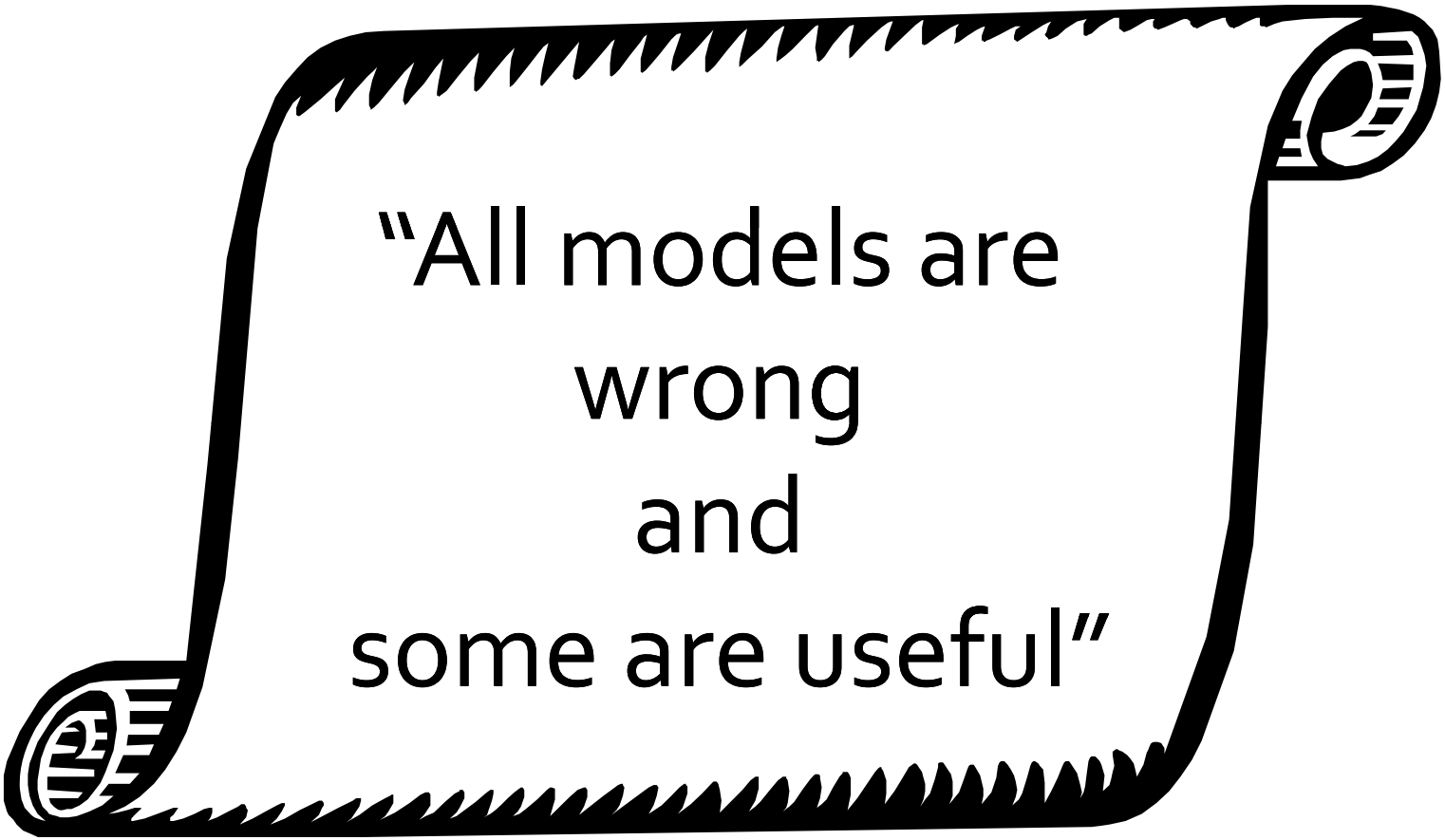
Modeling Philosophies & Application

Andrew Anthony "Tony" Havics, CHMM, CIH, PE
pH2, LLC
Avon, IN
Dollis Wright
QEPA
Denver, CO



- A. Susten, PhD, DABT
  Former Director of Science
  Agency for Toxic Substance and Disease Registry (ATSDR)

Overview

1. Assumptions
2. Limitations
3. Model Selection
4. Chemical Selection (previously considered)
5. Toxicology
6. Fate & Transport
7. Exposure
8. Sensitivity
9. Validation

1. Assumptions

- Discrete vs. Stochastic
  - Distribution v. Point Estimate
  - MLE, Mean, Median, Mode, Max, UCL
- Site-Region
  - Source strength & composition
  - Geology, Hydrogeology, and Hydrology
- Underlying Distributions
  - Normality vs Lognormality (or other)
- Scenarios

2. Limitations

- As Previous Slide
- Model Selection
- Physical or Measureable Constraints
  - Analytical techniques
  - Data availability
- Accuracy
  - Bias
  - Surrogate representation
- Precision
  - Inherent
  - Sensitivity

Parameters of Models for Risk Assessment

- Model Selection
- Chemical Selection
- Toxicology
  - RfD, RfC
  - SF or BMD
- Fate & Transport
  - Physico-Chem properties
  - Hydrogeologic Parameters
  - Model Specifics
- Exposure
  - Population
  - Events that predict dose or dose rate
  - Scenario
- Risk Endpoint

3. Model Selection

MODEL TYPES

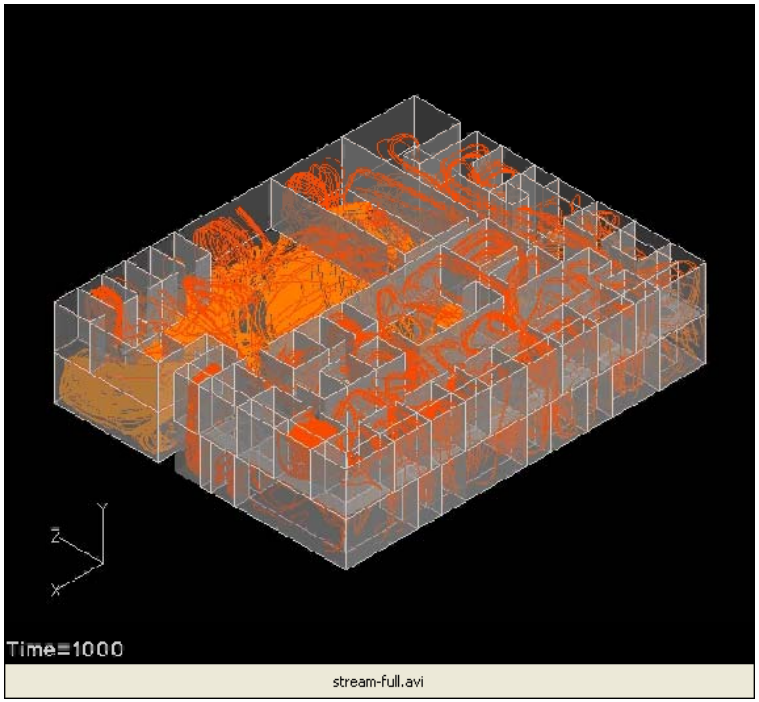
- Empirical-Deterministic
- Heuristic-Deterministic
- Empirical-Stochastic
- Heuristic-Stochastic

