A Field Example of Dioxin-Like Compound Transport in Consolidated Glacial Till

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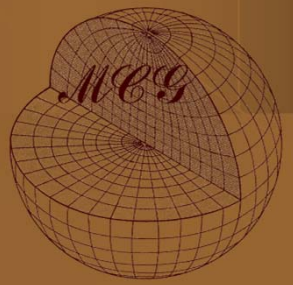
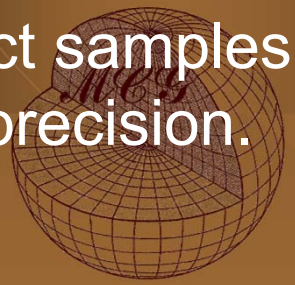


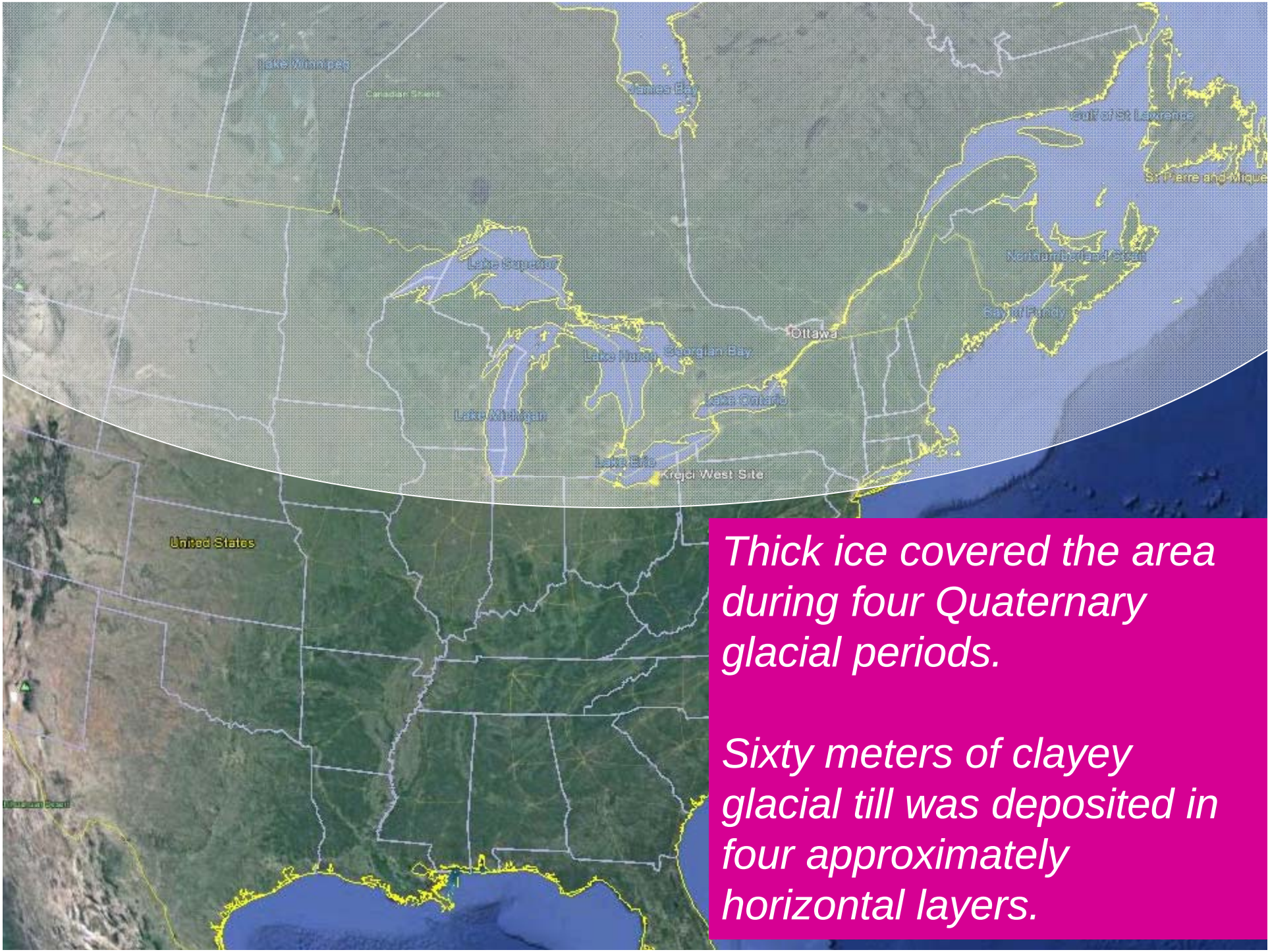
Purpose

- I will present measured dioxin and furan soil concentrations as they varied with depth beneath a former uncontrolled municipal and industrial dump.
- Ratios of retardation factors were back-calculated by fitting the one-dimensional advective-dispersive equation to the observed distributions of three congeners.
- I will compare ratios of retardation factors to expectations.
- Of secondary interest: Present the composite sampling method that was used to collect samples and that resulted in good measurement precision.



