Fraction of Organic Carbon in Soil

Application to Ohio EPA VAP Rules

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Technical Guidance Compendium (TGC) Reference

- **TGC # VA30007.14.001 – Sampling & Analysis of Fraction Organic Carbon (f_{oc}) in Soils - Revised January 2014**
- **Reasons:**
  - Provides for **less subjective** evaluation
  - Addresses **large correction factor errors**
  - Addresses **less conservative results** from ASTM method due to influence of carbonates
  - Addresses NFAs submitted with TOC concentrations **outside range of values** found in literature sources

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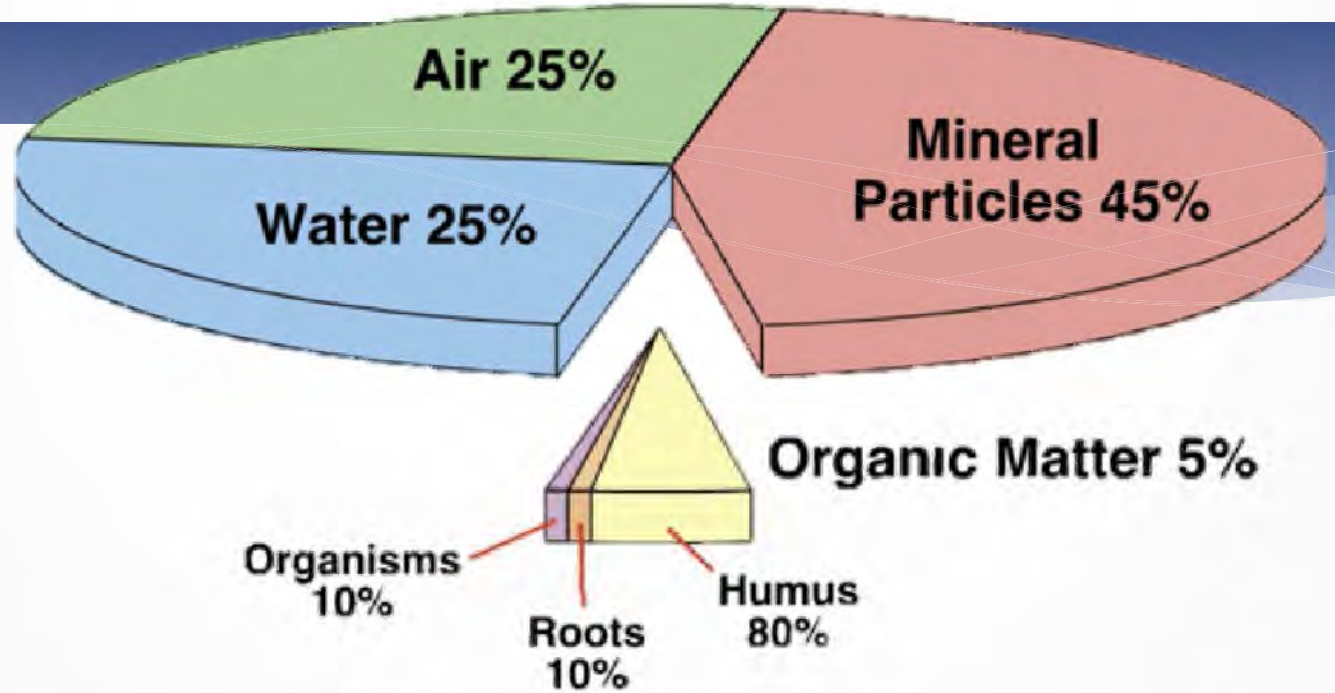


