West Lake Landfill
Organic Pollutant Phytoforensic Assessment

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Executive Summary:

Researchers at the Missouri University of Science and Technology was contacted in 2015 with a request to assess potential contamination in the area of West Lake Landfill (WLL). The primary concern was evaluating the presence of on-site pollutants and off-site migration of pollutants in the shallow hydrogeology of the area. As part of this request from the Missouri Attorney General’s Office, historical data from the site was evaluated and plant sampling was conducted in the WLL area for target pollutants that are typical from landfill operations and for radionuclides. Such sampling has been proven to delineate groundwater plumes for certain compounds and this methodology is termed phytoscreening and one of phytoforensic methods of assessing polluted environments for a limited group of pollutants with properties and characteristics that allow plant uptake and translocation.

Findings indicate contamination on-site for the WLL area, and the distribution of pollutants in the vegetation at WLL and surrounding properties is highly indicative of off-site migration. Pollutants detected most commonly were chlorinated-volatile organic compounds (ClVOCs) in the chlorinated ethane family and petroleum constituents benzene, toluene, ethylbenzene and o,m,p-xylenes (BTEX). These most commonly detected compounds were noted to be in clustered areas, supporting the conclusion that these particular contaminants were present in the subsurface rooting zone of the trees. Potential sources were considered and from the information reviewed, the most probably source of the pollution was concluded to be the WLL operations.

Site Background Information Considered:

Landfill activities dating back to pre-RCRA often included disposal of a wide variety of wastes that are currently not allowed for disposal in a municipal landfill (RCRA D landfill). Among these wastes, liquid industrial wastes were commonly disposed in large quantities. As a result landfill leachates from pre-RCRA landfills commonly contain a number of priority pollutants at elevated levels. According to an international review article by Kjeldsen et al “The most frequently found XOCs are the monoaromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) and halogenated hydrocarbons such as tetrachloroethylene and trichloroethylene (Table 6). These pollutants are also the ones found in the highest concentrations.” The article is an international compilation of over 80 reports and research articles and has been cited in over 600 scholarly works, thereby strongly supporting the findings of the article.

The West Lake Landfill (WLL) in a pre-RCRA landfill, having been in operation since the late 1940s or early 1950s, when waste was placed into the limestone quarry. WLL is not unusual in in terms of the presence of numerous priority pollutants in leachate and disposal of a variety of liquid wastes in WLL has been alleged (OU1 RI report 1990).

Leachate reports from WLL indicate that BTEX, Cl-VOCs, acetone, methyl ethyl ketone, and various other compounds are known to be present in the WLL disposal area and in leachate samples tested from sampling wells at WLL (Herst&Associates 2013). These compounds and other typical leachate constituents have repeatedly been identified in multiple wells since 2012 and upward trends in concentration have been noted (Herst&Associates 2013).
Air sampling in the area has confirmed the presence of benzene, toluene, o-, m-, p- xylenes naphthalene and phenanthrene are present in the area and likely emanating from the WLL property (DNR 2013-2015). Numerous other constituents and odors have been reported to occur from the WLL property

**Vegetation Sampling and Phytoforensics Applications**

Recent sampling of vegetation in a phytoforensic testing effort looked to assess the potential for off-site migration from the WLL. Sampling looked at a variety of on-site and off-site vegetation, sampling the tissues for a variety of volatile organic compounds (VOCs), particularly chlorinated VOCs and BTEX compounds (WLL Analytic report (Burken et al. 2015)). Plant sampling for subsurface pollutants has been termed phytoscreening and phytoforensics (Vroblesky et al. 1999, Vroblesky 2008, Burken et al. 2011). Phytoscreening has been applied for a wide variety of pollutants at many sites internationally.

Plants interact with the surrounding soil, water and air, extracting and releasing chemicals throughout their life cycle. Phytoscreening is based on the place-bound nature of plants, and the mass transfer abilities that allows plants to efficiently harvest all molecular constituents needed to be the dominant biomass on earth. Being place-bound, plants are ideal recorders of certain details about their surroundings. Plants have been used to assess weather/climate history, history of wild fire occurrence, volcanic eruptions, nuclear fallout, and earth quake history. These methods have been based on dendrochronology and dendrochemistry techniques, assessing data recorded in the rings of perennial trees. Phytoforensic methods are based on these combined properties of being place bound, having an intimate connection to the surroundings, and novel analytic techniques that allow for assessing the molecular chemical exposure of the plants to measure the chemical constituents and chemical activity of the surroundings in a semi-quantitative fashion. A summary schematic of chemical processes that allow plants to accumulate pollutants from their surroundings is depicted in Figure 1.

