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WORKSHOP REPORT

Considerations for Developing Leaching Test Methods for Semi- and Non-Volatile Organic Compounds

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WORKSHOP REPORT CONSIDERATIONS FOR DEVELOPING LEACHING TEST METHODS FOR SEMI- AND NON-VOLATILE ORGANIC COMPOUNDS

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NOTICE/DISCLAIMER

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, funded the preparation of this report under EPA Contract No. EP-D-11-006. The Office of Resource Conservation and Recovery also provided funding for the workshop. This report was subjected to the Agency's peer administrative review and is approved for publication as an EPA document. Statements captured in the discussion and summaries are those of the participants, not necessarily reflective of the EPA. Presentations are the responsibility of their authors and may represent opinions or personal points of view in some cases. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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FOREWORD

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods (and their cost-effectiveness) for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and in order to identify/anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development (ORD) to assist the user community and to link researchers with their clients.

Cynthia Sonich-Mullin, Director
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Office of Research and Development
U.S. Environmental Protection Agency

ABBREVIATIONS AND ACRONYMS

COC	Contaminants of Concern
DNAPL	Dense Non-Aqueous Phase Liquid
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EPA	Environmental Protection Agency
ERG	Eastern Research Group
EU	European Union
ISO	International Organization for Standardization
ISS	In Situ Solidification/Stabilization
LEAF	Leaching Environmental Assessment Framework
L/S	Liquid/Solid
LSP	Liquid Solid Partitioning
MCL	Maximum Contaminant Level
MGP	Manufactured Gas Plant
MSW	Municipal Solid Waste
NAPL	Non-Aqueous Phase Liquid
NRMRL	National Risk Management Research Laboratory
NVOC	Non-Volatile Organic Chemical
ORCR	Office of Resource Conservation and Recovery
ORD	Office of Research and Development
OSRTI	Office of Superfund Remediation and Technology Innovation
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PTFE	Polytetrafluoroethylene
RCRA	Resource Conservation and Recovery Act
SPLP	Synthetic Precipitation Leaching Procedure (EPA Method 1312)
SVOC	Semi-Volatile Organic Chemical
TCLP	Toxicity Characteristic Leaching Procedure (EPA Method 1311)
UVA	University of Virginia
VOC	Volatile Organic Chemical

1. INTRODUCTION

The workshop was hosted by the US Environmental Protection Agency (EPA) on September 16 and 17, 2015 in Arlington, VA to discuss developing leaching test methods for semi- and non-volatile organic compounds. The purpose of the workshop was to exchange information concerning how to evaluate the potential for release of semi- or non-volatile organic constituents at contaminated sites where sub-surface treatment approaches have been applied to control migration, and from waste that is disposed or re-used. The workshop also considered how to predict sub-surface leaching potential at the outer edge of the treated media, or in disposal or material re-use situations, at the unit or use boundary. Representatives from EPA and academia participated in the workshop. Workshop discussions focused on identifying technical issues for further consideration to support the development of tools that could be used to make determinations of protectiveness and regulatory compliance.

Representatives from the Office of Resource Conservation and Recovery (ORCR) and the Office of Superfund Remediation and Technology Innovation (OSRTI) identified several workshop objectives, including:

- Identify key parameters expected to govern leaching potential of semi- and/or non-volatile organic constituents from sub-surface treated media (e.g., soils) or disposed waste. The keys parameters will need to be considered in the development of leaching tests to provide more accurate source-term data that inform treatment and waste disposal decisions;
- Understand how to account for these parameters when evaluating release potential both at initial treatment and over time (in general, 50-100 years);
- Identify methodologies currently used to evaluate organic constituent leaching and their strengths and weaknesses;
- Understand whether the Leaching Environmental Assessment Framework (LEAF) established for inorganics can be adapted to evaluate leaching of organic constituents; and
- Explore how to leverage the best science available to facilitate decision-making.

During the workshop, the following key points related to Superfund site remediation were discussed to help frame workshop discussions:

- Treatment effectiveness is measured at the waste management area boundary;
- Clean-up levels are assumed to be known;
- Superfund generally deals with site-specific data and information rather than generic or national distributions of modeled fate and transport scenarios; and
- In situ treatment technologies most often used to treat organic contaminants in soil include soil vapor extraction for volatile organic chemicals (VOCs) and in situ solidification/stabilization (ISS) for semi-volatile organic chemicals (SVOCs) and non-volatile organic chemicals (NVOCs).

After the introductory remarks, there were a series of technical presentations followed by related technical discussions. The information from each presentation is summarized in the remainder of this report. The report also includes the three appendices listed below.

- Appendix A – Presents the workshop agenda,
- Appendix B – Provides a list of the meeting participants, and
- Appendix C – Contains the presentations.

2. PRESENTATIONS AND RELATED DISCUSSIONS

As described in the agenda found in Appendix A, the workshop included a series of presentations. The key points from each presentation are below including summary points from the group discussion that followed each presentation.

2.1 Presentation: Key parameters or drivers that govern the source term at the unit boundary for subsurface leaching of semi- (SVOC) and non-volatile (NVOC) organic chemicals

Key points from Dr. Charles Werth's (University of Texas – Austin) presentation:

- Factors that either retard or enhance leaching of semi- and non-volatile organics can include:
  - Adsorption/desorption;
  - Multi-phase partitioning; and
  - Equilibrium vs. diffusion controlled release.
- Complex matrices that influence leaching include natural components of soils, sorption amendments to sequester pollutants, and precipitates that encapsulate pollutants..
- Leaching is controlled by the <u>capacity</u> of the different phases for the organic chemical(s) of interest, and the <u>mass transfer rate</u> from each phase. As water moves through a phase, the solute goes through advection and dispersion; each phase holds some of the solute (water, non-aqueous phase liquids (NAPL) – organic or a mixture, and solid), which accumulate in the phases.
- It is possible to approximate leaching from sorbed and NAPL phases with a first order expression to illustrate dependence on the capacity of each phase for pollutant and mass transfer rate constant.
- The **air** phase holds little volatile organic chemicals (VOCs), semi-volatile organic chemicals (SVOCs) or non-volatile organic chemicals (NVOCs) relative to solid and NAPL phases and contributes little to leaching.
- As is it replenished, the **water** phase represents leachate and serves as a pollutant sink for other phase. The by presence of salts, co-solvents, dissolved organic matter (DOM), and colloids affects the capacity of the water phase.
  - Increasing ionic strength decreases the aqueous solubility;
    - Altered solubility is related to concentration of the salt
    - As the salt concentration increases, solubility decreases (lowers the capacity of the water)
  - Increasing co-solvent concentration increases the aqueous solubility (e.g., methanol – changes the structure of the water and increases the capacity of water to hold a solute); and
  - Increasing DOM concentration increases the apparent aqueous solubility (or association with macromolecules).
- Leaching capacity of **soils** and **sediments** depends on soil/sediment properties and chemical properties. Soils, sediments, and geosorbent amendments (e.g., char) can sorb large amounts of VOCs, SVOCs and NVOCs, and slowly release them.

  - Equilibrium capacity of these solids is determined by composition;
  - There are both absorption (or partitioning) and adsorption environments; and
    - The capacity of the soil partitioning environment for contaminants in absorption environments can be estimated and is often linear
    - Adsorption environments are more challenging to characterize, and it is impossible to predict adsorption; therefore, empirical models are often used
    - The capacity of adsorption environments for contaminants must be measured; the relationship between water and soil concentrations is typically nonlinear
  - Both partitioning and adsorption environments are often present in solids, and the contribution of partitioning and adsorption environments varies widely depending on the sorbent.

- Mass transfer processes can be complex and occur in parallel or in series.
- A simplified model that focuses on multi-phase partitioning and adsorption is needed to predict mass transfer rates.

Discussion

- Consider each phase and identify the capacity and subsequent mass transfer rate.
  - Capacity is relative to the solubility in water (high capacity = 1000x or more soluble in water); and
  - Mass transfer rate measured as velocity of leaching in a column (cm/min).
    - Fast = equilibrium
    - Medium = minutes to hour to days
    - Slow = many days to weeks/months
    - Very slow = years

- Cement amendments can be in block or granular form and the format can affect the diffusion length scale (a measure of how far the concentration has propagated over time).
  - Diffusion coefficient affects the time scale and can be challenging to predict (e.g., if a contaminant is trapped throughout the cement, the length scale is unknown);
  - For ISS with equal distribution of NAPL, expect fairly short length scales; and
  - For ISS with macro-encapsulation (boundary has no NAPL), expect very long length scales.

- The manufactured gas plant (MGP) industry is adding activated carbon to reduce leaching, and there are questions regarding whether the added components are improving performance.
- An important consideration related to mass transfer is the degree of mixing and conformity for laboratory prepared mixes compared to the long-term effects of actual treated materials observed in the field.
- Unmixed regions may dominate field results.
- The age of NAPL and its duration of contact to soil can influence the rate of leaching of organic constituents.

- Adding adsorption materials to dilute the concentration of contaminated particles can create another environment whereby new added capacity delays or slows leaching (increasing the length scale slows overall mass transfer rate).
- Participants discussed ISS conditions that are below the water table. As the water table rises and falls, pore spaces are occupied and emptied thereby changing the connectivity of space in the different phases.
  - VOC transport through gas phase can be fast (i.e., would have a large impact on the rate at which VOC would leave); and
  - Mass transfer of SVOCs in NAPLs would slow when water table goes down and increase again when water table re-rises back.

- Participants identified the following key considerations and questions for future work:
  - The capacity and mass transfer rate constants for each phase determine the relative contributions to leaching;
  - Consider and evaluate competing mechanisms when developing a framework to assess leaching;
  - Consider the conditions and integrity of materials over time (e.g., carbonation of weak cementitious material can influence product stability over time);
  - Simulation of the age of material can be an important factor;
  - Account for time scales – test at various states (initial, six months, accelerated aging);
    - Relate time scales of mass release to controlling process to design an experiment and interpret release/risk
  - Conduct background research to better understand mixing issues and how to account for differences between laboratory and field conditions (i.e., represent the potential for incomplete mixing and lack of mixing in the field);
  - Identify uncertainties that exist between laboratory and field conditions; and
  - Consider external factors (environmental conditions) that influence the integrity of materials (e.g., organoclays).

2.2 What is our field test experience related to organics leaching?

Key points from Dr. Craig Benson's (University of Virginia) presentation:

- Dr. Benson discussed his experiences relating barrier experiments in the laboratory to the field.
- He underscored the importance of understanding how the subtleties of experimental design components can dramatically influence results and predictive outcomes.
- Several key issues to consider when designing experimental protocols include:
  - Account for biological processes and activity of a system when designing experiments;
  - When running long-term experiments with small amounts of mass, pay significant attention to experimental design and apparatus – measure and conduct experiments on design components;
  - When dealing with small amounts of mass, exercise caution in the quantity of liquid to extract when sampling to avoid impact on mass transport processes;

  - Experimental apparatus can have a significant effect on outcome of transport experiments with hydrophobic organic contaminants at low concentrations;
  - Evaluate materials beforehand as sinks for organic contaminants, even in the most obscure components, to avoid false negatives;
  - Evaluate apparatus for unintended sinks for organic contaminants (e.g., O-ring);
  - Develop expectations for outcomes of experiments to provide a reality check on data;
  - Accurately model the breakthrough time using simple analytical methods to bracket expected boundaries;
  - Recognize the importance of quality control (positive and negative) and method blanks; and
  - Understand what you expect to see and measure why you do not.

Discussion

- Dr. Benson reiterated the potential importance of the relationship and influence of dissolved organic carbon (DOC) in experimental design following the discussion of DOM binding in Dr. Werth's talk.
  - Specifically, how DOC impacts binding and whether the mobility of contaminants would increase when using real groundwater with DOC over deionized water often used in the laboratory.

2.3 Estimation of Source Term Concentration for Organics Contained on Superfund Sites

Key points from Dr. Ed Barth's (EPA/ORD/NRMRL) presentation:

- Dr. Barth discussed some of the challenges EPA Regions face in providing a quick answer for evaluating "the source term at the waste management area" for remedies involving ISS of organic materials (including dense non-aqueous phase liquid [DNAPLs]).
- Dr. Barth discussed a variety of methods for pre-placement and post-placement evaluations. He indicated that EPA and other organizations have guidance for the evaluation of ISS for organics, but questioned whether there is too much emphasis on physical properties (UCS, hydraulic conductivity) and not enough emphasis on chemical bonding strength and leaching mechanisms, especially if free product is present on the site and if colloids are present in the site around water.
- He described one approach to evaluate barrier improvements with an emphasis on organoclays or activated carbon. Specifically, the focus would be to: (1) evaluate the bonding strength of activated carbon and organoclay, and (2) determine whether colloids interfere with bonding strength.
- Additional experimental design considerations specific to polycyclic aromatic hydrocarbons (PAHs), analytical techniques, and data interpretation techniques should include:
  - Reduction of PAHs in laboratory samples due to photochemical oxidation exposure;
  - Headspace volatilization;
  - Dilution;
  - Sorption onto glassware; and
  - Oil sheens on sample surface.

- Historical and current laboratory approaches (evaluated by EPA and being proposed by EPA regional contractors) that EPA Regions use to assess adequacy of treatment/containment processes include:
  - Application of a modification to the LEAF Method 1315;
  - Use of site groundwater;
  - Use of coated glassware;
  - Partitioning/NAPL saturation; and
  - Use of pore water models based upon partitioning.

Discussion

- Summary points discussed:
  - Some EPA Regional Offices have used leaching methods, beyond the toxicity characteristic leaching procedure (TCLP), to ascertain whether a treatment/containment process is either adequate to protect the public health and environment or as a comparison to other treatment technologies;
  - An array of challenge fluids is available to cover the range of extraction recovery; and
  - While bonding-strength indicator methods are available, they are rarely used in treatment evaluations.

- More guidance is required if EPA Regions are beginning to use a modification to LEAF Method 1315 to determine organic leaching.
- TCLP remains the regulatory standard for RCRA hazardous waste determinations and land disposal restrictions requirements and is widely used for ISS effectiveness determination.

2.4 European and international standards on leaching of organic contaminants, available tools and recent developments for assessment of organic contaminants

Key points from Hans van der Sloot's (Consultant – retired from the Energy Research Center of the Netherlands) presentation:

- Dr. van der Sloot provided an understanding of leaching methods currently in use and the status of standardization and validation in Europe.
- European standardization is split into different fields (soil, waste, mining waste, and construction products) and methods that may be field-specific. Many fields have boundaries that are interrelated and therefore, regulators are questioning whether methods need to be harmonized across fields to promote standardization.
- Dr. van der Sloot described parameter differences and adaptations among methods for organics and inorganics and noted many similarities.
- In response to earlier discussions on important parameters, Dr. van der Sloot noted:
  - Bioactivity/biodegradation is not addressed during the test itself, rather it is dealt with during sample preparation and storage; and
  - Address aging by testing at various states (initial, six months, accelerated aging), rather than designing for aging within the leaching test method itself.

- Important considerations identified through observations from European Union (EU) standardization activities for leaching standards for organics include:
  - The fundamental processes that characterize release behavior are not different, and in many cases information on both organic and inorganic substances is needed; and
  - Material requirements for the equipment and other parts contacting the eluate are adapted to meet requirements for both types of substances.
    - Glass column and stainless steel connections
    - In the column, quartz sand or glass beads are used instead of filters
    - It was noted that filtration commonly used for inorganic substances is unsuitable for organic substances – if needed, centrifugation is recommended

- Dr. van der Sloot also noted the importance of the relationship of organics leaching to DOC and complexation with DOC. He has observed an apparent correlation of PAH with DOC, hence, indirect pH dependence of PAH leaching. This observation further underscores the need to understand differing field conditions with the influence of DOC, where increased DOC can increase leaching potential.
- Dr. van der Sloot summarized important take-away messages from the EU experience developing methods for organics:
  - Adsorption to Material Surfaces
    - Match contacting surfaces to organic substances of interest
      - Do not use plastics (including Viton), rubber, polytetrafluoroethylene (PTFE) (PAHs adsorb to Teflon)
      - Glass, stainless steel preferable

  - Volatilization
    - VOCs are not considered; only semi- and non-volatile organic substances are considered

  - Colloid Formation
    - Because there is more colloid formation in a batch test compared to a column test, centrifuge eluate rather than use filtration, if at all needed

  - Eluate Analysis
    - Always measure pH and DOC; DOC varies as a function of pH and hence water insoluble organics associated with DOC have increased leachability as pH increases

  - Demonstrated Higher Release Values from Batch vs. Column Tests
    - Observations made during the development of International Organization for Standardization (ISO) standards for soil show batch tests resulted in higher release values in almost all cases due to higher turbidity and thus higher DOC levels in batch compared to column

  - Filtration and/or Centrifugation
    - In the German test, filtration and centrifugation are not used when the turbidity of the solution is below a certain value

- Additional key concepts that should be considered include:
  - Liquid-solid partitioning;
    - pH – indirectly relevant due to dependence of DOC on pH
    - Liquid-solid ratio
    - Redox – not directly relevant
    - Dissolution/sorption
    - Particulate and DOM interaction
    - Eluate Chemistry

  - Mass transport; and
    - Diffusivity
    - Surface area
    - Surface interactions (local equilibrium)

  - Limitations.
    - Degradation of organic substances (after results are available, happens in the analysis)
    - Degradation of organic matter and associated DOC formation (time-lapsed issue)
    - Sorption on many surfaces
    - Volatilization

- Important observations were shared, including:
  - Use of a common leaching conceptual framework and related standardized test methods will allow for comparability of results across contaminants, sources of contaminated materials, scenarios and regulatory jurisdictions.
  - Standardized tests show systematic release patterns for organic contaminants to further understanding of release mechanisms;
  - Methods are aimed to simultaneously address both inorganic and organic substances to facilitate ecotoxicity testing of eluates;
  - Dissolved organic matter plays an important role in release of semi- and non-volatile organic substances due to their association with DOC;
  - Transport properties are controlled by the substance itself and by the transport properties of DOC;
  - The pH dependence of DOC release is important because the association of organics with DOC impacts organics partitioning and transport;
  - Release of organic substances from monolithic products (e.g., stabilized waste and treated wood) is, primarily controlled by the release of DOC-bound organic substances and thus controlled by DOC release. DOC release from porous monolithic materials is about a factor 10 – 15 times slower than the release of soluble salts (e.g. Na+, K+, Cl-);
  - DOC-associated organic substances are not bioavailable for a range of organisms currently applied in ecotoxicity testing and thus have no toxic response;
  - Partitioning of DOM in sub-fractions (fulvic and humic substances) may prove important, in view of their different binding characteristics for organic contaminants; and
  - The use of soil adsorption coefficient (Koc) parameters allows the partitioning of organic contaminants to be estimated between particulate and DOM.

- There were no tests have addressed specifications for leaching water (i.e., specifications for pH and DOC) and therefore underscores the importance of a pH dependence test to understand the impacts.

2.5 What is LEAF for inorganics? What lead to its development? What was the process and timeline for developing and validating the methods?

Key points from Greg Helms' (EPA/ORCR) and Susan Thorneloe's (EPA/ORD/NRMRL) presentations:

- Greg Helms provided an overview of LEAF for inorganics, what led to its development and the process and timeline for developing and validating the methods.
- The TCLP is a generic leaching test representing an eluant pH = 4.98 (that of active decay phase in a municipal solid waste [MSW] landfill); TCLP is broadly used and in many cases inappropriately applied (e.g., at conditions not representative of the pH).
- Given the deficiencies and challenges of TCLP, EPA was urged to evaluate other more representative methods to estimate and predict leaching that provide a better representation of what is likely to occur.
- LEAF methods have broad applicability across materials and enable one to compare:
  - pH;
  - Liquid-to-solid (L/S) ratio; and
  - Particle size.

- LEAF results can be very useful when you gain economies of scale when analyzing waste management and re-use options for large quantities of waste.

Susan Thorneloe provided background on the importance of establishing methods that provided a more accurate depiction of leaching based on a range of environmental conditions. There was a need to have a more holistic understanding of the impact of air pollution control technologies at coal-fired power plants to ensure pollutant transfers were not delayed or shifted from one media into another. Acros the U.S., coal-fired power plants were implementing wider spread use of air pollution control technology such as the use of selective catalytic reduction for post-combustion NOx removal, electrostatic precipitators or fabric filters for particulate capture, sorbent injection for increasing mercury control, and flue gas desulfurization or other scrubber technologies to reduce acidic gases in the stack emissions. When these pollutants are transferred from the air stack at coal-fired power plants to the fly ash and other air pollution control residues, the concern is whether the pollutants may be later released when the air pollution control residues are utilized for beneficial use or land disposed. *[Thorneloe S.A., D.S. Kosson, F. Sanchez, A.C. Garrabrants and G. Helms (2010) "Evaluating the fate of metals in air pollution control residues from coal-fired power plants," Environmental Science and Technology, 44, 7351-7356.]*

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- LEAF is a collection of:

  - Four leaching methods;
  - Data management tools;
  - Geochemical speciation and mass transfer modeling;
  - Quality assurance/quality control; and

  - Integrated leaching assessment approaches.

- LEAF is designed to identify characteristic leaching behaviors for a wide range of materials and associated use and disposal scenarios to generate material- and site-specific source terms.
- LEAF is not a replacement for TCLP but instead is used when TCLP is not considered applicable or appropriate. Uses include:
  - Assess materials for beneficial use;
  - Evaluate treatment effectiveness (equivalent treatment determination);
  - Characterize potential release from high-volume materials; and
  - Corrective action (remediation decisions).

- LEAF provides a source term for future modeling and facilitates comparing data across materials when using a common framework.
- LEAF includes data management tools to facilitate implementation, including:
  - Spreadsheets to help manage data and pre-calculate required values (e.g., titration);
  - Form upload to the materials database; and
  - Software for processing and results visualization.
- Susan shared important lessons learned through the LEAF development, including:
  - Modifications to Methods 1313 and 1316;
    - Tolerance for contact time was added
    - Requirement that pH values be measured within one hour after separation of solids and liquids due to lack of buffering in aqueous samples

  - Modifications to Data Templates; and
    - Mandatory information is highlighted
    - Instructions more closely follow method text

  - Other Considerations.
    - Calibration of pH meters should cover entire pH range to extent possible
    - Reagents should be freshly prepared, stored in vessels of compatible materials (e.g., strong alkalis not be stored in borosilicate glass)
    - Laboratories should establish a QC regimen to check the quality of reagent water (method blanks are important)

- Susan discussed lessons learned from the validation effort and suggested the following:
  - Engage laboratories and ensure they follow the instructions;
  - Brief participating laboratories through interactive webinars;
  - Walk participating laboratories step-by-step through the process;
  - Conduct methods training;
  - Conduct QA/QC; and
  - Ensure conformance to the method.

2.6 Existing Tools and Limitations to Address Leaching of Organic Species

Key points from Dr. David Kosson's (Vanderbilt University) presentation:

- Dr. Kosson described the capabilities of existing leach test methods to measure factors that impact organic leaching.
- Dr. Kosson provided an overview of leaching control factors, including chemical factors and physical factors, coupled with release mechanisms of wash off, dissolution and diffusion.
- The distinction between simulation-based and characterization-based leaching approaches was discussed:
  - Simulation-based Leaching Approaches:
    - Designed to provide representative leachate under specified conditions, simulating a specific field scenario
    - Eluate concentration assumed to be leachate (source term) concentration
    - Simple implementation (e.g., single-batch methods like TCLP or Synthetic Precipitation Leaching Procedure [SPLP]) and interpretation (e.g., acceptance criteria)
    - Limitations
      - Lack of Representativeness of testing to actual disposal or use conditions
      - Results cannot be extended to scenarios that differ from simulated conditions
      - Basis for comparison of results from different materials is often unclear
  - Characterization-based Leaching Approach:
    - Evaluate intrinsic leaching parameters under broad range of conditions
    - More complex; sometimes requiring multiple leaching tests
    - Results can be used to conduct "what if" analyses of disposal or use scenarios
    - Provides a common basis for comparison across materials and scenarios
    - Materials testing databases allow for initial screening
- Dr. Kosson provided an overview of existing methods in practice and identified limitations for organic contaminants.
- LEAF methods were discussed, including the rationale and limitations for use with organics:

Table 2-1. LEAF Methods Overview

Method	Rationale	Limitations for Use with Organics
1313	• Designed to provide Availability and Liquid-Solid Partitioning (LSP) as a function of pH. Also provides acid/base titration and basis for chemical speciation modeling • Focus on end-state conditions (pH, L/S, DOC, etc.) • Particle size and contact intervals, mixing to approach equilibrium • Conceptual paradigm is applicable for organic species	• Availability determination approach not applicable for organics although some organic constituents or fractions thereof partition strongly to natural organic matter or NAPLs, resulting in a very readily available fraction for leaching and a more slowly or recalcitrant fraction for leaching. • pH domain beyond the relevant scenario pH not needed • Eluent and mixing conditions do not address potential for deflocculation and colloid formation (column test minimizes inadvertent release of DOC; can get higher results from batch testing vs column) • Provisions for selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses are not provided • Many methods do not provide sufficient guidance on what is "applicable"
1314	• Designed to provide LSP as a function of L/S (elution curve). Approximates initial pore water and linkages between individual species leaching (e.g., DOC & chloride complexation, depletion of one species leading to increased release of another) • Particle size, dimensions, flow rate, to approach equilibrium. Eluent to avoid deflocculation • Conceptual paradigm is applicable for organic species	• Availability determination approach not applicable for organics; percolation column approach can be used to indicate readily leachable fraction of organic contaminants but also must be sensitive to leaching kinetics. • pH domain beyond the relevant scenario pH not needed • Eluent and mixing conditions do not address potential for deflocculation and colloid formation (column test minimizes inadvertent release of DOC; can get higher results from batch testing compared to column) • Provisions for selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses are not provided • Many methods do not provide sufficient guidance on what is "applicable"

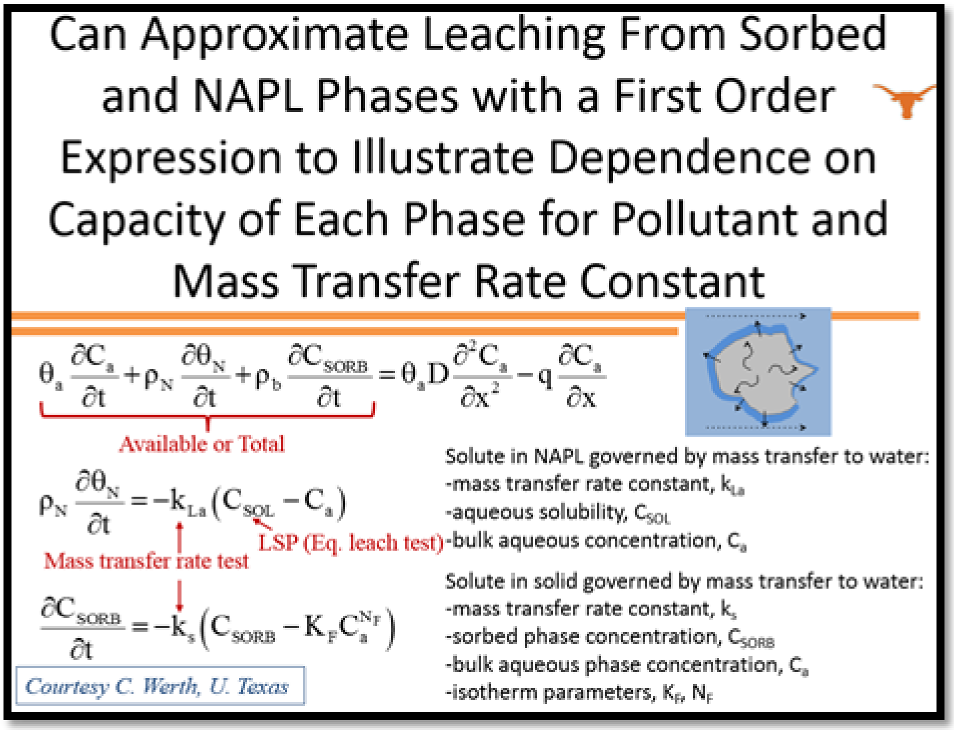
Table 2-1. LEAF Methods Overview

Method	Rationale	Limitations for Use with Organics
1315	• Designed to provide maximum release flux (mass transport rate) by maintaining dilute boundary condition • Closed vessels to minimize atmospheric exchange (CO_2, O_2) • Interpretation includes consideration of field scenario boundary conditions • Conceptual paradigm is applicable for organic species	• Provision for in-situ solid phase extraction not provided (variants have been developed but not standardized) • Provisions for selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses are not provided
1316	• Designed to provide LSP as a function of 0.5 ≤ L/S ≤ 10 mL/g dry material. Provides basis to approximate early leachate concentrations and determination of availability or solubility controlled leaching • Particle size and contact intervals, mixing to approach equilibrium • Conceptual paradigm is applicable for organic species	• Eluent and mixing conditions do not address potential for deflocculation and colloid formation resulting in a potential bias towards higher release estimates. • Provisions for selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses are not provided

- Key take-aways from Dr. Kosson's presentation include:
  - Measurement of intrinsic leaching characteristics and development of source terms based on mass balance, thermodynamic and mass transport principles provides a robust leaching assessment framework that is applicable to both inorganic and organic species;
  - Numerical modeling may be warranted when direct extension of laboratory results to field conditions is not applicable and analytical solutions are not available;
  - A tiered approach to source term estimation provides for a balance between extent of testing, complexity of source term development, and end-user needs, thus allowing users to assess the costs associated with specific tests compared to the benefits gained based on their needs;
  - Current LEAF test methods do not include specifications specific to many classes of organic species; and
  - Important factors that are not addressed **specifically for organics** include:
    - Selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses, maintaining "dilute" boundary conditions (for monoliths)
    - Use in source terms does not address NAPLs and vapor phase transport

Discussion

- The LEAF framework allows you to run computational what-if scenarios.
- It is important to understand the difference between exposure conditions and field conditions and make the appropriate modifications.
- As shown in the figure below, Dr. Kosson was able to relate the first order reaction equation addressed in Dr. Werth's talk that identifies key drivers with elements of LEAF methods that permit measurement of key components to predict leaching of organics. LEAF leaching test methods are designed to measure the available content, liquid-solid partitioning and mass transfer rates to facilitate development of scenario-specific leaching source terms.



Can Approximate Leaching From Sorbed and NAPL Phases with a First Order Expression to Illustrate Dependence on Capacity of Each Phase for Pollutant and Mass Transfer Rate Constant

$$\underbrace{\theta_a \frac{\partial C_a}{\partial t} + \rho_N \frac{\partial \theta_N}{\partial t} + \rho_b \frac{\partial C_{SORB}}{\partial t}}_{\text{Available or Total}} = \theta_a D \frac{\partial^2 C_a}{\partial x^2} - q \frac{\partial C_a}{\partial x}$$

$$\rho_N \frac{\partial \theta_N}{\partial t} = -k_{La}\left(C_{SOL} - C_a\right)$$

LSP (Eq. leach test)

Mass transfer rate test

$$\frac{\partial C_{SORB}}{\partial t} = -k_s\left(C_{SORB} - K_F C_a^{N_F}\right)$$

Solute in NAPL governed by mass transfer to water:
-mass transfer rate constant, k_{La}
-aqueous solubility, C_{SOL}
-bulk aqueous concentration, C_a

Solute in solid governed by mass transfer to water:
-mass transfer rate constant, k_s
-sorbed phase concentration, C_{SORB}
-bulk aqueous phase concentration, C_a
-isotherm parameters, K_F, N_F

Courtesy C. Werth, U. Texas

Figure 2-1. Association of First Order Expressions to LEAF Leaching Tests

- There is a need to make the jump to practical implementation, recognizing constraints and coming to a reasonable compromise.
- Understanding pH dependence is important given that there may be situations where the pH could shift over time and therefore influence leachability (e.g., if there is a breakdown of organic matter in capped material and subsequent influx of dissolved organic matter capable of mobilizing organics). Changes in pH also may occur in response to biological processes.