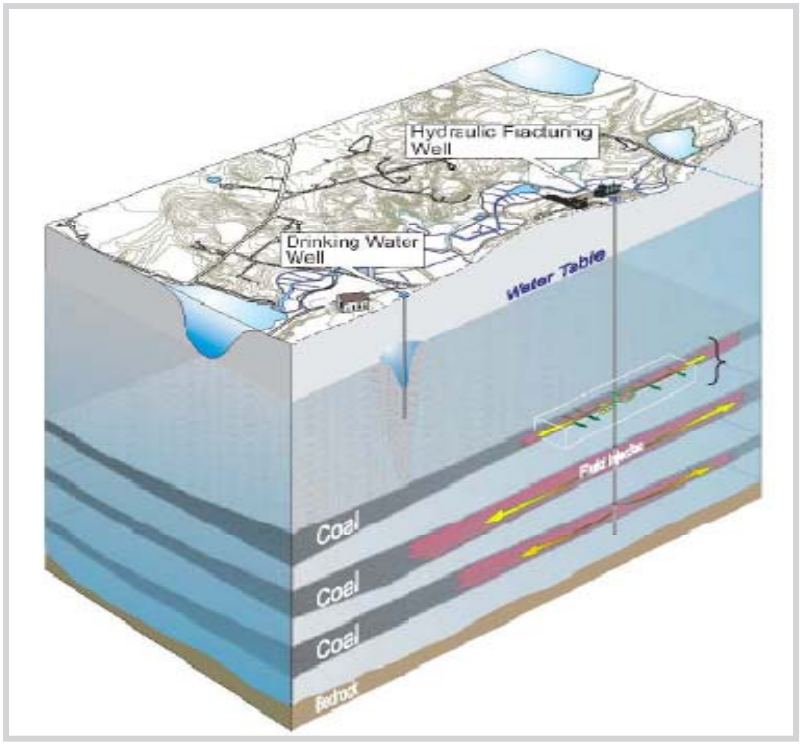
$$E_{max} = Q_B C_{v,eq} \left(\frac{D^{eff} A_B}{Q_B d}\right) \exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right) \Big/ \left[\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right) + \left(\frac{D^{eff} A_B}{Q_{soil}{}^{cr}}\right)\left(\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right) - 1\right)\right]$$

MODEL ASPECTS

- Empirical
  - Reynolds number
- Deterministic
  - Benzene = 5 ppm (max)
  - SA (man)= 3160 cm2/day
- Heuristic
  - Johnson Vapor intrusion model
- Stochastic
  - Distribution of a contaminant
  - Benzene GM = 1 ppm, GSD = 6
  - SA = $71.84 W^{0.425} H^{0.725}$ (Sendroy, 1954)

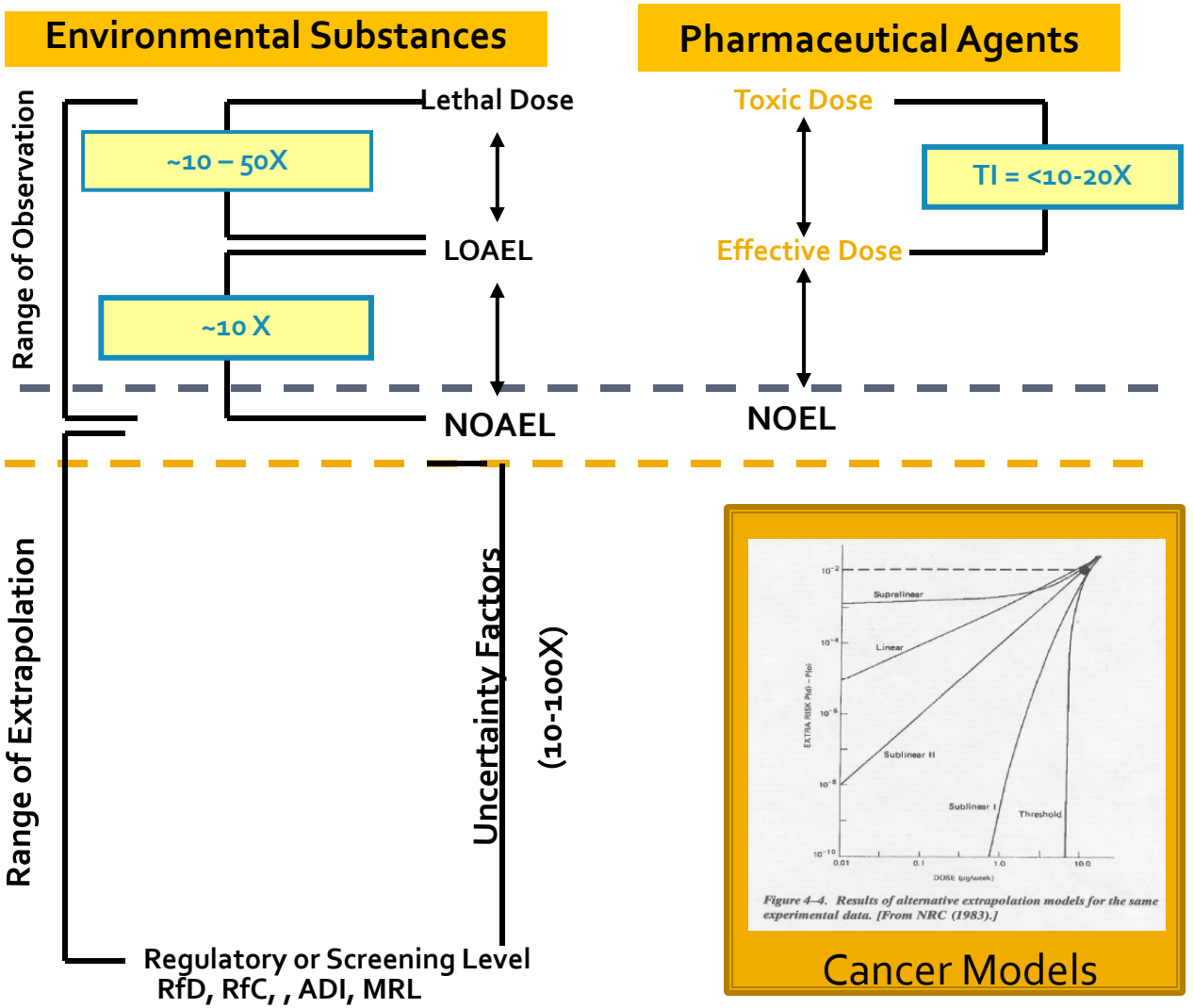
Models & Boundary Conditions





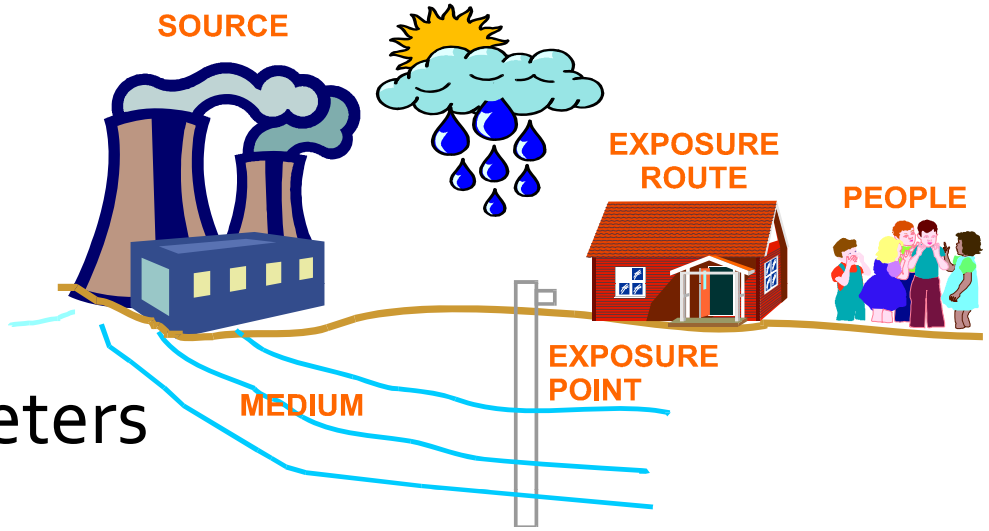
5. Toxicology

- Multiple end points
- Agent Relevancy
- Multiple Agents (mixtures)
- Background
- Unknown Parameters