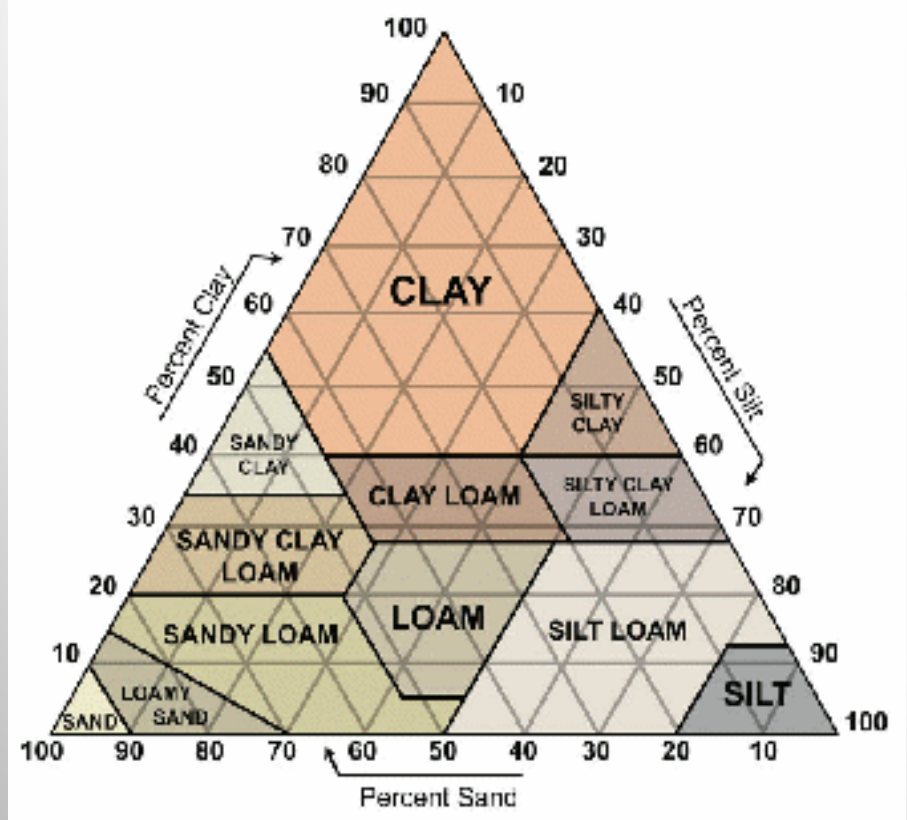
www.prescriptionsoilanalysis.com/files/images/soil_composition

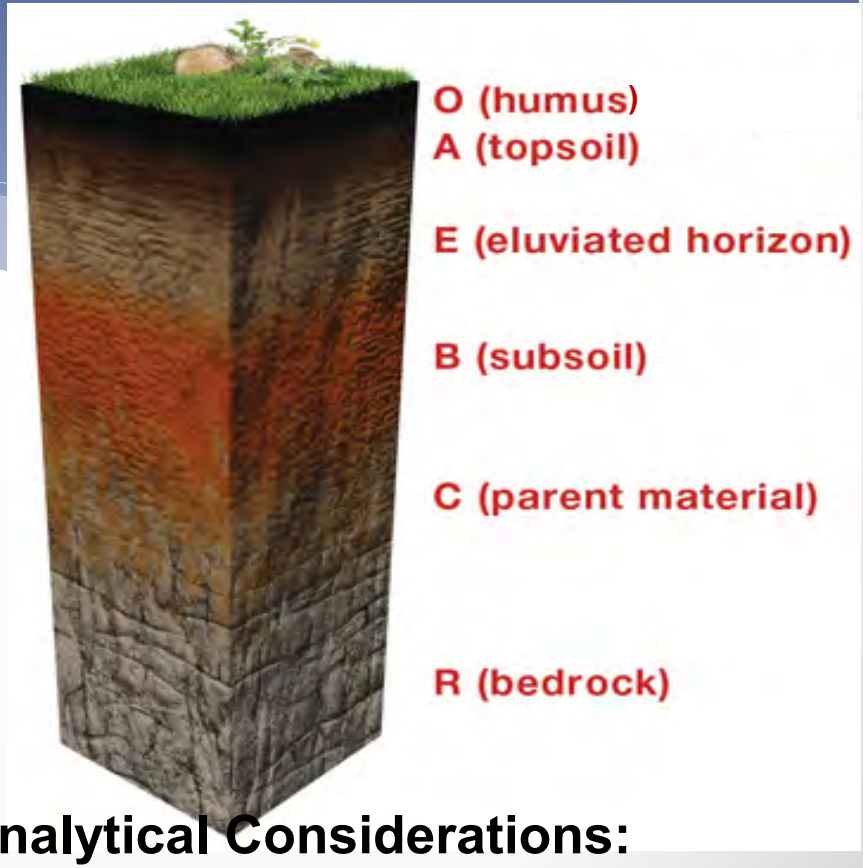
- Soil organic matter (SOM) ≠ Soil organic carbon (SOC)
  - SOM contains ≈ 58% SOC
  - **This is the fraction of organic carbon – *f*oc!**
    - ONLY an approximation!
    - Actual fraction is soil specific