3. WORKSHOP DISCUSSION

Additional discussion followed the conclusion of presentations and continued through the morning of Day 2. Discussion topics are summarized below and are organized by related topics.

3.1 Key Parameters that Drive Organics Leaching

- In measuring organic leaching, two systems are in effect: 1) a percolation system and 2) a diffusion system.
- There are many factors to consider, not all of which are always a concern; therefore, there is a need to identify the most important factors.
- Participants described external field considerations to consider when designing an organics leaching test:
  - Presence of a discrete organic phase;
  - Presence of SVOCs and VOCs;
  - Physical form of the material;
  - Groundwater velocity;
  - Water quality/composition;
    - DOC, which may vary seasonally
    - Ionic strength
    - pH
  - Bioavailability of study material;
  - Depth to groundwater;
  - Temperature;
    - Reasonably translating temperature fluctuations (laboratory vs. field)
    - Controlled conditions
  - Weathering may be a factor depending geographic location and whether waste is located above freeze-thaw line;
    - Diffusion
    - Extent of mixing/homogeneity
    - Durability testing
    - Diffusion changes based on degradation in material
    - Climate change factors, for example, seawater intrusion
  - Sampling to control microbial variables;
    - Representative and compositing sample collection; and
    - Consider whether remediation treatment itself could affect other areas of site (e.g., by changing the pH or adding DOC).

- Participants described analytical parameters that impact leaching of organic constituents:
  - pH;
  - Temperature;
  - Physical size and form of the material (granular or monolithic), which affects mass transport distances;
  - L/S or water contact time, velocity, and volume;

  - Composition of water used in testing;
    - Ionic strength
    - DOC
  - Test type: batch, column, or monolith;
  - Laboratory equipment compatibility and degradation (steel, coated glass, maybe Teflon);
    - Scale of apparatus
    - Preservation to prevent degradation
  - Local equilibrium;
  - Eluate composition;
  - Age of sample;
    - 90 day maximum age
  - Scale of apparatus;
  - Laboratory equipment suitable for testing organics;
  - Testing over time, to capture constituents that increase in solubility over time;
    - Design the leaching test to inform the decision maker about whether solidification/stabilization is an appropriate treatment
  - Location of material relative to boundary; and
  - Comparability of leaching test result with the analogous analytical test method (solid extraction).

- Other potentially problematic or confounding leaching factors include:
  - Reducing conditions cause chlorinated compounds to leach first;
  - Treatment may change diffusion behavior; and
  - Oily wastes present a challenge to evaluate because of physical constraints of the testing equipment and difficulties in interpreting the results.

3.2 Important Considerations for Methods Development

- Through the presentations, participants gained a better understanding about the fundamental mechanisms that affect the release of organics. The challenge now is to identify key drivers, balancing practicality and costs, while remaining scientifically defensible. A framework considering a phased or tiered approach may be appropriate to handle a broad range of waste materials.
- Participants expressed a desire to simplify the system, identify key parameters, and translate components into a first order reaction.
- The following questions are important to consider related to implementing an evaluation-based approach using both modeling and testing:
  - How much modeling?
  - How much leach testing?
  - Are we addressing materials evaluation?
  - Can modeling to isolate variability be developed?
- A participant noted that if a batch equilibrium test was conducted, one could run the test where the concentration in water was close to zero to permit the calculation of maximum flux out when the driving force concentration is known. One can relate max flux out to

calculate water out (percolation rate) to compare against a maximum contaminant level (MCL) (by transforming the first order rate equation to solve for MCL).

  - Only the bulk measurement is needed to understand the percolation rate

- A step function could be an input for comparative assessment (i.e., current state, remediated state or measure of treatment effectiveness).

- The difference of results between batch and flow-through systems was discussed and when to use each.
  - Column tests provide a practical dilution curve
  - Batch tests provide an indication for bounding modeling conditions and provide a worst case scenario where if concentrations are below regulatory thresholds there is no need to test further

- The following issues are related to organic leaching and leach testing:
  - Mobility of NAPL
  - Impact of mixing
  - Durability of treatment technology
  - Effective compliance monitoring at sites to assess treatment effectiveness
  - Quality assurance and quality control protocols to measure whether what was built was as designed
  - Performance specifications for ISS
  - Uniformity of solidification/stabilization amendment mixing)

- Other considerations related to test specifications:
  - An opportunity exists to modify existing methods to address material and head space requirements to meet the needs for both inorganic and organic substances whereby a single method could exist that addresses any required protocol deviations that may be substance-specific
  - Requirements for leaching tests and analytical techniques can be collectively addressed if a larger system is designed or a wider column is used
  - Cleanup levels with very low detection levels will require large volumes of waste material to adequately assess
  - In partitioning testing, it may be necessary to measure DOC in solid and aqueous phase as DOC will vary in different environments
  - If material contains a high levels of DOC (e.g., from natural organic matter), testing results will likely result in increases in mobility of organic compounds.

3.3 Considerations Related to Source Materials and Constituents of Concern

- Participants discussed how NAPLs will initially dominate phases, followed by partitioning environments, and then adsorption environments.
  - It is possible to flush the system or conduct an extraction to isolate NAPL and then separate from what is sorbed to understand the capacity of the fraction; otherwise, another approach is to use the total mass

  - If the fraction capacity is known, how fast the NAPL is flushed would indicate the mass transfer rate
  - The mass transfer rate could then be parameterized for a leaching test
  - MCL could be used with known volume of water to back calculate representative velocity – Representative velocity is the ratio of mass that comes out in a certain volume of water to predict retention time

- With regards to NAPL leaching:
  - A batch equilibrium test would evaluate mass transfer, and provide an upper limit (worst case)
  - A column test with pulverized material would estimate flux from stabilized material

- EPA presented preliminary data for organic contaminant groups found at Superfund sites to introduce the discussion of disposal scenarios and wastes that may require leaching testing for organics. Based on an analysis of Superfund decision documents (e.g., Records of Decision, Amended Records of Decision), both volatile and semi-volatile organic contaminants are common at Superfund sites. For example:
  - Halogenated volatile organic compounds (primarily chlorinated VOCs) are contaminants of concern (COCs) at approximately 70 percent of these sites
  - PAHs are COCs at half of the sites, and other semi-volatile organic (e.g., pesticides/herbicides, polychlorinated biphenyl (PCBs) are also common
  - Based on four recent years (Fiscal Years 2009-2012), 18 decision documents include a solidification/stabilization remedy for organic contaminants. Of these, about half have or may have NAPLs, and about half are using solidification/stabilization as a pretreatment prior to offsite disposal
  - Common contaminant distinguishing characteristics include:
    - Polarity
    - Hydrophobicity
    - Non-Ionic
    - Ionic (not likely a problem but pH can become an issue)
  - Priority organics of concern include:
    - Organo-metallic compounds
    - Combined contaminants
    - Mercury

- The 40 constituents regulated in the 1990 Toxicity Characteristic (TC) Rule may be a good starting point for organic constituents for which to consider testing. Note that the TC Rule was developed at a time when MSW landfills did not have liners and many industries of today did not exist; therefore, some of the underlying assumptions are dated.
  - Could initially consider the basic parameters that govern the release of the majority of organic contaminants and situations, recognizing there will be exceptions, and then design a flexible system that can accommodate most constituents and matrices

- Some organic contaminants are recalcitrant, transform in the environment, and are toxic at low levels; the potential occurrence and toxicity of daughter products is also a concern, as well as preventing them from mobilizing into groundwater.

- Participants briefly discussed scenarios where leaching of organics may be of concern:
  - Leaching related to industrial waste is the focus EPA's Resource Conservation and Recovery Act (RCRA) program
  - Waste pharmaceuticals (expired products) management was mentioned, but workshop participants noted direct exposure is also a concern in addition to leaching
  - The need to identify specific examples of scenarios that may be most problematic for leaching was discussed
  - From an EU perspective, a lesson learned was to develop methods based on the material rather than the application to reduce the number of duplicative test methods

- Participants discussed scenarios where leach tests would be needed:
  - For Superfund, EPA is managing old contaminated sites
  - For RCRA, EPA is dealing with newly generated waste. Focus is primarily on the existing list of approximately 40 constituents listed in the regulation, but also dealing with industries that did not exist at the time of regulation. The primary focus is on industrial waste

- Could consider worst case scenarios (e.g., weathering scenario that includes degraded [crumbled] source material) from a chemical and physical stability perspective when designing leaching tests to account for a wide range of external conditions to ensure test results reflect worst case conditions.
- Concrete is another example of a material that often cracks under external conditions and may be best represented by a monolithic sample in the laboratory, rather than a pulverized sample. The movement of constituents through concrete depends on the movement of water by gravity and interconnectedness of cracks.
- Regarding representative site samples, Dr. van der Sloot indicated that research from a heterogeneous MSW landfill site showed that the composition of the leachate was rather homogeneous and consistent throughout the face of excavation.
- Testing a composite sample by the full tests in conjunction with single step tests (own pH batch) on spatially distributed samples can be used to place site-wide variability in perspective to the more detailed information provided by the full testing of a composite sample. This approach provides for detailed information at reasonable cost.
- Laboratory quality assurance and quality control procedures, including sample preparation techniques and separation procedures, are important.
- Conducting training and outreach (e.g., through webinars) for both policymakers, regulators and laboratories could improve stakeholders' understanding of the factors that affect organics leaching and important nuances related to conducting leaching tests.

3.4 Applicability of LEAF Methods

- Participants reiterated that a leaching framework is a scientific evaluative tool that provides more accurate characterization of leaching that can be considered within a regulatory decision framework.

- It is important to consider the purpose of the leaching test (define how the data will be used), desired testing output, and define a decision pathway such as an elution curve, L/S equilibrium, mass transfer, or NAPL concentration.
- The LEAF How-to Guide that is currently being developed for inorganic constituents describes the suite of tests, the use of simplified screening level testing, as well as more detailed characterization to compare results to known thresholds. The document offers guidance on how to select the appropriate test for the material of interest. LEAF methods can be useful for evaluating multiple inorganic contaminants with unknown release potential.
- Suggested applications of a leaching test framework at waste cleanup sites included:
  - To estimate contribution of a source material to mass flux and transport, given heterogeneous distribution of contaminants often seen at contaminated sites;
  - To support treatability studies and provide insight on the best combination of remedial technology to use; and
  - To support performance monitoring.

- A leaching test framework could be useful to make a “go” or “no go” decision for whether to apply stabilization treatment.
  - Leaching test methods may be used to estimate release rate at the physical boundary of the treated/stabilized waste as an indicator of performance

- Participants were reminded that leaching test methods evaluate the leaching potential of the *source material*; leach test results are then used in fate and transport modeling to predict future groundwater concentrations.
- The LEAF testing methods are basic scientific tools that offer results that can then be evaluated within the context of a specific scenario. The existing LEAF framework established for inorganic contaminants is flexible enough that the specific context of the waste material can be considered **after** generating test results. This logic is in contrast to TCLP where the context of the waste material is considered **prior to** testing.
- Participants discussed how to evaluate whether methods adequately predict leaching. Dr. van der Sloot noted that the EU does not currently have data on organics to compare what was predicted through testing and modeling to what was observed in the field, but through the sustainable landfill project such data should be available in 2016.
  - It would be best to integrate laboratory testing, modeling, and field results to assess the accuracy of predictions based on laboratory data (analogous to the approaches taken for inorganic contaminants, e.g., Lab-to-Field study). No or very limited data is available today.

Appendix A

Workshop Agenda

USEPA Workshop on Considerations for Developing Leaching Test Methods for Semi- and Non-Volatile Organic Compounds

Workshop Agenda

Presentation/Discussion	Objective(s)	Presenter or Moderator
Day 1: September 16, 2015 (Wednesday)		
Welcome, Logistics, and Introductions		Linda Fiedler, OSRTI
Workshop Objectives	Purpose of workshop for ORCR and OSRTI	Greg Helms - ORCR Robin Anderson - OSRTI
Key Parameters or Drivers that Govern the Source Term at the Unit Boundary for Subsurface Leaching of Semi- (SVOC) and Non-Volatile (NVOC) Organic Chemicals	Identify factors that either retard or enhance leaching of semi- and non-volatile organics (e.g., adsorption/ desorption/multi-phase partitioning, equilibrium vs diffusion controlled release).	Charles Werth, University of Texas – Austin
What is our field test experience related to organics leaching? *Estimation of Source Term Concentration for Organics Contained on Superfund Sites*	What problems are being encountered in real-world applications from estimation of source term concentration at the unit boundary using present methods?	Craig Benson, University of Virginia Ed Barth, ORD/NRMRL
European and International Standards on Leaching of Organic Contaminants, Available Tools and Recent Developments for Assessment of Organic Contaminants	Provide understanding of what currently is in use and the status of standardization and validation.	Hans van der Sloot, Consultant (retired from the Energy Research Center of the Netherlands)
What is LEAF for inorganics? What lead to its development? What was the process and timeline for developing and validating the methods?	Provide understanding of work done to develop and validate LEAF.	Greg Helms, ORCR Susan Thorneloe, ORD/NRMRL
What laboratory methods are available to measure the factors that impact leaching of semi- and non-volatiles?	Identify laboratory methods that measure the factors that impact organics leaching.	Greg Helms (Moderator)
Existing Tools and Limitations to Address Leaching of Organic Species	Describe capabilities of existing leach test methods to measure factors that impact organic leaching, and which factors existing methods cannot address.	David Kosson, Vanderbilt University
Day 2: September 17, 2015 (Thursday)		
Review of Day 1		Greg Helms, ORCR
What are the capabilities of existing leach test methods to measure factors that impact leaching of semi- and non-volatiles?	Discuss capabilities of existing leach test methods to measure factors that impact organic leaching, and which factors existing methods cannot address.	Greg Helms (Moderator)
What are the source materials, matrices and constituents of potential concern and how are these considered in determining the reference materials?	Identify reference materials, representative matrices, and constituents.	Dave Jewett, ORD (Moderator)
Closing Remarks and Adjournment		Linda Fiedler

Appendix B

Workshop Participants

USEPA Workshop on Considerations for Developing Leaching Test Methods for Semi- and Non-Volatile Organic Compounds
Workshop Participants List

Name	Organization
USEPA	
Robin Anderson	Office of Superfund Remediation and Technology Innovation (OSRTI)
Linda Fiedler	OSRTI
David Bartenfelder	OSRTI
Greg Gervais	OSRTI
Pamela Barr	OSRTI
Jeff Heimerman	OSRTI
Kathy Davies	Region III
Greg Helms	Office of Resource Conservation and Recovery (ORCR)
Schatzi Fitz-James	ORCR
Shen-Yi Yang	ORCR
Christie Langlois	ORCR
Susan Thorneloe	Office of Research and Development (ORD)/National Risk Management Research Laboratory (NRMRL) (Research Triangle Park)
David Jewett	ORD/NRMRL (Ada)
Ed Barth	ORD/NRMRL (Cincinnati)
Kelly Smith	ORD/NRMRL (Cincinnati)
OTHER PARTICIPANTS	
David Kosson	Vanderbilt University
Hans van der Sloot	Consultant (retired from the Energy Research Center of the Netherlands)
Craig Benson	University of Virginia
Charley Werth	University of Texas (Austin)
Molly Rodgers	Eastern Research Group, Inc. (ERG) (EPA Contractor)
Katie Connolly	ERG (EPA Contractor)

Appendix C

Workshop Presentations

Key parameters or drivers that govern the source term at the unit boundary for subsurface leaching of semi- (SVOC) and non-volatile (NVOC) organic chemicals

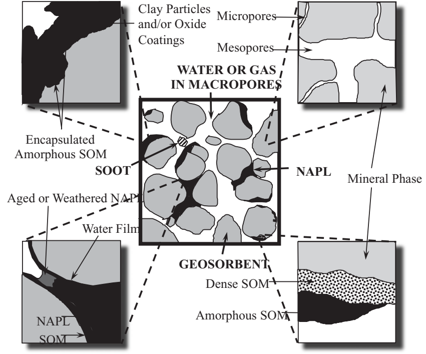
Charles Werth

Civil, Architectural, and Environmental Engineering

UT Austin

VOCs, SVOCs and NVOCs Are in Air, Water, Solid, & NonAqueous Liquid Phases

Solid Phases Include:
1) Natural Components of Soils and Sediments
2) Sorption Amendments to Sequester Pollutants
3) Precipitates that Encapsulate Pollutants



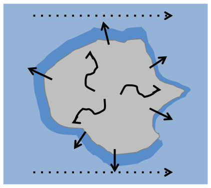
Luthy et al., ES&T, 1992

Leaching is Controlled By the Capacity of the Different Phases for the Organic of Interest, and the Mass Transfer Rate from Each Phase

This Can Be Expressed Mathematically By the Simplified Expression Below For Pollutant Removal Mechanisms in Leachate

$$\theta_a \frac{\partial C_a}{\partial t} + \rho_N \frac{\partial \theta_N}{\partial t} + \rho_b \frac{\partial C_{SORB}}{\partial t} = \theta_a D \frac{\partial^2 C_a}{\partial x^2} - q \frac{\partial C_a}{\partial x}$$

Solute accumulation in leachate	Solute accumulation in NAPL	Solute accumulation in solids	Solute dispersion /diffusion in leachate	Solute advection in leachate

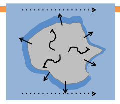


Mass Transfer Between Phases: ∿ →

Mass Transport in Water: ⋯⋯⋯→

Can Approximate Leaching From Sorbed and NAPL Phases with a First Order Expression to Illustrate Dependence on Capacity of Each Phase for Pollutant and Mass Transfer Rate Constant

$$\theta_a \frac{\partial C_a}{\partial t} + \rho_N \frac{\partial \theta_N}{\partial t} + \rho_b \frac{\partial C_{SORB}}{\partial t} = \theta_a D \frac{\partial^2 C_a}{\partial x^2} - q \frac{\partial C_a}{\partial x}$$



$$\rho_N \frac{\partial \theta_N}{\partial t} = -k_{La}\left(C_{SOL} - C_a\right)$$

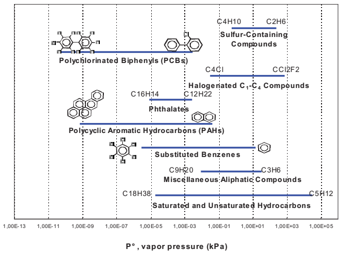
Solute in NAPL governed by mass transfer to water:
-mass transfer rate constant, k_{La}
-aqueous solubility, C_{SOL}
-bulk aqueous concentration, C_a

$$\frac{\partial C_{SORB}}{\partial t} = -k_s\left(C_{SORB} - K_F C_a^{N_F}\right)$$

Solute in solid governed by mass transfer to water:
-mass transfer rate constant, k_s
-sorbed phase concentration, C_{SORB}
-bulk aqueous phase concentration, C_a
-isotherm parameters, K_F, N_F

Air Phase Holds Little SVOCs or NVOCs Relative to Solid and NAPL Phases, and Contributes Little to Leaching

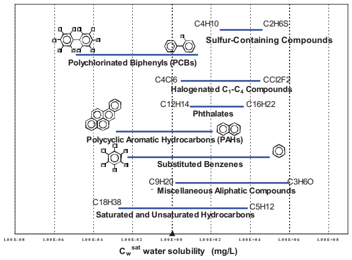
- Capacity of air to hold contaminants is very small (<< 1%)
  - low fugacity capacity, or low P^{sat}
- Mass transfer between air and leachate water is relatively fast
  - seconds to minutes



(modified from Schwarzenbach et al., 1993)

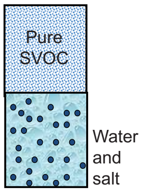
Water Phase Represents Leachate, and Serves As a Pollutant Sink For Other Phases As It is Replenished

- Capacity of water to hold SVOCs and NVOCs is typically small
- Is affected by presence of salts, cosolvents, dissolved organic matter (DOM), & colloids



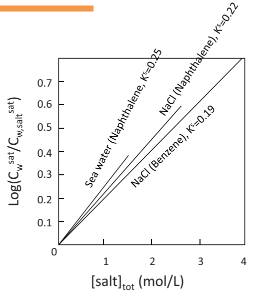
(modified from Schwarzenbach et al., 1993)

Increasing Ionic Strength Decreases the Aqueous Solubility



$$\log\frac{C_w^{sat}}{C_{w,sal}^{sat}} = K^S C_{sal}\left[\frac{mol}{L}\right]$$

$$C_{w,sal}^{sat} = C_w^{sat}\exp\left(-K^S C_{sal}/2.3\right)$$



K^S = "salting out" constant, (~ 0.15-0.3; e.g. Benz = 0.19, Naph = 0.22 in NaCl solutions)

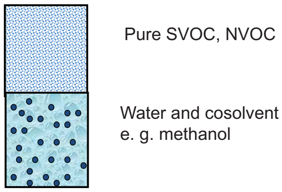
C_{wsal}^{sat} = saturation concentration in water with salt [mol L^{-1}; g L^{-1}]

C_w^{sat} = saturation concentration in distilled water [[mol L^{-1}; g L^{-1}]

C_{sal} = salt concentration [mol L^{-1}]

(Schwarzenbach et al., 1993)

Increasing Co-Solvent Concentration Increases the Aqueous Solubility



$$\log\frac{C_{w,Co}^{sat}}{C_w^{sat}} = \sigma f_{Co}$$

$$C_{w,Co}^{sat} = C_w^{sat}\exp(\sigma f_{Co})$$

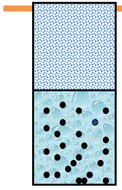
$C_{w,Co}^{sat}$ = saturation concentration in presence of cosolvent [mol/L; g/L]

f_{Co} = fraction of cosolvent [-]

σ = solubilization constant [-] or "cosolvency power"

σ increases with decreasing water solubility of the cosolvent σ (increasing hydrophobicity K_{ow}.)

Increasing Dissolved Organic Matter Concentration Increases the Apparent Aqueous Solubility



$$\frac{C_{w,DOC}^{sat}}{C_w^{sat}} = 1 + f_{DOC}K_{DOC}$$

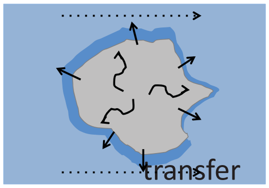
$$C_{w,DOC}{}^{sat} = C_w{}^{sat} + C_w{}^{sat} f_{DOC}K_{DOC}$$

$C_{w,DOC}^{sat}$ = saturation concentration in presence of DOC [mol L^{-1}; g L^{-1}]
f_{DOC} = fraction of dissolved organic carbon [kg L^{-1}] (e.g.: Humic-, fulvic acids, surfactants)
K_{DOC} = partitioning coefficient organic carbon / water (L kg^{-1}).

K_{DOC} increases with decreasing water solubility (increasing K_{ow}) of the solute and increasing hydrophobicity or molecular weight the DOC ($K_{DOC} \leq K_{ow}$)

Soils, Sediments, and Geosorbent Amendments Can Sorb Large Amounts of VOCs, SVOCs and NVOCs, and Slowly Release Them

- Leaching capacity of soils and sediments depends on soil/sediment properties and chemical properties
- Leaching rate depends on concentration gradient between sorbed phase and water, and mass rate constant



$$\frac{\partial C_{SORB}}{\partial t} = -k_s\left(C_{SORB} - K_F C_a^{N_F}\right)$$

Equilibrium Capacity of These Solids is Determined by Composition

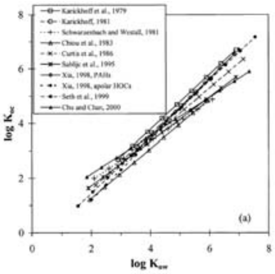
- There are both absorption (or partitioning) and adsorption environments
  - Partitioning environments
    - Relatively unweathered and/or recent soil organic matter
    - Capacity to hold contaminants can be large, and depends on amount of this organic matter
    - Mass transfer from this soil organic matter is relatively fast (hours to days) compared to soil adsorption environments
      - Can assume equilibrium partitioning at low water flow rates
      - At higher water flow rates can approximate as first order

Capacity of Soil Partitioning Environment for Contaminants Can be Estimated

- Relationship between concentrations in water and recent soil organic matter is often ~linear
  - $K_d = C_{sorbed} / C_{water}$
- K_d can be directly related to amount of organic matter and hydrophobicity of chemical
  - $K_d = K_{oc} * f_{oc}$
  - Where
    - $K_{oc} \sim K_{ow}$

Many Relationships K_{oc} and K_{ow} Have Been Proposed and There is Lots of Supporting Data

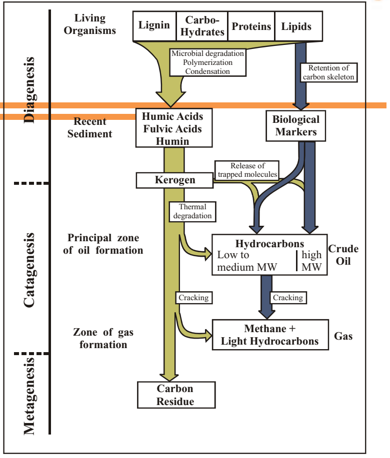
- The relationship by Karickhoff et al. (1979) is perhaps the most common
  – $\log(K_{oc}) = 1.00 * \log(K_{ow}) - 0.21$



Adsorption Environments Are More Challenging to Characterize

- Adsorption Environments
  – Thermally altered and/or condensed organic matter and black carbon
    - E.g., Soot, charcoal, kerogen
  – Mineral Surfaces, e.g., Clays
  – Composite Amendments
    - Organoclays, activated carbon embedded in cements
- Capacity to hold contaminants can be very large, and depends on many factors, e.g., microporosity, surface area, and surface charge
- Mass transfer from adsorption environments can be very slow
  – Leaching for months to years to decades

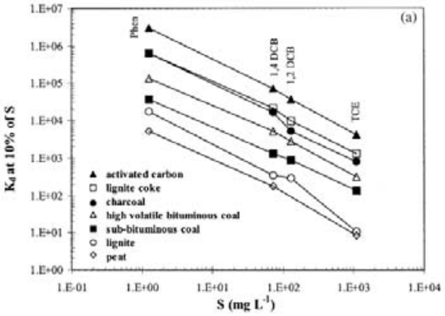
Natural Materials Become Thermally Altered Over Geologic Time With Burial



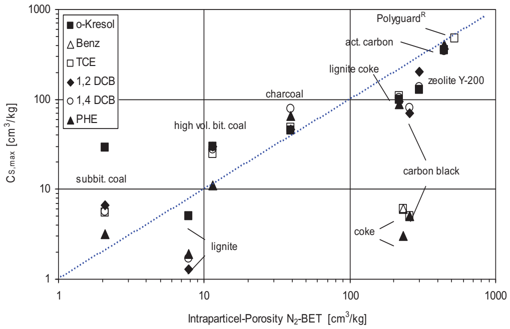
Some Thermally Altered Sorbents Are Anthropogenic in Origin

- Soot
  – Combustion product of hydrocarbons
- Char
  – Solid phase residual from biomass burning
- Activated Carbon
  – Solid phase residual from biomass burning, followed by activation by exposure to acid, oxidizing, or reducing conditions at elevated temperature

The Extent of Adsorption Varies with Sorbate and Sorbent



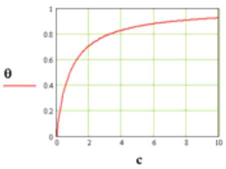
The Extent of Sorption Has Been Related to Surface Area, Pore Volume, and Microporosity



HOCs from water at 20°C, N_2 from gas phase at –196°C

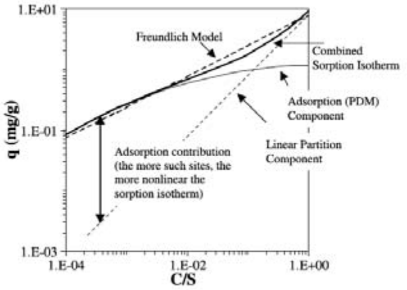
Capacity of Adsorption Environments for Contaminants Must Be Measured

- Relationship between water and soil concentrations is typically nonlinear
  - The Freundlich equation is often used to model data
    - $C_{sorbed} = K_F \, C_{water}^{n_F}$
  - The Langmuir isotherm equation is also used
    - $C_{sorb}/C_{sorb,max} = K_{ads}C_{water} / (1 + K_{ads} \, C_{water})$



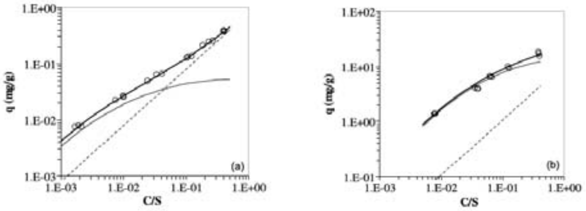
Both Partitioning and Adsorption Environments are Often Present in Solids

- Two-part models used to capture sorption to both environments simultaneously
  - $q_T = q_{ab} + q_{ad}$



Allen-King et al., AWR, 2002

The Contribution of Partitioning and Adsorption Environments Varies Widely Depending on the Sorbent



- (left) Pyrene sorption to the silty/clayey aquitard material and (right) 1,4-dichlorobenzene sorption to subbituminous coal

Allen-King et al., AWR, 2002

Mass Transfer from Adsorption Environments is Thought to Be Diffusion Controlled

- Contaminants diffuse through:
  - tortuous matrices of inflexible organic matter
  - pores in minerals and between cemented mineral fragments
- In some cases a retarded diffusion concept has been invoked
  - E.g., Diffusion through internal pores of particle that is retarded by sorption to pore walls
  - Not a practical modeling approach

Slow Mass Transfer is Often Approximated with a First Order Mass Transfer Expression

- Recall the single 1^0 mass transfer expression

$$\frac{\partial C_{SORB}}{\partial t} = -k_s\left(C_{SORB} - K_F C_a^{N_F}\right)$$

- In some cases two or more first order expressions are used in parallel to describe mass transfer from multiple adsorption environments

$$\frac{\partial C_{SORB,Part}}{\partial t} = -k_{s,Part}\left(C_{SORB,Part} - K_d C_a\right)$$

$$\frac{\partial C_{SORB,Adsorb}}{\partial t} = -k_{s,Adsorb}\left(C_{SORB,Adsorb} - K_F C_a^{N_F}\right)$$

Poorly Sorbing Solid Phases Are Also Present in Samples Analyzed for Leaching

- Cements used to encapsulate solid waste materials like contaminated soils
- Oxidized potassium permanganate that precipitates around soil and NAPL phases and creates a diffusion barrier
- Composites of these materials that also contain adsorbents
  - E.g., activated carbon embedded in cements

Precipitates Create Serial Barriers to Leaching

- Reduces permeability so increases diffusion length scale in stagnant water
- Create a solid barrier that only allows contaminant release through hindered diffusion
  - If precipitates contain adsorbents, then have retarded diffusion

