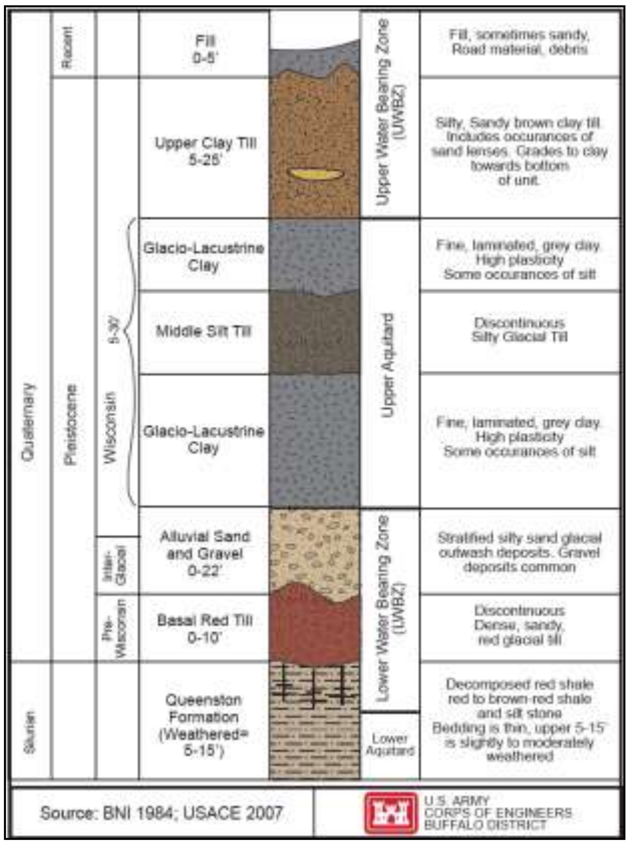


Figure 2. Hydrostratigraphy at NFSS

The regional groundwater flow in the UWBZ is generally to the northwest towards the Niagara River and Lake Ontario. The average horizontal gradients typically range between 0.0012 and 0.0074 m/m, which reflects the flat lake plain environment surrounding the site (Figure 4) [6]. Groundwater seasonally fluctuates and average of 2.4 feet and is most pronounced in wells with no sand lenses [1,2]. This flow field is interrupted on the site by incised drainage ditches that are penetrate the UWBZ and intercept adjacent groundwater. The hydrologic influence of the ditches is most pronounced in the summer and fall seasons, when vegetation in the ditches evapotranspires what the little surface-water collects central and tributary ditches.

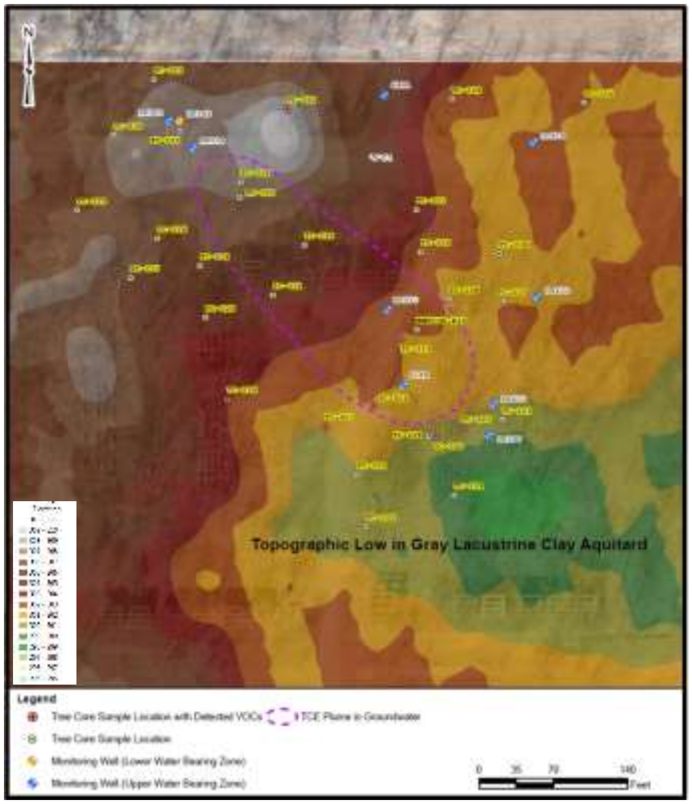


Figure 3. VOC Impacts in Groundwater and Tree Cores Above Interpolated Topographic Surface of the Gray Lacustrine Clay Aquitard