Consideration of Soil Characteristics

Structural considerations:

- Where in the soil profile are we?
  - Horizons: O, A, E, B and C
- What soil type do we have?
  - Texture: percent sand, silt and clay





Analytical Considerations:

Composition:

Inorganic constituents

Organic constituents

Processes

Biological

Anthropogenic

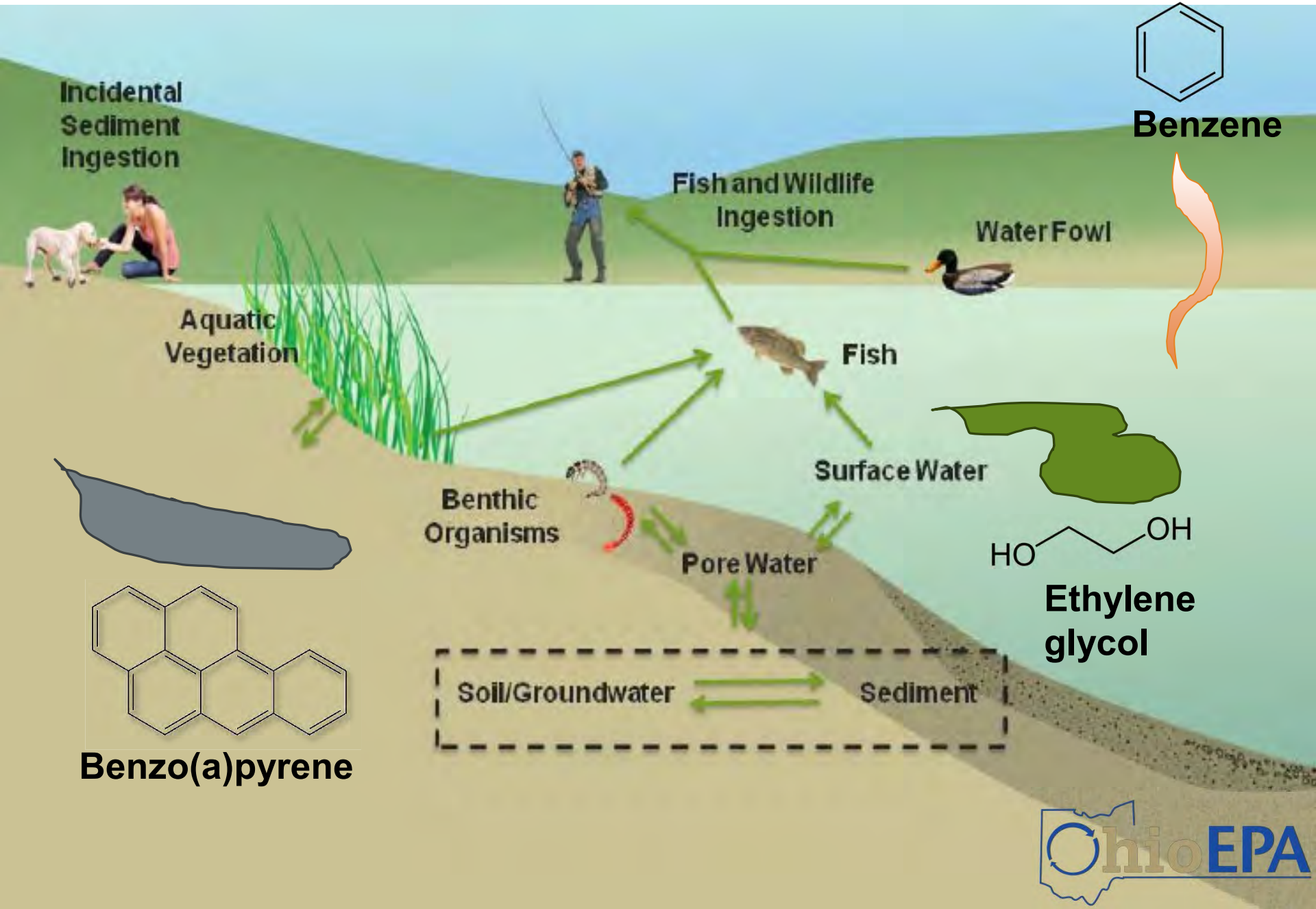
Organic Chemicals of Concern (COCs) - Behavior & $f$oc in Soil Systems

Behavior – Parameters

- Is it volatile? – Henry's Law Constant – H'
- Is it soluble? – Solubility - S
- Does it "sorb" to the SOM? - Organic carbon coefficient - Koc
- Does it dissolve in fat vs. water?
  - Octanol water coefficient – Kow
- Where K is a partition coefficient

Organic chemical behavior governed by partition coefficients!