---

Contribution of Contaminants Originally in Trapped NAPL to Leachate Can Be Large

- Can be a pure NAPL, or a NAPL mixture
- Mass transfer is typically described by first order process

$$\rho_N \frac{\partial \theta_N}{\partial t} = -k_{La}\left(C_{SOL} - C_a\right)$$

Pure NAPL

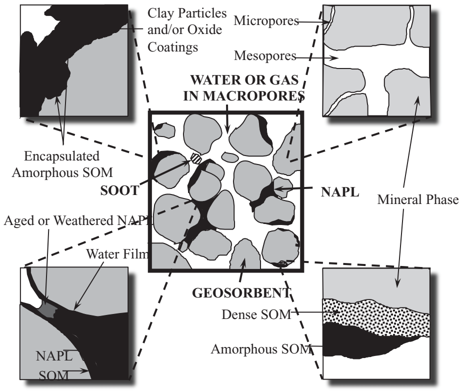
$$\rho_N \frac{\partial \theta_{N,i}}{\partial t} = -k_{La,i}\left(x_i C_{SOL,i} - C_{a,i}\right)$$

NAPL mixture, x_i=mole fraction

- Mass transfer from NAPL is relatively fast compared to adsorption environments
  - Can be limiting if diffusion length scales through low permeability zones are large and at high water velocities

---

Recall the Different Phases That Contribute to Leaching



Mass Transfer Processes Can Be in Parallel or in Series

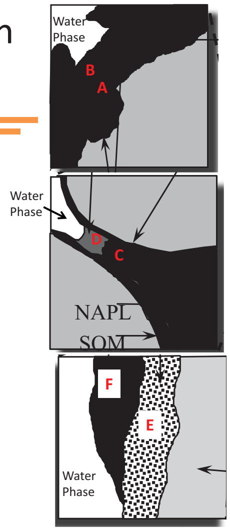
A → B → Water Phase (Series)

C → D → Water Phase (Series)

E → F → Water Phase (Series)
↘ Water Phase

(Parallel)

(Parallel)

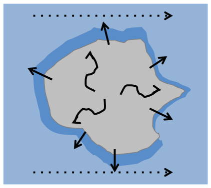


Many Models Have Been Developed to Describe These Mass Transfer Processes

- Recall the simple leaching model with mass transfer in parallel that I showed earlier

$$\theta_a \frac{\partial C_a}{\partial t} + \rho_N \frac{\partial \theta_N}{\partial t} + \rho_b \frac{\partial C_{SORB}}{\partial t} = \theta_a D \frac{\partial^2 C_a}{\partial x^2} - q \frac{\partial C_a}{\partial x}$$

$$\left.\begin{array}{l} \rho_N \dfrac{\partial \theta_N}{\partial t} = -k_{La}\left(C_{SOL} - C_a\right) \\ \\ \dfrac{\partial C_{SORB}}{\partial t} = -k_s\left(C_{SORB} - K_F C_a^{N_F}\right) \end{array}\right\} \text{In Parallel}$$



The Capacity and Mass Transfer Rate Constants for Each Phase Determine the Relative Contributions to Leaching

Phase	Capacity	Mass Transfer Rate
Air	Low	Fast
Water	Low	NA
Soil (Partitioning)	High	Medium/Fast
Soil (Adsorption)	Very High	Very Slow
Black Carbon	Very High	Very Slow
Composites	Medium/High	Slow/Medium
Cement	Low	Slow/Medium
OrganoClays	High	Slow/Medium
NAPL	High	Medium/Fast

The Contact Time of Water, or Water Flow Rate, Determines How Far Mass Transfer Processes Are From Equilibrium

- Can use dimensional numbers to evaluate
- First Damkohler Number, Da_1
  - $Da_1 = L\, k_s / v$
    - L=length of leachate sample along flow direction (L)
    - k_s = mass transfer rate constant (t^{-1})
    - v = average linear velocity ($L\, t^{-1}$)
  - Large Da_1, close to equilibrium
  - Small Da_1, mass transfer important

Issues with Organic Transport in Physical Models of Barrier Systems

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University of Virginia
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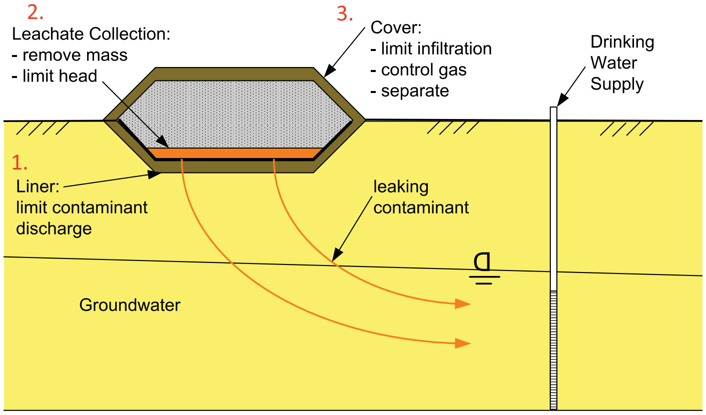
Modern Waste Containment Systems



2.
Leachate Collection:
- remove mass
- limit head

3.
Cover:
- limit infiltration
- control gas
- separate

Drinking
Water
Supply

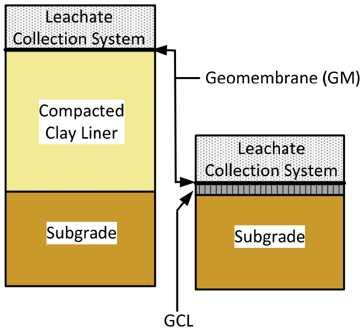
1.
Liner:
limit contaminant
discharge

leaking
contaminant

Groundwater

Highly engineered systems that are protective of the environment

Single Composite Liner Systems



Leachate Collection System

Compacted Clay Liner

Subgrade

Geomembrane (GM)

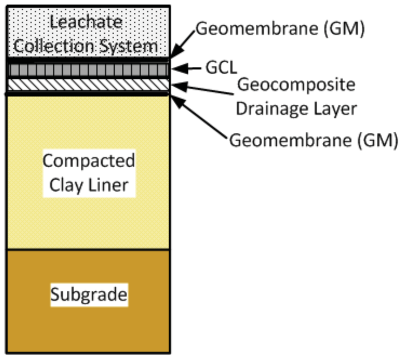
Leachate Collection System

Subgrade

GCL

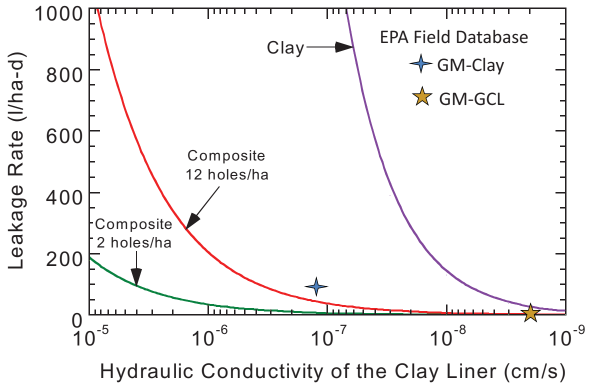
- Synthetic geomembrane and natural clay-based layer work synergistically and have very low leakage rates.
- Exceptionally strong track record for wide range of waste streams world wide.
- Very long lifetimes expected, 1000+ yr

Double Composite Liner Systems

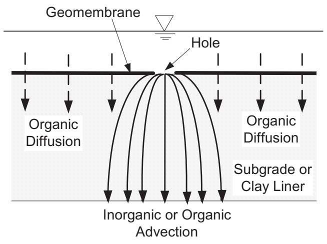


- Double systems with leak detection essentially eliminates release of constituents.
- Found to be extremely effective worldwide, but conservatism may not be necessary.

Liner Leakage

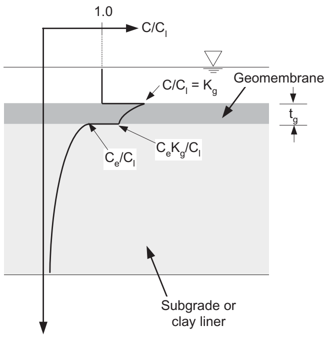


Advective-Diffusive Transport through Holes



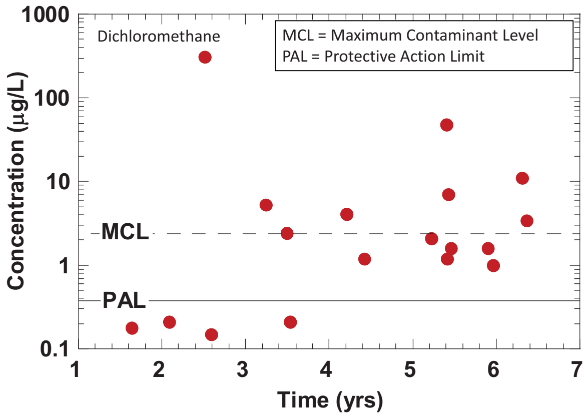
Requires 3-D numerical transport analysis

Diffusive Transport through Intact Geomembrane

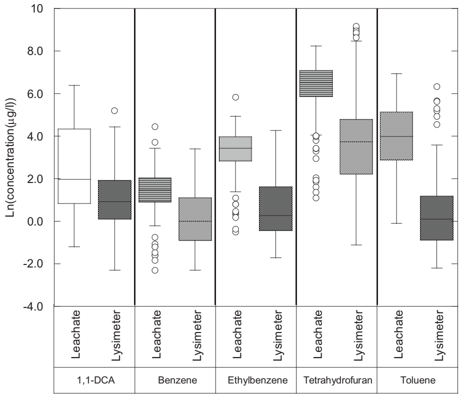


Requires 1-D numerical transport analysis

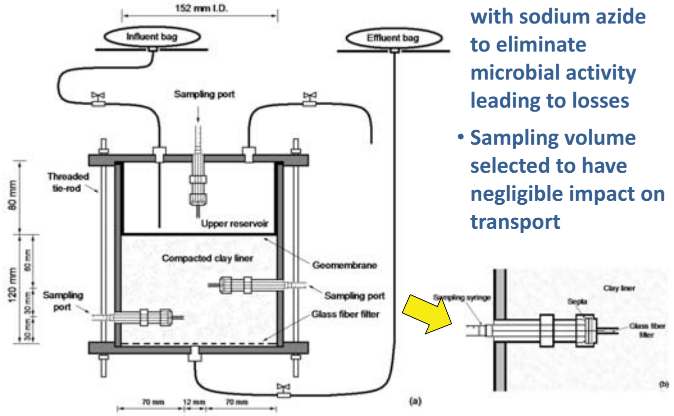
VOCs in Lysimeters Beneath Liners in Wisconsin



Leachate & Lysimeter Concentrations

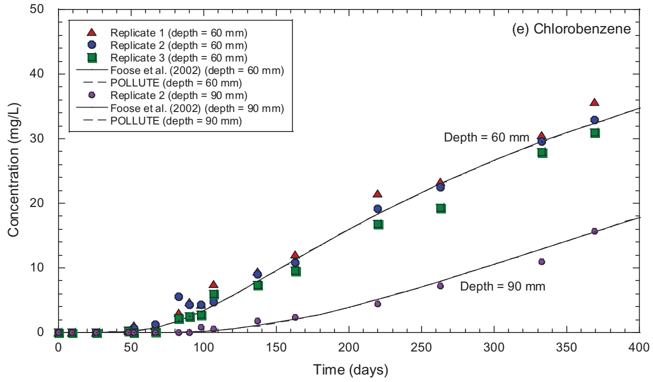


Composite Liner VOC Transport Experiments

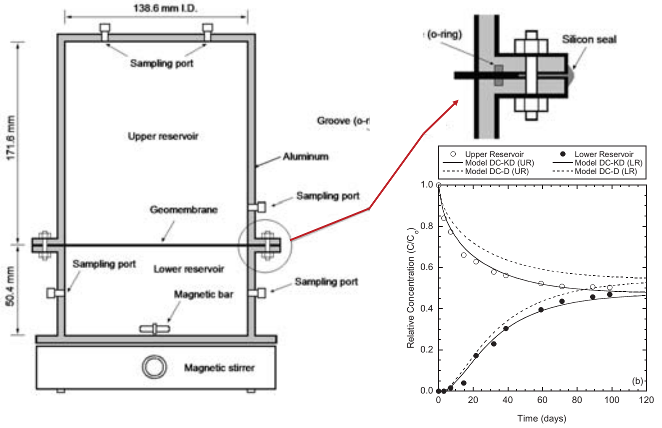


- Reservoir spiked with sodium azide to eliminate microbial activity leading to losses
- Sampling volume selected to have negligible impact on transport

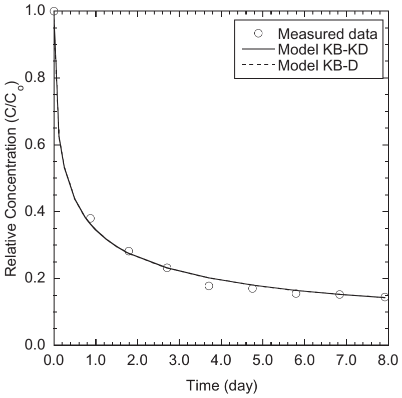
VOC Concentrations in Clay Liner with Model Predictions



Dual Compartment Tests for Diffusion (D_g) & Partition (K_g) Coefficients for Geomembrane

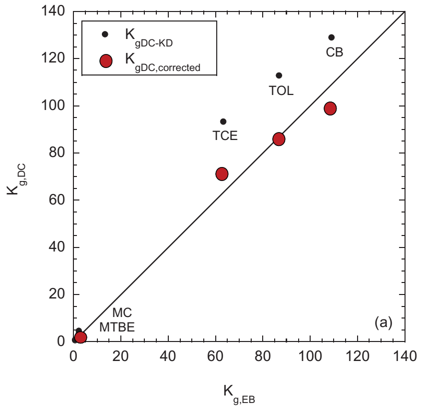


Kinetic Batch Tests for Diffusion (D_g) & Partition (K_g) Coefficients for Geomembrane



- Model fits provides D_g & K_g.
- Acceptable if geomembrane is homogeneous material.

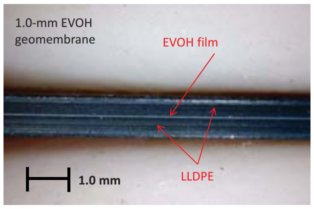
Partition (K_g) Coefficients for Geomembrane: Double Compartment vs. Kinetic Batch

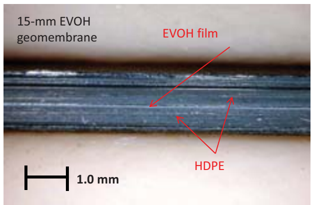


- Bias from double compartment due to loss in flange.
- Eliminating loss results in good agreement.

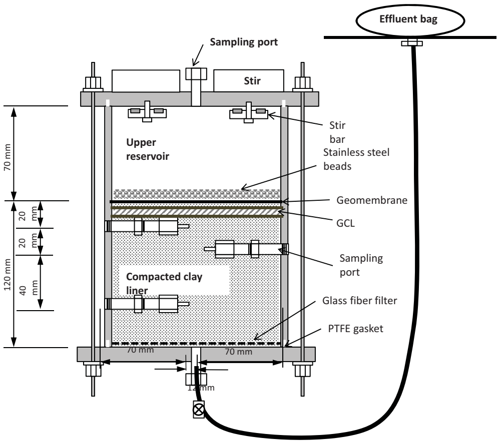
Co-Extruded EVOH Geomembrane

- Ethyl vinyl alcohol (EVOH) core
- PE jacket (LLDPE or HDPE)
- Tie sheet to bind EVOH and HDPE

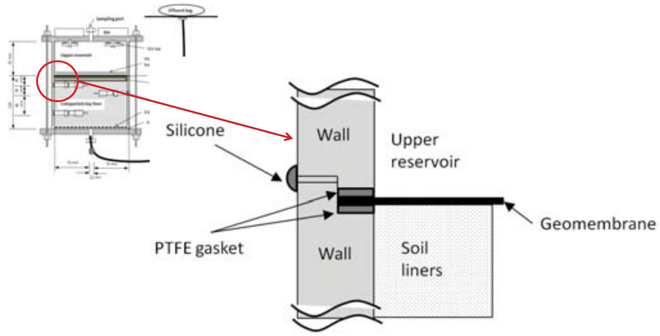




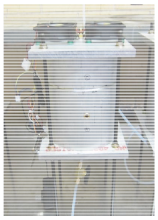
Columns for EVOH Composite Liner Tests

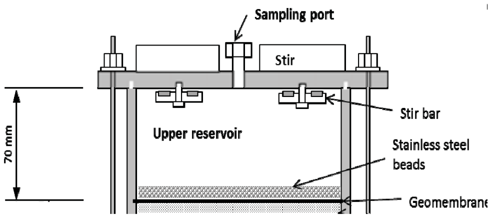


New Flange Design



Well Mixed Upper Boundary

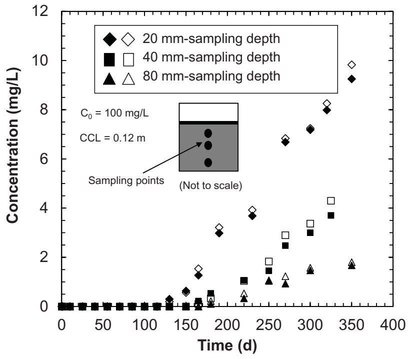




Column Tests for EVOH Composite Liner Experiments

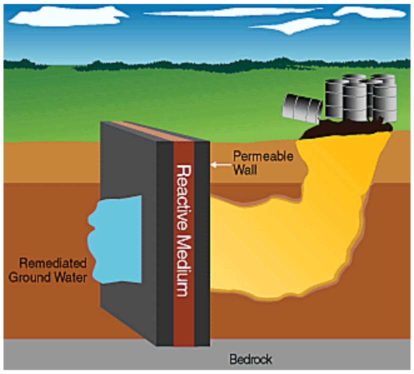
PTFE bag including DDI water to apply hydraulic gradient to liner

TCE Concentrations in Clay Component of EVOH Composite Liner



- Repeatable.
- Good agreement with theory (not shown).

Reactive Barrier Strategy for Creosote



For creosote containment:

- Impermeable to DNAPL
- Permeable to ground water
- Remove PAHs dissolved in ground water flowing thru barrier.

Create a **V**ariably **P**ermeable **R**eactive **B**arrier – **VPRB**

What are Organoclays?

- Na bentonite (high montmorillonite content) exchanged with quaternary ammonium cations
- Cation characteristic binds molecule to clay surface. Organic component provides sorption site for PAHs
- Benzyltriethylammonium or hexadecyltrimethyl-ammonium

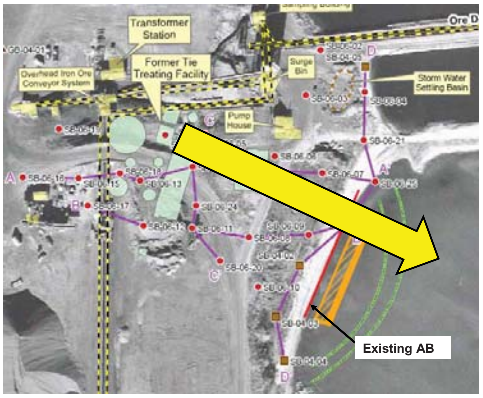
Creosote Remediation – Michigan's Upper Peninsula

UP is a major source of iron ore.

Load iron ore onto ships for transfer to Chicago rail terminals.

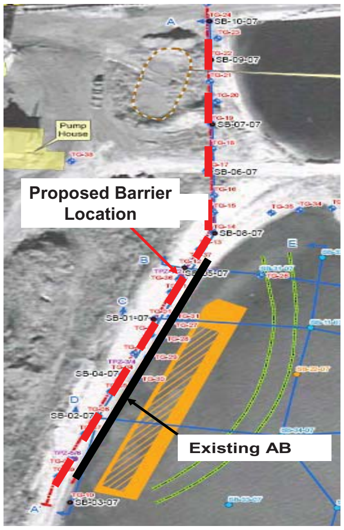
Creosote used for railroad tie treating for iron ore lines.

Site Aerial View – Iron Ore Loading Facility
Upper Peninsula, Michigan



Railroad tie-treating facility where ties soaked in creosote (wood preservative).

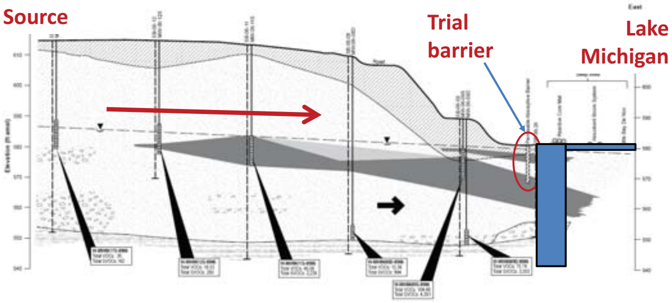
Creosote residue from pits migrated thru subsurface & ultimately to lake.



Full-Scale Barrier

- Cover broad area to ensure all stringers are captured.
- Key into underlying clay aquitard.
- Polish effluent into Lake Michigan using subaqueous cap (organoclay coremat)

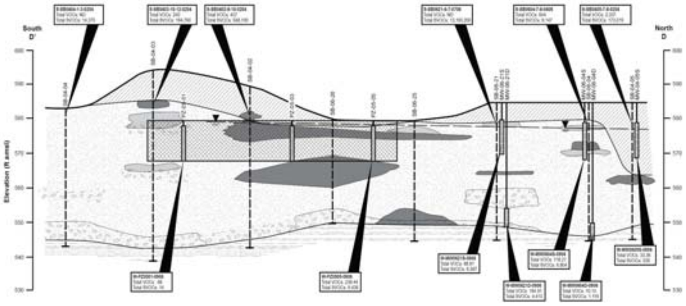
Cross-Section Parallel to Flow



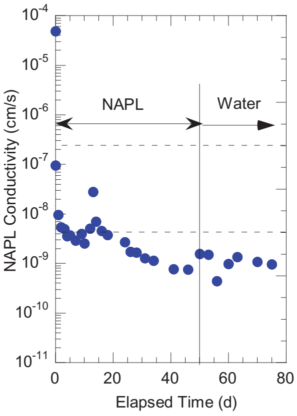
Creosote discharging into lake creating "hot spots"

Ground water with dissolved PAH emanating into Lake Michigan

Cross-Section Perpendicular to Flow (looking upstream)



Hydraulic Conductivity Record



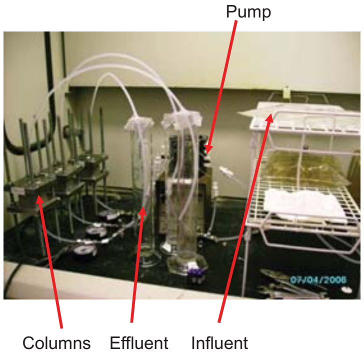
Material	Hydraulic Conductivity (cm/s)
PM-199	$7.6\text{x}10^{-10}$ (for DNAPL) $9.6\text{x}10^{-10}$ (for water)
ET-1	$3.4\text{x}10^{-9}$
EC-199	$3.7\text{x}10^{-10}$ (for DNAPL) $1.1\text{x}10^{-9}$ (for water)
0% PM-199	$4.1\text{x}10^{-5}$
10% PM-199	$2.6\text{x}10^{-6}$
25% PM-199	$8.6\text{x}10^{-9}$
50% PM-199	$2.8\text{x}10^{-9}$

- ***Nearly im*permeable to DNAPL, but varies by clay.**
- **Can obtain similar low K with a sand blend.**

PM-199

ET-1

Aqueous-Phase Column Experiments



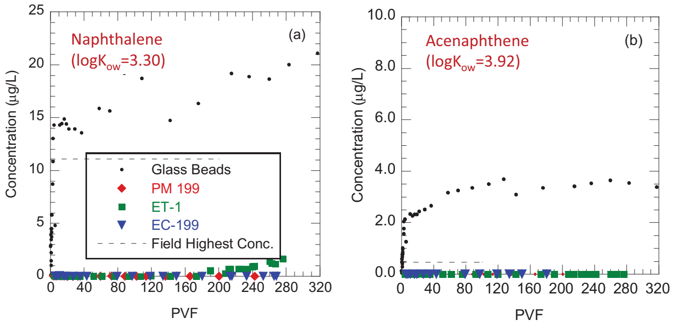
Objective:

- **Evaluate organoclay under flow-through conditions**
- **Determine if parameters from batch tests provide reasonable predictions of sorption under flow through conditions.**

Breakthrough from Batch Adsorption Data (time to breakthrough at MCL)

Thickness of Barrier (m)	Material	PVF to MCL in Column Test	Longevity (yr) at 1 m/yr
0.5 m	PM-199	1843	307
	ET-1	148	24
	EC-199	920	154
	25% PM-199	461	77
	50% PM-199	922	154
1.0 m	PM-199	1843	614
	ET-1	148	49
	EC-199	920	307
	25% PM-199	461	154
	50% PM-199	922	307

Effluent from Organoclay Columns



- **Breakthrough of naphthalene (above DL) in ET-1 organoclay (lowest OC fraction) ~ 190 PVF**
- **No other breakthrough in 10 months.**

Summary Remarks

- Experimental apparatus can have a significant effect on outcome of transport experiments with hydrophobic organic contaminants at low concentrations.
- Evaluate materials beforehand as sinks for organic contaminants, even in the most obscure components. Avoid false negative.
- Evaluate apparatus for unintended sinks for organic contaminants.
- Develop expectations for outcomes of experiments to provide reality check on data.

Acknowledgements

- US Department of Energy, Environmental Management, Consortium for Risk Evaluation with Stakeholder Participation (CRESP)
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- Wisconsin Department of Natural Resources
- Kuraray America Inc.
- CETCO
- Union Pacific Railroad Corporation

Estimation of Source Term Concentration for Organics Contained on Superfund Sites

Ed Barth, PhD, PE, CIH, RS, BCEE

National Risk Management Research Laboratory (NRMRL)

Office of Research and Development

Cincinnati, OH

Purpose of Presentation

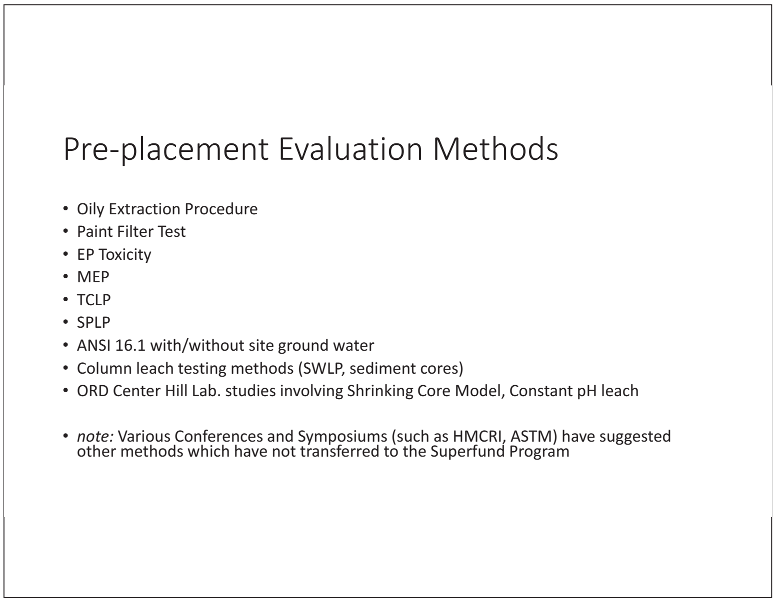
- Briefly describe and present examples to illustrate how EPA Regional Offices (Superfund Program) and EPA Office of Research and Development (ORD) have historically and currently evaluated “the source term at the unit boundary” for remedies involving on-site containment of organic materials (including DNAPLs)

Various Types of DNAPL Sites

- Petroleum
- Wood Preserving (Creosote, PCP)
- MGP
- Organic Compound Formulation Industries
- Waste Recycling Industries

Remediation options for DNAPL contaminated soil *and sediments*

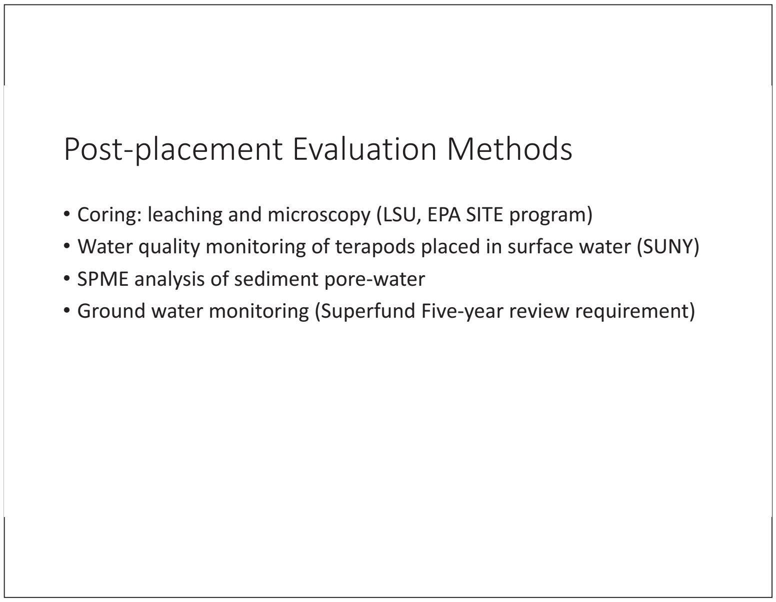
- Containment (cap, slurry wall)
- Product Extraction and Recovery
- In-situ solidification/stabilization (ISS)
- ISS w additives (carbon or organoclays)
- Complete or partial degradation via in-situ heating, in-situ combustion, in-situ chemical treatment (oxidation, de-chlorination), or in-situ bioremediation



Pre-placement Evaluation Methods

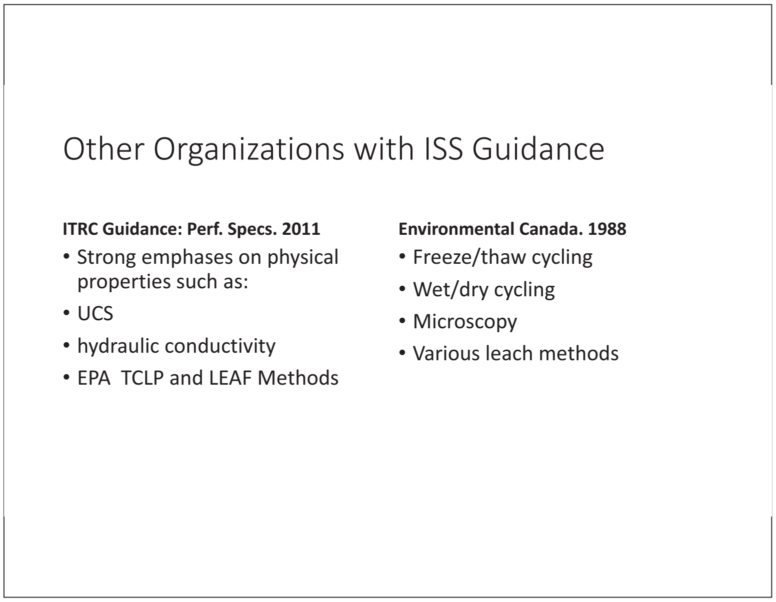
- Oily Extraction Procedure
- Paint Filter Test
- EP Toxicity
- MEP
- TCLP
- SPLP
- ANSI 16.1 with/without site ground water
- Column leach testing methods (SWLP, sediment cores)
- ORD Center Hill Lab. studies involving Shrinking Core Model, Constant pH leach

- *note:* Various Conferences and Symposiums (such as HMCRI, ASTM) have suggested other methods which have not transferred to the Superfund Program



Post-placement Evaluation Methods

- Coring: leaching and microscopy (LSU, EPA SITE program)
- Water quality monitoring of terapods placed in surface water (SUNY)
- SPME analysis of sediment pore-water
- Ground water monitoring (Superfund Five-year review requirement)



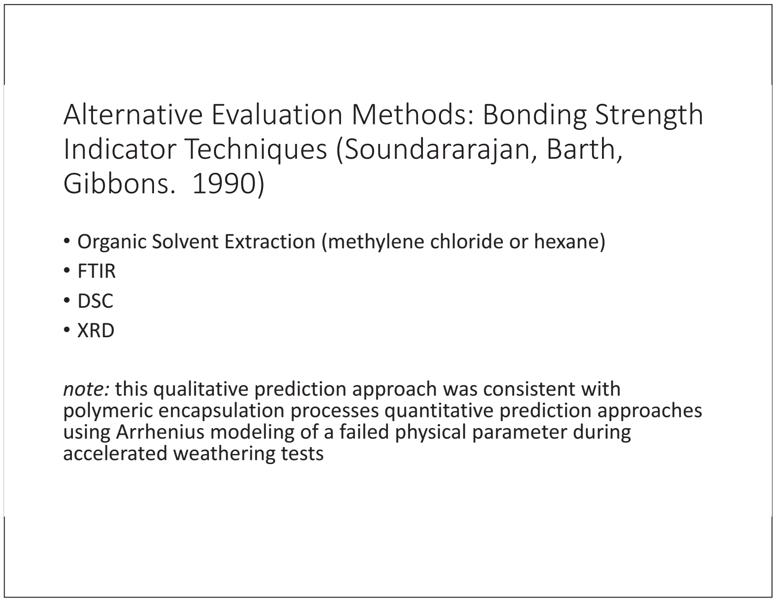
Other Organizations with ISS Guidance

ITRC Guidance: Perf. Specs. 2011

- Strong emphases on physical properties such as:
- UCS
- hydraulic conductivity
- EPA TCLP and LEAF Methods

Environmental Canada. 1988

- Freeze/thaw cycling
- Wet/dry cycling
- Microscopy
- Various leach methods



Alternative Evaluation Methods: Bonding Strength Indicator Techniques (Soundararajan, Barth, Gibbons. 1990)

- Organic Solvent Extraction (methylene chloride or hexane)
- FTIR
- DSC
- XRD

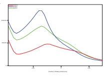
note: this qualitative prediction approach was consistent with polymeric encapsulation processes quantitative prediction approaches using Arrhenius modeling of a failed physical parameter during accelerated weathering tests

Further Bonding Strength Indicator Techniques (Johnston, Barth, Chattopadhyay. 2012)

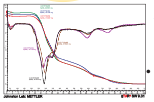
- Containment/Challenge of containing a DNAPL soup (Mukherji, et al. 1997)
- Sequential extraction test (similar to Tessier series except last stage)
- Consideration of facilitated transport (via low vs. high colloid competion environment)

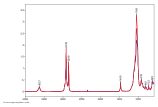
- *note*: In a separate study, pore water extraction via centrifuge (sediments) appears to be another predictive tool

Structural, Spectroscopic, and Sorption Studies of Alkylammonium Modified Clay Minerals



Characterization





- Structural Methods
  - Powder X-ray diffraction:
    - Target d-spacing of ~ 3.8 nm corresponding to intercalation fo 2 layers of DMDODA in clay interlayer
  - Thermal analysis:
    - TGA to confirm surface loading of DMDODA in clay interlayer. Target surface loading: 44% OM; 35% OC
    - Assess thermal stability of clay and influence of organic cation on dehydroxylation
- Spectroscopic
  - FTIR Spectroscopy
    - Gain molecular insight about the interaction of the organic cation with the clay mineral.
    - Molecular probe of alkyl chain ordering. Measure of organophilicity of organoclay

Lessons Learned: "Normalize" for Mass Balance Concerning PAHs analytical techniques?