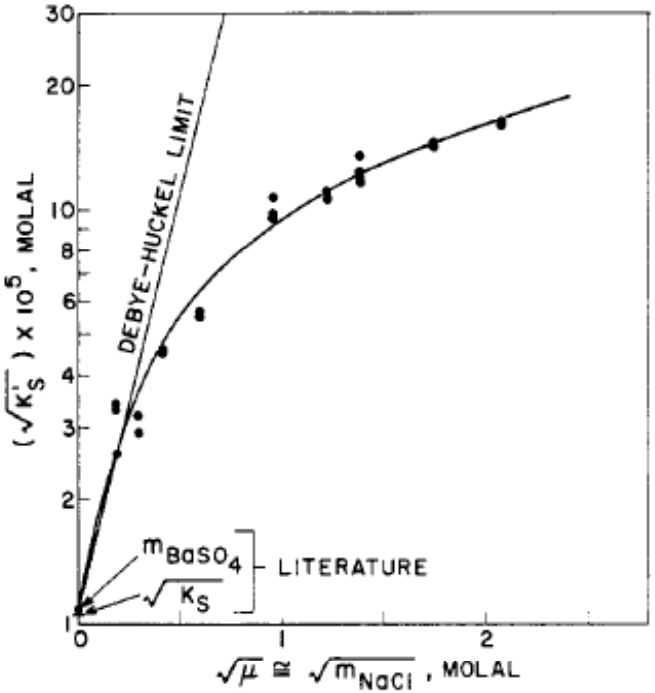
6. Fate & Transport

- Phys-Chem properties
  - Solubility
  - Retardation
  - Log K_{ow}, K_d
- Hydrogeologic Parameters
  - Depth to GW
  - Porosity, Hydraulic Conductivity
- Model Specifics
  - Distance to Point of Exposure (POE)
  - Decay v. no Decay
  - Liner or no Liner

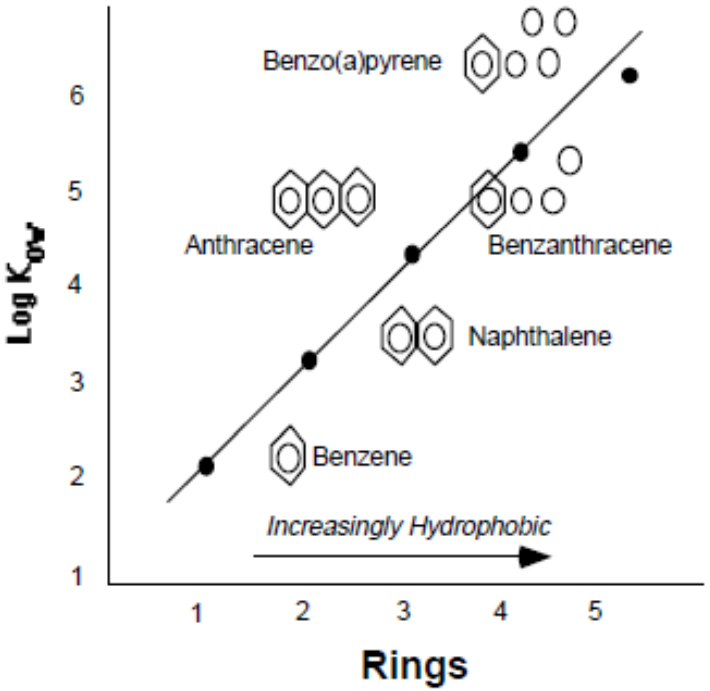


Phys-Chem properties

- Log K_{ow}
- Solubility



Variation in K's for $BaSO_4$ with ionic strength (NaCl) at 25C



Piwoni, Basic Concepts of Contaminant Sorption at Hazardous Waste Sites, EPA-540-4-90-053, 1-7, 1990

Hydrogeologic Parameters - Hydraulic Conductivity

$$V_h = \frac{K_{ha} x I}{n_e}$$

$d - V_h * t$

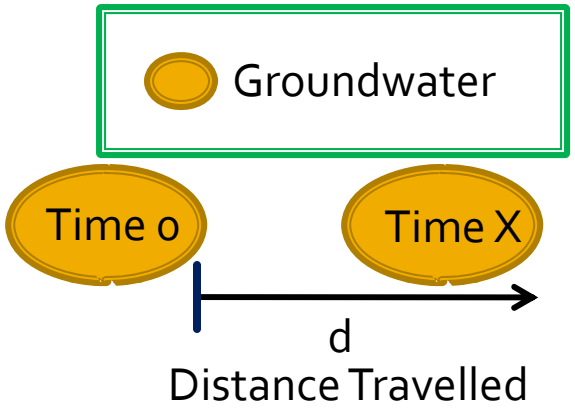
V_h = Velocity (horizontal) in direction of flow (flow rate of groundwater)

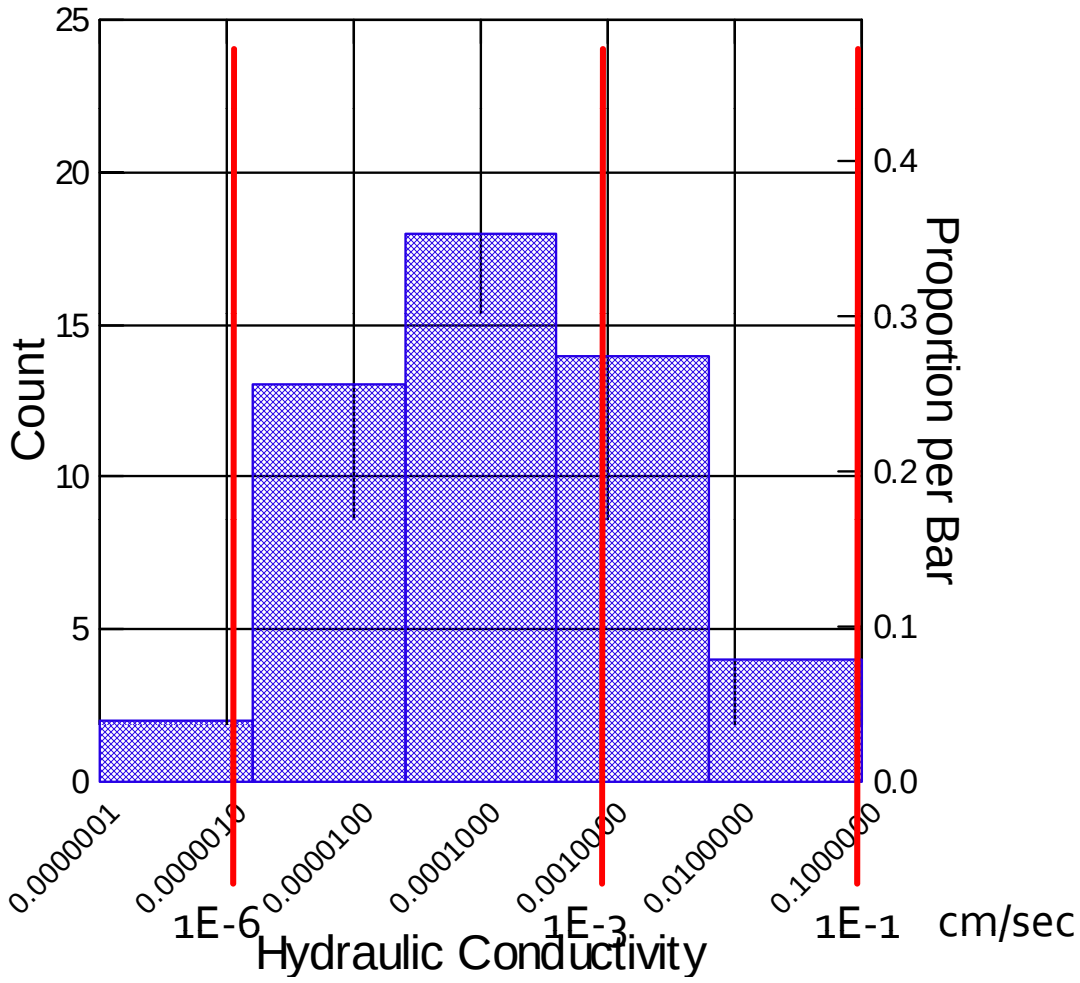
K_{ha} = Average Hydraulic Conductivity (horizontal) (resistance from soil)