Plume delineations have been proven to correlate to groundwater and to vapor phase pollutant concentrations (Struckhoff et al. 2005, Larsen et al. 2008). Recent research has correlated direct push, passive sampling, gas phase sampling, and traditional groundwater sampling (Holm et al. 2011, Shetty et al. 2013, Algreen et al. 2015, Rein et al. 2015). The Burken laboratory at Missouri S&T has performed analysis on samples from over 60 sites including 8 countries and 14 states. Among these sites, landfills have been sampled in 3 states, with each showing detections of VOCs in areas of leachate migration. Phytoscreening and dendrochemistry methods also fit the basis of the Daubert criteria. The fundamental hypothesis is the transfer of water and vapors from the subsurface to the above ground tissues. Testing has been conducted at laboratory and field scale, with consistent proof of concept from hypothesis to testing at ‘mega sites’. Peer review has consistently reinforced the validity, with the initial seminar paper cited over 120 times (Vroblesky et al. 1999) and guidance documents have been generated nationally and internationally. Technical guidance documents have been published in the EU and in the US (Trapp et al. 2007, Vroblesky 2008, Holm et al. 2011). Reliability has been assessed, with a prevalence in error for false negatives, wherein plants underpredict chemical activity in the subsurface due to degradation, poor rooting structure of specific plants, or decreased water transpiration due to toxicity or poor health.
Figure 1 Concepts of phytoforensics transfer of environmental pollutants to plants, exhibiting the environmental processes whereby plants accumulate environmental pollutants from their surroundings. (Burken et al. 2011)

Phytoscreening Applicability
Phytoscreening has been most commonly applied for Cl-VOCs. Phytoscreening has also been used for BTEX detection and recently methods have been developed for perchlorate, RDX and HMX (Yuan 2013, Limmer et al. 2015). In all cases, the transport of organic pollutants and perchlorate from the subsurface has resulted in a presence of the contaminant molecules in the above ground tissues. The transfer of subsurface pollutants to the above ground tissues is a complex pathway. The specific transport efficiency varies among compounds, primarily as a function of the molecular physicochemical properties. The efficiency is most commonly called transpiration stream concentration factor (TSCF) first coined by Briggs (Briggs et al. 1982) when proposing a single variable model based
on the octanol water partition coefficient (K_{ow}). This uptake model has since been assessed and refined to consider multiple chemical properties, multiple root transport pathways (apoplastic, symplastic, apoplastic bypass), and multiple chemical phase processes (dissolved and vapor) (Trapp and McFarlane 1995, Burken and Schnoor 1998, Trapp 2002, Dettenmaier et al. 2009, Limmer and Burken 2014). Overall transport and residence of pollutant molecules in plants must consider mobility in the subsurface, potential rhizosphere and bulk soil degradation prior to uptake, sorption and immobilization in plant tissues, degradation in-planta, endophytic degradation (Trapp and Pussemier 1991, Trapp and McFarlane 1995, Burken and Schnoor 1997, Burken et al. 2001, Trapp 2002, Trapp 2004, Doty 2008, Barac et al. 2009, Weyens et al. 2010). Overall the transfer rate can be highly variable for different site conditions and plant types. However, at the majority of sites sampled in phytoscreening efforts have revealed a positive correlation for the specific site.

Phytoscreening Limitations

Phytoscreening for subsurface pollutants has numerous intrinsic limitations for assessing groundwater pollutants. Primarily the plant roots must have direct contact with the contaminated media. Rooting depth and depth to groundwater may limit plant uptake, however for vapor-phase contaminants direct uptake of the vapors can occur with limited or no direct contact with the true water table (Struckhoff et al. 2005, Vroblesky 2008, Holm et al. 2011). Separation of the polluted media and the roots by a clean water source has also been reported, such as the case of a 'diving plume' where a freshwater source can force a contaminant plume lower (Landmeyer et al. 2000).

High biodegradation rates can also limit plant uptake (Holm et al. 2011) as shown for BTEX compounds (Weishaar et al. 2009). Biodegradation of BTEX at the root surface can be at highly elevated rates (Weishaar et al. 2009, Cook and Hesterberg 2013, Le Fevre et al. 2014). Degradation rates are influenced by transpiration rates, exudation of organics from roots, enhanced desorption rates, and enhanced oxygenation rates from diurnal water removal fluctuations.