- Reduction of PAHs in lab samples due to photochemical oxidation exposure (Kochaney and Maguire. 1994)
- Headspace volatilization
- Dilution
- Sorption onto glassware
- Oil sheens on sample surface

Some Current Approaches Used by USEPA Regions (proposed by EPA contractors)

- LEAF methods
- Site ground water
- Coated Glassware
- Partitioning/NAPL saturation
- Pore water models based upon partitioning

Case Study: Atlantic Wood Industry, VA: Use of OC for in-situ application at Atlantic Wood Site

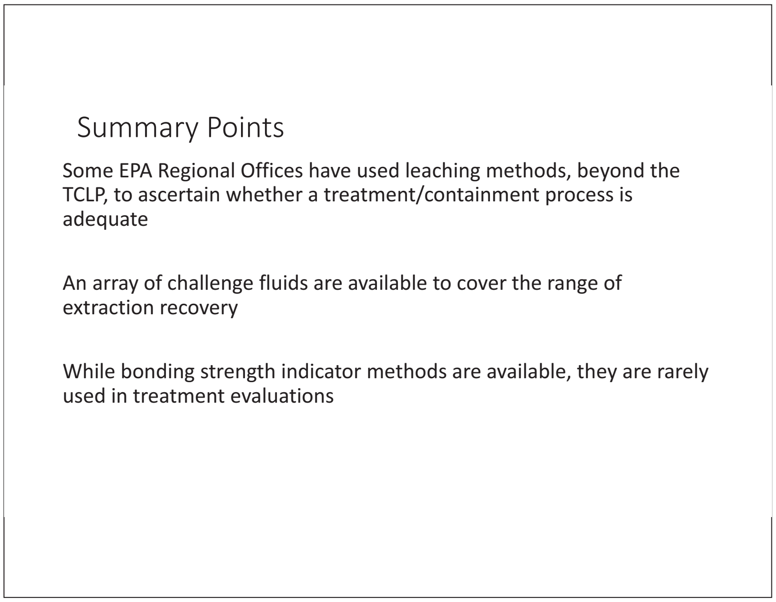
Atlantic Wood Industry Site

- Region 3 contacted ORD because TCLP criteria for PCP (0.001 mg/l) could not be met with cement based process
- Based upon previous ORD work with Dr. Stephen Boyd of MSU, ORD suggested the use of OC
- Addition of organoclay greatly reduced the TCLP value of PCP, but not below criteria established for the site

Case Study: Gowanus Canal, NY: ISS of NAPL Contaminated Sediments

Gowanus Canal Treatability Study (Niemet, et al. 2015 and Gentry et al., 2015)

- SPLP
- EPA Method 1315M: modified for organics: methanol extraction, PDMS lined leaching vessel
- Dean-Stark fluid pore saturation to indicate NAPL mobility



Summary Points

Some EPA Regional Offices have used leaching methods, beyond the TCLP, to ascertain whether a treatment/containment process is adequate

An array of challenge fluids are available to cover the range of extraction recovery

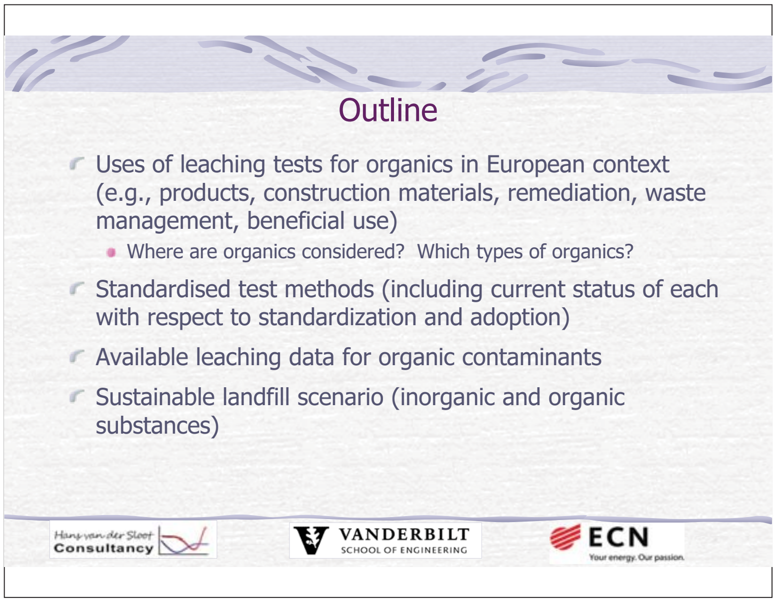
While bonding strength indicator methods are available, they are rarely used in treatment evaluations

European and international standards on leaching of organic contaminants, available tools and recent developments for assessment of organic contaminants

Hans van der Sloot[1], David Kosson[2], and Andre van Zomeren[3]

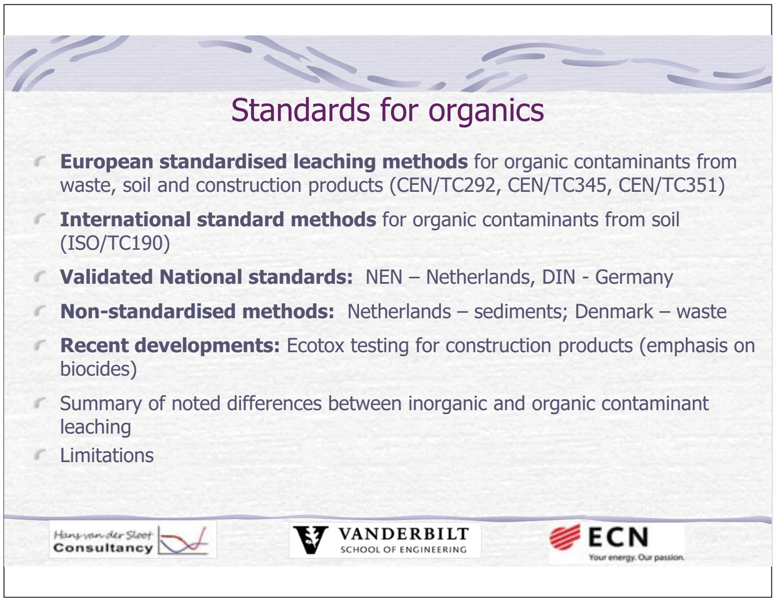
[1] Hans van der Sloot Consultancy, Langedijk, The Netherlands
[2] Vanderbilt University, Nashville, TN
[3] Energy Research Centre of the Netherlands, Petten, The Netherlands

USEPA Workshop on the Measurement of Leaching of Semi- and Non-Volatile Organic Compounds September 16, 2015, Washington



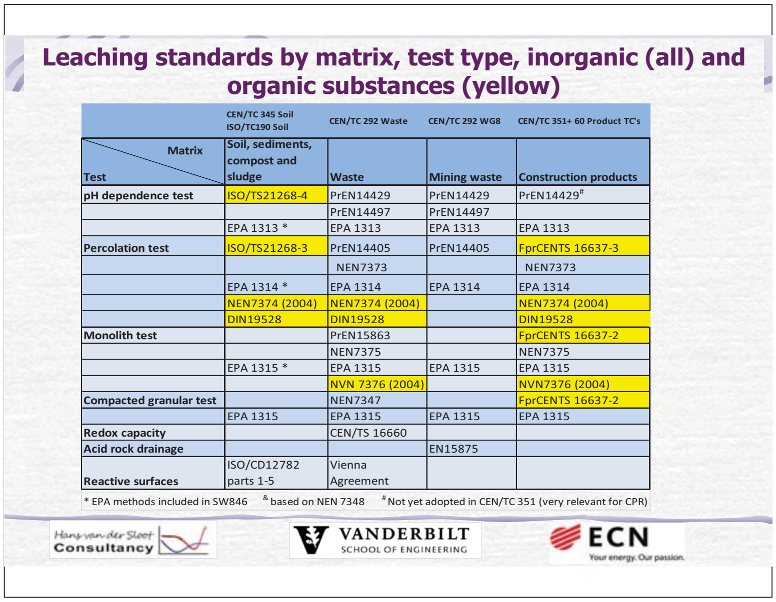
Outline

- Uses of leaching tests for organics in European context (e.g., products, construction materials, remediation, waste management, beneficial use)
  - Where are organics considered? Which types of organics?
- Standardised test methods (including current status of each with respect to standardization and adoption)
- Available leaching data for organic contaminants
- Sustainable landfill scenario (inorganic and organic substances)



Standards for organics

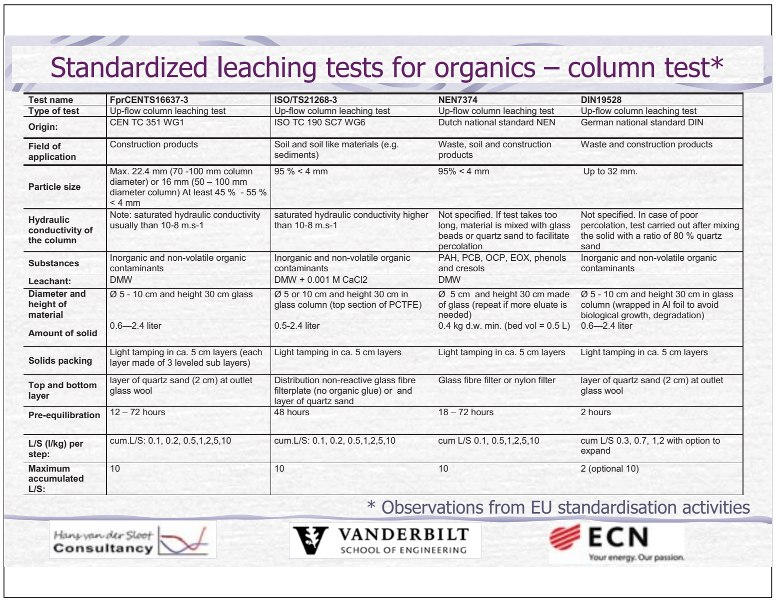
- **European standardised leaching methods** for organic contaminants from waste, soil and construction products (CEN/TC292, CEN/TC345, CEN/TC351)
- **International standard methods** for organic contaminants from soil (ISO/TC190)
- **Validated National standards:** NEN – Netherlands, DIN - Germany
- **Non-standardised methods:** Netherlands – sediments; Denmark – waste
- **Recent developments:** Ecotox testing for construction products (emphasis on biocides)
- Summary of noted differences between inorganic and organic contaminant leaching
- Limitations



Leaching standards by matrix, test type, inorganic (all) and organic substances (yellow)

	CEN/TC 345 Soil ISO/TC190 Soil	CEN/TC 292 Waste	CEN/TC 292 WG8	CEN/TC 351+ 60 Product TC's
Matrix / Test	**Soil, sediments, compost and sludge**	**Waste**	**Mining waste**	**Construction products**
pH dependence test	ISO/TS21268-4	PrEN14429	PrEN14429	PrEN14429[#]
		PrEN14497	PrEN14497	
	EPA 1313 *	EPA 1313	EPA 1313	EPA 1313
Percolation test	ISO/TS21268-3	PrEN14405	PrEN14405	FprCENTS 16637-3
		NEN7373		NEN7373
	EPA 1314 *	EPA 1314	EPA 1314	EPA 1314
	NEN7374 (2004)	NEN7374 (2004)		NEN7374 (2004)
	DIN19528	DIN19528		DIN19528
Monolith test		PrEN15863		FprCENTS 16637-2
		NEN7375		NEN7375
	EPA 1315 *	EPA 1315	EPA 1315	EPA 1315
		NVN 7376 (2004)		NVN7376 (2004)
Compacted granular test		NEN7347		FprCENTS 16637-2
	EPA 1315	EPA 1315	EPA 1315	EPA 1315
Redox capacity		CEN/TS 16660		
Acid rock drainage			EN15875	
Reactive surfaces	ISO/CD12782 parts 1-5	Vienna Agreement		

* EPA methods included in SW846 [&] based on NEN 7348 [#] Not yet adopted in CEN/TC 351 (very relevant for CPR)



Standardized leaching tests for organics – column test*

Test name	FprCENTS16637-3	ISO/TS21268-3	NEN7374	DIN19528
Type of test	Up-flow column leaching test	Up-flow column leaching test	Up-flow column leaching test	Up-flow column leaching test
Origin:	CEN TC 351 WG1	ISO TC 190 SC7 WG6	Dutch national standard NEN	German national standard DIN
Field of application	Construction products	Soil and soil like materials (e.g. sediments)	Waste, soil and construction products	Waste and construction products
Particle size	Max. 22.4 mm (70 -100 mm column diameter) or 16 mm (50 – 100 mm diameter column) At least 45 % - 55 % < 4 mm	95 % < 4 mm	95% < 4 mm	Up to 32 mm.
Hydraulic conductivity of the column	Note: saturated hydraulic conductivity usually than 10-8 m.s-1	saturated hydraulic conductivity higher than 10-8 m.s-1	Not specified. If test takes too long, material is mixed with glass beads or quartz sand to facilitate percolation	Not specified. In case of poor percolation, test carried out after mixing the solid with a ratio of 80 % quartz sand
Substances	Inorganic and non-volatile organic contaminants	Inorganic and non-volatile organic contaminants	PAH, PCB, OCP, EOX, phenols and cresols	Inorganic and non-volatile organic contaminants
Leachant:	DMW	DMW + 0.001 M CaCl2	DMW	
Diameter and height of material	Ø 5 - 10 cm and height 30 cm glass	Ø 5 or 10 cm and height 30 cm in glass column (top section of PCTFE)	Ø 5 cm and height 30 cm made of glass (repeat if more eluate is needed)	Ø 5 - 10 cm and height 30 cm in glass column (wrapped in Al foil to avoid biological growth, degradation)
Amount of solid	0.6—2.4 liter	0.5-2.4 liter	0.4 kg d.w. min. (bed vol = 0.5 L)	0.6—2.4 liter
Solids packing	Light tamping in ca. 5 cm layers (each layer made of 3 leveled sub layers)	Light tamping in ca. 5 cm layers	Light tamping in ca. 5 cm layers	Light tamping in ca. 5 cm layers
Top and bottom layer	layer of quartz sand (2 cm) at outlet glass wool	Distribution non-reactive glass fibre filterplate (no organic glue) or and layer of quartz sand	Glass fibre filter or nylon filter	layer of quartz sand (2 cm) at outlet glass wool
Pre-equilibration	12 – 72 hours	48 hours	18 – 72 hours	2 hours
L/S (l/kg) per step:	cum.L/S: 0.1, 0.2, 0.5,1,2,5,10	cum.L/S: 0.1, 0.2, 0.5,1,2,5,10	cum L/S 0.1, 0.5,1,2,5,10	cum L/S 0.3, 0.7, 1,2 with option to expand
Maximum accumulated L/S:	10	10	10	2 (optional 10)

* Observations from EU standardisation activities

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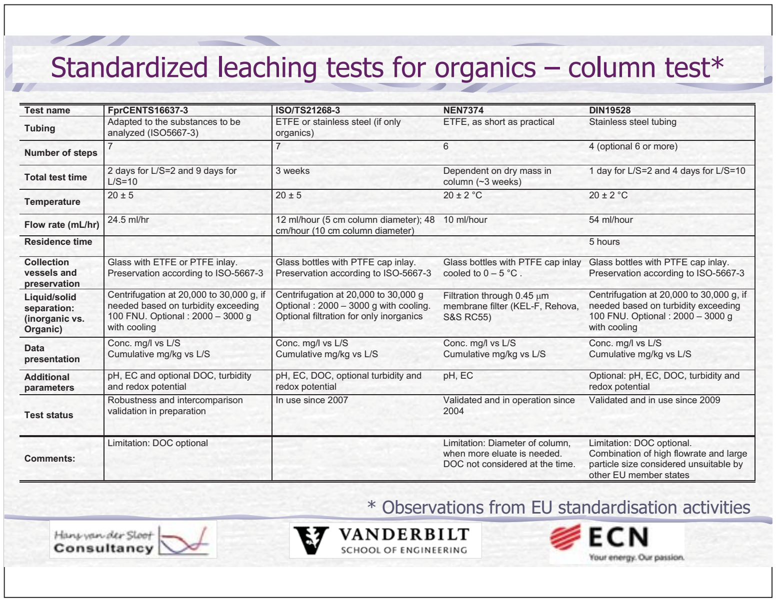

Standardized leaching tests for organics – column test*

Test name	FprCENTS16637-3	ISO/TS21268-3	NEN7374	DIN19528
Tubing	Adapted to the substances to be analyzed (ISO5667-3)	ETFE or stainless steel (if only organics)	ETFE, as short as practical	Stainless steel tubing
Number of steps	7	7	6	4 (optional 6 or more)
Total test time	2 days for L/S=2 and 9 days for L/S=10	3 weeks	Dependent on dry mass in column (~3 weeks)	1 day for L/S=2 and 4 days for L/S=10
Temperature	20 ± 5	20 ± 5	20 ± 2 °C	20 ± 2 °C
Flow rate (mL/hr)	24.5 ml/hr	12 ml/hour (5 cm column diameter); 48 cm/hour (10 cm column diameter)	10 ml/hour	54 ml/hour
Residence time				5 hours
Collection vessels and preservation	Glass with ETFE or PTFE inlay. Preservation according to ISO-5667-3	Glass bottles with PTFE cap inlay. Preservation according to ISO-5667-3	Glass bottles with PTFE cap inlay cooled to 0 – 5 °C .	Glass bottles with PTFE cap inlay. Preservation according to ISO-5667-3
Liquid/solid separation: (inorganic vs. Organic)	Centrifugation at 20,000 to 30,000 g, if needed based on turbidity exceeding 100 FNU. Optional : 2000 – 3000 g with cooling	Centrifugation at 20,000 to 30,000 g Optional : 2000 – 3000 g with cooling. Optional filtration for only inorganics	Filtration through 0.45 μm membrane filter (KEL-F, Rehova, S&S RC55)	Centrifugation at 20,000 to 30,000 g, if needed based on turbidity exceeding 100 FNU. Optional : 2000 – 3000 g with cooling
Data presentation	Conc. mg/l vs L/S Cumulative mg/kg vs L/S	Conc. mg/l vs L/S Cumulative mg/kg vs L/S	Conc. mg/l vs L/S Cumulative mg/kg vs L/S	Conc. mg/l vs L/S Cumulative mg/kg vs L/S
Additional parameters	pH, EC and optional DOC, turbidity and redox potential	pH, EC, DOC, optional turbidity and redox potential	pH, EC	Optional: pH, EC, DOC, turbidity and redox potential
Test status	Robustness and intercomparison validation in preparation	In use since 2007	Validated and in operation since 2004	Validated and in use since 2009
Comments:	Limitation: DOC optional		Limitation: Diameter of column, when more eluate is needed. DOC not considered at the time.	Limitation: DOC optional. Combination of high flowrate and large particle size considered unsuitable by other EU member states

* Observations from EU standardisation activities

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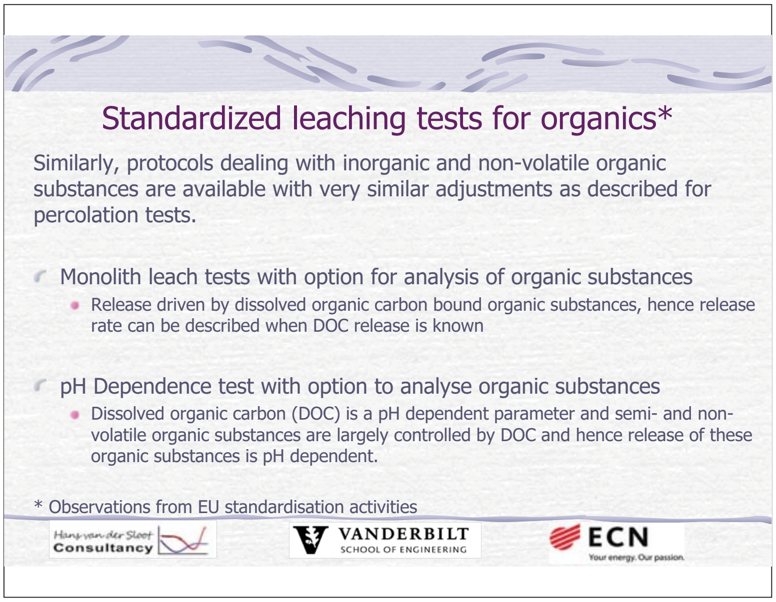

Standardized leaching tests for organics*

Similarly, protocols dealing with inorganic and non-volatile organic substances are available with very similar adjustments as described for percolation tests.

- Monolith leach tests with option for analysis of organic substances
  - Release driven by dissolved organic carbon bound organic substances, hence release rate can be described when DOC release is known
- pH Dependence test with option to analyse organic substances
  - Dissolved organic carbon (DOC) is a pH dependent parameter and semi- and non-volatile organic substances are largely controlled by DOC and hence release of these organic substances is pH dependent.

* Observations from EU standardisation activities

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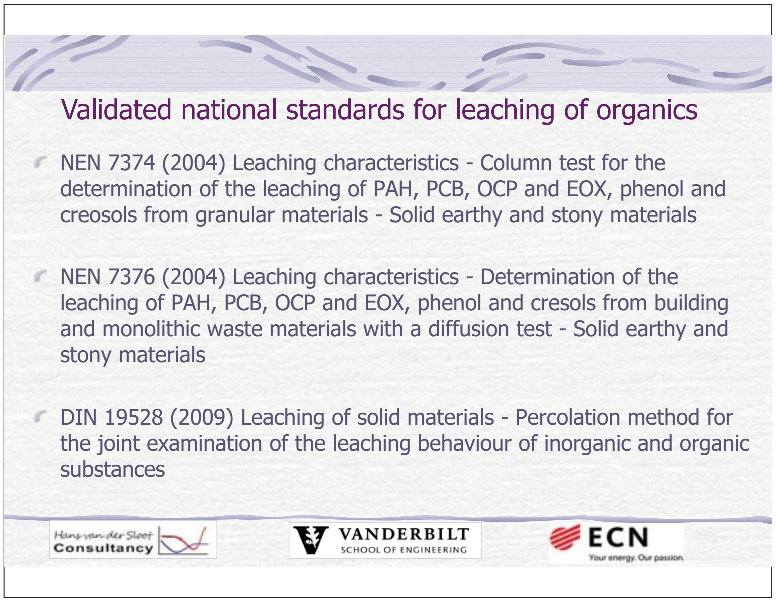

Validated national standards for leaching of organics

- NEN 7374 (2004) Leaching characteristics - Column test for the determination of the leaching of PAH, PCB, OCP and EOX, phenol and creosols from granular materials - Solid earthy and stony materials
- NEN 7376 (2004) Leaching characteristics - Determination of the leaching of PAH, PCB, OCP and EOX, phenol and cresols from building and monolithic waste materials with a diffusion test - Solid earthy and stony materials
- DIN 19528 (2009) Leaching of solid materials - Percolation method for the joint examination of the leaching behaviour of inorganic and organic substances

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Performance data for leaching of organic contaminants

NEN 7374 (2004)	PAH	PCB	EOX	Phenols, cresols
Within lab variability S_r	25 %	15 %	12 %	3 %
Between lab variability S_R		42 %	42 %	14 %

DIN 19528 (2009)	ΣPAH	Naphtalene	Anthracene
Within lab variability S_r	13 %	10 %	12 %
Between lab variability S_R	50 %	45 %	45 %

DIN 19528 (2009)	Pyrene	Chrysene	Benzo[a]pyrene
Within lab variability S_r	10 %	27 %	60 %
Between lab variability S_R	45 %	48 %	80 %

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Main features of leaching standards for organics*

CEN and ISO Standards are suitable for inorganic and organic substances.

- The first and foremost reason is that the basis of testing and the use of test results in environmental judgment of release is not fundamentally different.
- In many cases information on both inorganic and organic substances is needed.
  - Running one test has economic advantages (equipment occupation, cost).
  - Ecotox testing requires eluates containing all substances of interest.
- Material requirements for the equipment and other parts getting in contact with the eluate are adapted to meet requirements for both type of substances. Glass column and stainless steel connections.
- In the column, quartz sand or glass beads are used instead of filters.
- Filtration commonly used for inorganic substances is unsuitable for organic substances. If needed, centrifugation is prescribed.
- Test limited to non-volatile organic substances at ambient conditions.

* Observations from EU standardisation activities

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Non-standardized tests for organics

- Static method for porewater analysis (Solid Phase Micro Extraction (SPME), Semipermeable Membrane Devices (SPMD), Solid Phase Extraction Disks (SPE disks) and Tenax extraction. Applied in the Netherlands for bioavailability of organic contaminants in sediments and soils.
  - Limitation: useful method, but does not provide insight in long term behaviour
- Leaching tests for non-volatile organic compounds. Recirculation column procedure derived from the CEN/TC292 procedure.
  - Inconsistent batch test results prompted this development. Test was developed as a compliance test procedure. However, results are not easy to interpret.
- Modified diffusion test procedure (Nordtest report TR577)
  - Same basic test method as defined in CEN/TC292, CEN/TC351 and EPA 1315, but modified with a strong sorbing solid or liquid phase to create a zero boundary condition.

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Available data on leaching of organics

- Dutch, German, Danish and Swedish leaching data
  - pH dependence 14 samples
  - Percolation 108 samples
  - Monolith leaching 82 samples
- Ecotox testing in connection with leach testing (Study Umwelt Bundes Amt, Germany)
- Modelling for partitioning of organic contaminants between free, DOC and POM associated forms - Role of DOC and POM for organic contaminant mobility.