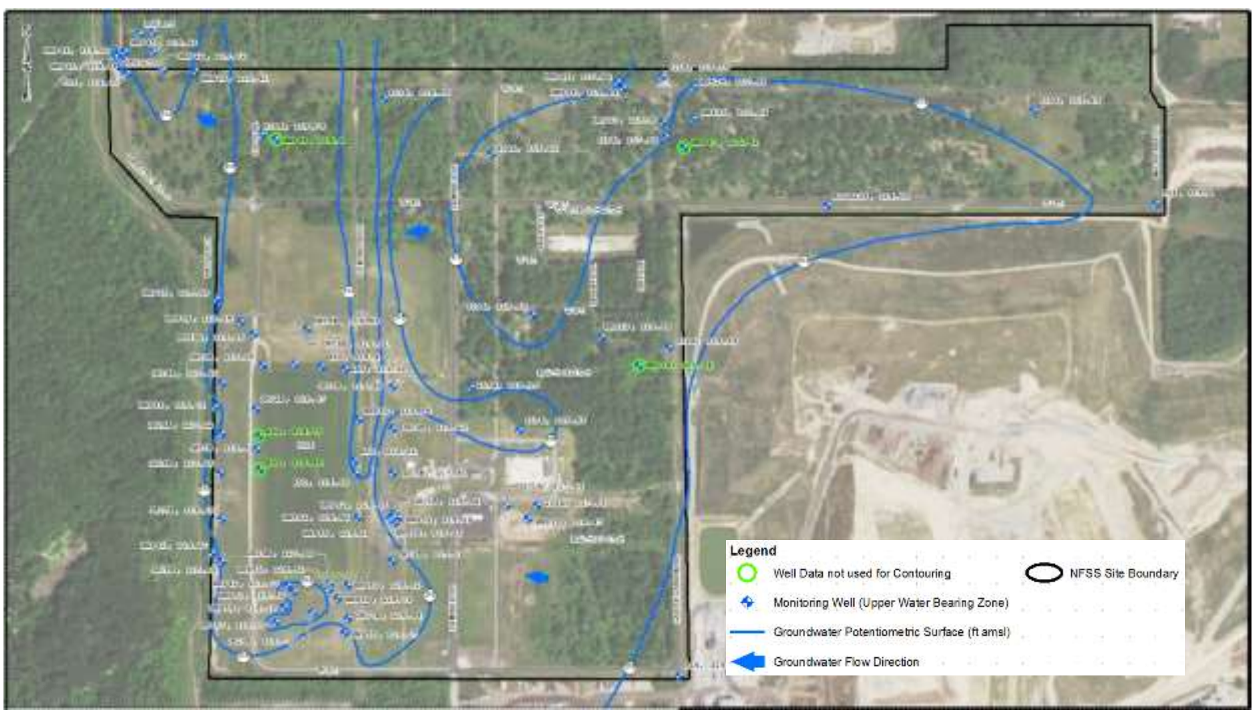


Figure 4. NFSS UWBZ Potentiometry – April 2015

Site contamination

Thirty years of groundwater sampling at the NFSS produced results that indicate the groundwater quality in the UWBZ is naturally poor due to high salinity and mineralization [1,2,3,4]. This condition is indicative of a low recharge and low permeability (silty clay) flow system, where groundwater velocities range near 0.3 meter per year (m/y) (1.0 foot per year [ft/y]). This slow flow allows natural soil minerals to dissolve and chemically saturate (or mineralize) the groundwater with total dissolved solids (TDS) and calcium/magnesium sulfates. The natural water quality in the LWBZ is relatively higher in salinity, total dissolved solids, sulfate species, and several metals that do not have drinking water standards (e.g., calcium, magnesium, potassium, sodium). This higher mineralization is derived from the long residence times for groundwater flow into and through the LWBZ, which includes a flowpaths through upper clayey sediments and LWBZ south of the site, where shallow gradients produce very low flow velocity [6].