How Organic Chemicals Partition in the Environment



Importance of Partitioning on Fate and Transport of Organic Contaminants

- **Partitioning behavior** – determines which "compartment" (soil/water/air) contaminant concentrates in

- Described by **partition coefficient, Kd** – this
- GOVERNS fate and transport

- Measured by **Koc** (L/kg)– ***soil organic carbon partition coefficient*** - chemical specific property – values found in Ohio EPA CIDARS database or US EPA RSL database (REGION 9)

- **Kd = Koc * *ƒ*oc – thus, Kd is normalized to *ƒ*oc**

- ***ƒ*oc - fraction of organic carbon** (%) in vadose zone or soil layer appropriate to the compartment being evaluated

Thus, Kd depends on *ƒ*oc - an important and sensitive parameter in many environmental evaluations!

Partioning Behavior: Applicable Ohio EPA VAP Rules and Guidance

* TGC VA30009.07.031 - Utilizes **Soil Partitioning Coefficient (Kd)** in **leaching evaluation**

* OAC 3745-300-08(C)(3)(b) – Utilizes **Kd** to develop **Generic Direct Contact Soil Standards**

* OAC 3745-300-08(C)(3)(e) – Utilizes **Kd** in calculations of **Property-Specific Soil Saturation** concentration for a constituent

* OAC 3745-300-07(G)– Utilizes **Kd** in **Modeling**
  * **SESOIL** - fate and transport of chemicals in ground water
  * Ohio EPA - Sample Collection and Evaluation of Vapor Intrusion (VI) to Indoor Air Guidance Document, May 2010 and US EPA OSWER **Johnson and Ettinger (J&E)** Model
    * SL-ADV to model chemical behavior **VI pathway**

Soil Sampling Considerations

sciencewithmoxieblogspot.com

What is being determined?

OAC 3745-300-07(E)(2) Phase II characterize lateral extent & characteristics of unsaturated soils to evaluate **contaminant attenuation capacity**

How many?

OAC 3745-300-07(E)(1) - **10% of total population or 8,** whichever is greater

ProUCL defines sample population needed to develop a 95% LCL as **8 or more**

How to sample?

- Use correct tools
- Understand sources of error
- Chose randomly
- Sample representatively

***Avoid anthropogenic sources of contamination ***

Sampling Protocols & Guidance:

Gerlach and Nocerino, 2003: http://www.epa.gov/esd/cmb/pdf/guidance.pdf

Mason, 1992: http://www.epa.gov/OUST/cat/mason

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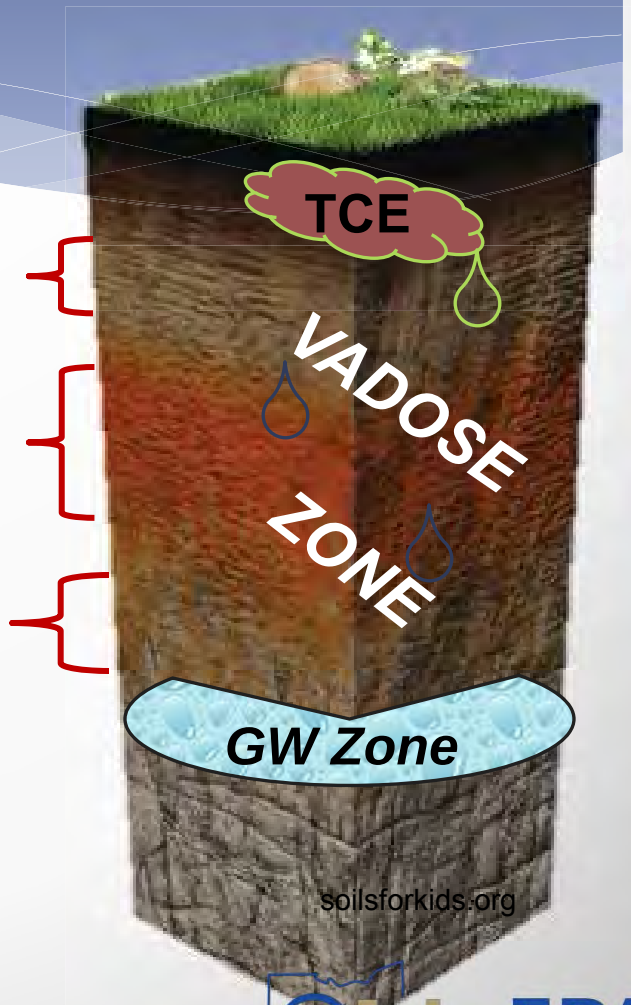
Depth Weighted Averaging in Soil Profile: Relationship between *f*oc & Density - ρ (Rho)