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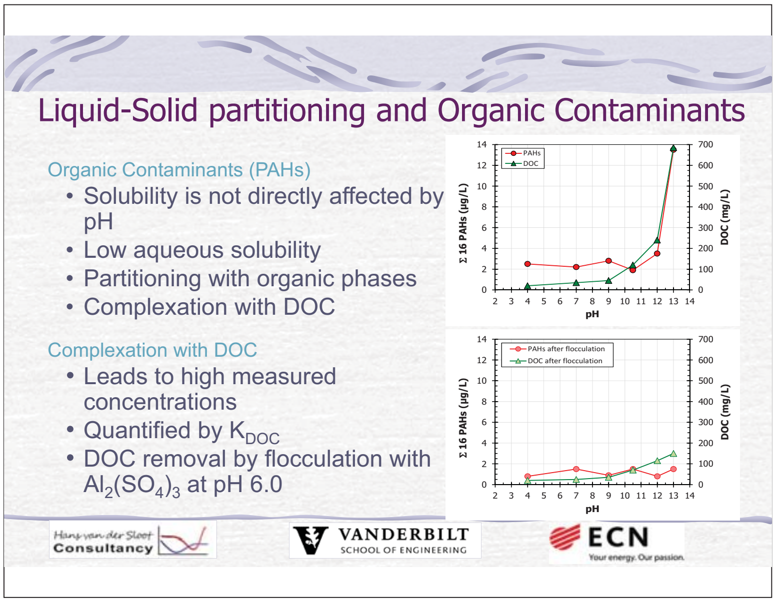

Liquid-Solid partitioning and Organic Contaminants

Organic Contaminants (PAHs)

- Solubility is not directly affected by pH
- Low aqueous solubility
- Partitioning with organic phases
- Complexation with DOC

Complexation with DOC

- Leads to high measured concentrations
- Quantified by K_{DOC}
- DOC removal by flocculation with $Al_2(SO_4)_3$ at pH 6.0

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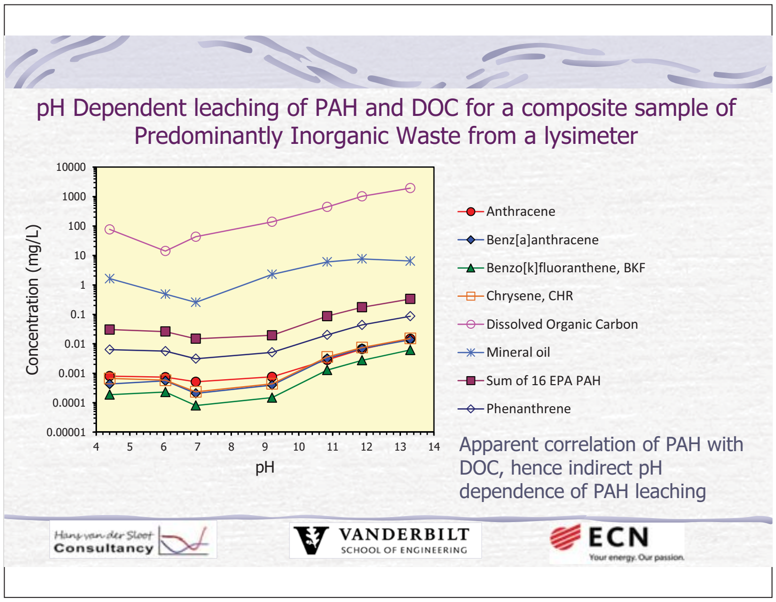

pH Dependent leaching of PAH and DOC for a composite sample of Predominantly Inorganic Waste from a lysimeter

Apparent correlation of PAH with DOC, hence indirect pH dependence of PAH leaching

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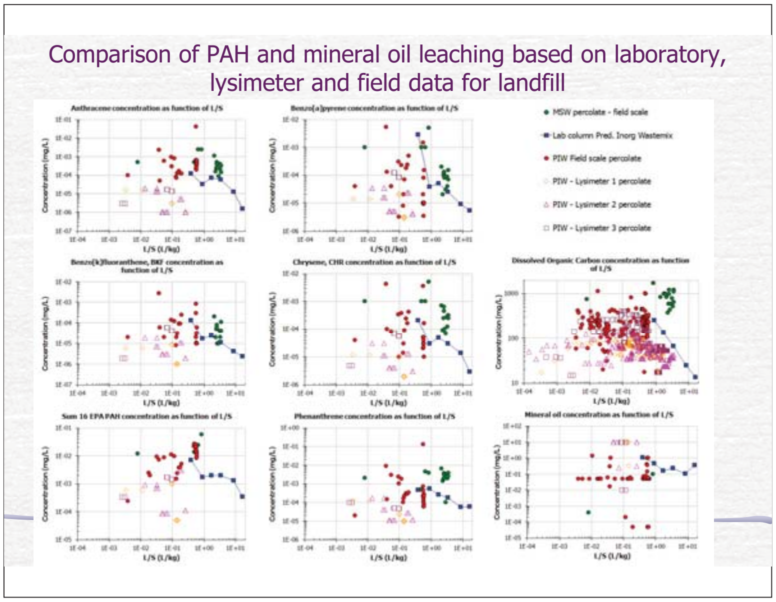
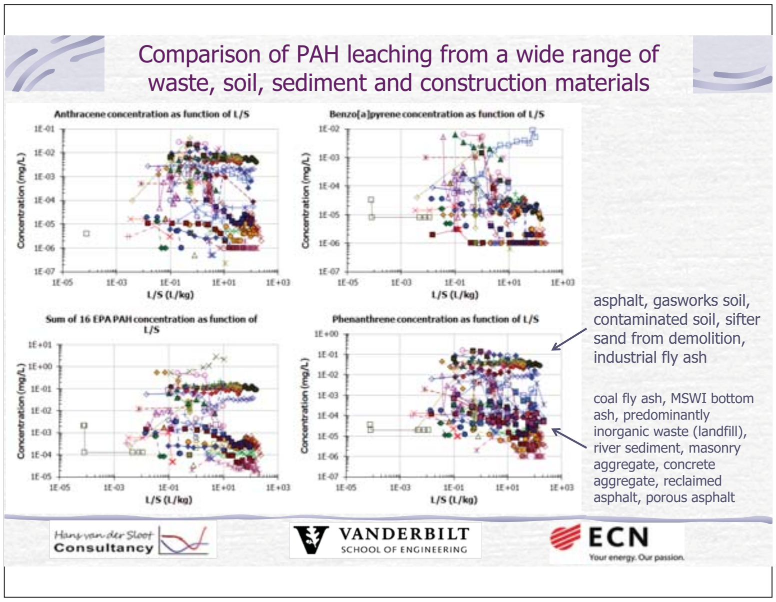


Comparison of PAH and mineral oil leaching based on laboratory, lysimeter and field data for landfill



Comparison of PAH leaching from a wide range of waste, soil, sediment and construction materials

asphalt, gasworks soil, contaminated soil, sifter sand from demolition, industrial fly ash

coal fly ash, MSWI bottom ash, predominantly inorganic waste (landfill), river sediment, masonry aggregate, concrete aggregate, reclaimed asphalt, porous asphalt

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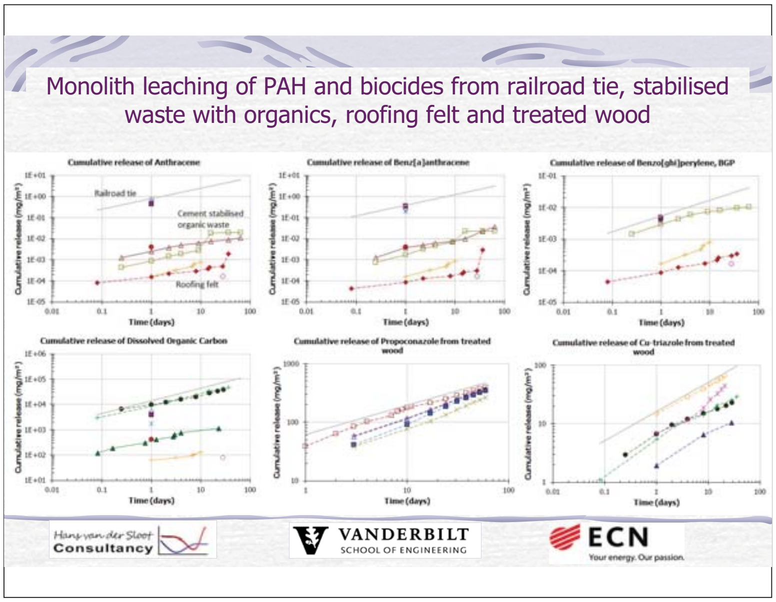
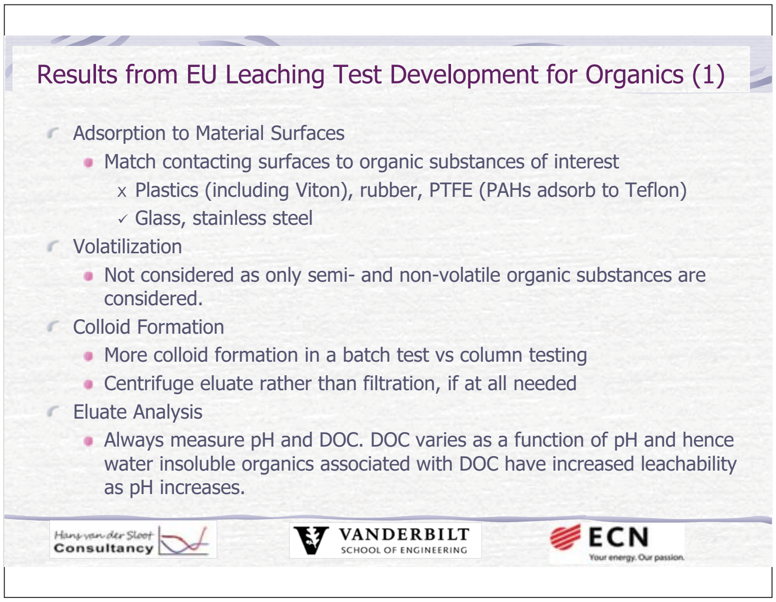
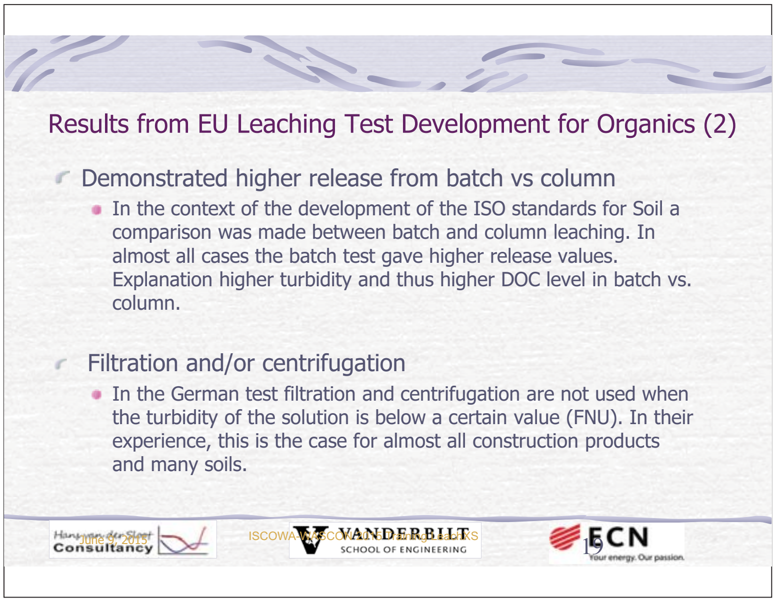


Monolith leaching of PAH and biocides from railroad tie, stabilised waste with organics, roofing felt and treated wood



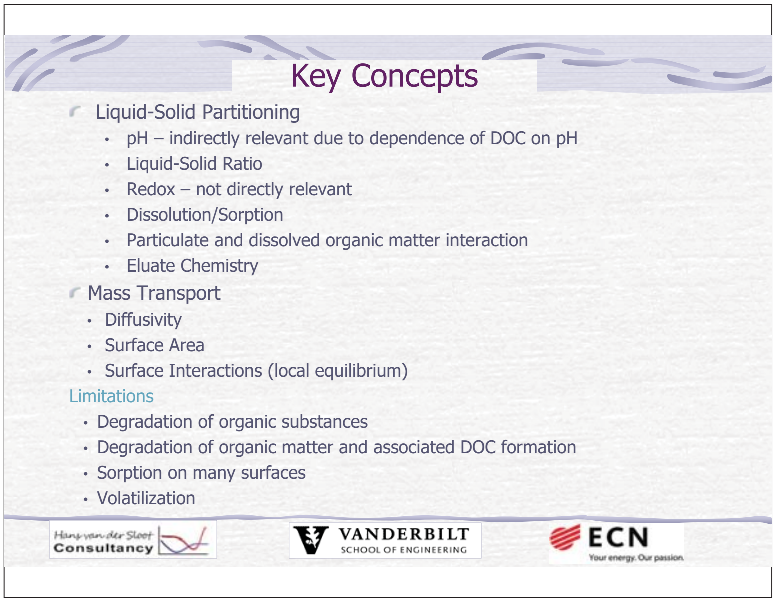
Results from EU Leaching Test Development for Organics (1)

- Adsorption to Material Surfaces
  - Match contacting surfaces to organic substances of interest
    - x Plastics (including Viton), rubber, PTFE (PAHs adsorb to Teflon)
    - ✓ Glass, stainless steel
- Volatilization
  - Not considered as only semi- and non-volatile organic substances are considered.
- Colloid Formation
  - More colloid formation in a batch test vs column testing
  - Centrifuge eluate rather than filtration, if at all needed
- Eluate Analysis
  - Always measure pH and DOC. DOC varies as a function of pH and hence water insoluble organics associated with DOC have increased leachability as pH increases.



Results from EU Leaching Test Development for Organics (2)

- Demonstrated higher release from batch vs column
  - In the context of the development of the ISO standards for Soil a comparison was made between batch and column leaching. In almost all cases the batch test gave higher release values. Explanation higher turbidity and thus higher DOC level in batch vs. column.
- Filtration and/or centrifugation
  - In the German test filtration and centrifugation are not used when the turbidity of the solution is below a certain value (FNU). In their experience, this is the case for almost all construction products and many soils.

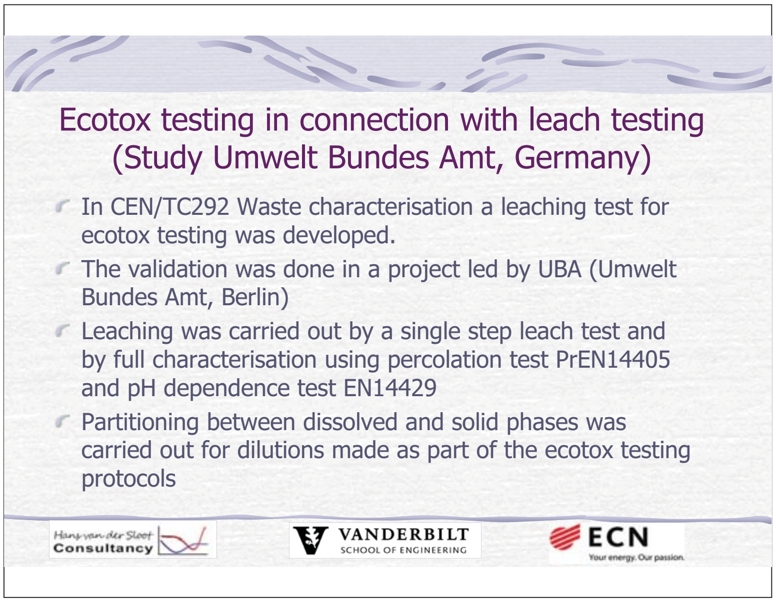


Key Concepts

- Liquid-Solid Partitioning
  - pH – indirectly relevant due to dependence of DOC on pH
  - Liquid-Solid Ratio
  - Redox – not directly relevant
  - Dissolution/Sorption
  - Particulate and dissolved organic matter interaction
  - Eluate Chemistry
- Mass Transport
  - Diffusivity
  - Surface Area
  - Surface Interactions (local equilibrium)

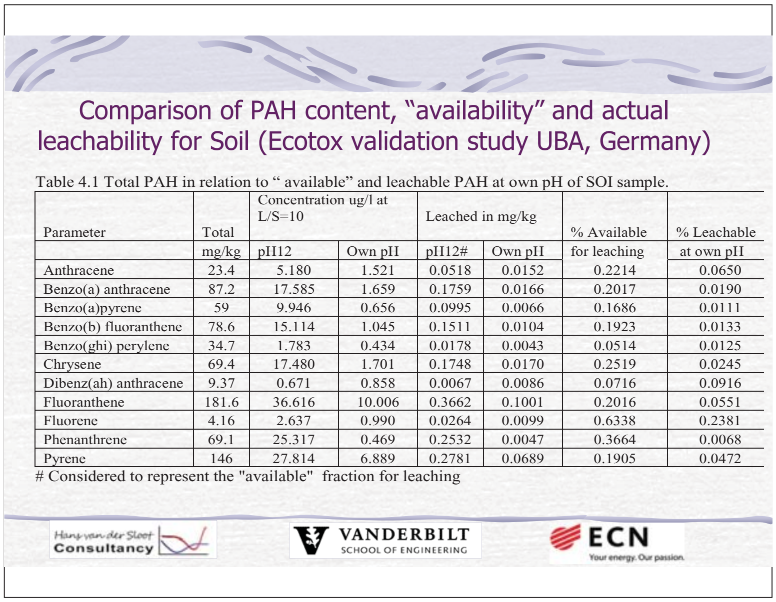
Limitations

- Degradation of organic substances
- Degradation of organic matter and associated DOC formation
- Sorption on many surfaces
- Volatilization



Ecotox testing in connection with leach testing (Study Umwelt Bundes Amt, Germany)

- In CEN/TC292 Waste characterisation a leaching test for ecotox testing was developed.
- The validation was done in a project led by UBA (Umwelt Bundes Amt, Berlin)
- Leaching was carried out by a single step leach test and by full characterisation using percolation test PrEN14405 and pH dependence test EN14429
- Partitioning between dissolved and solid phases was carried out for dilutions made as part of the ecotox testing protocols

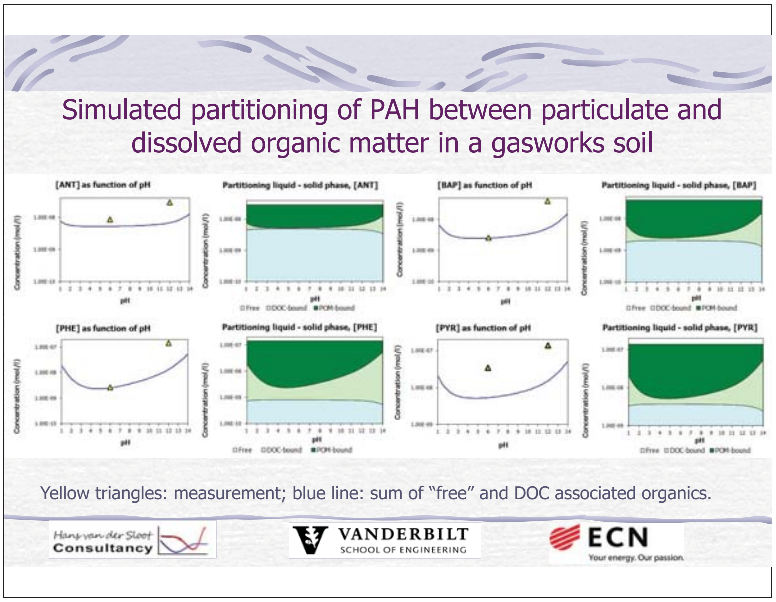


Comparison of PAH content, "availability" and actual leachability for Soil (Ecotox validation study UBA, Germany)

Table 4.1 Total PAH in relation to " available" and leachable PAH at own pH of SOI sample.

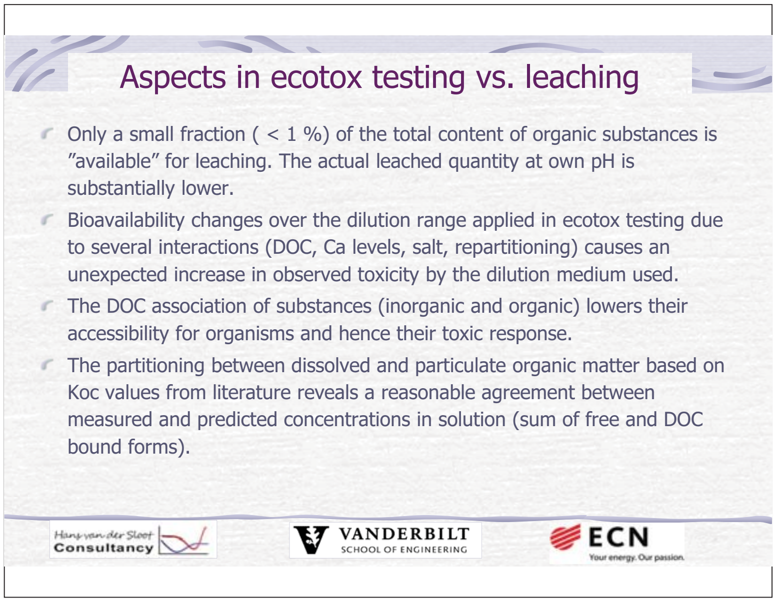
Parameter	Total	Concentration ug/l at L/S=10		Leached in mg/kg		% Available	% Leachable
	mg/kg	pH12	Own pH	pH12#	Own pH	for leaching	at own pH
Anthracene	23.4	5.180	1.521	0.0518	0.0152	0.2214	0.0650
Benzo(a) anthracene	87.2	17.585	1.659	0.1759	0.0166	0.2017	0.0190
Benzo(a)pyrene	59	9.946	0.656	0.0995	0.0066	0.1686	0.0111
Benzo(b) fluoranthene	78.6	15.114	1.045	0.1511	0.0104	0.1923	0.0133
Benzo(ghi) perylene	34.7	1.783	0.434	0.0178	0.0043	0.0514	0.0125
Chrysene	69.4	17.480	1.701	0.1748	0.0170	0.2519	0.0245
Dibenz(ah) anthracene	9.37	0.671	0.858	0.0067	0.0086	0.0716	0.0916
Fluoranthene	181.6	36.616	10.006	0.3662	0.1001	0.2016	0.0551
Fluorene	4.16	2.637	0.990	0.0264	0.0099	0.6338	0.2381
Phenanthrene	69.1	25.317	0.469	0.2532	0.0047	0.3664	0.0068
Pyrene	146	27.814	6.889	0.2781	0.0689	0.1905	0.0472

Considered to represent the "available" fraction for leaching



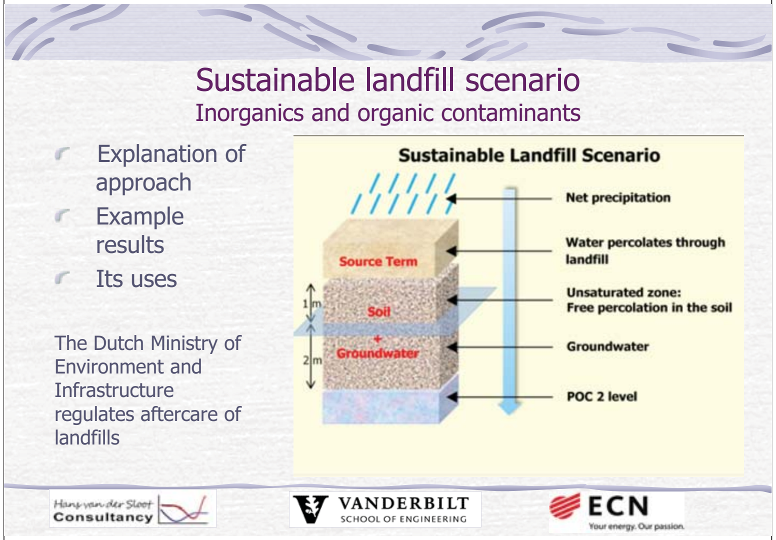
Simulated partitioning of PAH between particulate and dissolved organic matter in a gasworks soil

Yellow triangles: measurement; blue line: sum of "free" and DOC associated organics.



Aspects in ecotox testing vs. leaching

- Only a small fraction (< 1 %) of the total content of organic substances is "available" for leaching. The actual leached quantity at own pH is substantially lower.
- Bioavailability changes over the dilution range applied in ecotox testing due to several interactions (DOC, Ca levels, salt, repartitioning) causes an unexpected increase in observed toxicity by the dilution medium used.
- The DOC association of substances (inorganic and organic) lowers their accessibility for organisms and hence their toxic response.
- The partitioning between dissolved and particulate organic matter based on Koc values from literature reveals a reasonable agreement between measured and predicted concentrations in solution (sum of free and DOC bound forms).

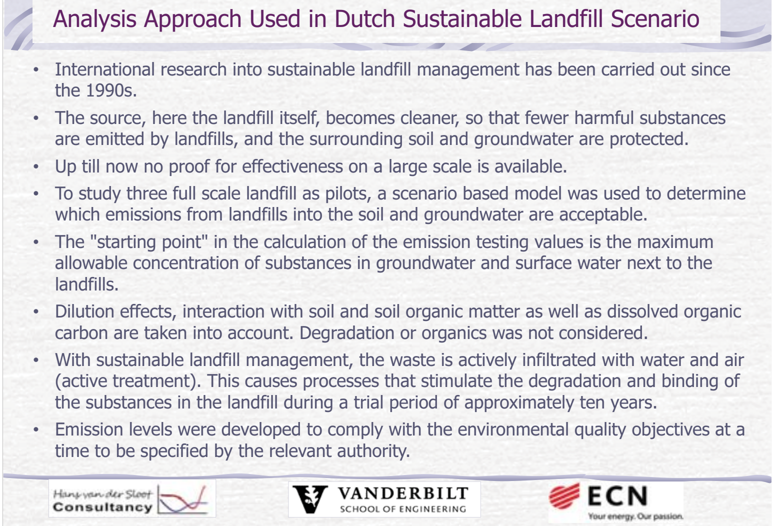


Sustainable landfill scenario

Inorganics and organic contaminants

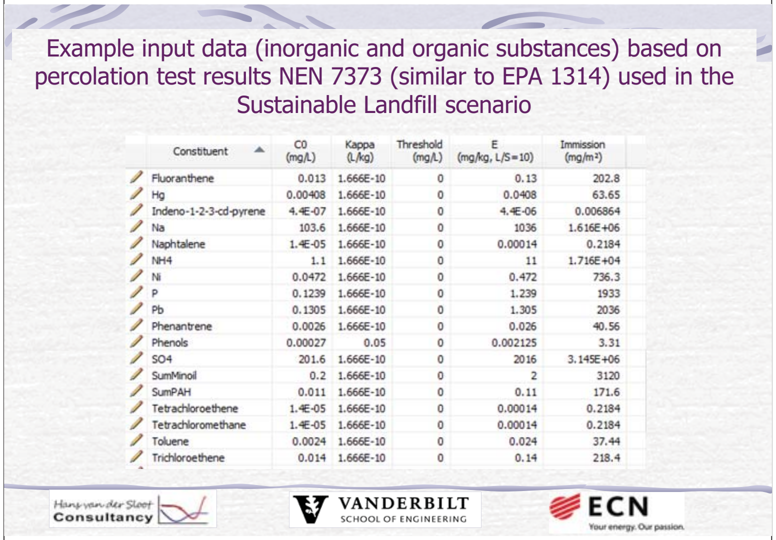
- Explanation of approach
- Example results
- Its uses

The Dutch Ministry of Environment and Infrastructure regulates aftercare of landfills



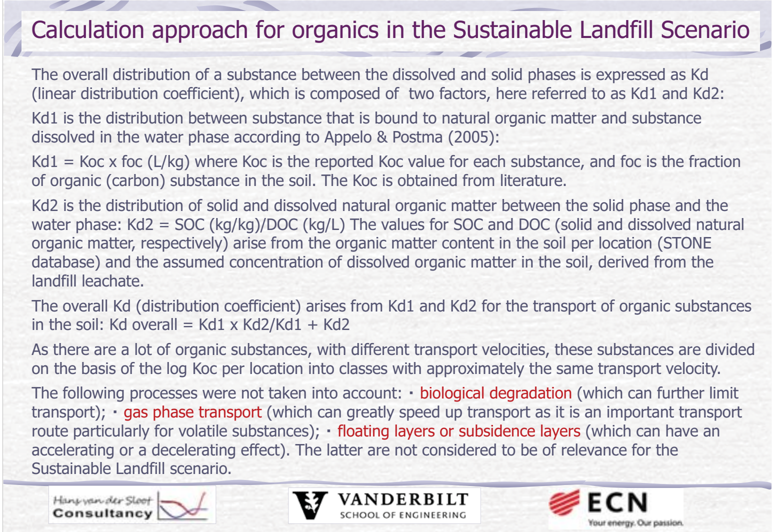
Analysis Approach Used in Dutch Sustainable Landfill Scenario

- International research into sustainable landfill management has been carried out since the 1990s.
- The source, here the landfill itself, becomes cleaner, so that fewer harmful substances are emitted by landfills, and the surrounding soil and groundwater are protected.
- Up till now no proof for effectiveness on a large scale is available.
- To study three full scale landfill as pilots, a scenario based model was used to determine which emissions from landfills into the soil and groundwater are acceptable.
- The "starting point" in the calculation of the emission testing values is the maximum allowable concentration of substances in groundwater and surface water next to the landfills.
- Dilution effects, interaction with soil and soil organic matter as well as dissolved organic carbon are taken into account. Degradation or organics was not considered.
- With sustainable landfill management, the waste is actively infiltrated with water and air (active treatment). This causes processes that stimulate the degradation and binding of the substances in the landfill during a trial period of approximately ten years.
- Emission levels were developed to comply with the environmental quality objectives at a time to be specified by the relevant authority.



Example input data (inorganic and organic substances) based on percolation test results NEN 7373 (similar to EPA 1314) used in the Sustainable Landfill scenario

Constituent	C0 (mg/L)	Kappa (L/kg)	Threshold (mg/L)	E (mg/kg, L/S=10)	Immission (mg/m²)
Fluoranthene	0.013	1.666E-10	0	0.13	202.8
Hg	0.00408	1.666E-10	0	0.0408	63.65
Indeno-1-2-3-cd-pyrene	4.4E-07	1.666E-10	0	4.4E-06	0.006864
Na	103.6	1.666E-10	0	1036	1.616E+06
Naphtalene	1.4E-05	1.666E-10	0	0.00014	0.2184
NH4	1.1	1.666E-10	0	11	1.716E+04
Ni	0.0472	1.666E-10	0	0.472	736.3
P	0.1239	1.666E-10	0	1.239	1933
Pb	0.1305	1.666E-10	0	1.305	2036
Phenantrene	0.0026	1.666E-10	0	0.026	40.56
Phenols	0.00027	0.05	0	0.002125	3.31
SO4	201.6	1.666E-10	0	2016	3.145E+06
SumMinoil	0.2	1.666E-10	0	2	3120
SumPAH	0.011	1.666E-10	0	0.11	171.6
Tetrachloroethene	1.4E-05	1.666E-10	0	0.00014	0.2184
Tetrachloromethane	1.4E-05	1.666E-10	0	0.00014	0.2184
Toluene	0.0024	1.666E-10	0	0.024	37.44
Trichloroethene	0.014	1.666E-10	0	0.14	218.4



Calculation approach for organics in the Sustainable Landfill Scenario

The overall distribution of a substance between the dissolved and solid phases is expressed as Kd (linear distribution coefficient), which is composed of two factors, here referred to as Kd1 and Kd2:

Kd1 is the distribution between substance that is bound to natural organic matter and substance dissolved in the water phase according to Appelo & Postma (2005):

Kd1 = Koc x foc (L/kg) where Koc is the reported Koc value for each substance, and foc is the fraction of organic (carbon) substance in the soil. The Koc is obtained from literature.

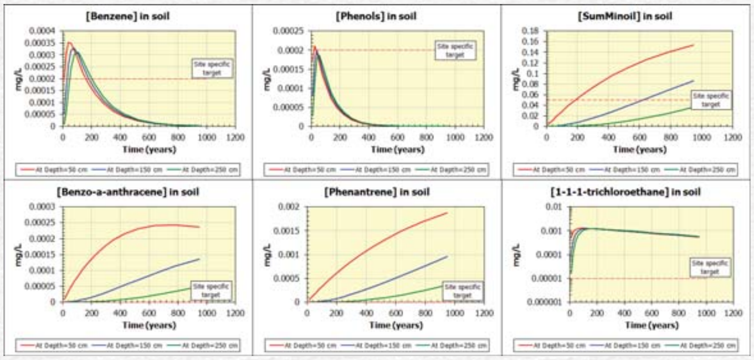
Kd2 is the distribution of solid and dissolved natural organic matter between the solid phase and the water phase: Kd2 = SOC (kg/kg)/DOC (kg/L) The values for SOC and DOC (solid and dissolved natural organic matter, respectively) arise from the organic matter content in the soil per location (STONE database) and the assumed concentration of dissolved organic matter in the soil, derived from the landfill leachate.