The UWBZ was further degraded by radionuclide and organic compound handling and storage methods that contaminated underlying and nearby soil and groundwater (Figure 1). Remedial actions to address site impacts occurred through 1991. Subsequent FUSRAP investigations indicate that the following residual contamination still exists above risk-based goals: uranium-238 and -235 series, arsenic, boron, cadmium, antimony, methylene chloride, and trichlororethylene (TCE) and associated byproducts [1,3,4]. The widest impacts to groundwater are derived from historic uranium-residue handling. However, the VOC impacted area exhibits very high soil and groundwater concentrations that may pose risk to a construction worker receptor, thus these soil and groundwater impacts may undergo remediation.

RESULTS

VOC Area Tree Core Sampling

The sampling of soil and groundwater in the northern area of the site for VOCs was augmented with 47 tree-core samples taken from an array of species in the impacted area. The tree cores were collected using a Haglof corer (5-millimeter diameter) and the wood samples (nominally two to three full cores per vial) were placed in VOC-sample containers; sample containers were immediately sealed to minimize air exposure, which is important in the literature [5,7,8].

Thirty-three (33) trees were sampled in the summer and 15 in the fall of 2016, which is an optimal time for most species due to maximum canopy and soil-moisture demand [7,8]. During the fall-season sampling, two trees also yielded sap samples that were collected and analyzed; one pair fruit also was sampled. The tree species and number sampled in the VOC area include:

- One (1) Pear – *Pyrus* (both wood and fruit sample)
- One (1) Pin Oak - *Quercus palustris*
- One (1) Fire Cherry - *Prunus pensylvanica*
- Two (2) Black Willow - *Salix nigra*
- Three (3) Green Ash - *Fraxinus pennsylvanica*
- Five (5) American Elm - *Ulmus Americana*
- Seven (7) Black Locust - *Robinia pseudoacacia*
- Twenty-seven (27) Cottonwood - *Populus deltoids*
    - 12 trees in the summer of 2016
    - 15 trees in the fall of 2016

Of the 47 trees, seven Cottonwoods and one Black Locust (TC-033) yielded detectable concentrations of either tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-Dichloroethene (cis-1,2-DCE) and/or trans-1,2-Dichloroethene (trans-1,2-DCE). The Black Locust grows within an area of near very high soil and groundwater concentrations.