Chemical properties also preclude uptake, even when intimate contact of polluted media and roots exists. The predominant chemical property that limits uptake and all biodegradability is the tendency to be absorbed to organic matter, most often called the octanol-water partition coefficient (K_{ow}), most often designated by the Log K_{ow} value or Log P (Briggs et al. 1982, Sicbaldi et al. 1997, Burken and Schnoor 1998, Dettenmaier et al. 2009). Compounds above a Log K_{ow} over 4.0 are considered to have greatly reduced and the increasingly low bioavailability outside of the root suggests that phytoscreening is not applicable at Log K_{ow} over 4.0. Recent research has indicated that uptake is also influenced by molecular weight, hydrogen bond donors hydrogen bond acceptors (Limmer and Burken 2014), the same properties that are used to predict trans-membrane migration of orally administered drugs (Lipinski et al. 1997). The similarities are not surprising given the similarity of the biological membranes involved. Investigations also indicate polar surface area (PSA) and rotatable bonds are two other molecular descriptors often used in drug screening and have impact on plant uptake and translocation of organic pollutant molecules (Limmer and Burken 2014). From this work a new method of assessing plant uptake was posed, in generating 'desirability functions' predicting the likelihood of plant uptake. Desirability functions were combined to calculate the quantitative estimate of plant translocation (QEPT_{w}) given a set of weights to the uptake impacts of the noted chemical properties above (Limmer and Burken 2014). The new estimation method is in close agreement with the previous models on plant uptake, reaffirming that the pollutants noted in this phytoforensic screening are predicted to undergo rapid uptake and efficient transport in vascular plants.

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**Sampling and Analytic Methods.**

Sampling methods for plant tissues in the field has varied among the target analyte, available vegetation, and techniques developed by different sampling teams and laboratories. Plant sampling methods have varied from tree core collection with increment borer (Ma and Burken 2002, Vrobesky 2008) or increment hammer (Holm et al. 2011, Limmer et al. 2011), branch sampling (Gopalakrishnan et al. 2007, Gopalakrishnan et al. 2009), bark sampling (Simonich and Hites 1995, Simonich and Hites 1995), \textit{in-planta} solid phase samplers (SPSs), \textit{in-planta} Solid Phase Microextraction (SPME) (Limmer et al. 2013, Shetty et al. 2013, Limmer et al. 2014), and transpiration stream physical extraction (Yuan 2013, Limmer et al. 2015). All methods are targeting sample isolation with the target analyte molecule in a form to be prepared for chemical analysis.

Sample analysis has varied widely based on available techniques and instrumentation and on the target analyte. The most prevalent methods are gas chromatography (GC) analyte separation, and detection of chlorinated solvents with electron capture detection (ECD). GC-ECD is highly sensitive for detection of halogenated compounds such as chlorinated VOCs, the most common targets for phytoscreening. For hydrocarbon analysis, GC with Flame Ionization Detection (FID) or Photo Ionization Detection (PID) are most common. GC paired with Mass Spectrometry (GC-MS) has also been commonly applied, with sample identification being possible. In limited cases, direct plant sampling using field portable GC-MS has been applied, where the volatilized gases from trees growing on polluted sites (Limmer et al. 2014).

Headspace sampling has been employed most often for getting analyte molecules on column. The volatility of ClVOCs and BTEX create a sampling location in the sample vial headspace that is relatively clean from interfering molecules from the plant tissue matrix. Headspace methods are commonly a direct gas sample form the headspace injected to the GC. The application of SPME to headspace sampling had greatly increased the analysis sensitivity through a rapid concentrating step for the analyte molecules prior to putting the sample on column (Limmer et al. 2011). Use of time weighted average (TWA) sampling with SPME can increase analytic sensitivity multiple fold (Sheehan et al. 2012).

For non-volatile compounds, phytoscreening has been less prevalent. Analytic challenge associated with the organic matrix of the plant tissues make analyte isolation and quantification is a limiting aspect to developing the screening techniques. New methods of physically extracting the plant tissue liquids has allowed for advancing phytoforensic methods for compounds such as pesticides, explosives, and energetics. Freeze and centrifuge methods for removing plant liquids were developed and used in connection with liquid chromatography (LC) at Missouri S&T laboratories (Mu et al. 2012, Yuan 2013, Limmer et al. 2015). Detection of RDX, HMX, DNAN and other explosives was accomplished with dual MS for LC-MS-MS analysis. Traditional liquid extraction was also applied for confirmation of the freeze-centrifuge methods (Karnjanapiboonwong et al. 2012).