Example - Normalizing *f*oc for ρ:

3 samples @ 2 – 4 ft. ρ = 0.98
*f*oc = 3.2 %

3 samples @ 6 – 8 ft. ρ = 1.2
*f*oc = 1.2 %

3 samples @ 8 – 10 ft. ρ = 1.5
*f*oc = 0.7 %



*f*oc 95 % UCL VALUE:

w/o ρ normalization	with ρ normalization
1.68	1.47

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Protection of GW Meeting Unrestricted Potable Use Standards (POGWMUPUS)

Ohio EPA VAP TGC VA30007.14.007 – Separation Distance Between Source Area and GW:

- At least 30 feet clay/clayey silt? Qualitative demonstration possible
- Less than 30 feet? Demonstration likely to be quantitative
- Less than 15 feet? Weight of evidence not usually acceptable

- **Both** require evaluation of partition coefficient **(kd)** therefore, analysis of ***f*oc** may be warranted
- Soil characteristics to assist in attenuation demonstration:
  - **Bulk density, soil pH and *f*oc**

Application of *f*oc in Soil Leaching and Soil Saturation Calculations

Ohio EPA VAP Leaching document:

* http://epa.ohio.gov/portals/30/vap/docs/sec-g-att.pdf

US EPA Soil Leaching Guidance:

* http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/chemicals/SSG_nonrad_technical.pdf

What should I use and when?

* **Screening -** Simple partitioning formula - TGC #VA30009.07.031 – Inherently conservative
* **Generic Values** – OAC 3745-300-08 Appendix - Generic Numerical Direct Contact Soil Standards – *f*oc defaults used in development
* **Property Specific Methods** – Utilizes Equation OAC 3745-300-09(H)(5) with property specific inputs - includes input for *f*oc
* **Modeling Options** – TGC VA30007.09.032 (formerly VA30007.05.05) – Use of RBCA Tool Kit ® and SAM to Evaluate Leaching - provides guidance - more complex modeling options

Soil Leaching & Saturation Equations

For Leaching to GW:

Soil Partitioning Coefficient Equation

$$Cs = foc * Koc * Cw$$

Where Cs = allowable soil conc.

- soil screening number, ppm (mg/kg)

***f*oc = fraction OC soil, unit less**

Koc = OC partition coefficient carbon (chemical specific), L/kg

Cw = water quality standard (MCL/background/risk-based), ppm (mg/L)

Note: Product of *f*oc and Koc is AKA Kd (soil adsorption coefficient)

For COC without a Generic Standard: Property Specific Saturation Equation

$$C_{sat} = \frac{S}{\rho_b}\left(K_d\,\rho_b + \theta_w + H'\theta_a\right)$$

Where C_{sat} = allowable soil conc. (mg/kg)

S = water solubility (mg/L water)

ρb = dry soil bulk density (kg/L)

Kd = soil – water partition coefficient (L/kg)

($K_d = K_{oc}$ x f_{oc})

Koc = soil OC /water partition coefficient (L/kg)

foc = fraction OC of soil (g/g) – default is 0.6%

θw = water – filled soil porosity (L_{water}/ L_{soil})

H' = dimensionless Henry's Law constant

θa = air – filled porosity (L_{pore}/ L_{soil})

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Allowable Soil Leaching Concentrations: Comparison of Screening, Generic & PS Equations

Chlorinated Solvent	Koc L/kg	Partitioning Equation (screening) ƒoc = 0.3% mg/kg	Generic Leach Based Soil Values (derived from SESOIL) mg/kg	Property Specific Partioning Equation ƒoc = 1.2% mg/kg
PCE	95.0	0.001	0.03	5.70
TCE	60.7	0.001	0.05	3.60
VC	24.7	0.0001	0.010	0.520
1,2,4 –TMB	614	0.03	---	110