The overall Kd (distribution coefficient) arises from Kd1 and Kd2 for the transport of organic substances in the soil: Kd overall = Kd1 x Kd2/Kd1 + Kd2

As there are a lot of organic substances, with different transport velocities, these substances are divided on the basis of the log Koc per location into classes with approximately the same transport velocity.

The following processes were not taken into account: • biological degradation (which can further limit transport); • gas phase transport (which can greatly speed up transport as it is an important transport route particularly for volatile substances); • floating layers or subsidence layers (which can have an accelerating or a decelerating effect). The latter are not considered to be of relevance for the Sustainable Landfill scenario.

Evaluation results (concentration as a function of time in the soil solution at 1-2 m depth) Sustainable Landfill Scenario



Observations (1)

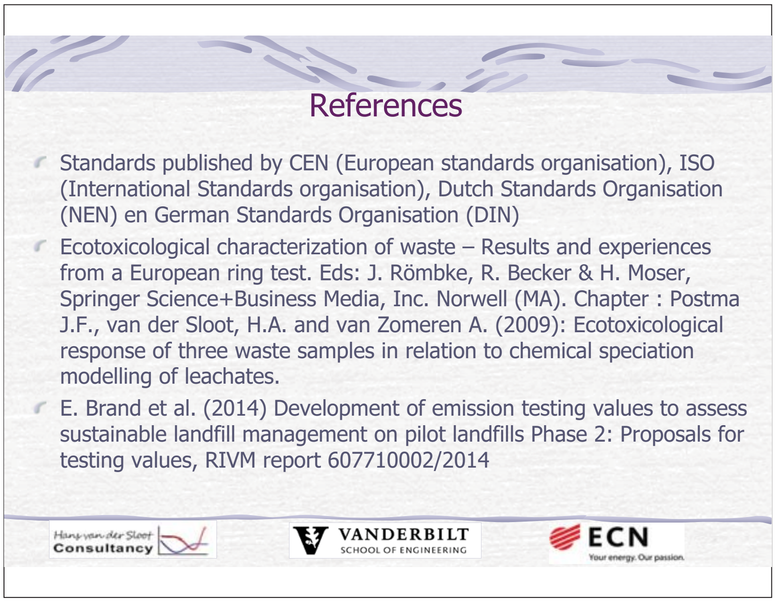
- Validated test methods for organic substances available at national level.
- Validation of tests suitable for organic substances in construction products up for validation in 2017, when the robustness work that will start in early 2016 is finished (CEN/TC351).
- Standardised tests show systematic release patterns for organic contaminants allowing understanding of release mechanisms
- Methods have been aimed to deal with inorganic and organic substances simultaneously to facilitate ecotox testing of eluates

Observations (2)

- The role of dissolved organic matter is important in release of semi- and non-volatile organic substances due to their association with DOC
- The transport properties are not controlled only by the substance itself, but also by the transport properties of DOC
- The pH dependence of DOC release is important because of the association of organics with DOC impacts organics partitioning and transport
- Release of organic substances from monolithic products (stabilised waste and treated wood) is to a large extent controlled by release of DOC bound organic substances and thus controlled by DOC release. DOC release from porous monolithic materials is about a factor 10 – 15 slower than soluble salts (e.g. Na^+, K^+, Cl^-)

Observations (3)

- DOC associated organic substances are not bioavailable for a range of organisms and thus have no toxic response (example: gaswork soil UBA study)
- Partitioning of dissolved organic matter in subfractions (fulvic and humic substances) may prove important in view of their different binding characteristics for organic contaminants
- The use of Koc parameters allows the partitioning of organic contaminants to be estimated between particulate and dissolved organic matter
- Sustainable landfill scenario considers leaching test results in conjunction with transport, dilution and attenuation to determine leaching test thresholds for regulation.



References

- Standards published by CEN (European standards organisation), ISO (International Standards organisation), Dutch Standards Organisation (NEN) en German Standards Organisation (DIN)
- Ecotoxicological characterization of waste – Results and experiences from a European ring test. Eds: J. Römbke, R. Becker & H. Moser, Springer Science+Business Media, Inc. Norwell (MA). Chapter : Postma J.F., van der Sloot, H.A. and van Zomeren A. (2009): Ecotoxicological response of three waste samples in relation to chemical speciation modelling of leachates.
- E. Brand et al. (2014) Development of emission testing values to assess sustainable landfill management on pilot landfills Phase 2: Proposals for testing values, RIVM report 607710002/2014

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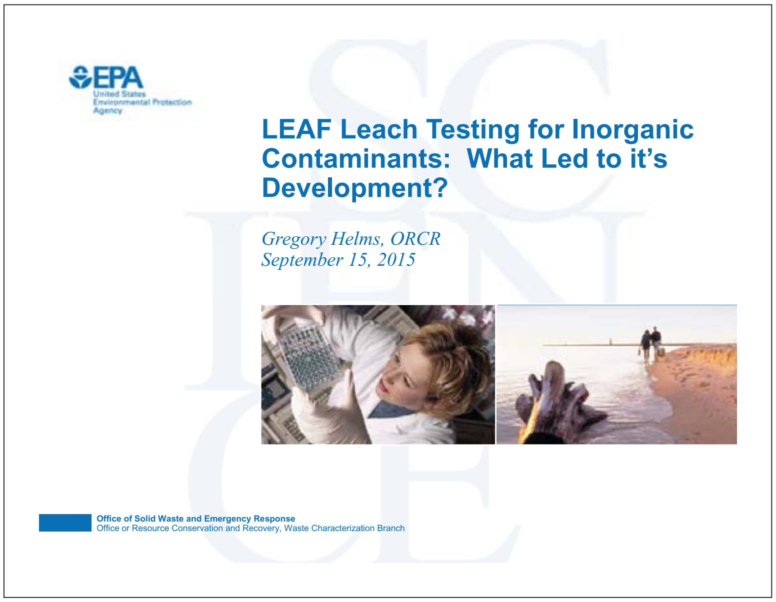


LEAF Leach Testing for Inorganic Contaminants: What Led to it's Development?

Gregory Helms, ORCR
September 15, 2015

What Led to LEAF Development?

- TCLP is EPA's regulatory test and most used leaching test.
  - Developed to implement the national RCRA regulatory program (not tailored to be site-specific).
  - Based on RCRA def of hazardous waste ("may pose hazard when improperly managed").
  - Simulates plausible mis-management scenario for waste disposal (i.e., co-disposal with municipal solid waste).
- Because it is the regulatory test, TCLP is used even when not required by regulation:
  - EPA SAB has twice (1991,1999) expressed concern about over-broad use of TCLP.
  - Conditions at most contaminated sites do not resemble MSW/TCLP conditions.

What Led to LEAF Development?

- ORCR experienced several program problems related to use of TCLP in the late 1990s:
- The LDR treatment standard and hazardous waste delisting for K088 based on TCLP data resulted in environmental releases:
  - Arsenic was leaching from the K088 disposal monofill at levels more than 100x the TCLP results (monofill leachate pH 13)
  - EPA withdrew the delisting and instituted disposal restrictions for delisted waste.
- EPA was successfully sued on use of TCPL data to establish the LDR standard by an aluminum company.
  - The court said that models of the environment must bear a reasonable relationship to the situation they are intended to represent.

What Led to LEAF Development?

- TCLP Program Issues (cont):

- In responding to legal challenges to TCLP use in determining the hazardousness of mineral processing wastes, the Agency was urged to consider using SPLP instead.
- TCLP was used in the end, but EPA agreed to conduct a review of leaching tests and their use in Agency Waste management programs

Superfund Use of Leach Tests for S/S Projects

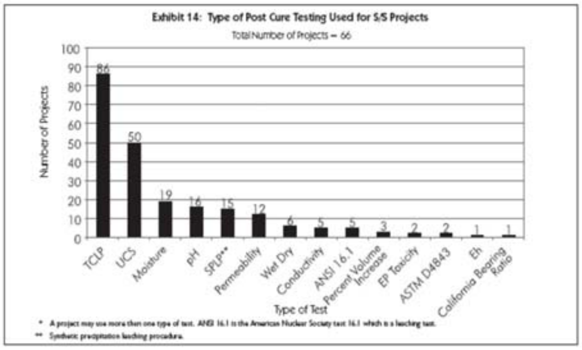


Exhibit 14: Type of Post Cure Testing Used for S/S Projects

Total Number of Projects = 66

* A project may use more than one type of test. ANSI 16.1 is the American Nuclear Society test 16.1 which is a leaching test.

** Synthetic precipitation leaching procedure.

What Led to LEAF Development?

- EPA's Science Advisory Board (SAB) has in the past expressed concern about the Agency's use of Leaching Tests:
  - In a 1991 report, the SAB expressed concern about the over-broad use of the test, particularly where test conditions did not match site conditions.
  - SAB expressed concern about several technical aspects of TCLP (e.g., colloid formation)
  - SAB urged the Agency to develop test methods which would:
    - Consider the significant parameters affecting leaching.
    - Consider conditions of the disposal site.
    - Be supported by field validation and repeatability studies.
    - Be supplemented by leaching and source term modeling.
  - In 1999 the SAB reiterated many of the concerns expressed in the 1991 report.

What Led to LEAF Development?

- EPA initiated a program to identify and validate a next-generation of leach testing approaches
  - Goals in selection of appropriate tests included:
    1. General applicability to a broad range of wastes/secondary materials
    2. Consideration of conditions that affect leaching
    3. Flexibility to allow tailoring for a range of applications

---

What Led to LEAF Development?

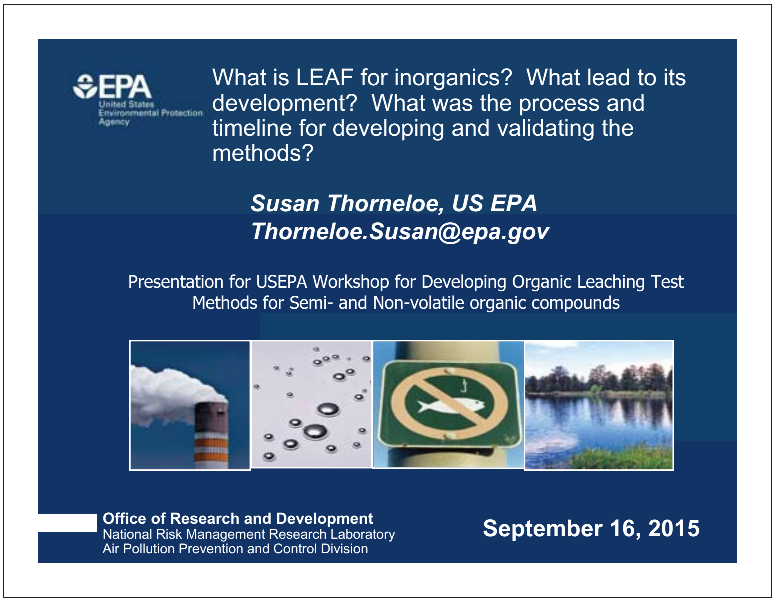
- 2003 SAB Consultation
- When LEAF research on CCR leaching was begun, ORCR/ORD consulted with the SAB about the approach being taken.
  - SAB was in particular asked its advice about the relative importance of the parameters affecting leaching that are incorporated into LEAF.
  - SAB did not disagree, but noted that other factors are sometimes important and urged flexibility in testing.
  - SAB also urged the Agency to develop leaching tests that included leaching or organic constituents.

LEAF Addresses Many SAB Concerns

- Most tests (including TCLP & SPLP) assess leaching potential for a single set of conditions:
  - Tests tend to focus in initial conditions; final test leaching conditions are often unknown.
- However, final test conditions represent conditions under which leaching actually occurs
- Site conditions can have a significant impact on leaching:
  - Metal solubility and aqueous-solid partitioning vary with pH.
  - Infiltration rates vary nationally (varying weather, soil type)
  - Redox conditions can determine which metal salts are present (and so change solubility).
  - Site conditions can change over time.

Program Use of LEAF

- Intended for situations where a tailored assessment is needed, and the conditions differ from TCLP, and TCLP is not required by RCRA regulations
  - Evaluating treatment effectiveness for corrective action/site remediation where LDR treatment standards are not triggered
  - Hazardous waste delisting
  - Assessment of non-hazardous materials for beneficial reuse
  - Characterizing potential release from high-volume materials
- CAMU regulations can allow use of alternatives to TCLP for assessing stabilization treatment effectiveness if the alternative more accurately reflects conditions at the site that affect leaching. See: 40 CFR 264.552(e)(4)(iv)(F)



What is LEAF for inorganics? What lead to its development? What was the process and timeline for developing and validating the methods?

Susan Thorneloe, US EPA
Thorneloe.Susan@epa.gov

Presentation for USEPA Workshop for Developing Organic Leaching Test Methods for Semi- and Non-volatile organic compounds

Office of Research and Development
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division

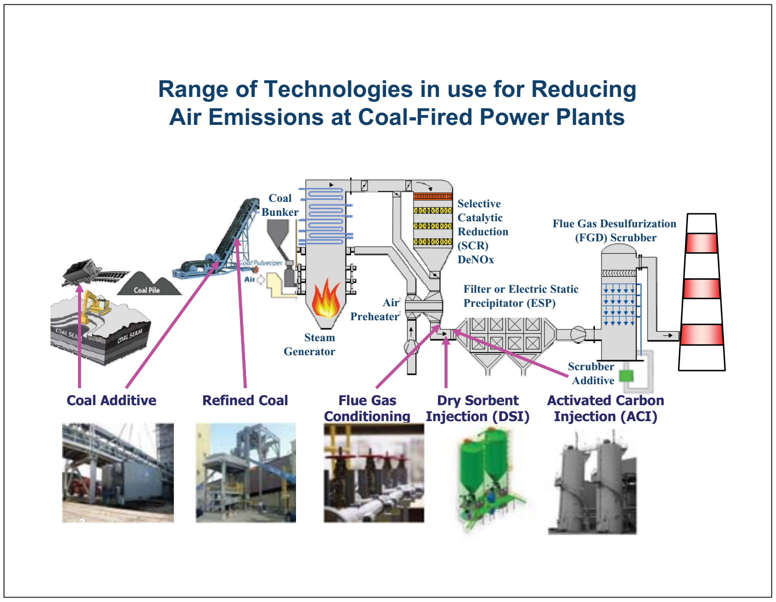
September 16, 2015

Objective

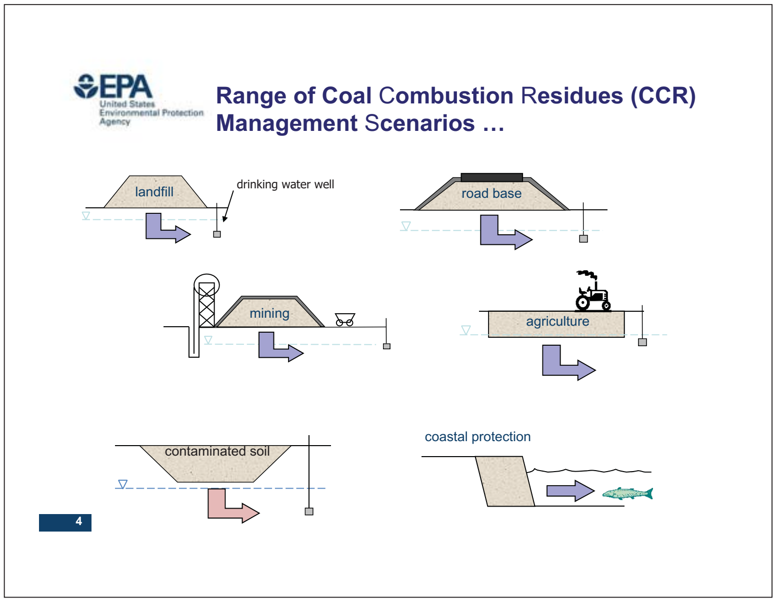
Provide understanding of work to develop and validate:

EPA Method 1313	Liquid-Solid Partitioning as a Function of Eluate pH using a Parallel Batch Procedure
EPA Method 1314	Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio (L/S) using an Up-flow Percolation Column Procedure
EPA Method 1315	Mass Transfer Rates in Monolithic and Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure
EPA Method 1316	Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio using a Parallel Batch Procedure

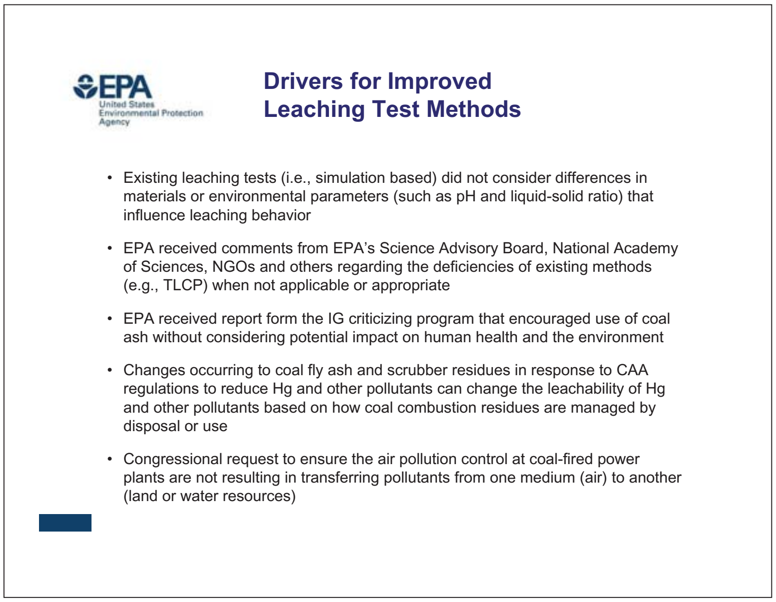
Posted as "New Validated Methods" to SW-846 *on Aug 2013*



Range of Technologies in use for Reducing Air Emissions at Coal-Fired Power Plants



Range of Coal Combustion Residues (CCR) Management Scenarios …

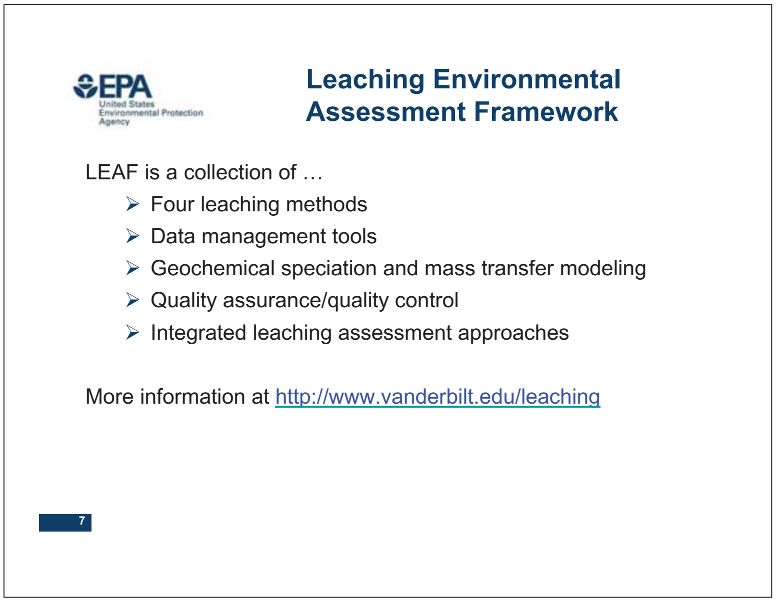


Drivers for Improved Leaching Test Methods

- Existing leaching tests (i.e., simulation based) did not consider differences in materials or environmental parameters (such as pH and liquid-solid ratio) that influence leaching behavior
- EPA received comments from EPA's Science Advisory Board, National Academy of Sciences, NGOs and others regarding the deficiencies of existing methods (e.g., TLCP) when not applicable or appropriate
- EPA received report form the IG criticizing program that encouraged use of coal ash without considering potential impact on human health and the environment
- Changes occurring to coal fly ash and scrubber residues in response to CAA regulations to reduce Hg and other pollutants can change the leachability of Hg and other pollutants based on how coal combustion residues are managed by disposal or use
- Congressional request to ensure the air pollution control at coal-fired power plants are not resulting in transferring pollutants from one medium (air) to another (land or water resources)

Use of LEAF in Source Term Development

- Used to evaluate range of fly ashes and scrubber residues to develop material- and site-specific source terms for land disposal of CCRs
- Data led to EPA's decision to allow use of coal fly ash for substitute for portland cement for encapsulated uses. EPA's decision was based on use of LEAF data to evaluate potential leaching from monoliths where fly ash is used as replacement for cement.
- "How to" Guidance for use of LEAF data has source term derivations for (1) coal ash used as embankment fill; (2) contaminated soil remediation; and (3) solidified waste treatment. Expect release in next 6 months. Will be updated as source terms are expanded to other applications.
- Continue to see broader use of LEAF by industry, academia, and commercial labs.
- The EU has developed methods comparable to LEAF for source term In parallel, the EU has developed methods comparable to LEAF for source term evaluation. China, Australia, Israel, and the EU are adopting comparable methods.
- Once CCR evaluation was completed, OSWER requested that LEAF be validated for adoption to SW-846. Over 20 labs were involved using 4 different reference materials for each of the 4 LEAF methods. Work began in 2010 and completed in 2013.

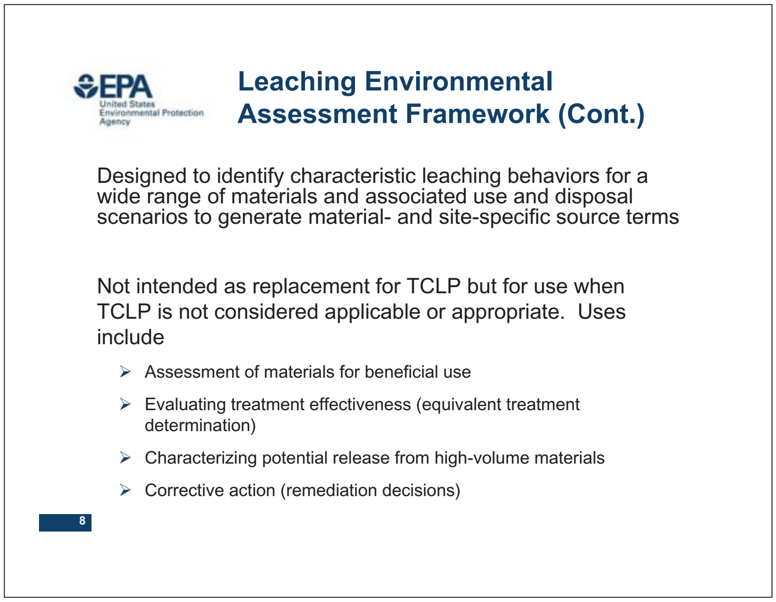


Leaching Environmental Assessment Framework

LEAF is a collection of …

- Four leaching methods
- Data management tools
- Geochemical speciation and mass transfer modeling
- Quality assurance/quality control
- Integrated leaching assessment approaches

More information at http://www.vanderbilt.edu/leaching

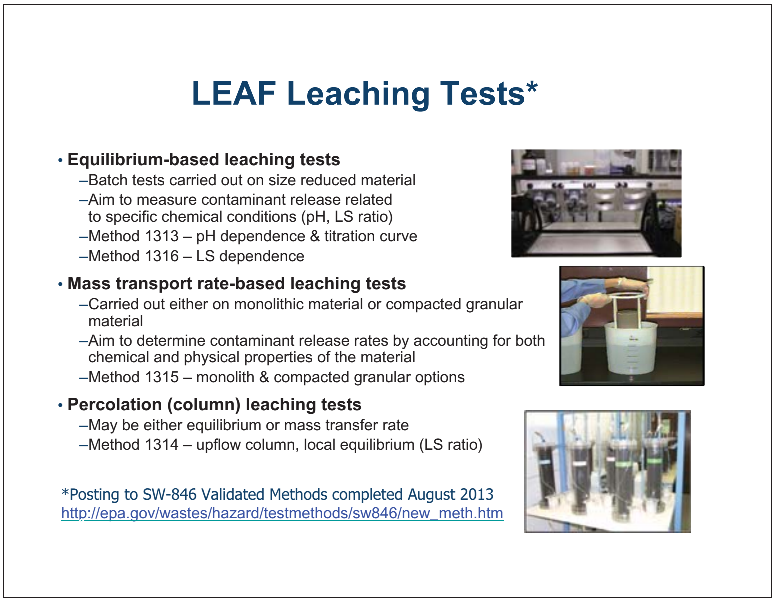


Leaching Environmental Assessment Framework (Cont.)

Designed to identify characteristic leaching behaviors for a wide range of materials and associated use and disposal scenarios to generate material- and site-specific source terms

Not intended as replacement for TCLP but for use when TCLP is not considered applicable or appropriate. Uses include

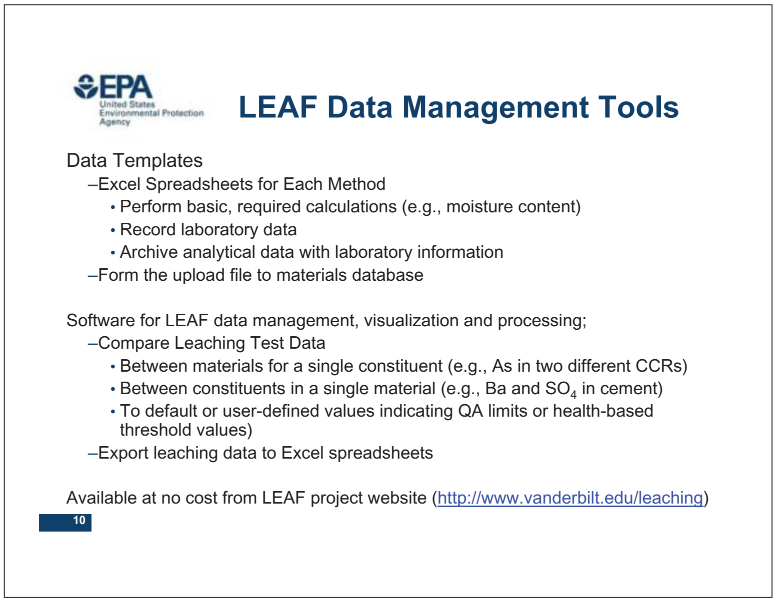
- Assessment of materials for beneficial use
- Evaluating treatment effectiveness (equivalent treatment determination)
- Characterizing potential release from high-volume materials
- Corrective action (remediation decisions)



LEAF Leaching Tests*

- **Equilibrium-based leaching tests**
  - –Batch tests carried out on size reduced material
  - –Aim to measure contaminant release related to specific chemical conditions (pH, LS ratio)
  - –Method 1313 – pH dependence & titration curve
  - –Method 1316 – LS dependence
- **Mass transport rate-based leaching tests**
  - –Carried out either on monolithic material or compacted granular material
  - –Aim to determine contaminant release rates by accounting for both chemical and physical properties of the material
  - –Method 1315 – monolith & compacted granular options
- **Percolation (column) leaching tests**
  - –May be either equilibrium or mass transfer rate
  - –Method 1314 – upflow column, local equilibrium (LS ratio)

*Posting to SW-846 Validated Methods completed August 2013
http://epa.gov/wastes/hazard/testmethods/sw846/new_meth.htm

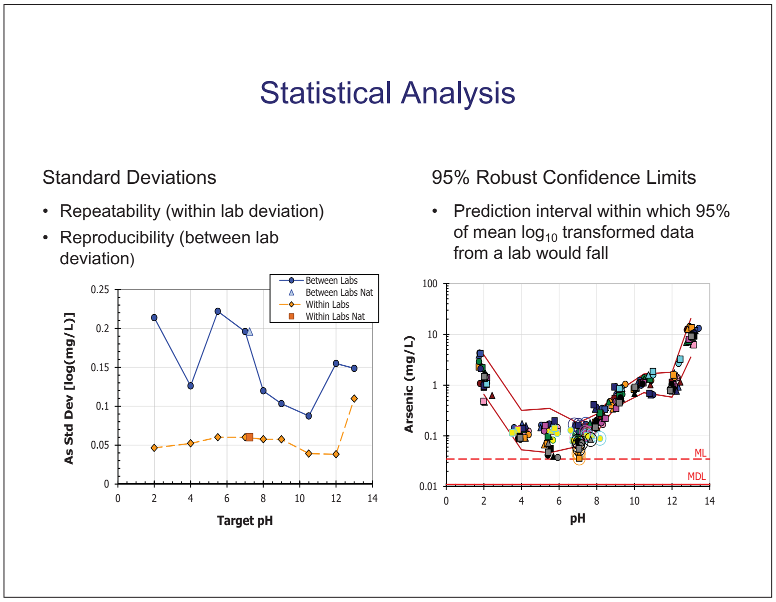


LEAF Data Management Tools

Data Templates
- –Excel Spreadsheets for Each Method
  - Perform basic, required calculations (e.g., moisture content)
  - Record laboratory data
  - Archive analytical data with laboratory information
- –Form the upload file to materials database

Software for LEAF data management, visualization and processing;
- –Compare Leaching Test Data
  - Between materials for a single constituent (e.g., As in two different CCRs)
  - Between constituents in a single material (e.g., Ba and SO_4 in cement)
  - To default or user-defined values indicating QA limits or health-based threshold values)
- –Export leaching data to Excel spreadsheets

Available at no cost from LEAF project website (http://www.vanderbilt.edu/leaching)



Statistical Analysis

Standard Deviations
- Repeatability (within lab deviation)
- Reproducibility (between lab deviation)

95% Robust Confidence Limits
- Prediction interval within which 95% of mean $\log_{10}$ transformed data from a lab would fall

Validation of LEAF Test Methods

Multi-lab Round-robin Testing
Academic,
Commercial,
Government and
International Labs

Materials
Coal Fly Ash
Contaminated Soil
Solidified Waste
Brass Foundry Sand

EPA 600/R-12/623
EPA 600/R-12/624

Validation Acknowledgements

Participating Labs – Domestic

- Government
    - ❑ Oak Ridge National Lab
    - ❑ Pacific Northwest National Lab
    - ❑ Savannah River National Lab
    - ❑ U.S. EPA- Research Triangle Park, NC
- Academia
    - ❑ Ohio State University
    - ❑ University of Wisconsin – Madison
    - ❑ University of Missouri – Rolla
    - ❑ Vanderbilt University
- Commercial
    - ❑ ARCADIS-US, Inc.
    - ❑ TestAmerica Laboratories, Inc.
    - ❑ URS Corporation

Other participating labs – international

- DHI (Denmark)
- Energy Research Centre of the Netherlands

Support

- Electric Power Research Institute (EPRI)
- Recycled Materials Research Center (RMRC)
- Tennessee Valley Authority (TVA)

LEAF Methods Focus Group

Validation Lessons Learned

Modifications to Methods 1313 and 1316

- Tolerance for contact time have been added
- Requirement that pH values to be measured within 1 hr after separation of solids and liquids due to lack of buffering in aqueous samples

Modifications to Data Templates

- Mandatory information has been highlighted
- Instructions more closely follow method text

Other Recommendations

- Calibration of pH meters should cover entire pH range to extent possible
- Reagents should be freshly prepared, stored in vessels of compatible materials (e.g., strong alkalis not be stored in borosilicate glass)
- Labs should establish a QC regimen to check the quality of reagent water (method blanks are important)

Laboratory-to-Field Relationships

- Provides understanding of leaching assessment fundamentals
- 10 Cases of large-scale field analysis coupled with laboratory testing for 7 different materials
    - -Coal combustion residues (fly ash, scrubber residues
    - -Inorganic waste (mixed origin)
    - -Municipal solid waste (MSW)
    - -MSW incinerator bottom ash
    - -Cement-stabilized MSW incinerator fly ash
    - -Portland cement mortars and concrete

L E A F

Leaching Environmental Assessment Framework

EPA

Leaching Test Relationships, Laboratory-to-Field Comparisons and Recommendations for Leaching Evaluation using the Leaching Environmental Assessment Framework

EPA 600/R-14/061

LEAF Method Validation Steps

- Agreements with labs to conduct validation of individual methods
- Obtain or develop samples for analysis
- Prepare and deliver kits with equipment and samples for each lab and method
- Receive Excel spreadsheets with results from each lab for each material and method
- Statistical analysis of samples to evaluate inter- and intra- laboratory variability
- Documentation of results into two reports representing two batch equilibrium methods and two mass transfer methods
- Reviews and publication of EPA report
- Posting of validated methods onto SW-846 web site

Conclusions for LEAF Validation

LEAF methods for inorganics

- have been found to provide data needed for assessing release behavior under range of field conditions for use and disposal scenarios
- can be used to evaluate leaching behavior of a wide range of materials using a tiered approach that considers the effect of leaching on pH, liquid-to-solid ratio, and physical form
- were validated working with 20 different labs and posted on the SW846 website as validated methods

Research has been coordinated with international community resulting in leveraging expertise, data, and helping provide harmonization in leaching methods so that comparable data is provided when evaluating use of industrial by-products or treatment and remediation effectiveness

Field to lab report showed good comparison between lab and field data using geochemical speciation modeling for processes not easily evaluated in lab (i.e., oxidation and carbonation). Able to explain leaching behavior and found LEAF is good predicator of ultimate fate of inorganics.