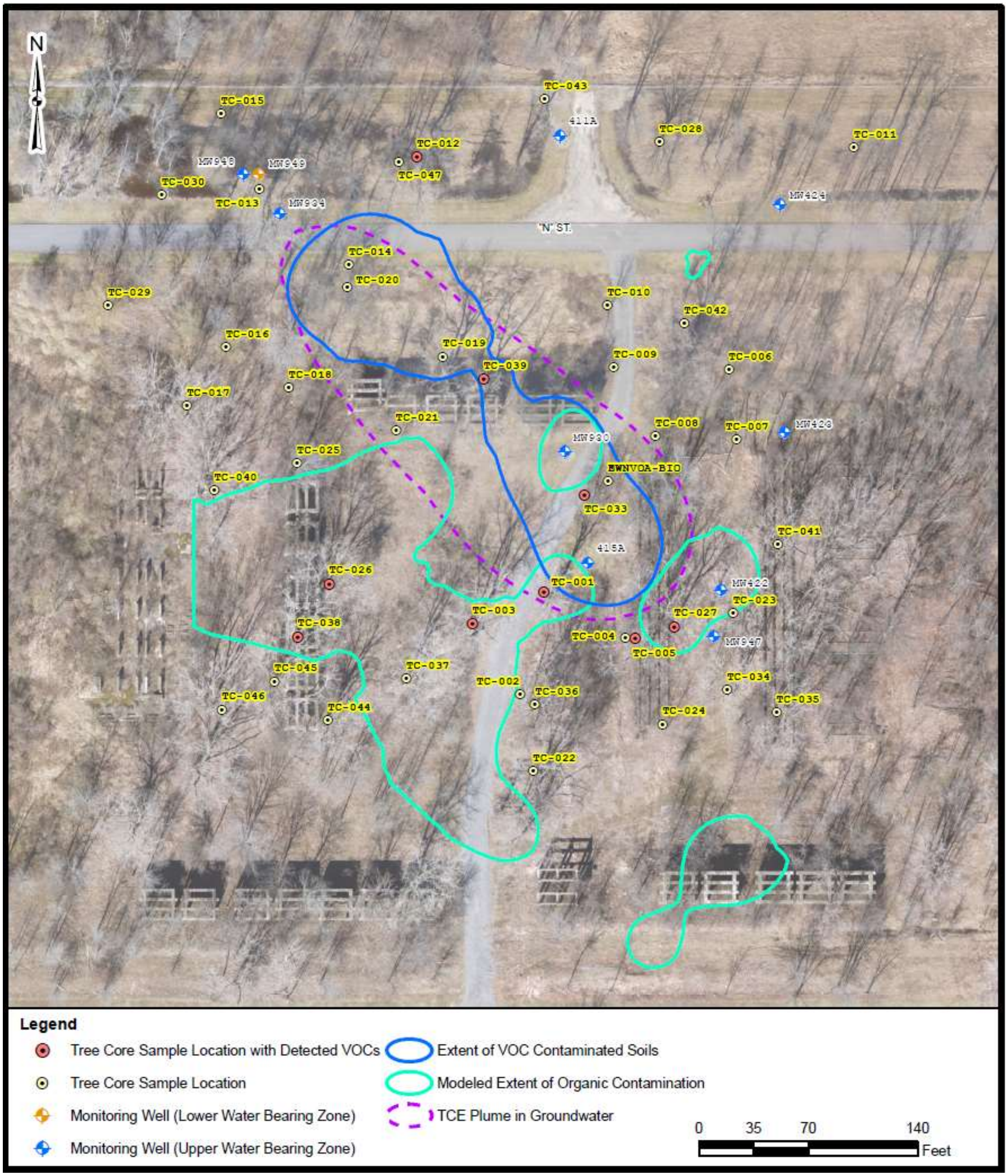
The VOC detections in wood and sap samples are listed below in Table I.

Table I. VOC Detections in Tree Samples at NFSS

Tree Location	VOC Detected	Result (µg/kg)
TC-001	Tetrachloroethene (PCE)	22.0
	Trichloroethene (TCE)	17.0
	cis-1,2-Dichloroethene (cis-12DCE)	120.0
	trans-1,2-Dichloroethene (trans-12DCE)	2.3
TC-003	Tetrachloroethene (PCE)	1.5
	Trichloroethene (TCE)	0.65
	cis-1,2-Dichloroethene (cis-12DCE)	2.0
TC-005	Tetrachloroethene (PCE)	1.3
	cis-1,2-Dichloroethene (cis-12DCE)	27.0
	trans-12-Dichloroethene (trans-12DCE)	1.2
TC-012	cis-1,2-Dichloroethene (cis-12DCE)	5.5
TC-026	cis-1,2-Dichloroethene (cis-12DCE)	7.0
TC-027	Tetrachloroethene (PCE)	4.2
	Trichloroethene (TCE)	4.4
	cis-1,2-Dichloroethene (cis-12DCE)	12.0
TC-033	Tetrachloroethene (PCE)	22.0
	Trichloroethene (TCE)	5.5
	cis-1,2-Dichloroethene (cis-12DCE)	31.0
TC-033 Duplicate	Tetrachloroethene (PCE)	28.0
	Trichloroethene (TCE)	9.4
	cis-1,2-Dichloroethene (cis-12DCE)	68.0
TC-039	Tetrachloroethene (PCE)	20.0
TC-038-W*	cis-1,2-Dichloroethene (cis-12DCE)	0.53 µg/L

NOTE: * Sap sample.

Figure 5 shows the combined soil and groundwater data (VOC plume), along with VOC results from the tree cores and sap. Soil and groundwater samples from the VOC area exhibit concentrations of PCE up to 75,600 µg/kg and 5.61E8 µg/L (noticeable product phase), respectively. The VOC detections provide evidence of plant uptake into the harder softwoods, like Cottonwood, which is also documented by the U.S. Geological Service (USGS) [4]. The distribution of the tree results indicates that VOCs may exist south of the current plume and thus an area to investigate for VOC impacts during potential remedial design.