The roughly 200,000 m² Krejci Dump Site was a former municipal and industrial dump and salvage located within the Cuyahoga Valley National Park in Summit County, Ohio, USA.

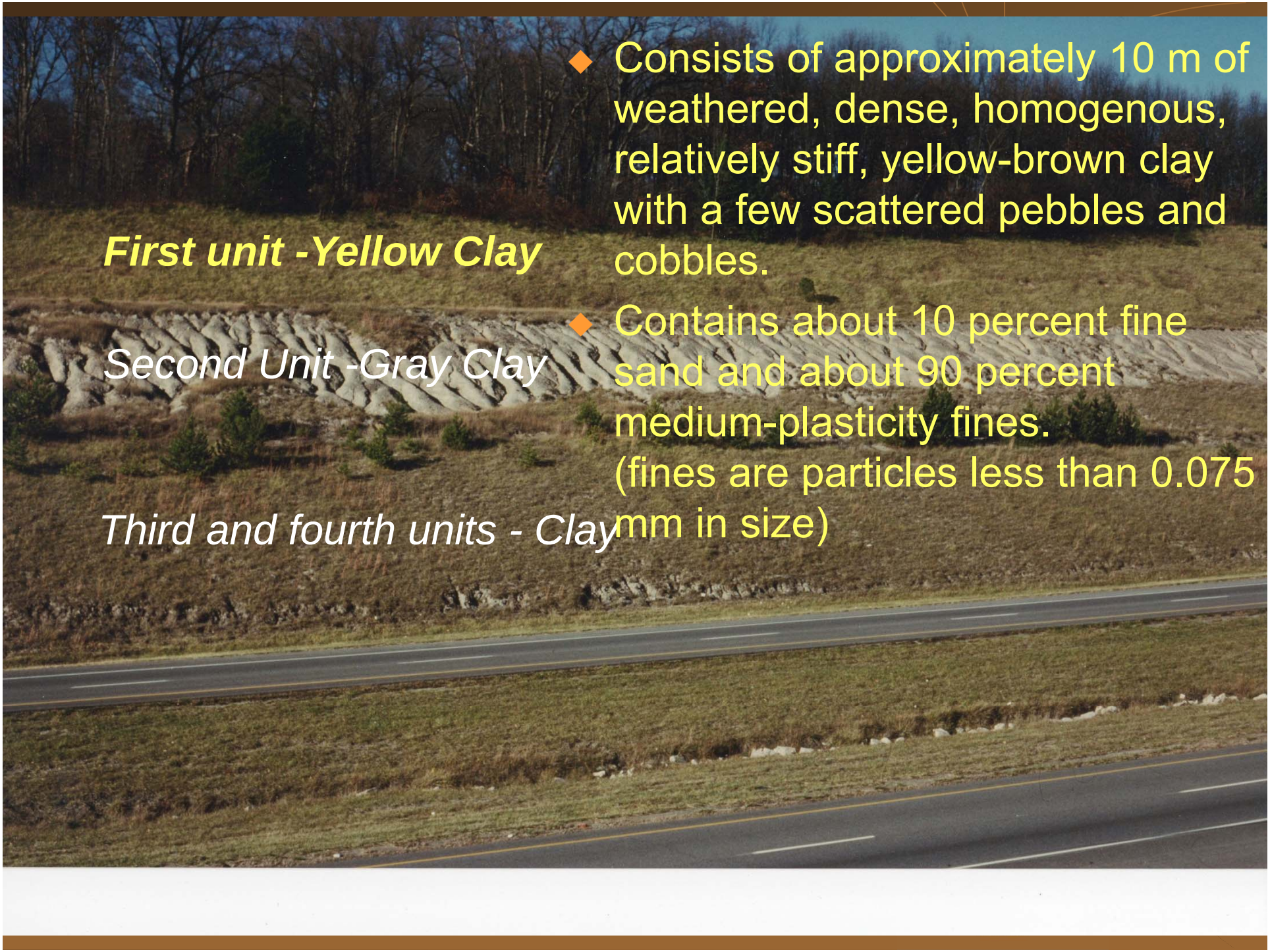

Lake Winnipeg
Canadian Shield
James Bay
Gulf of St Lawrence
St Pierre and Miquelon
Lake Superior
Northumberland Strait
Bay of Fundy
Ottawa
Lake Huron
Georgian Bay
Lake Ontario
Lake Michigan
Lake Erie
Krejci West Site
United States
Appalachian Mountains
Washington
The site is approximately 30 km south of Lake Erie between the industrial cities of Cleveland and Akron Ohio.