Supporting Documentation for LEAF Validation

- D.S. Kosson, H.A. van der Sloot, F. Sanchez, and A.C. Garrabrants (2002) “An integrated framework for evaluating leaching in waste management and utilization of secondary materials,” Environmental Engineering Science, 19(3), 159-204.
- Background Information for the Leaching Environmental Assessment Framework Test Methods, EPA/600/R-10/170, Dec 2010
- Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Leaching Tests for Inclusion into SW-846: Method 1313 and Method 1316, EPA 600/R-12/623, Sept 2012
- Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Leaching Tests for Inclusion into SW-846: Method 1314 and Method 1315, EPA 600/R-12/624, Sept 2012
- Laboratory-to-Field Comparisons for Leaching Evaluation using the Leaching Environmental Assessment Framework (LEAF), EPA 600/R-14/061, Sept 2014.

Supporting Documentation for use of LEAF to evaluate coal combustion residues (CCRs)

- S.A. Thorneloe, D.S. Kosson, F. Sanchez, A.C. Garrabrants, and G. Helms (2010) “Evaluating the Fate of Metals in Air Pollution Control Residues from Coal-Fired Power Plants,” Environmental Science & Technology, 44(19), 7351-7356.
- Characterization of Coal Combustion Residues from Electric Utilities - Leaching and Characterization Data, EPA-600/R-09/151, Dec 2009
- Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control, EPA-600/R-08/077, July 2008
- Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb 2006

Supplementary Slides on CCR Evaluation

U.S. range of observed total content and leaching test results (5.4 ≤ pH ≤ 12.4) for 34 fly ash samples and 20 FGD gypsum samples

	Indicator Values		Fly Ash		FGD Gypsum	
	TC (µg/L)	*MCL (µg/L)*	*Total Content (mg/kg)*	*Leaching Concentration (µg/L)*	*Total Content (mg/kg)*	*Leaching Concentration (µg/L)*
Hg	200	2	0.1- 1.5	<0.01-0.50	0.01-3.1	<0.01-0.66
Sb	-	6	3-14	<0.3-11,000	0.14-8.2	<0.3-330
As	5,000	10	17-510	0.32-18,000	0.95-10	0.32-1,200
Ba	100,000	2,000	50-7,000	50-670,000	2.4-67	30-560
B	-	7,000*	NA	210-270,000	NA	12-270,000
Cd	1,000	5	0.3-1.8	<0.1-320	0.11-0.61	<0.2-370
Cr	5,000	100	66-210	<0.3-7,300	1.2-20	<0.3-240
Mo	-	200	6.9-77	<0.5-130,000	1.1-12	0.36-1,900
Se	1,000	50	1.1-210	5.7-29,000	2.3-46	3.6-16,000
Tl	-	2	0.72-13	<0.3-790	0.24-2.3	<0.3-1,100

* Indicates DWEL value rather than MCL. **Red** text indicates where leaching concentrations are greater than indicator values but does not reflect fate and transport modeling. From ES&T 2010 publication.

Indicator Values: TC = Toxicity characteristic value; DWEL – drinking H_2O equivalent level; MCL – Maximum contaminant level

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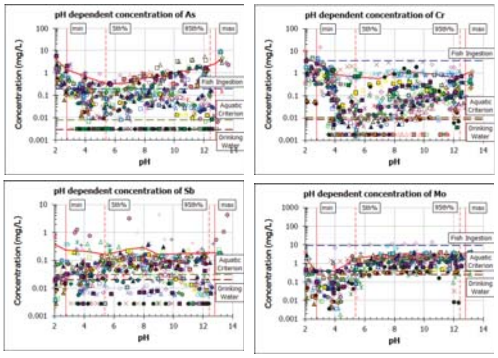
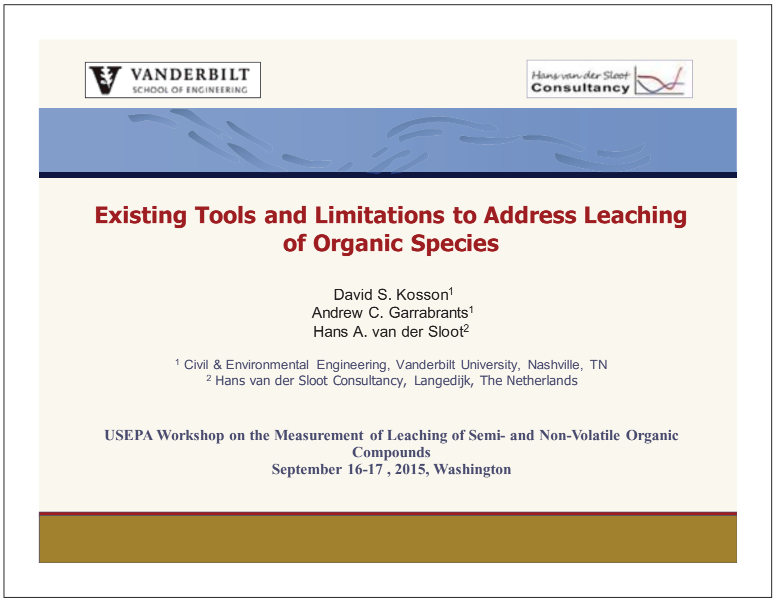
United States Environmental Protection Agency

Illustration of why LEAF is Needed



- COPCs leaching from CCRs have been found to span up to 4 orders of magnitude
- Acceptability appears to be CCR and/or use specific

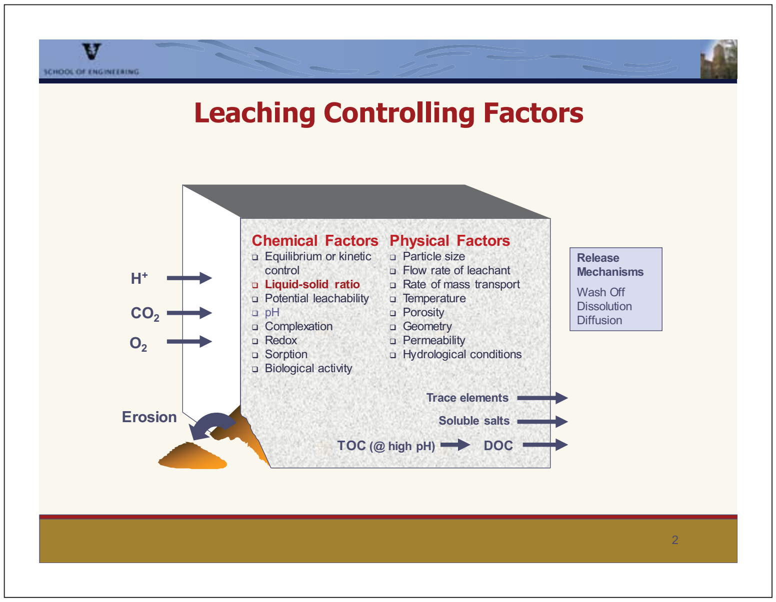


Existing Tools and Limitations to Address Leaching of Organic Species

David S. Kosson[1]
Andrew C. Garrabrants[1]
Hans A. van der Sloot[2]

[1] Civil & Environmental Engineering, Vanderbilt University, Nashville, TN
[2] Hans van der Sloot Consultancy, Langedijk, The Netherlands

USEPA Workshop on the Measurement of Leaching of Semi- and Non-Volatile Organic Compounds
September 16-17 , 2015, Washington

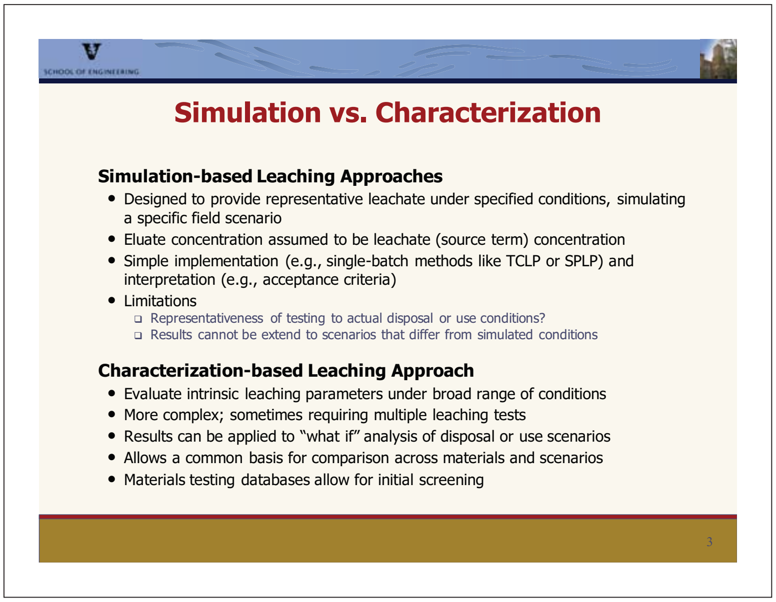


Leaching Controlling Factors

Chemical Factors
- ☐ Equilibrium or kinetic control
- ☐ **Liquid-solid ratio**
- ☐ Potential leachability
- ☐ pH
- ☐ Complexation
- ☐ Redox
- ☐ Sorption
- ☐ Biological activity

Physical Factors
- ☐ Particle size
- ☐ Flow rate of leachant
- ☐ Rate of mass transport
- ☐ Temperature
- ☐ Porosity
- ☐ Geometry
- ☐ Permeability
- ☐ Hydrological conditions

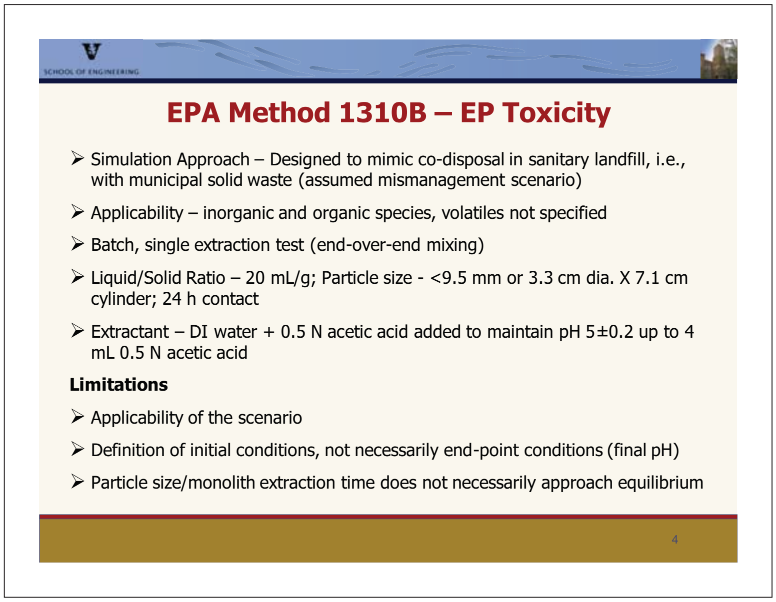
Release Mechanisms
Wash Off
Dissolution
Diffusion



Simulation vs. Characterization

Simulation-based Leaching Approaches
- Designed to provide representative leachate under specified conditions, simulating a specific field scenario
- Eluate concentration assumed to be leachate (source term) concentration
- Simple implementation (e.g., single-batch methods like TCLP or SPLP) and interpretation (e.g., acceptance criteria)
- Limitations
  - ☐ Representativeness of testing to actual disposal or use conditions?
  - ☐ Results cannot be extend to scenarios that differ from simulated conditions

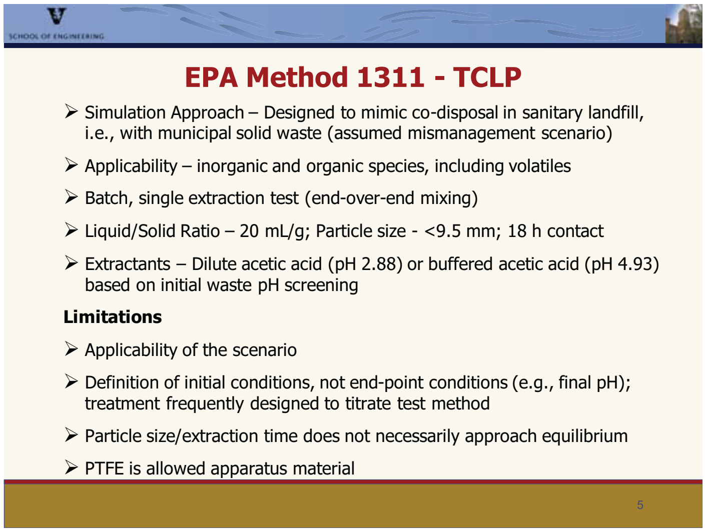
Characterization-based Leaching Approach
- Evaluate intrinsic leaching parameters under broad range of conditions
- More complex; sometimes requiring multiple leaching tests
- Results can be applied to "what if" analysis of disposal or use scenarios
- Allows a common basis for comparison across materials and scenarios
- Materials testing databases allow for initial screening



EPA Method 1310B – EP Toxicity

- ➢ Simulation Approach – Designed to mimic co-disposal in sanitary landfill, i.e., with municipal solid waste (assumed mismanagement scenario)
- ➢ Applicability – inorganic and organic species, volatiles not specified
- ➢ Batch, single extraction test (end-over-end mixing)
- ➢ Liquid/Solid Ratio – 20 mL/g; Particle size - <9.5 mm or 3.3 cm dia. X 7.1 cm cylinder; 24 h contact
- ➢ Extractant – DI water + 0.5 N acetic acid added to maintain pH 5±0.2 up to 4 mL 0.5 N acetic acid

Limitations
- ➢ Applicability of the scenario
- ➢ Definition of initial conditions, not necessarily end-point conditions (final pH)
- ➢ Particle size/monolith extraction time does not necessarily approach equilibrium

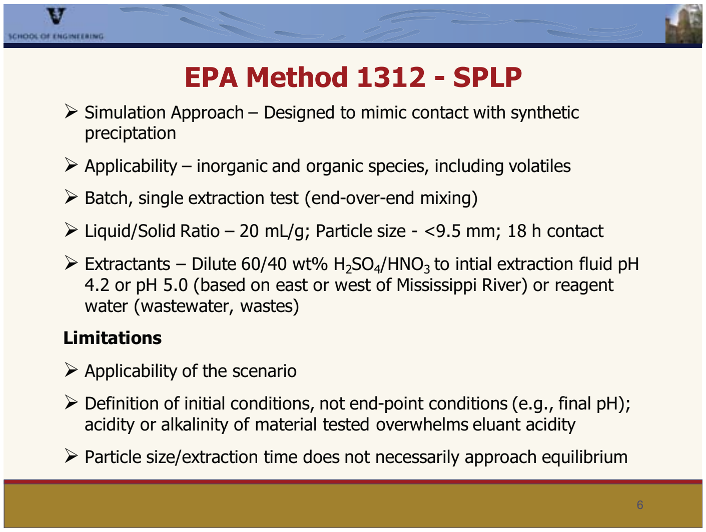


EPA Method 1311 - TCLP

- Simulation Approach – Designed to mimic co-disposal in sanitary landfill, i.e., with municipal solid waste (assumed mismanagement scenario)
- Applicability – inorganic and organic species, including volatiles
- Batch, single extraction test (end-over-end mixing)
- Liquid/Solid Ratio – 20 mL/g; Particle size - <9.5 mm; 18 h contact
- Extractants – Dilute acetic acid (pH 2.88) or buffered acetic acid (pH 4.93) based on initial waste pH screening

Limitations

- Applicability of the scenario
- Definition of initial conditions, not end-point conditions (e.g., final pH); treatment frequently designed to titrate test method
- Particle size/extraction time does not necessarily approach equilibrium
- PTFE is allowed apparatus material

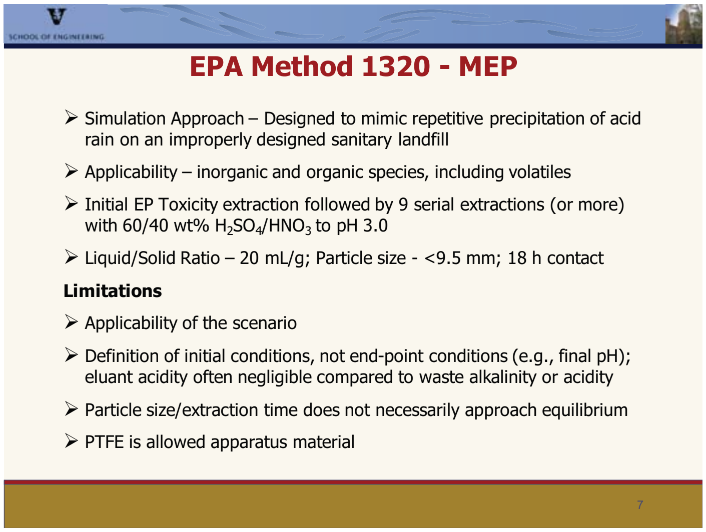


EPA Method 1312 - SPLP

- Simulation Approach – Designed to mimic contact with synthetic preciptation
- Applicability – inorganic and organic species, including volatiles
- Batch, single extraction test (end-over-end mixing)
- Liquid/Solid Ratio – 20 mL/g; Particle size - <9.5 mm; 18 h contact
- Extractants – Dilute 60/40 wt% H_2SO_4/HNO_3 to intial extraction fluid pH 4.2 or pH 5.0 (based on east or west of Mississippi River) or reagent water (wastewater, wastes)

Limitations

- Applicability of the scenario
- Definition of initial conditions, not end-point conditions (e.g., final pH); acidity or alkalinity of material tested overwhelms eluant acidity
- Particle size/extraction time does not necessarily approach equilibrium

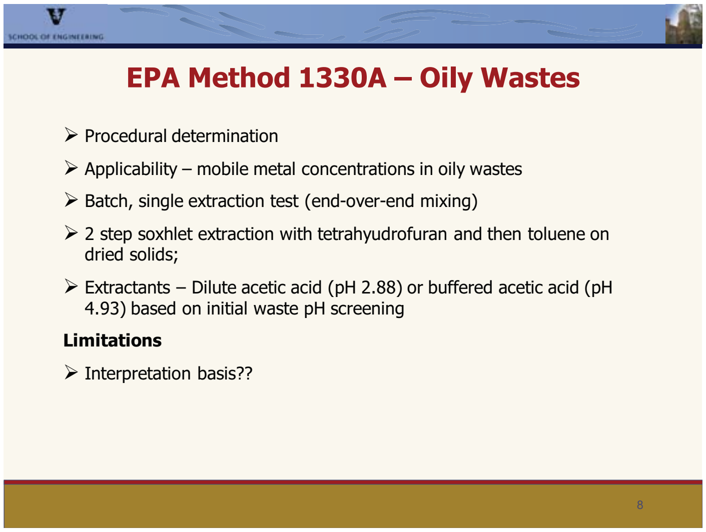


EPA Method 1320 - MEP

- Simulation Approach – Designed to mimic repetitive precipitation of acid rain on an improperly designed sanitary landfill
- Applicability – inorganic and organic species, including volatiles
- Initial EP Toxicity extraction followed by 9 serial extractions (or more) with 60/40 wt% H_2SO_4/HNO_3 to pH 3.0
- Liquid/Solid Ratio – 20 mL/g; Particle size - <9.5 mm; 18 h contact

Limitations

- Applicability of the scenario
- Definition of initial conditions, not end-point conditions (e.g., final pH); eluant acidity often negligible compared to waste alkalinity or acidity
- Particle size/extraction time does not necessarily approach equilibrium
- PTFE is allowed apparatus material



EPA Method 1330A – Oily Wastes

- Procedural determination
- Applicability – mobile metal concentrations in oily wastes
- Batch, single extraction test (end-over-end mixing)
- 2 step soxhlet extraction with tetrahyudrofuran and then toluene on dried solids;
- Extractants – Dilute acetic acid (pH 2.88) or buffered acetic acid (pH 4.93) based on initial waste pH screening

Limitations

- Interpretation basis??

L E A F

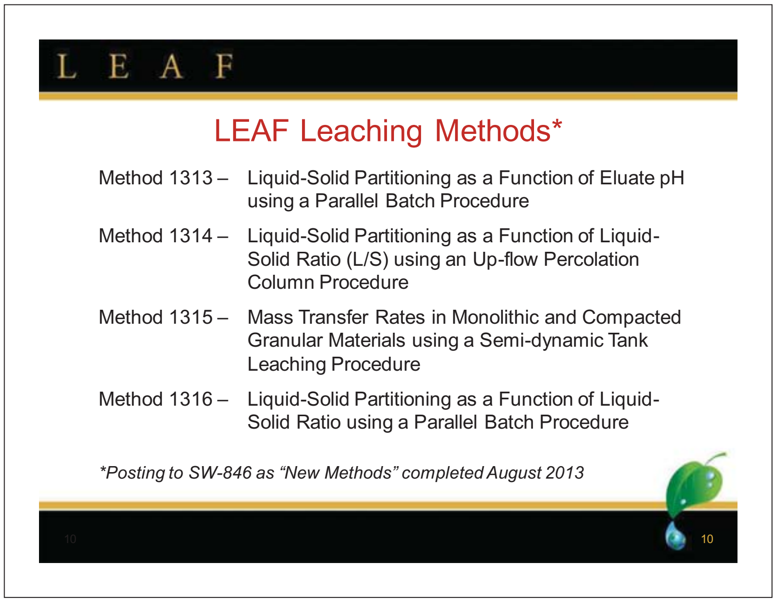
Leaching Environmental Assessment Framework

A Decision Support System for Beneficial Use and Disposal Decisions in the United States and Internationally…

- Four leaching test methods
- Data management tools
- Geochemical speciation and mass transfer modeling
- Quality assurance/quality control for materials production
- Integrated leaching assessment approaches

… designed to identify characteristic leaching behaviors for a wide range of materials and scenarios.

More information at http://www.vanderbilt.edu/leaching



L E A F

LEAF Leaching Methods*

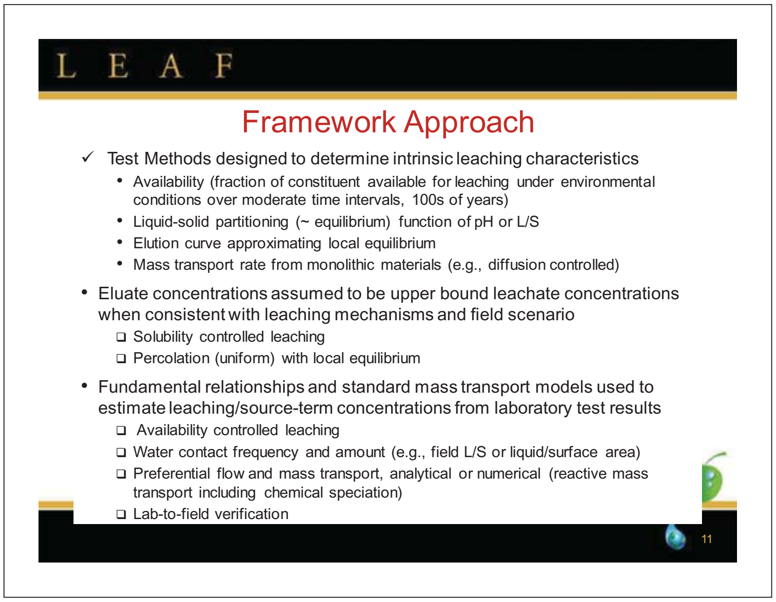
Method 1313 – Liquid-Solid Partitioning as a Function of Eluate pH using a Parallel Batch Procedure

Method 1314 – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio (L/S) using an Up-flow Percolation Column Procedure

Method 1315 – Mass Transfer Rates in Monolithic and Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure

Method 1316 – Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio using a Parallel Batch Procedure

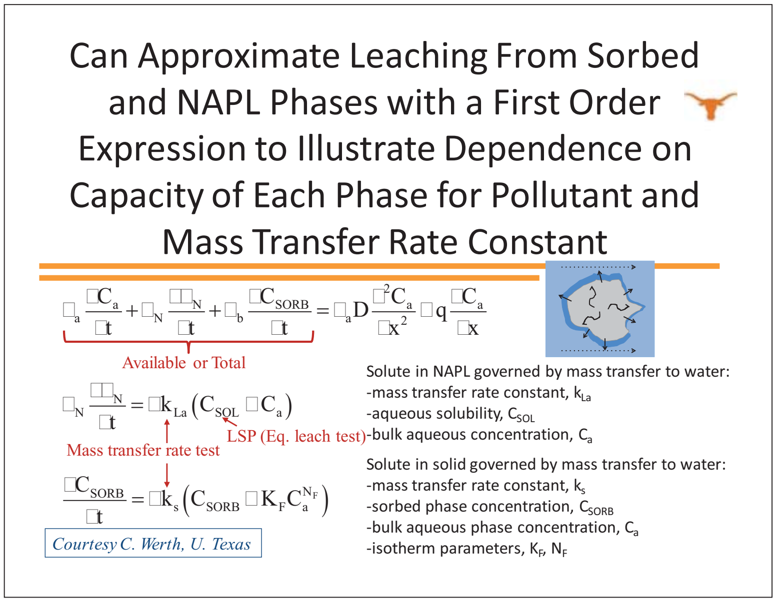
**Posting to SW-846 as "New Methods" completed August 2013*



L E A F

Framework Approach

- ✓ Test Methods designed to determine intrinsic leaching characteristics
  - Availability (fraction of constituent available for leaching under environmental conditions over moderate time intervals, 100s of years)
  - Liquid-solid partitioning (~ equilibrium) function of pH or L/S
  - Elution curve approximating local equilibrium
  - Mass transport rate from monolithic materials (e.g., diffusion controlled)
- Eluate concentrations assumed to be upper bound leachate concentrations when consistent with leaching mechanisms and field scenario
  - ☐ Solubility controlled leaching
  - ☐ Percolation (uniform) with local equilibrium
- Fundamental relationships and standard mass transport models used to estimate leaching/source-term concentrations from laboratory test results
  - ☐ Availability controlled leaching
  - ☐ Water contact frequency and amount (e.g., field L/S or liquid/surface area)
  - ☐ Preferential flow and mass transport, analytical or numerical (reactive mass transport including chemical speciation)
  - ☐ Lab-to-field verification



Can Approximate Leaching From Sorbed and NAPL Phases with a First Order Expression to Illustrate Dependence on Capacity of Each Phase for Pollutant and Mass Transfer Rate Constant

$$\underbrace{\square_a \frac{\square C_a}{\square t} + \square_N \frac{\square\square_N}{\square t} + \square_b \frac{\square C_{SORB}}{\square t}}_{\text{Available or Total}} = \square_a D \frac{\square^2 C_a}{\square x^2} \square q \frac{\square C_a}{\square x}$$

$$\square_N \frac{\square\square_N}{\square t} = \square k_{La} \left(C_{SOL} \square C_a \right)$$

LSP (Eq. leach test)

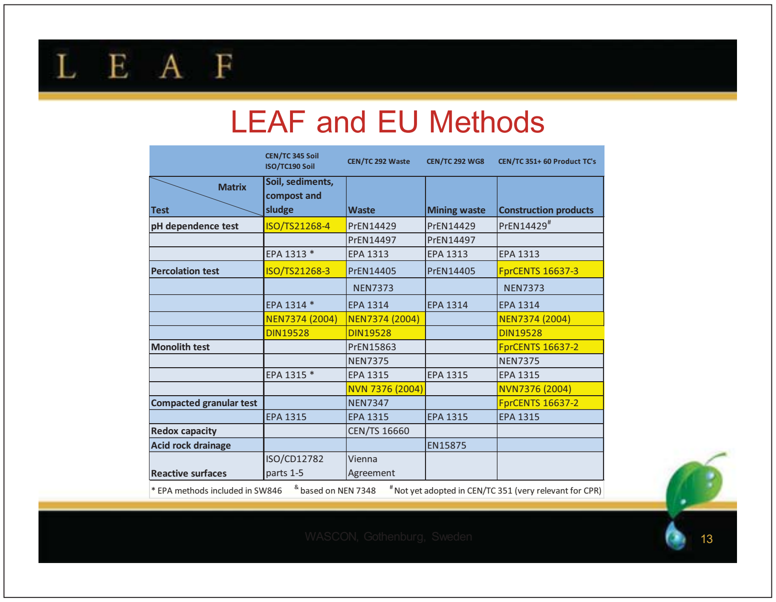
Mass transfer rate test

$$\frac{\square C_{SORB}}{\square t} = \square k_s \left(C_{SORB} \square K_F C_a^{N_F} \right)$$

Courtesy C. Werth, U. Texas

Solute in NAPL governed by mass transfer to water:
-mass transfer rate constant, k_{La}
-aqueous solubility, C_{SOL}
-bulk aqueous concentration, C_a

Solute in solid governed by mass transfer to water:
-mass transfer rate constant, k_s
-sorbed phase concentration, C_{SORB}
-bulk aqueous phase concentration, C_a
-isotherm parameters, K_F, N_F