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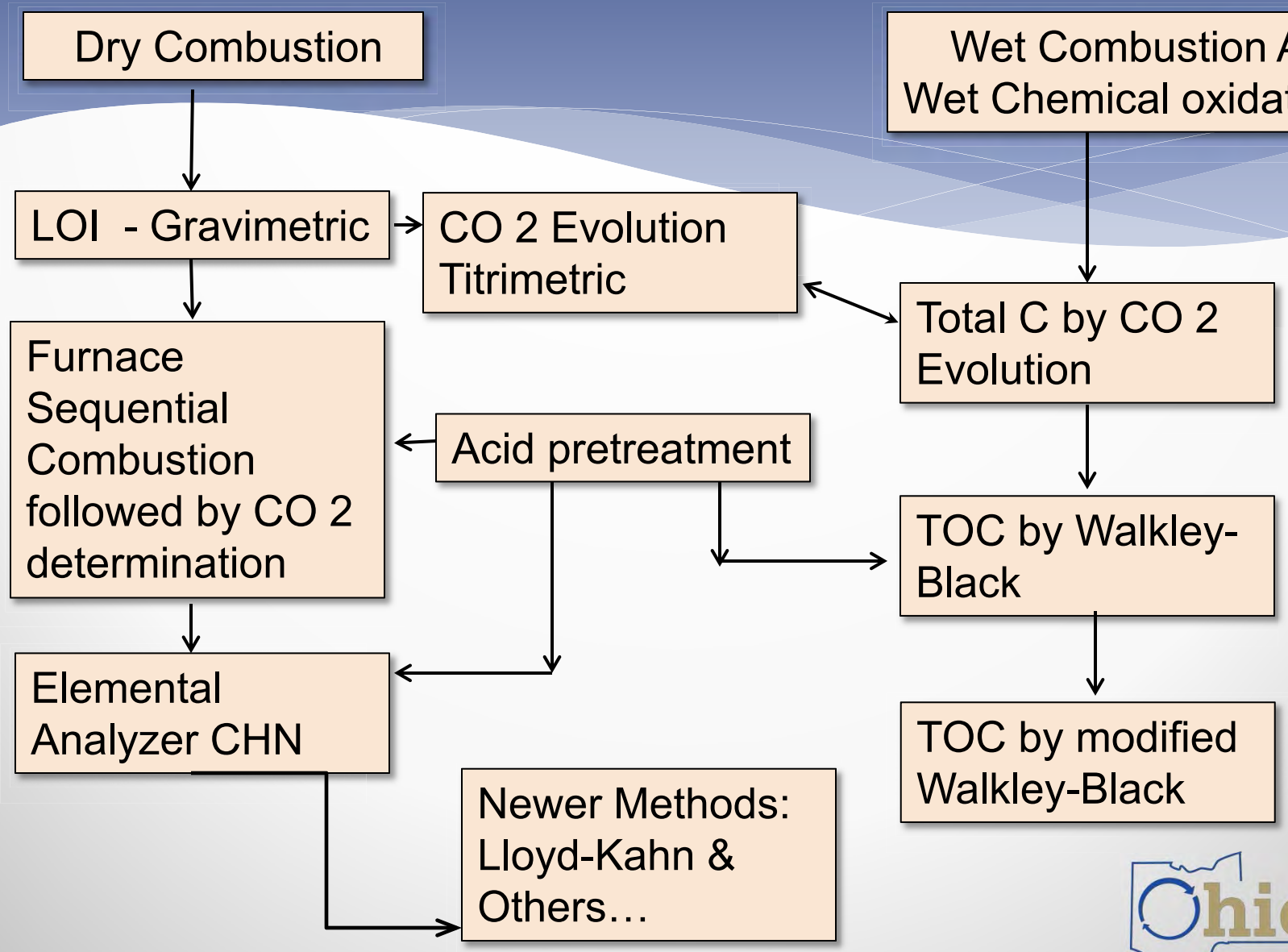
Johnson & Ettinger Modeling Exercise of VI Pathway: Interaction between koc, *f*oc & Volatility (H')

- **Advanced Soil Screening Model (SL-Adv)**
  - **Inputs: Silty-clay for first layer, defaults for all other values <u>except</u> foc**