I = Hydraulic Gradient (head pressure)

n_e = Porosity (effective) (void space that can be moved through)

t = time





28 Site Locations in DJ & Piceance

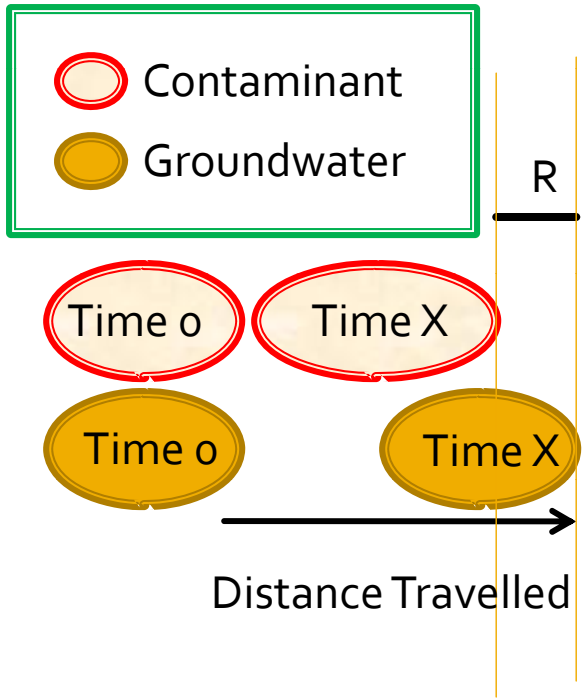
Hydrogeologic Parameters - Hydraulic Conductivity

V_h = ??
K_{ha} = 0.001 cm/sec
Average Hydraulic Conductivity (horizontal)
DJ highest value (most 0.001-0.0001)
K_{ha} = 2.83 ft/day
I = 0.01 ft/ft
n_e = 0.25
Assume R = 1.5 for Benzene

V_c for Benzene @ 1E-6
0.028 ft/yr
V_c for Benzene @1E-3
27.5 ft/yr

Retardation Values (examples)

Ethanol	1.04
Methanol	1.04
MTBE	1.09
Benzene	~1.59



$V_c = V_h / R$

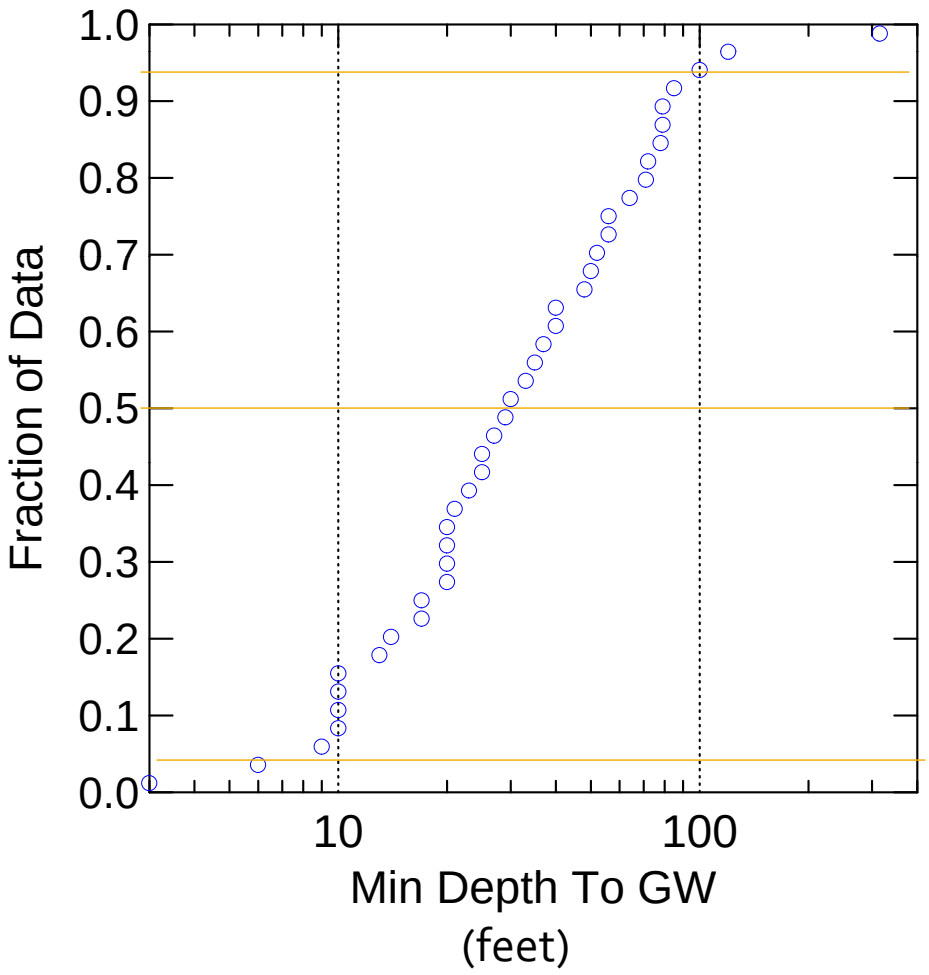
R depends on soil matrix and contaminant type
V_c = Velocity of contaminant in direction of flow
V_h = Velocity (horizontal) in direction of flow
R = Retardation Coefficient

Hydrogeologic Parameters – Depth to GW

N of cases	42
Minimum	**3.0**
Maximum	315.0
Median	**29.5**
Mean	**45.0**
Standard Dev	51.1
5 % Quantile	**7.8**
95 % Quantile	**108.0**
95% CI Lower	**29.0**
95% CI Upper	60.9

Data from Actual Drilling Locations in DJ and Piceance

Which one do we use?
Is this a policy question or a scientific selection?