DRAFT Figure 5. Tree-core Results and Observed TCE Plume

The southerly extension of the plume on Figure 5 (see detections at TC-003 and TC-026) may be partially controlled by a depression in the contact between the UWBZ and underlying aquitard, as depicted on Figure 3. The trees with VOC detections near a western portion of the depression may indicate a larger source area or multiple sources. To better understand the distribution of VOCs in the tank cradle area (legacy LOOW operations), additional tree-core samples will be taken as a surrogate for invasive soil and groundwater sampling near and under the thick concrete foundations. The Cottonwoods and Poplars that are found within and near these structures are candidates for tree-core sampling to assess whether uncharacterized soil impacts occur near and under the structures.

Phytomanagment of groundwater sources

The observed capability for native species to uptake VOCs opens opportunities to use phytoextractive techniques for site remediation and/or maintenance. The Interstate Technology & Regulatory Council (ITRC) defines phytoextraction as “the ability of plants to take up contaminants into the roots and translocate them to the above-ground shoots or leaves. For contaminants to be extracted by plants, the constituent must be dissolved in the soil water and come into contact with the plant roots through the transpiration stream. Alternatively, the uptake may occur through vapor adsorption onto the organic root membrane in the vadose zone. Once adsorbed, the contaminant may dissolve into the transpiration water or be actively taken up through plant transport mechanisms [8].”

Organic chemicals taken up by the plant may be 1) stored in the plant biomass via lignification (covalent bonding of the chemical or its by-products into the lignin of the plant), 2) sequester it into the cell vacuoles of above-ground tissues (as opposed to in root cells), or 3) metabolized through phytodegradation or phytovolatilization via the transpiration stream exiting the plant [7]. Figure 6 conceptualizes the phytoextraction mechanisms that can influence soil and groundwater concentrations [7].

Figure 6. Phytoextraction Mechanisms to Capture Soil and Groundwater Contaminants [8].

The octanol-water partition coefficient, log K_{ow}, for organic chemicals is specifically linked to plant uptake; log K_{ow} values between 1 and 3.5 promote uptake and plant transfer. Values greater than 3.5 signify chemicals that are more hydrophobic, non-polar, and generally not sufficiently soluble in the transpiration stream; these VOCs can be bound strongly to the root surface and not easily translocated into the plant xylem (sap fluids). Chemicals that are highly polar and very water soluble (log K_{ow} <1.0) are not sufficiently sorbed by the roots, nor are they actively transported through plant membranes due to their high polarity [7,8].

Common log K_{ow} values (ranges) for the VOCs at the NFSS include the following [5,7,8]:

- Tetrachloroethene = 2.03 - 2.83
- Trichloroethene = 1.43 - 2.33
- cis-1,2-Dichloroethene = 1.25 - 1.86
- Vinyl Chloride (VC) = 0.60 - 1.27

Consequently, the NFSS tree-core data reflect compounds that are most susceptible to phytoextraction and thus supports the viability of using phytoextractive species to support site options. The presence of vinyl chloride in underlying soils and groundwater, but not in the tree cores, indicates this compound is not phytoextractive by the native Cottonwood species. However, tree-root penetration in soils may promote VC degradation by increasing air porosity in the deeper soils and provide vapor exhalation pathways from deeper soils.

Although the evidence for phytoextraction has been observed at the NFSS, the removal rates of VOCs from the clayey soils is dependent on the evapotranspiration rates for water, which vary with species and plant age. Hybrid Poplars were estimated to evapotranspire 38 to 3,030 liters (10 to 800 gallons) per day per tree for 1-year to 5-year old trees. Cottonwoods vary between 14 and 3,030 liters (3.75 to 800 gallons) per day per tree for 1.5-year to 19-year old trees [8]. These rates correlate with observations from a 0.4-hectare (1-acre) stand of 2170 hybrid poplars that together removed about 8.7-million liters (2.3-million gallons) of water per acre per day. This plot equates to a grid of 5-year old trees spaced 6 meters (20 feet) apart, each removing about 4,000 liters (1,060 gallons) per tree per day [7,8].