Compound	foc	Risk based Soil Conc.
	%	µg/kg (ppb)
Vinyl Chloride	0.2	110
Koc (L/kg) = 19	0.4	110
H' = 1.24	0.8	110
	1	110
	2	110
1,2,4 Tri-methylbenzene	0.2	4780
Koc (L/kg) = 1350	0.4	9470
H' = 0.25	0.8	18900
	1	23600
	2	47000

The Evolution of Carbon Analytical Methods



Laboratory Methods Overview…

Dry Combustion

Advantages:

- Established method
- high throughput
- Faster processing
- Bulk discount for volume processing

Disadvantages

- High capitol cost for elemental analyzer
- Correction factor issues – subject to error unless sample size and processing are done to account for $f$oc content

Chemical Oxidation

Advantages:

- Suited to more soil types
- Has evolved over time

Disadvantages:

- Generates chemical wastes that contain chromium
- Slower processing

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Recent Studies Evaluating TOC Analytical Methods

- **Tivet, et al, 2011** – found un-modified Walkley-Black (WB) and gravimetric methods **overestimate** $f$oc
- **Wang, et al, 2012** – found modified WB (MWB) yielded accurate determinations of $f$oc in calcareous soils
- **Dias et al,2013** – found that dry combustion with elemental analyzer results comparable to MWB and provided accurate determination of $f$oc in calcareous soils
- **Wendt & Hauser, 2013** – found errors in sampling for TOC using fixed depth methods – developed a depth weighted averaging method

ASTM D2974 - the "Method Du Jure"

A loss on ignition (LOI) gravimetric method

* Easy to perform
* Developed for geotechnical vs. soil chemical applications
* Developed for analysis of peat soils

Not appropriate for most OHIO soils!

* **Does not account for the carbonate fraction**
* **OVERESTIMATES f_{oc} –leads to less conservative determinations**

Un-Modified Walkley -Black

* Wet chemistry method
* Widely known and used by labs
* Acceptable for some soil types – **BUT NOT Calcareous**
* Employs a correction factor –
  * Published factors range from 1.7 -2.0
  * **Factor SHOULD be determined for each soil type! IS ANYONE DOING THIS?**

* **OVER-ESTIMATES f_{oc}**, so may not be conservative enough for risk assessment or leaching demonstration

Modified Walkley-Black

- **Modified to**:
  - Release CO_2 from recalcitrant carbonates
  - Uses heating step in digestion
  - Calibrated against an organic carbon standard
- Accounts for inorganic soil carbon
- **Well suited for analysis of glacial till soils found in Ohio & our TGC recommends this method**

Other Methods…

* **Elemental analyzer:**
  * Lloyd-Kahn

* If you are unsure whether a particular method is acceptable, send us the SOP for review

Actual *f*oc Values from VAP Projects

Location	*f*oc Value (%)	Method
1. Cleveland, Cuyahoga County	0.25	WB
2. Lorain, Lorain County	3.20	LOI
3. Cincinnati, Hamilton County	2.00	LOI
4. Columbus, Franklin County	1.25	MWB
5. Mansfield, Richland County	0.50	WB
6. New Boston, Scioto County	0.26	WB

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Scenarios under the VAP

- **When should you consider using defaults?**
  - When COC conc. close to screening values
  - When COC conc. exceeds generic screening values by orders of magnitude

- **When should you consider sampling for *f*oc instead of using defaults?**
  - The soil COC conc. exceeds screening & close to generic standard
  - Presence of COCs in soil & compliance with GW standards at property boundary required
  - Property boundary close to area of COC source
  - Upper GW layer contaminated & doesn't meet UPUS

    < 30 feet separation between upper and lower GW layers

    lower GW meets UPUS (POGMUPUS)

What is Ohio EPA looking for?

* **Sampling methodology**
  * Appropriate depth in soil profile - consideration of bulk density
  * Enough samples to calculate statistically valid 95% LCL OR use of lowest $f$oc value

Analytical Method:

* Method considers and differentiates inorganic vs. organic carbon
* Analytical result falls within range of values found in the literature, or can be substantiated if significantly higher

Take Home Message

- Consider **pathways** influenced by **$f$oc – plan ahead – include** in sampling and analysis plan
- Consider **cost to analyze** vs. using defaults – **does it make a difference** in final determination?
- Consider **where** contaminants are in soil profile - **$f$oc decreases dramatically** with depth
- Remember – **sampling just as important** as analysis
- **Take care with your $f$oc – a driving force in many determinations!**

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Questions?

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THANK YOU

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