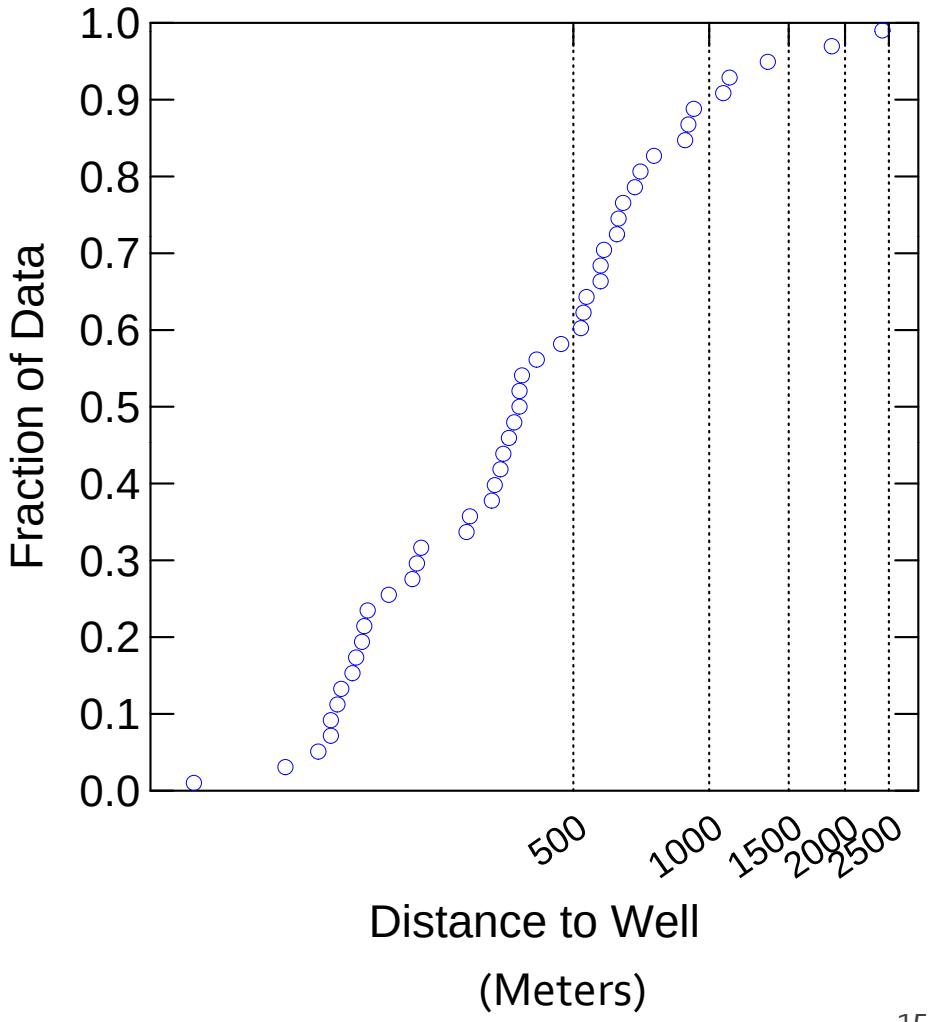


Model Specifics
- Distance to Point of Exposure (POE

N of cases	49
Minimum	**72.0**
Maximum	2420.0
Median	**380.0**
Mean	**514.9**
Standard Dev	451.5
5 % Quantile	**135.0**
95 % Quantile	**1376.0**
95% CI Lower	**385.3**
95% CI Upper	644.6

Data from Actual Drilling Locations in DJ and Piceance

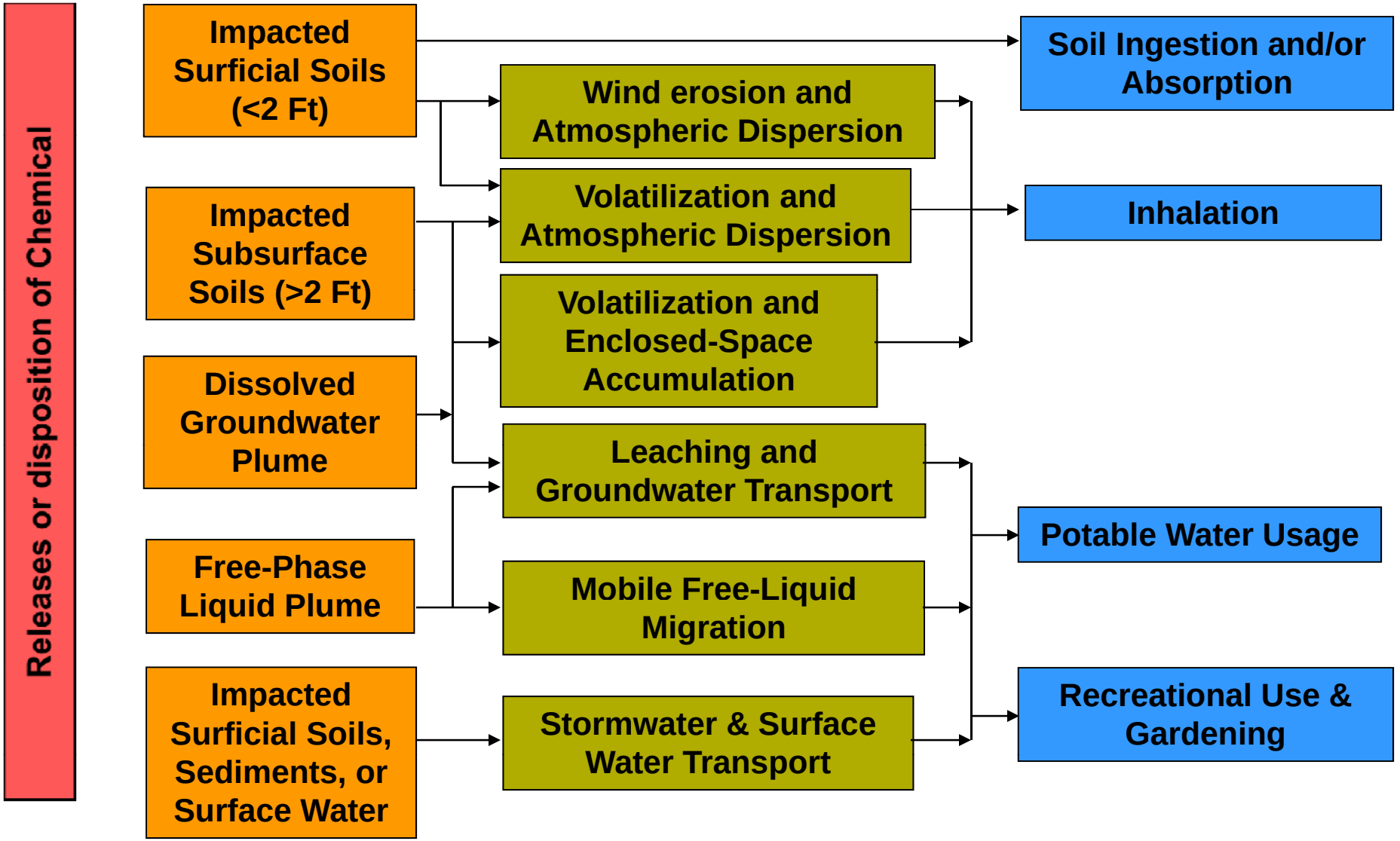
Note: Some typical setbacks 150, 300, 800, 1600 m



6. Exposure

- Population/Resources
  - Resources (water, air)
  - Non-human health
  - Human health
- Events that predict dose or dose rate
  - Completed vs. non-completed pathways
  - Time of exposure
  - Rate of exposure
- Scenario
  - Pathway(s) Selection
  - Additivity vs. independence

Exposure Pathways



ASTM E 1739, Standard Guide For Risk-Based Corrective Action Applied At Petroleum Release Sites. American Society for Testing and Materials, Conshohoken, PA. . November 1995; ASTM: *ASTM E 1739-95 (2002), Standard Guide For Risk-Based Corrective Action Applied At Petroleum Release Sites*. American Society for Testing and Materials, Conshohocken, PA. 2002.