**Site-Specific Data Assessment**

The results from phytoscreening around the WLL property revealed ClVOCs and BTEX in a many samples from different areas, both on and off sites. Two off-site areas of indicate a high probability for off-site pollutant transport. The spatial distribution of the detections in and around WLL varied among the contaminants. The ClVOCs were detected most frequently in the northwest area of WLL property near the closed demolition landfill and OU1, and off property to the north-northeast across St. Charles Rock road from the entrance to WLL. The second area was near South Quarry and West...
OU2 to the southwest along and across the Old St. Charles Road and the closed section of the Old St. Charles road near the water district impoundments. Summary maps of PCE and TCE concentrations in the collected tree cores are presented in Figure 9 of the analytic report (Burken et al. 2015) and figure 2 below.

The occurrence of the ClVOCs in grouped area and in multiple trees is a strong indication of subsurface pollutants in the specific area and in the shallow subsurface horizon occupied by the rooting zone of the trees. Similar in-planta concentrations and contaminant profiles are indicative of a subsurface plume for these compounds. Chlorinated VOCs are the most prevalent groundwater pollutants in the US, and are commonly associated with landfill leachate (Kjeldsen et al. 2002). The detections of ClVOCs was predominantly on or adjacent the WLL property with the exception of two lone detections that were not co-located or showing in a cluster of surrounding vegetation. These detections are likely not attributed to the WLL property.

Concentrations of cDCE were low and only detected on the WLL property in limited samples. Analytic sensitivity of cDCE is roughly two orders of magnitude lower than PCE and PCE as noted above. cDCE is a daughter product (metabolite) of reductive dechlorination processes that can degrade these ClVOCs in-situ.

![Figure 2 Mapped tree core concentrations for TCE and PCE for trees samples in April 2015 at WLL. Also shown as Figure 9 of the WLL analytic report (Burken et al. 2015).](image)

BTEX were detected across larger areas in the WLL surroundings and with greater frequency than the ClVOCs. During the phytoforensic sampling BTEX hydrocarbon pollutants were detected most frequently in the north west area of WLL property in OU1, and off-property in two clustered areas. These areas are to the north-northeast across St. Charles Rock Road from the entrance to WLL and to the southwest along the perimeter of the South Quarry and across the Old St. Charles Road continuing along the closed section of the Old St. Charles road adjacent to West Lake OU2 and continuing to the water district impoundments. Toluene and Benzene detections were more frequent along the Old St. Charles road and further to the east along the entire length of the WLL property.
adjacent the South Quarry and West Lake OU2. Summary maps of toluene and benzene concentrations in the collected tree cores are presented in Figure 3.

One cluster of benzene detection was noted in an area not adjacent to the WLL property. This cluster was along Crossroads Industrial Drive, and was directly adjacent to a heavy machinery and vehicle sales and rental facility. A number of other vehicle intensive operations are located along Crossroads Industrial Drive and may be possible sources of this cluster of detections. Benzene has been detected in air sampling in this light industrial area around WLL on occasions and not attributed to WLL on some occasions. Based on the proximity to other potential sources, this Crossroads Industrial Drive cluster of benzene detections may have a number of potential sources.

![Figure 3 Mapped tree core concentrations for Benzene and Toluene for trees samples in April 2015 at WLL. Also shown as Figure 9 of the WLL analytic report (Burken et al. 2015).](image)

Clusters of vegetation adjacent to South Quarry and West Lake OU2 that have elevated BTEX in multiple samples are also in an area of groundwater with BTEX detection as well. Groundwater analysis from this area and leachate analysis from South Quarry have revealed elevated concentrations of benzene and toluene as well as other constituents such as acetone and 4-Methyl-2-pentanone (MIBK), which were not targeted in the phytoscreening analysis.

The cluster of BTEX detections extending along the southwest perimeter of South Quarry and proximity to the South Quarry and West Lake OU2 have the probable source in or near the sanitary landfill of the South Quarry. BTEX compounds are the most prevalent of leachate constituents in surveys of multiple leachate studies and are commonly noted as markers for identifying leachate migration (Christensen et al. 2001, Kjeldsen et al. 2002, Baun et al. 2004).