VOC-impacted soil distributions indicate about 2,525 cubic meters (3,302 yards) of soil requires remediation, along with about 12,500 liters (8,965 gallons) of contact groundwater [5]. This volume could be reduced by planting phytoextractive species in the VOC area as a maintenance action during the period between remedial decision making and remediation. This interim maintenance measure would have capital costs (clearing, planting, initial maintenance), but otherwise be passive until potential remedial design options were was funded.

Phytoextractive trees also provide a maintenance option that would be coupled with a removal option to further reduce residual soil and groundwater VOC concentrations. A planting plan would be designed to passively “polish” soil residuals remaining after a removal remedy achieves remedial goals. This technology coupling would increase future site re-use options via the enhanced attenuation of VOCs (e.g., passively removing residual VOCs lessen vapor intrusion risks should buildings be built in the plume area).

In addition to the extraction of VOCs from the subsurface, the replacement of non-extractive species with extractive Cottonwoods (for example) over and near other groundwater impacts (e.g., metals or radionuclides) will increase the seasonal evapotranspiration rates and promote greater soil-moisture deficits in the UWBZ [7,8]. The evapotranspiration rates for maturing cottonwood seem to vary around 3,030 liters (800 gallons) per day per tree, which would equate to an array of extraction wells pumping at 2.1 liters per minute (0.55 gallons per minute). This rate is significantly greater than well yields observed during NFSS sampling events.

Consequently, the use of phytoextraction techniques would limit groundwater transport by 1) decreasing groundwater recharge, 2) depressing seasonal groundwater levels, 3) lengthening the period of low groundwater levels, and 4) promoting a lower saturation in the UWBZ, all of which would lessen the ability for contaminants to affect other media via groundwater.

CONCLUSION

Groundwater contamination near legacy radioactive-residue storage areas and LOOW operational corridors provide an opportunity to assess phytoextractive technologies as part of the NFSS management program. Since site remediation may not occur for over 10 years, the interim management of soil impacts will ensure that groundwater does not spread contamination via diffusion to other media or soil. Although the groundwater is not considered a consumptive resource due to naturally high salinity and poor quality, a phytomanagment program would be a low-cost and passive technique to minimize soil impacts and groundwater contamination (i.e., control volumetric growth of soil impacts).

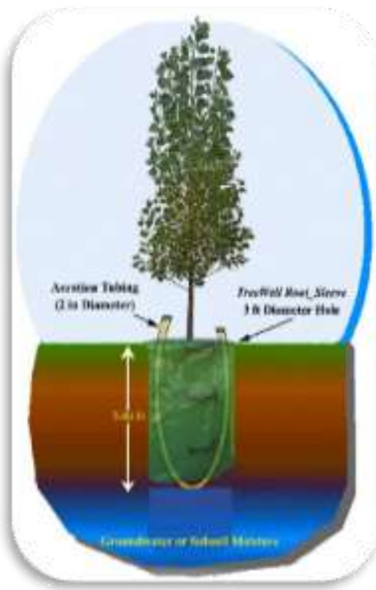


Figure 7. Tree-well Conceptualization [7,8]

The propagation of hybrid Poplar or native Cottonwood trees as a passive phytoextractive technology at the NFSS is viable. Such phytoextraction arrays (tree plots) also can employ “tree-well” systems (e.g., EnPhySys) to promote aggressive root development and to increase the phytoextractive potential of the trees (Figure 7). Additional supportive investigations that would sample leaves and pruned tree parts may be conducted to verify VOC uptake and transpiration in the plant. Should a maintenance array of trees be planted, the subsurface hydrogeologic conditions also would be assessed to estimate groundwater and VOC extraction characteristics, along with geochemical changes derived from the presence of the vegetation (i.e., changes caused by lower soil moisture and increased air permeability).

In areas where groundwater is impacted with only uranium, site vegetation samples did not show radionuclide uptake (e.g., radium, thorium, and uranium isotopes). For these areas, phytoextraction would be used to further reduce seasonal soil moisture, which will depress water levels and transport mechanisms, and promote geochemical conditions that lower uranium solubility, as seen in the late summer and fall when groundwater levels are lowest. The phytomanagement success metrics would be 1) plume and source management via hydraulic control, 2) VOC uptake and transpiration to deplete soil concentrations, and 3) promotion of seasonal geochemical (reducing) conditions that lower both uranium solubility in groundwater and promote reductive dechlorination of the VOC plume.

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