7. Sensitivity

- Purposes of a sensitivity analysis
  - to quantify the uncertainty in the calibrated model caused by uncertainty in the estimates of parameters, stresses, and boundary conditions
  - to identify the model inputs that have the most influence on model calibration and predictions
  - Sensitivity (S)

$$S = \Delta Y/\Delta X \qquad = \text{change in y / change x}$$

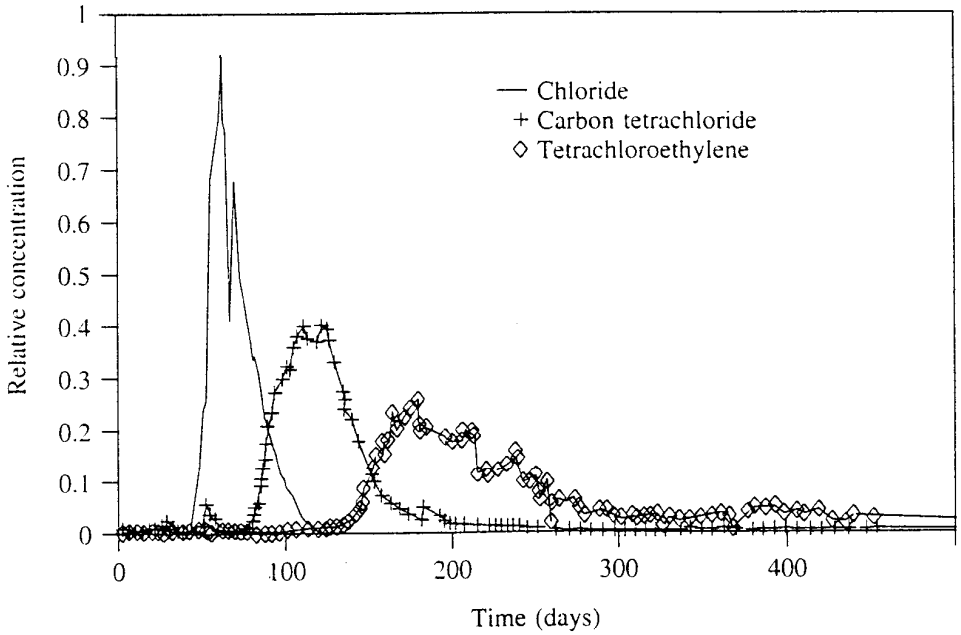
  - Normalized sensitivity*

$$S^{y}_{x} = \quad (\Delta Y_x/Y)/(\Delta X/X) \quad = \frac{\text{change in y (with respect to x) relative to y}}{\text{change in x relative to x}}$$

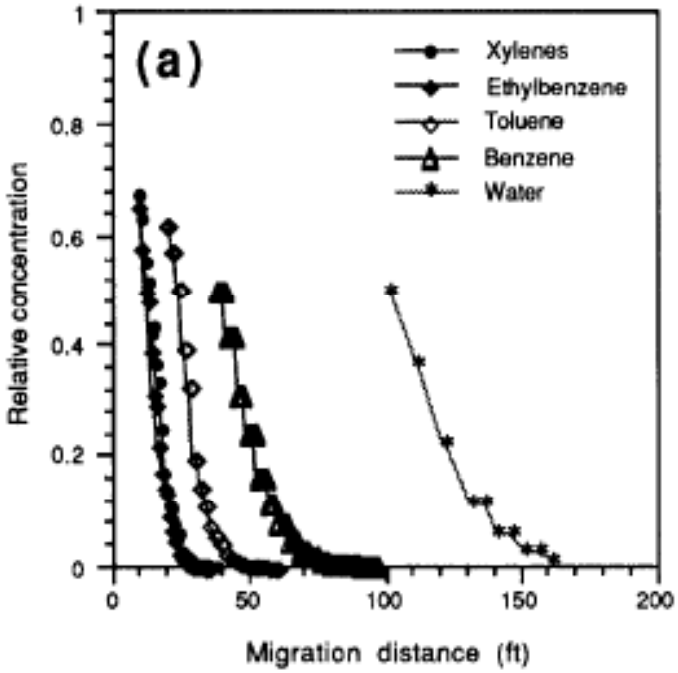
  - Guidance: ASTM, D5611-94, Standard Guide for Conducting a Sensitivity Analysis for a Ground-Water Flow Model Application, 2002

*Norton, Algebraic sensitivity analysis of environmental models, Environ Model & Soft, 23, 963-972, 2008

Hydrogeologic Parameters -Retardation Effects



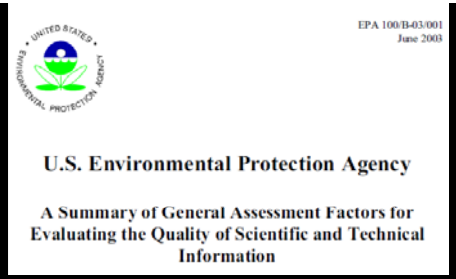
Example of retardation-based reduction in concentration



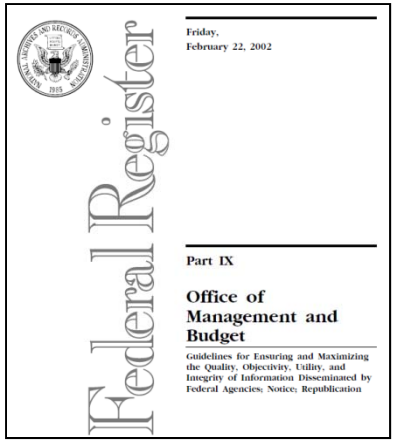
BTEX transport modeling results for hydraulic dispersion using 0.2% organic carbon in a sandy aquifer after 100 days migration. [K=20 ft/day, I = 0.01, n = 0.2].

Yang, GW Contaminant Plume Differentiation and Source Determination Using BTEX Concentration Ratios, Ground Water, 33, 6, 927-935, 1995

8. Validation?



- Intentional Spill/Injection
  - Field scale
  - Lab Scale
- Field Examples
- Parallel Models
  - Radon and landfill gases
  - Other plumes (Plume size examples)
- Health & Media Assessments



Example: Domenico Limitations

- Error potential sensitive to high values of longitudinal dispersivity
- Generally 3 approaches for estimating longitudinal dispersivity (αx)
  - αx = 10% of plume length
  - αx = 10% of L
  - $\alpha x = 0.83(\log_{10} L)^{2.414}$

$$C(x,y,z,t) = \left(\frac{C_o}{8}\right)\exp\left\{x/2\alpha_x\left[1-\left(1+4\lambda\alpha_x/v\right)^{\frac{1}{2}}\right]\right\} erfc\left\{\left[x-vt\left(\sqrt{1+4\lambda\alpha_x/v}\right)\right]/2\sqrt{\alpha_x vt}\right\}$$
$$\left\{erf\left[(y+Y/2)/2\sqrt{\alpha_y x}\right]-erf\left[(y-Y/2)/2\sqrt{\alpha_y x}\right]\right\}\left\{erf\left[(z+Z/2)2\sqrt{\alpha_z x}\right]-erf\left[(z-Z/2)/2\sqrt{\alpha_z x}\right]\right\}$$

- Minimal error when Pe >6
  - Where Pe = VL/ αx
  - V = GW velocity; L = distance to POE