Unknown compounds were noted in tree cores analyses for Cl-VOCs and BTEX, as peaks occurred at consistent peak retention times and with notable peak areas, i.e. relating to elevated concentrations. Three individual peaks were noted repeatedly, with detections in at least 20 of the tree core samples.
Two typical peaks within the BTEX analyses at a retention time of 2.3 minutes (8 tree cores) and 3.9 minutes (12 tree cores) and one within the Cl-VOC analyses at 1.37 minutes (4 tree cores), as noted in the analytic report (Burken et al. 2015). The plotting of the unknown compound detections revealed a spatial clustering of the samples with the unknown peaks, indicating a likely subsurface source of these compounds in these areas. These tree cores were then reanalysed by SPME-GC-MSD. In comparison to the background sample, no significant peaks within the targeted retention times for the unknown contaminants in any background samples. The specific chemical structure and chemical properties of the unknown chemicals are not yet known. To further investigate the identification of the unknown contaminants observed within initial analyses, fresh samples should be taken and directly analyzed by SPME-GC-MSD to assist in identification. Sample degradation due to the storage time between the initial analyses and attempted identification by MSD could have occurred to limit the ability to identify the contaminants.

Resampling in August 2015 revealed BTEX and the Unknown 2 again in the area along Old St. Charles road affirming presence of these pollutants in the rooting zone of the vegetation along the roadway near the WLL property boundary and perimeter of South Quarry. Detected levels did change from the April 2015 sampling as is often observed (Limmer et al. 2014) and likely attributed to changes in the transpiration rates off the vegetation, changing in the soil water content, and altered degradation rates in the rhizosphere. These factors are all interrelated and have been shown to alter contaminant fate and transport rates.

**Figure 4 Mapped tree core concentrations for Benzene, Toluene, and ‘Unknown 2’ for trees samples in April 2015 at WLL. Also shown as Figure 12 of the WLL analytic report (Burken et al. 2015)**

**Summary Assessment of Phytoforensic Analysis and Historical Data,**

Phytoforensic methods are a proven method for screening subsurface pollutants in a semi quantitative manner for pollutants that reside in the near-surface profile. This environmental volume is general considered to be up to 10 m deep and extent laterally is in the similar range, but can vary greatly due to differences in tree species, rooting conditions and soil properties. Plants can uptake pollutants that reside in multiple phases, including dissolved in groundwater, in vapor phase, or absorbed to soil. The intrinsic value of the phytoscreening approach is the ability to screen large areas, with spatial resolution only limited by the presence of adequate vegetation. In the sampling
endeavor undertaken as part of this study, over 200 trees were sampled in less than two days with
data produced in a matter of weeks total.

Presence of target analytes in multiple trees covering large areas are clear indicators of subsurface pollutants in the rooting zone. Presence of BTEX and unknown pollutants in the area of Old St. Charles Road along the South Quarry and West Lake OU2 are likely due to subsurface migration of leachate in groundwater or soil vapor transport from the WLL site. BTEX detection was noted in a large number of trees covering a length of roughly 900 meters along the Old St. Charles Road – WLL property boundary.

Presence of BTEX and CIVOCs in the leachate samples from the WLL property, presence in local groundwater samples collected off-property support the opinion that the BTEX contamination originated from the WLL property. Potential sources in the area are limited, with a petroleum station at the west end of Old St. Charles road being removed decades prior to the sampling. The nearest probably source to the noted contamination is WLL.

The timing of the pollution cannot be fully determined, however degradation rates of BTEX are typically high in the near surface profile, and particularly in the rooting zone of trees. CIVOCs are more persistent than BTEX in the shallow subsurface, as the oxic conditions of the vadose zone occupied by tree roots typically does not support the reductive dechlorination process. Degradation rates for BTEX in the rhizosphere of perennial trees has been noted at many times higher than unplanted soils and the bulk soil degradation rate is also noted to be higher in the general vegetated area, due to the dynamic nature of plant-groundwater-soil vapor interactions (Weishaar et al. 2009, Lefevre et al. 2013, Wilson et al. 2013, Le Fevre et al. 2014, Nichols et al. 2014, Yadav et al. 2014). Given the relatively rapid degradation rates of BTEX and the shallow profile of phytoscreening analysis, the opinion is supported that the source of the BTEX is recent and likely a continuing source, particularly along South Quarry and West Lake OU2 western perimeters.


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