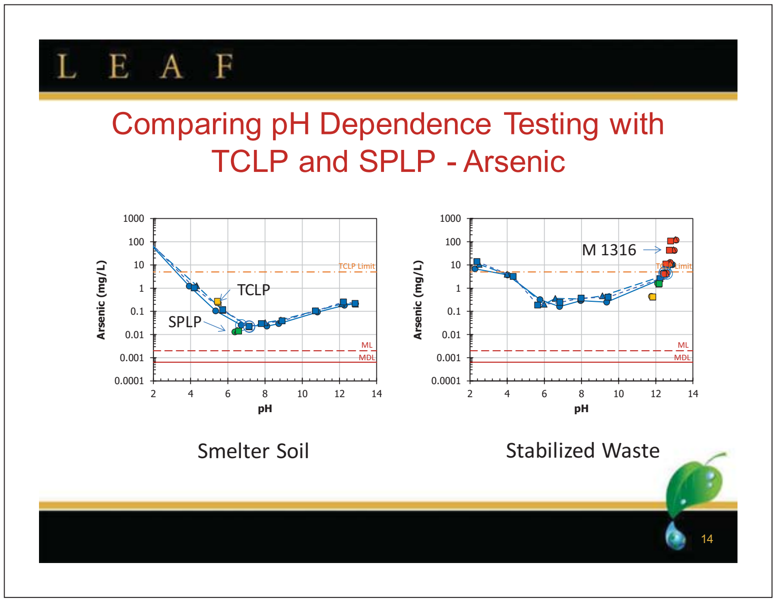


LEAF and EU Methods

	CEN/TC 345 Soil ISO/TC190 Soil	CEN/TC 292 Waste	CEN/TC 292 WG8	CEN/TC 351+ 60 Product TC's
Test / **Matrix**	**Soil, sediments, compost and sludge**	**Waste**	**Mining waste**	**Construction products**
pH dependence test	ISO/TS21268-4	PrEN14429	PrEN14429	PrEN14429#
		PrEN14497	PrEN14497	
	EPA 1313 *	EPA 1313	EPA 1313	EPA 1313
Percolation test	ISO/TS21268-3	PrEN14405	PrEN14405	FprCENTS 16637-3
		NEN7373		NEN7373
	EPA 1314 *	EPA 1314	EPA 1314	EPA 1314
	NEN7374 (2004)	NEN7374 (2004)		NEN7374 (2004)
	DIN19528	DIN19528		DIN19528
Monolith test		PrEN15863		FprCENTS 16637-2
		NEN7375		NEN7375
	EPA 1315 *	EPA 1315	EPA 1315	EPA 1315
		NVN 7376 (2004)		NVN7376 (2004)
Compacted granular test		NEN7347		FprCENTS 16637-2
	EPA 1315	EPA 1315	EPA 1315	EPA 1315
Redox capacity		CEN/TS 16660		
Acid rock drainage			EN15875	
Reactive surfaces	ISO/CD12782 parts 1-5	Vienna Agreement		

* EPA methods included in SW846 & based on NEN 7348 # Not yet adopted in CEN/TC 351 (very relevant for CPR)

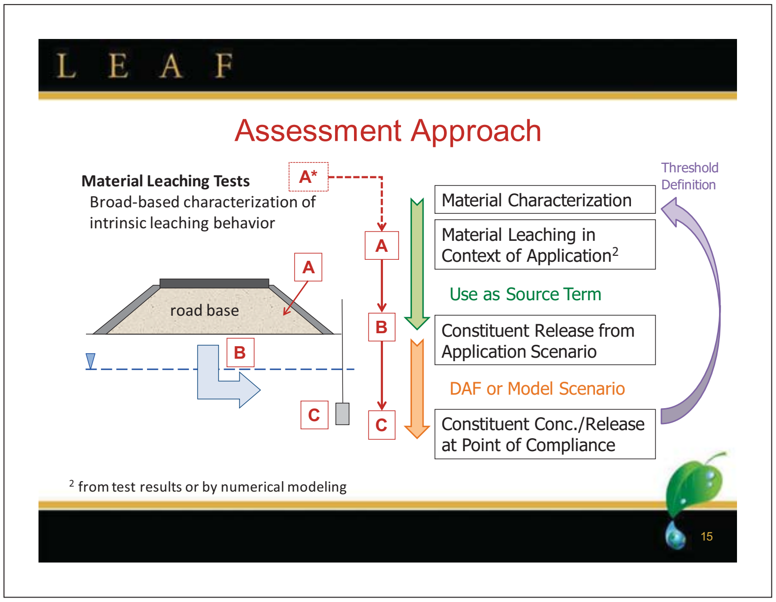
WASCON, Gothenburg, Sweden



Comparing pH Dependence Testing with TCLP and SPLP - Arsenic

Smelter Soil

Stabilized Waste



Assessment Approach

Material Leaching Tests
Broad-based characterization of intrinsic leaching behavior

Threshold Definition

Material Characterization

Material Leaching in Context of Application^2

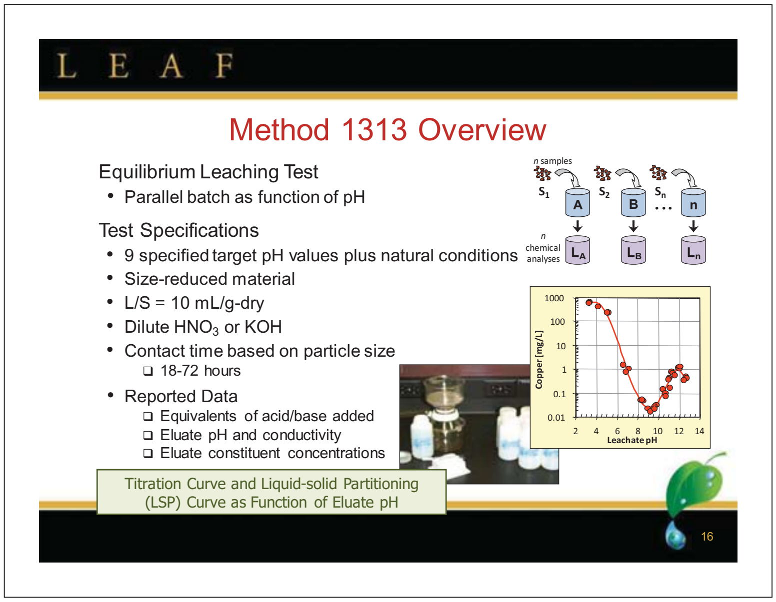
Use as Source Term

Constituent Release from Application Scenario

DAF or Model Scenario

Constituent Conc./Release at Point of Compliance

[2] from test results or by numerical modeling

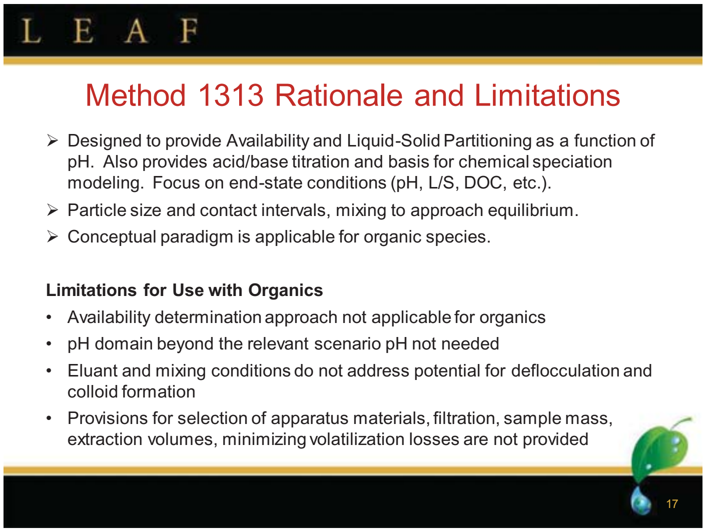


Method 1313 Overview

Equilibrium Leaching Test
- Parallel batch as function of pH

Test Specifications
- 9 specified target pH values plus natural conditions
- Size-reduced material
- L/S = 10 mL/g-dry
- Dilute HNO_3 or KOH
- Contact time based on particle size
  - ❑ 18-72 hours
- Reported Data
  - ❑ Equivalents of acid/base added
  - ❑ Eluate pH and conductivity
  - ❑ Eluate constituent concentrations

Titration Curve and Liquid-solid Partitioning (LSP) Curve as Function of Eluate pH

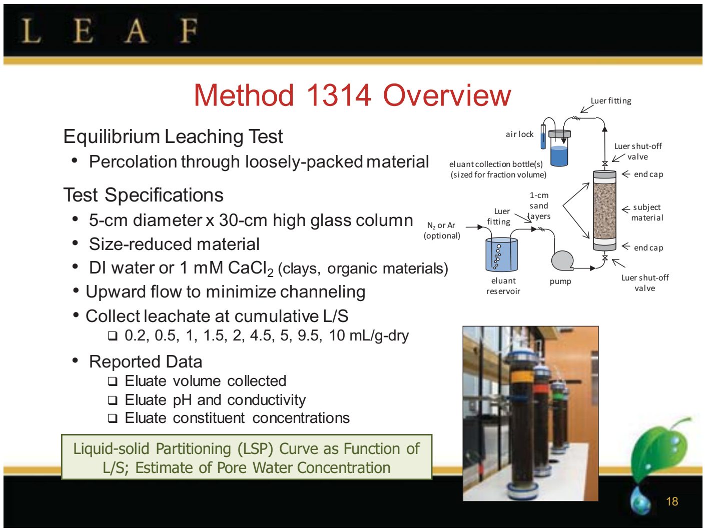


Method 1313 Rationale and Limitations

- ➢ Designed to provide Availability and Liquid-Solid Partitioning as a function of pH. Also provides acid/base titration and basis for chemical speciation modeling. Focus on end-state conditions (pH, L/S, DOC, etc.).
- ➢ Particle size and contact intervals, mixing to approach equilibrium.
- ➢ Conceptual paradigm is applicable for organic species.

Limitations for Use with Organics

- Availability determination approach not applicable for organics
- pH domain beyond the relevant scenario pH not needed
- Eluant and mixing conditions do not address potential for deflocculation and colloid formation
- Provisions for selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses are not provided



Method 1314 Overview

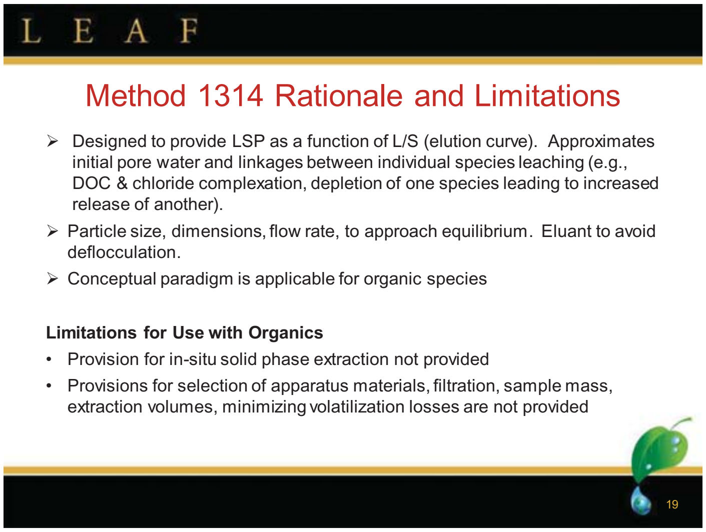
Equilibrium Leaching Test

- Percolation through loosely-packed material

Test Specifications

- 5-cm diameter x 30-cm high glass column
- Size-reduced material
- DI water or 1 mM $CaCl_2$ (clays, organic materials)
- Upward flow to minimize channeling
- Collect leachate at cumulative L/S
  - ❑ 0.2, 0.5, 1, 1.5, 2, 4.5, 5, 9.5, 10 mL/g-dry
- Reported Data
  - ❑ Eluate volume collected
  - ❑ Eluate pH and conductivity
  - ❑ Eluate constituent concentrations

Liquid-solid Partitioning (LSP) Curve as Function of L/S; Estimate of Pore Water Concentration

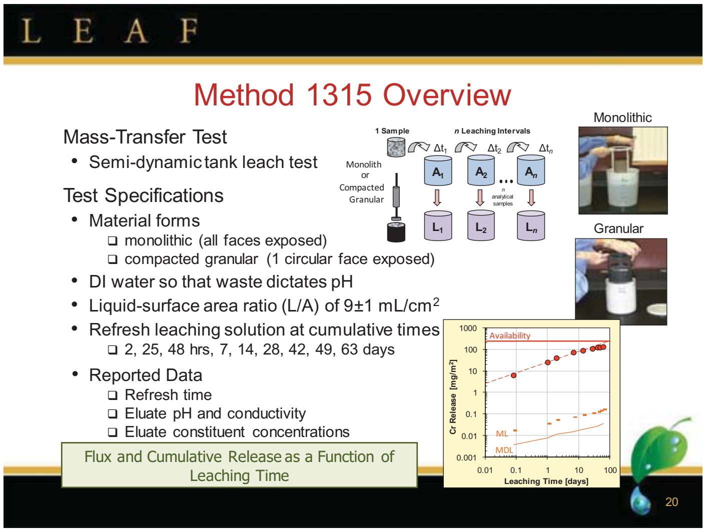


Method 1314 Rationale and Limitations

- ➢ Designed to provide LSP as a function of L/S (elution curve). Approximates initial pore water and linkages between individual species leaching (e.g., DOC & chloride complexation, depletion of one species leading to increased release of another).
- ➢ Particle size, dimensions, flow rate, to approach equilibrium. Eluant to avoid deflocculation.
- ➢ Conceptual paradigm is applicable for organic species

Limitations for Use with Organics

- Provision for in-situ solid phase extraction not provided
- Provisions for selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses are not provided



Method 1315 Overview

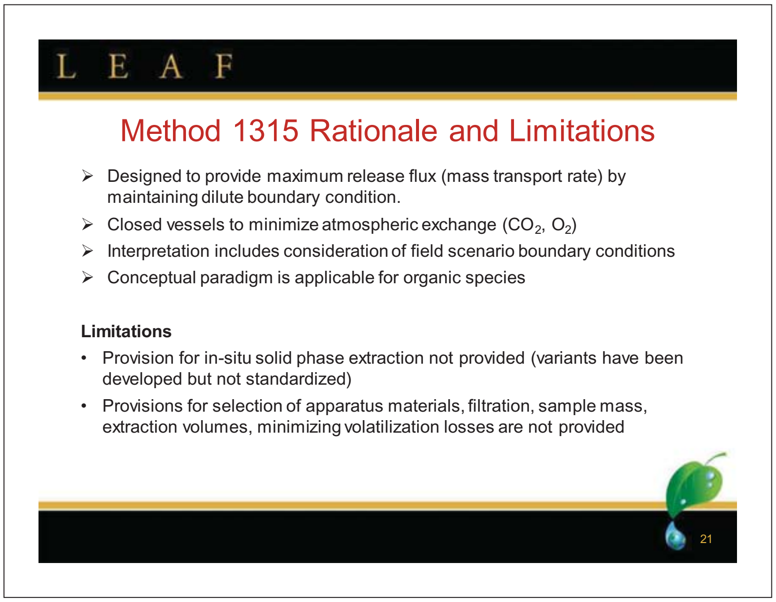
Mass-Transfer Test

- Semi-dynamic tank leach test

Test Specifications

- Material forms
  - ❑ monolithic (all faces exposed)
  - ❑ compacted granular (1 circular face exposed)
- DI water so that waste dictates pH
- Liquid-surface area ratio (L/A) of 9±1 mL/cm^2
- Refresh leaching solution at cumulative times
  - ❑ 2, 25, 48 hrs, 7, 14, 28, 42, 49, 63 days
- Reported Data
  - ❑ Refresh time
  - ❑ Eluate pH and conductivity
  - ❑ Eluate constituent concentrations

Flux and Cumulative Release as a Function of Leaching Time

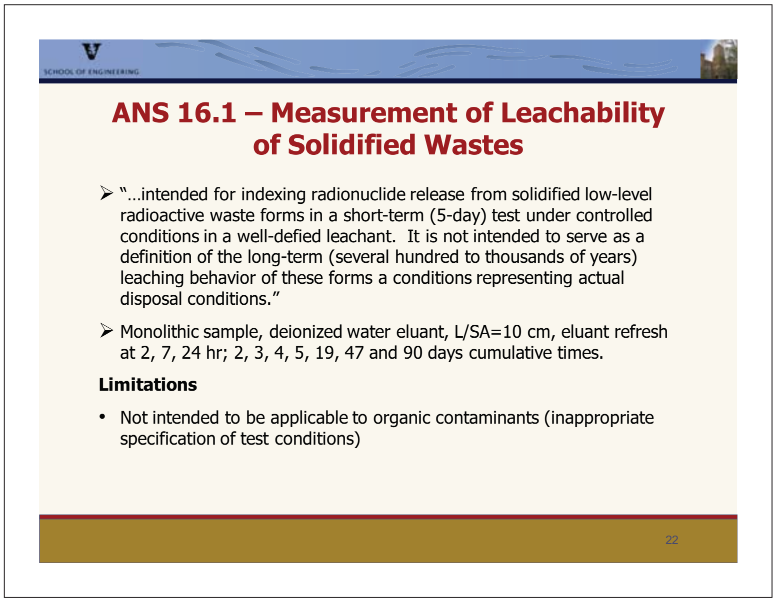


Method 1315 Rationale and Limitations

- Designed to provide maximum release flux (mass transport rate) by maintaining dilute boundary condition.
- Closed vessels to minimize atmospheric exchange (CO_2, O_2)
- Interpretation includes consideration of field scenario boundary conditions
- Conceptual paradigm is applicable for organic species

Limitations

- Provision for in-situ solid phase extraction not provided (variants have been developed but not standardized)
- Provisions for selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses are not provided

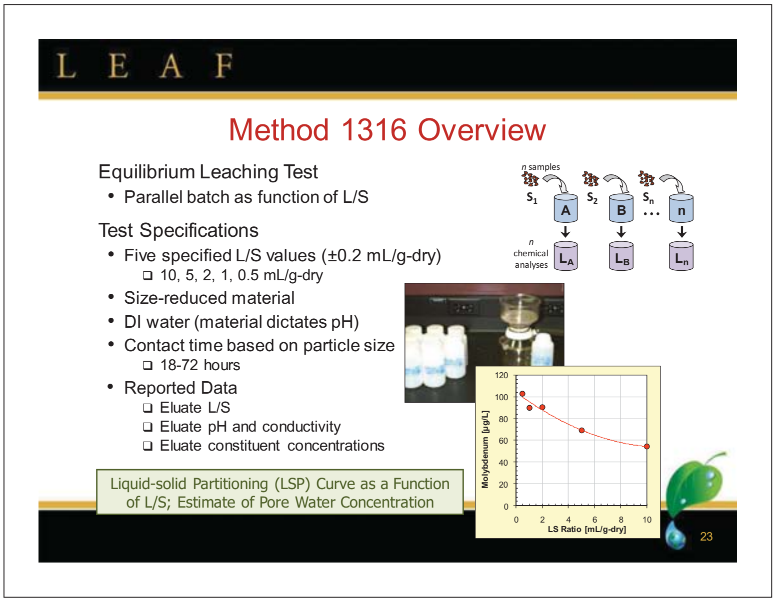


ANS 16.1 – Measurement of Leachability of Solidified Wastes

- "...intended for indexing radionuclide release from solidified low-level radioactive waste forms in a short-term (5-day) test under controlled conditions in a well-defied leachant. It is not intended to serve as a definition of the long-term (several hundred to thousands of years) leaching behavior of these forms a conditions representing actual disposal conditions."
- Monolithic sample, deionized water eluant, L/SA=10 cm, eluant refresh at 2, 7, 24 hr; 2, 3, 4, 5, 19, 47 and 90 days cumulative times.

Limitations

- Not intended to be applicable to organic contaminants (inappropriate specification of test conditions)



Method 1316 Overview

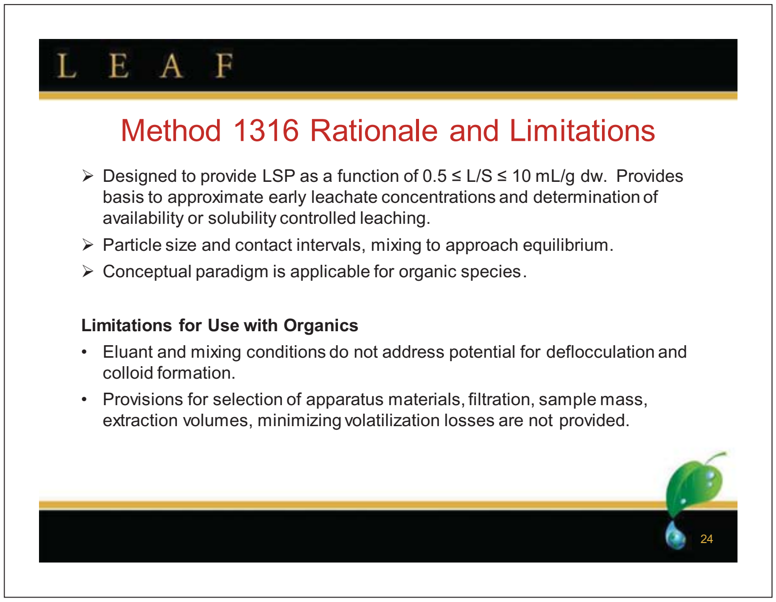
Equilibrium Leaching Test

- Parallel batch as function of L/S

Test Specifications

- Five specified L/S values (±0.2 mL/g-dry)
  - 10, 5, 2, 1, 0.5 mL/g-dry
- Size-reduced material
- DI water (material dictates pH)
- Contact time based on particle size
  - 18-72 hours
- Reported Data
  - Eluate L/S
  - Eluate pH and conductivity
  - Eluate constituent concentrations

Liquid-solid Partitioning (LSP) Curve as a Function of L/S; Estimate of Pore Water Concentration

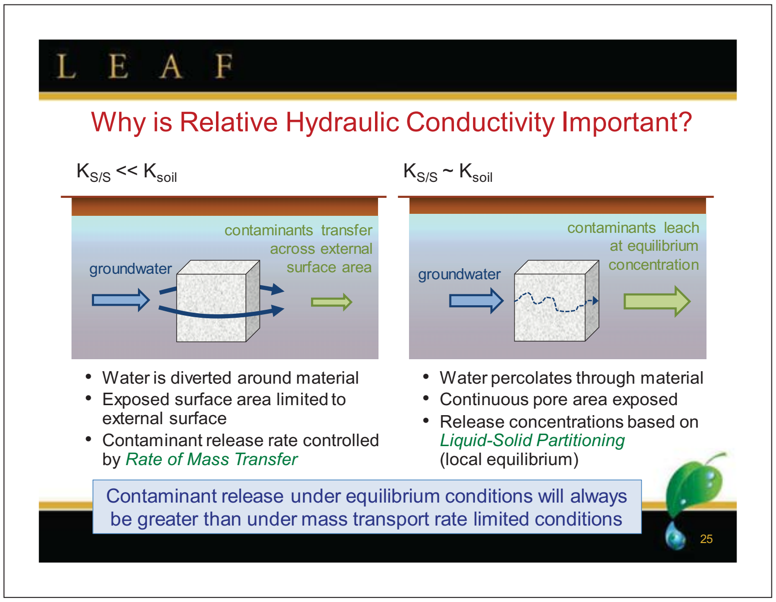


Method 1316 Rationale and Limitations

- Designed to provide LSP as a function of $0.5 \leq L/S \leq 10$ mL/g dw. Provides basis to approximate early leachate concentrations and determination of availability or solubility controlled leaching.
- Particle size and contact intervals, mixing to approach equilibrium.
- Conceptual paradigm is applicable for organic species.

Limitations for Use with Organics

- Eluant and mixing conditions do not address potential for deflocculation and colloid formation.
- Provisions for selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses are not provided.



Why is Relative Hydraulic Conductivity Important?

$K_{S/S} << K_{soil}$

- Water is diverted around material
- Exposed surface area limited to external surface
- Contaminant release rate controlled by *Rate of Mass Transfer*

$K_{S/S} \sim K_{soil}$

- Water percolates through material
- Continuous pore area exposed
- Release concentrations based on *Liquid-Solid Partitioning* (local equilibrium)

Contaminant release under equilibrium conditions will always be greater than under mass transport rate limited conditions

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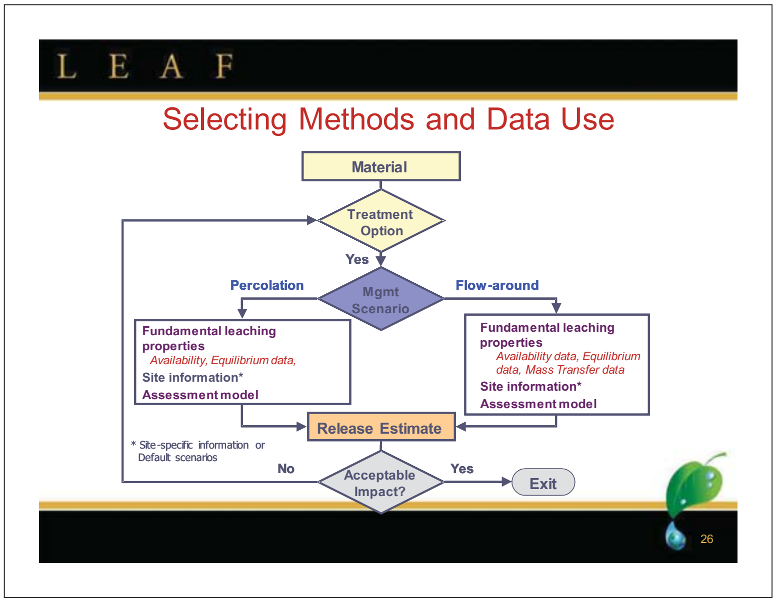


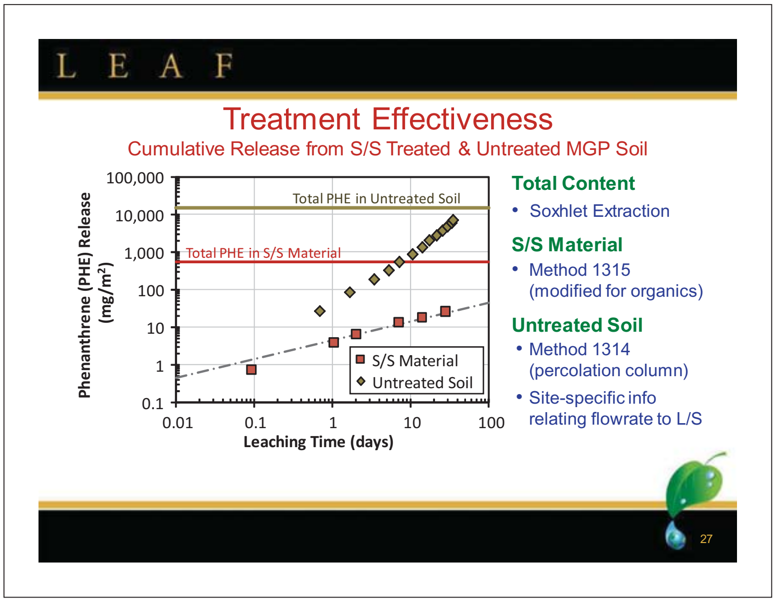
Selecting Methods and Data Use

Fundamental leaching properties
Availability, Equilibrium data,
Site information*
Assessment model

Fundamental leaching properties
Availability data, Equilibrium data, Mass Transfer data
Site information*
Assessment model

Release Estimate

* Site-specific information or Default scenarios



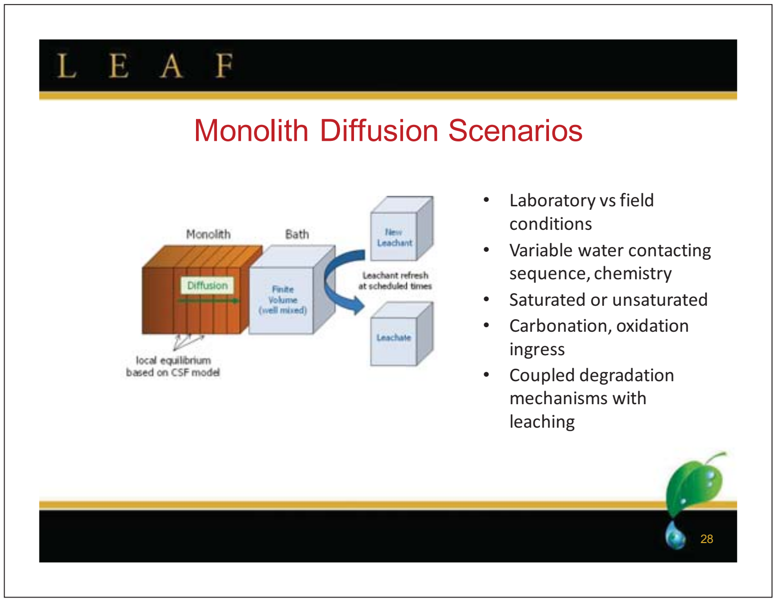
Treatment Effectiveness

Cumulative Release from S/S Treated & Untreated MGP Soil

Total Content
- Soxhlet Extraction

S/S Material
- Method 1315 (modified for organics)

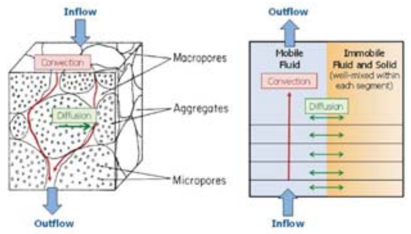
Untreated Soil
- Method 1314 (percolation column)
- Site-specific info relating flowrate to L/S



Monolith Diffusion Scenarios

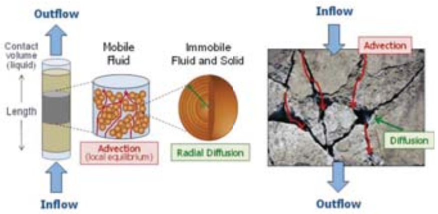
- Laboratory vs field conditions
- Variable water contacting sequence, chemistry
- Saturated or unsaturated
- Carbonation, oxidation ingress
- Coupled degradation mechanisms with leaching

Percolation with Mobile-Immobile Zones Scenarios



- Laboratory vs. field conditions
- Variable water flow rate, chemistry
- Effects of preferential flow

Percolation with Radial Diffusion Scenarios



- Laboratory vs field conditions
- Cracked materials or packed beds
- Effects of preferential flow
- Variable water flow rate, chemistry

Lab & Field Scenario Rationale and Limitations

- Development of source terms follows a tiered approach, with simple approximation (reasonable bounding) used based on mass balance, chemical thermodynamic, and mass transport principles.
- More complex models used to provide basis for developing leaching source terms under conditions that are not direct applications of laboratory test data or simple analytical solutions (e.g., finite bath leaching from monolith, evolving boundary conditions and chemistry). Includes consideration of sorptive phases, aqueous phase complexation, NOM, DOC, redox, etc.
- Conceptual paradigm is applicable for organic species.

Limitations

- Does not include consideration of NAPLs, vapor phase transport, biodegradation/transformation.

Conclusions

- Measurement of intrinsic leaching characteristics and development of source terms based on mass balance, thermodynamic and mass transport principles provides a robust leaching assessment framework that is applicable to both inorganic and organic species.
- Numerical modeling is required when direct extension of laboratory results to field conditions is not applicable and analytical solutions are not available.
- A tiered approach to source-term estimation provides for a balance between extent of testing, complexity of source-term development, and end-user needs.
- Current LEAF test methods do not include specifications specific to many classes of organic species. Important factors that are not addressed ***specifically for organics*** include selection of apparatus materials, filtration, sample mass, extraction volumes, minimizing volatilization losses, maintaining "dilute" boundary conditions (for monoliths). Use in source terms does not address NAPLS and vapor phase transport.