Thick ice covered the area during four Quaternary glacial periods.

Sixty meters of clayey glacial till was deposited in four approximately horizontal layers.


First unit -Yellow Clay
Second Unit -Gray Clay
Sand layer
Third and fourth units - Clay
A nearby road cut shows some of the characteristics of the till units.

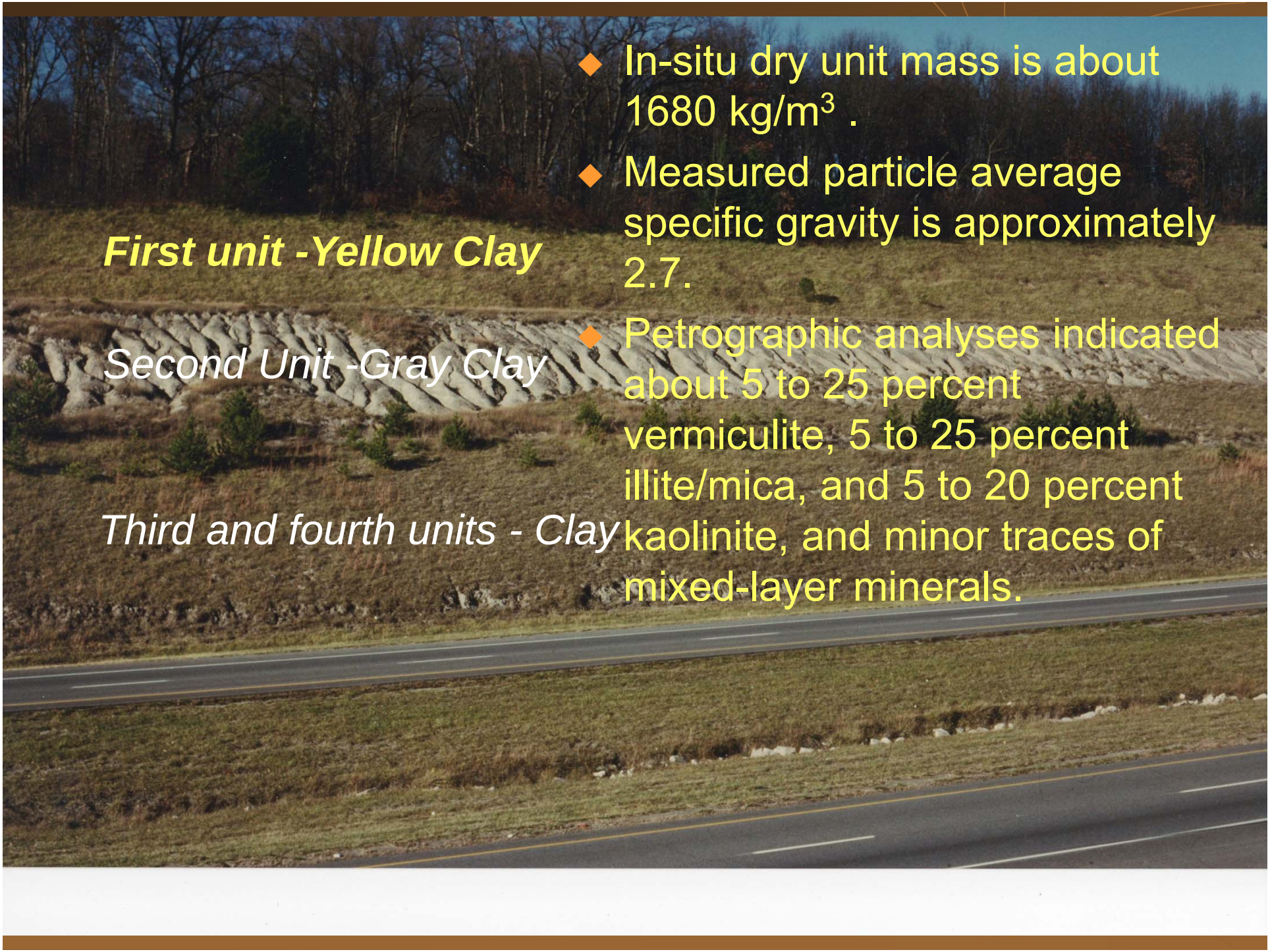


First unit -Yellow Clay

Second Unit -Gray Clay

Third and fourth units - Clay

- Consists of approximately 10 m of weathered, dense, homogenous, relatively stiff, yellow-brown clay with a few scattered pebbles and cobbles.
- Contains about 10 percent fine sand and about 90 percent medium-plasticity fines. (fines are particles less than 0.075 mm in size)