Domenico, P.A. : An Analytical Model for Multidimensional Transport of a Decaying Contaminant Species. *J Hydrology*, 91: 49–58, 1987; Domenico, P.A. and G.A. Robbins: A New Method of Contaminant Plume Analysis. *Ground Water*, 23, 4: 476–485. *1985;* West, M.R., B.H. Kueper, and M.J. Ungs: On the Use and Error of Approximation in the Domenico (1987) Solution. *Ground Water*, 45, 2: 126–135. 2007.; Guyonnet, D. and C. Neville: Dimensionless Analysis of Two Analytical Solutions for 3-D Solute Transport in Ground Water. *J Contaminant Hydrology*, 75: 141–153. 2004;
also EPA at http://www.epa.gov/ada/csmos/domenico.html

Groundwater Media Assessment

- URS 2006 – Garfield County*
- SEO database. The number of wells completed in each aquifer is shown below:
  - Alluvial aquifer: 48 wells
  - Wasatch aquifer: 388 wells
  - Both aquifers (Al and Tw): 5 wells
  - Unidentified or incomplete log: 9 wells
- **Benzene was not detected in domestic water wells in the study area**

- COGA 2008
- Baseline and post drilling water and monitoring wells within a ½ mile radius of the sampling sites were reviewed.
- **None of the private well samples exceeded drinking water standards.**

* URS, Phase 1, Hydrogeologic Characterization of the Mamm Creek Area In Garfield County, March 23, 2006 – for Board of County Commissioners Garfield County, Colorado

Points

- Assumptions & Limitations are inherent in models
- They come from
  - Scenario Selection
  - Parameter Selection
  - Model Design
  - Regulatory and Physical Constraints
- Understand the pitfalls and performance
- Once a model has been selected, the parameters will drive the model
- It is best to use real life data in addition to Maximum Likelihood Estimators (MLEs) to get a feel for a model's response
- Check the response for sensitivity & validity

Acknowledgments

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- Mark K. Leverson, PG, Principal Hydrogeologist, URS

Modeling Philosophies & Application

Andrew A Havics, CHMM, CIH, PE[1] and Dollis Wright[2]
[1]pH2, LLC
[2]QEPA

The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Models are mere surrogate test fields for answering a question(s) or solving a problem expediently. They can be physical analogs or computer-based (Bear, 1972). Regardless, they all begin with a framework and a set of assumptions and limitations that go along with that framework. As a result, all models are wrong, but some are useful. Assumptions and limitations begin before selecting models but also arise from the selection or specialized application of a model. In terms of fracing and Risk Assessment (RA), there are several places where models and parameters must be chosen to complete hazard identification including chemical selection, fate & transport, exposure assessment, and risk determination aspects. Furthermore, to evaluate the model(s) chosen, and at a minimum qualitative assess or rank their values of data (response/output), an analysis of sensitivity and validity of the models should be completed. The level of complexity in the model, its use, and evaluation will be based on a number of factors derived for the purposes, objectives and goals of the model's use, many of which may be directed by policy.

Assumptions, leading to Limitations

Beginning with the assumptions, there are *de facto* policy aspects. The first is whether the parameters for the models will be either (a) discrete - single point values, or (b) stochastic - continuous function of the probability of a value. By choosing a discrete model, one must then decide what are the appropriate parameters, constraints, or additional assumptions. For instance, should one use a Maximum Likelihood Estimator (MLE), Mean, Median, Maximum, or some stochastic upper limit as the single point value input. Compiled or repeated use of maximums or extreme values in equations, such as hydrogeologic data or human exposure estimates, increase the likelihood of overestimating risk and in some cases the cost of subsequent actions; but this must be weighed against benefits of communicating the level of conservatism and the simplicity of using it as a screening tool. At some point, the weight of evidence surrounding the parameter such as distance to point of exposure (POE) must be assessed and a professional judgment made. In certain cases, regulatory restrictions will determine initial estimates. In the case of fracing, the source material composition by basin will influence the selection of a parameter, e.g., the chemicals of interest and their anticipated concentrations. Again, regulatory stipulations, such as pre-treatment can and will affect the selection of an *appropriate* input value. Furthermore the geology & hydrogeology of a region or local area can also influence chemical selection and fate and transport parameters, whether the selection of PAHs from coalbed deposits or hydraulic conductivity of a formation. Based on

these variations, it is clear from the science that a single model of predicting fate, transport, or risk (or even one method of regulatory control) should not be applied to all locations.

Limitations

There are limitations in model selection, either constrained from the geology/hydrogeology, or constrained from the chemical side (metal versus organic), from the media of concern selected or from the pathways of anticipation. The limitation of sufficient, good quality or robust data will certainly restrict the use of stochastic estimates, but will also require a good analysis of sensitivity. The models themselves can (and usually are) created to permit a bias in the way of either over- or under-prediction of transport or exposure depending on how values are selected. Thus, a listing of all input values as well as the model structure should be available in any prediction using a model. There are limitations that are derived from precision of the model, and those that come from precision of the parameters. Calibrating the model to known field scenarios or lab-based experiments can provide an estimate of that precision. An analysis of sensitivity should follow to gage the relative importance of model variability versus model sensitivity.

Model Selection

By default, model selection restricts options. The more complex the model, generally the more costly, the more difficult to assess precision, the more difficult to understand the results and communicate them. One should consider the value of model refinement and model complexity relative to any gain in understanding the ultimate endpoint - risk. Regardless, in selecting a model, boundary conditions must be chosen and applied. In some models, these will drive fate and transport more than others. Because boundary conditions are likely to differ between geologic formation, application of one model from one formation to another should proceed cautiously.

Toxicology in the RA Model

In terms of RA, orders of magnitude are the norm. For toxicologists 3 times 3 is 10, and this level of rounding or semi- to multi-order-of-magnitude math pervades. First, one must recognize that parameters for doses that represent safe levels from toxic endpoints are selected with certain safety and uncertainty factors built in. For non-cancer agents these are typically 10- to 100-fold lower than No Observed Adverse Effect Levels (NOAELs) which are usually 10-50 times lower than Lowest Observed Adverse Effect Levels (LOAELs) [Dourson, 1996; Haber, 2002]. These are based on many studies indicating ratios of low or no response to a response between species and over differing times (days-months-years) and generally represent a conservative estimate times another conservative estimate. If less data is available or equivocal, a Benchmark Dose Level (BMDL) approach can be applied first; it brings a more stochastic approach to another deterministic aspect [EPA, 2000]. Examples are Barium (300-fold factor) [EPA, 2005] and Benzene (<10 factor) [ATSDR, 2007]. For cancer agents, risk is usually presumed to follow a straight from a projected 95% confidence limit to zero, thus is intentionally conservative in its application. The ultimate acceptable risk level is a policy decision but usually ranges in the 1 in 100,000 to 1 in 1,000,000 for residential settings and 1 in

10,000 to 1 in 100,000 for commercial or industrial settings [Kocher, 1991]. For comparison sake, one can consider two scenarios - a) struck by lightning and b) killed in a vehicle accident, both over a lifetime. The first, the lightning strike, is on the order of 6 in 1,000,000, the second (vehicular death) is about 1-2 in 100 people. Basic risk aside, there are assumptions or defaults that must be made with regard to multiple pathways from fate and transport, multiple routes of exposure, multiple toxic endpoints, and multiple mixtures. The most sensitive toxic endpoint, say liver damage, would generally be used. Generally, all doses are added for multiple routes of exposure or multiple pathways. As for mixtures of chemicals, this is a policy aspect and can range from no summing of risk, to summing only like toxic endpoints, to summing all aspects. Even after consideration of risk is made, there are potential limitations such as background amounts of an agents (e.g., arsenic in soils), and lack of tox data for additives or proprietary mixtures. The lack of data might be able to be handled using a control banding technique (Nelson, et al., 2011). Ultimately, the chemical selection and fate and transport aspects cannot be divorced from the models or the remainder of the RA, and science and policy must find consensus.

Fate & Transport

The selection or input of physical-chemical properties such as solubility, retardation, and Log Octanol Water partition coefficient (Log K_{ow}), can drive an equation in terms of fate and transport. There are, however, certain generalities as well as pitfalls in their selection and use. K_{ow} within a group of chemicals can be estimated within reason, but the value can easily affect transport estimates but will also affect dermal exposure. Barium Sulfate ($BaSO_4$) is generally considered to be relatively insoluble, but it can become more soluble, thus available for transport and human uptake, in the presence of high chlorides (Templeton, 1960). High chlorides were found present in our study and the dissolved Barium also tended to rise with increasing chlorides. Despite these effects, the effect of the hydrogeology in the Colorado pathway scenarios was not affected by this in terms of showing a significant risk.

Hydrogeologic parameters can vary widely from region to region and formation to formation. Thus, either a conservative selection or field data should be used. Because hydraulic conductivity (K_{ha}) can significantly influence transport models, a review of 28 sites in the DJ and Piceance were selected for detailed assessment of hydrogeological parameters including hydraulic conductivity. Each location was reviewed to establish local a geologic and hydrogeologic setting, and data from the vicinity on these aspects was then gathered. K_{ha} ranged from 0.01-0.0000001 cm/sec, with most values in the 0.001-0.0001 range, and the hydraulic conductivity appeared log normally distributed, which was expected. Using this data (and other representative data from the region) for Benzene with a retardation value of 1.5, the velocity of the benzene might be expected to be 27.5 ft/year at a K_{ha} of 1E-3 versus 0.028 ft/yr at a K_{ha} of 1E-6. One can see the necessity for gathering and entering relevant data into a model. For the modeling in the Colorado study, a K_{ha} of 3.63E-3 was ultimately used, driven by regulatory concerns [CDPHE, 2007].

Similarly for leaching from pits, the depth to groundwater (GW), can strongly affect transport. For the Colorado study, water well logs from <= 1.5 miles from each well pad in the DJ and

Piceance were pulled from state records and depth to GW evaluated. A total of 42 water wells provided sufficient data for analysis. The distribution appeared lognormal. Values ranged from 3 to 315 feet with the 5% quantile at 7.8 feet. Ultimately, 3.3, 9.8, and 20 feet (1, 3, 6.1 m) estimates were used in the modeling. The wells logs also were used to estimate point of exposure (POE) assuming the distance from the oil well directly to the water well. The results ranged from 72 to 2,420 meters (236-7,939 feet) with a 5% quantile at 135 m (442 feet). For the study, the minimum distance of 72 meters was selected by the risk assessor as a POE for the subsequent modeling; however, a 5% quantile value would likely be a reasonable maximum likelihood estimator (MLE). One should note that the 72 m is not likely as regulation restrictions have mandated setbacks to wells of 91-183 m (300-600 feet) with more stringent distances proposed [COGCC, 2008], again, a limitation imposed from outside the science. As a surrogate reference, one could consider plume data from 604 actual sites from other states for known significant pure product releases (only diluted fluids and solids are expected present in the O&G sites) reveal 75% are under 200 ft and most are shrinking [Newell, 1998].

Exposure

Several assumptions go into the exposure assessment process and a number of limitations also arise from this. The first is the selection of what is the exposed resource/population at risk, and it may be a natural resource such as water quality, a defined ecosystem to include fish or ducks, or human health. The toxicity of copper exposure to humans is less significant than to fish; the use of a typical surface water in Colorado isn't quite the recreation use that it might be for typical default scenario the EPA RAGS [EPA, 1989a, 1989b, 1991a, 1991b] or the ASTM RBCA [2002] and thus parameters of exposure might be overestimated. On the other hand, dust generation may be more than that usually considered by EPA or ASTM, as might be irrigation for grass. Furthermore, the determination of the need for a specific fate and transport model to assess these pathways will be controlled by their selection in the first place. Because the selection of completed pathways can be significant in any RA, there is a strong need for accurate transport models. The discrete selection of what is and what isn't complete must be considered in light of typical patterns of use, along with distances and relevant geophysical parameters. It is often driven by the media selected as "contaminated" or of concern. In the study in Colorado a number of media were selected and each relevant pathway was assessed with some form of fate and transport model. Media were:

Solids placed in Pits
Liquids in Subsurface Pits
Fracing Fluid placed in pits
Fracing Fluid placed in containers
Produced Water placed in containers
Produced Water placed in pits
Drilling fluids in drilling
Drilling fluids in pits

Thus, leaching from pits and migration to groundwater followed by transport to a residential well was modeled. On the other hand, because houses are not built on waste pits and distance

to houses are so great, direct vapor intrusion was not considered a complete pathway. Because each completed pathway leads to exposure, the dose from each was assessed as additive. Thus the removal of a pathway also removes a potential dose. However, because multiple pathways and thus exposures and doses are modeled on the same population (e.g., person), an overestimate of real exposure is likely to arise. This is where stochastic modeling is very useful. The RA was completed using a variety of assumptions, details of the RA are provided in the QEPA report [QEPA, 2008].

Sensitivity

A sensitivity assessment should be performed on any model, even if crudely done, unless the RA itself evaluates multiple scenarios such that sensitivity to basic parameters is obvious. That said, the purpose of a sensitivity analysis is: (a) to quantify the uncertainty in the calibrated model caused by uncertainty in the estimates of parameters, stresses, and boundary conditions, and (b) to identify the model inputs that have the most influence on model calibration and predictions. ASTM has provided guidelines for assessing GW models in this fashion (ASTM, 2002). A direct sensitivity analysis involves checking the response after varying a particular parameter through a range of values, or alternatively, taking the derivative of the response function and plotting that. Because not all parameters are based on the same scale, a normalized sensitivity measure can be used to more equally evaluate different parameters (Norton, 2008). Even so, this author has found normalizing to the data range (R) or 5%-95% quantile range provides a better representative of response relative to the expected range of values for a parameter.

Validation

It is useful at some point to validate the prediction of a model. This can be accomplished by pre-planned injections, correlating actual (unintentional) releases, running parallel models, or evaluating health outcomes or using biomarkers in the case of RA. The first option has been accomplished for petroleum releases by intentionally injection product into outdoor locations and indoors in laboratory setting, but not at great depths. Correlations to actual field data have been limited or proprietary in nature. Parallel models are run in select situations but don't offer real world calibration. in the case of the Domenico model used in the Colorado study, it has been evaluated for some aspects and found to have errors where the longitudinal dispersivity parameters are high or where the Peclet number (Pe) is low (Guyonnet, 2004; West, 2007) or the study, the Pe was in the range of 80-180. As a follow up in the 2008 study, a review of a 2006 groundwater data study (URS, 2006) from wells in one basin for the O&G drilling locations was conducted, and additional data reviewed (as available) for the site locations in the 2008 RA. For the 2006 study, no Benzene (the most likely contaminant given the local conditions) was detected. For the 2008 review some BTEX compounds were identified, but none of the chemicals was over their respective drinking water limits; also, confounding sources could not be ruled out where detections were observed.

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