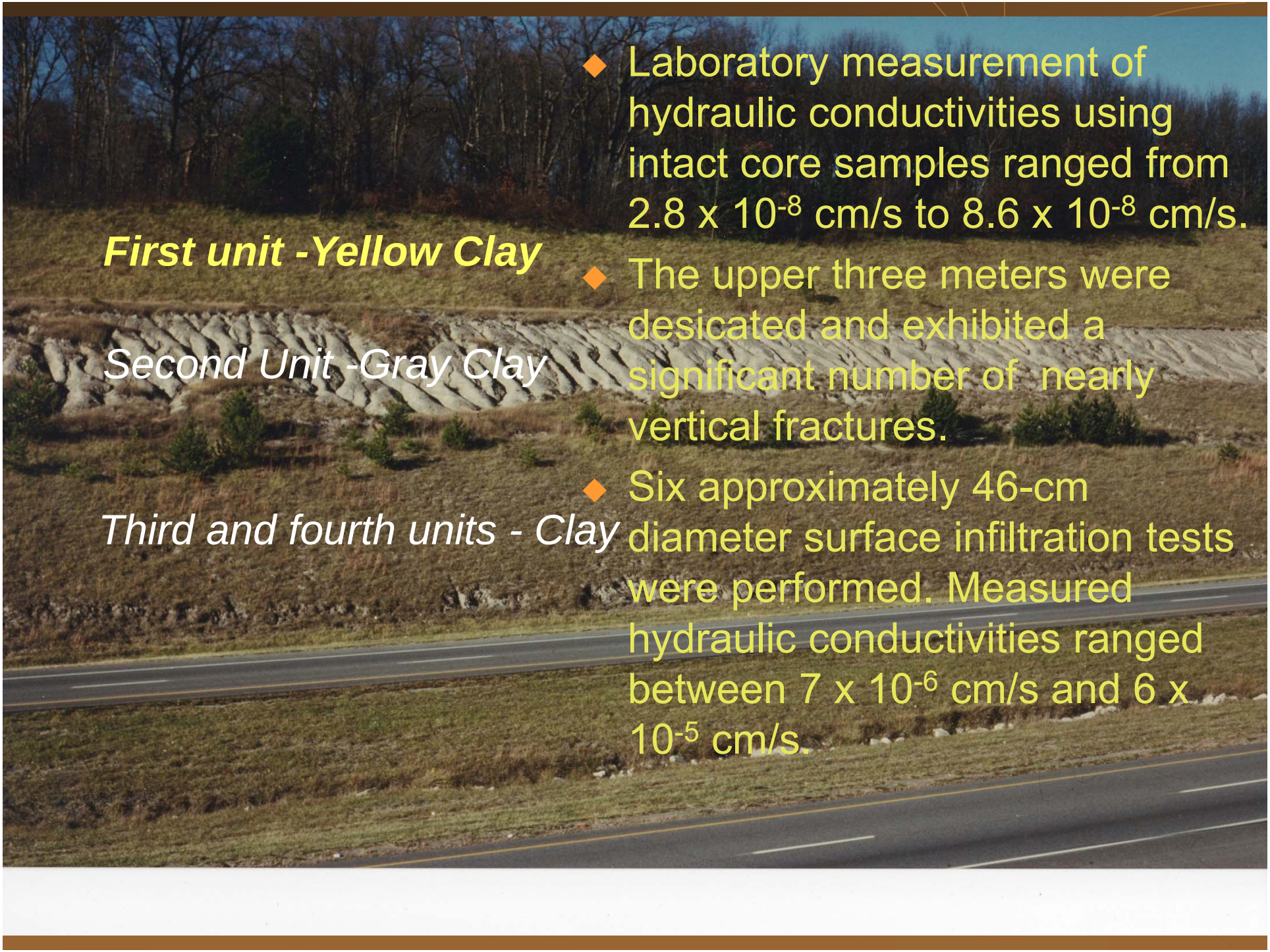


First unit -Yellow Clay

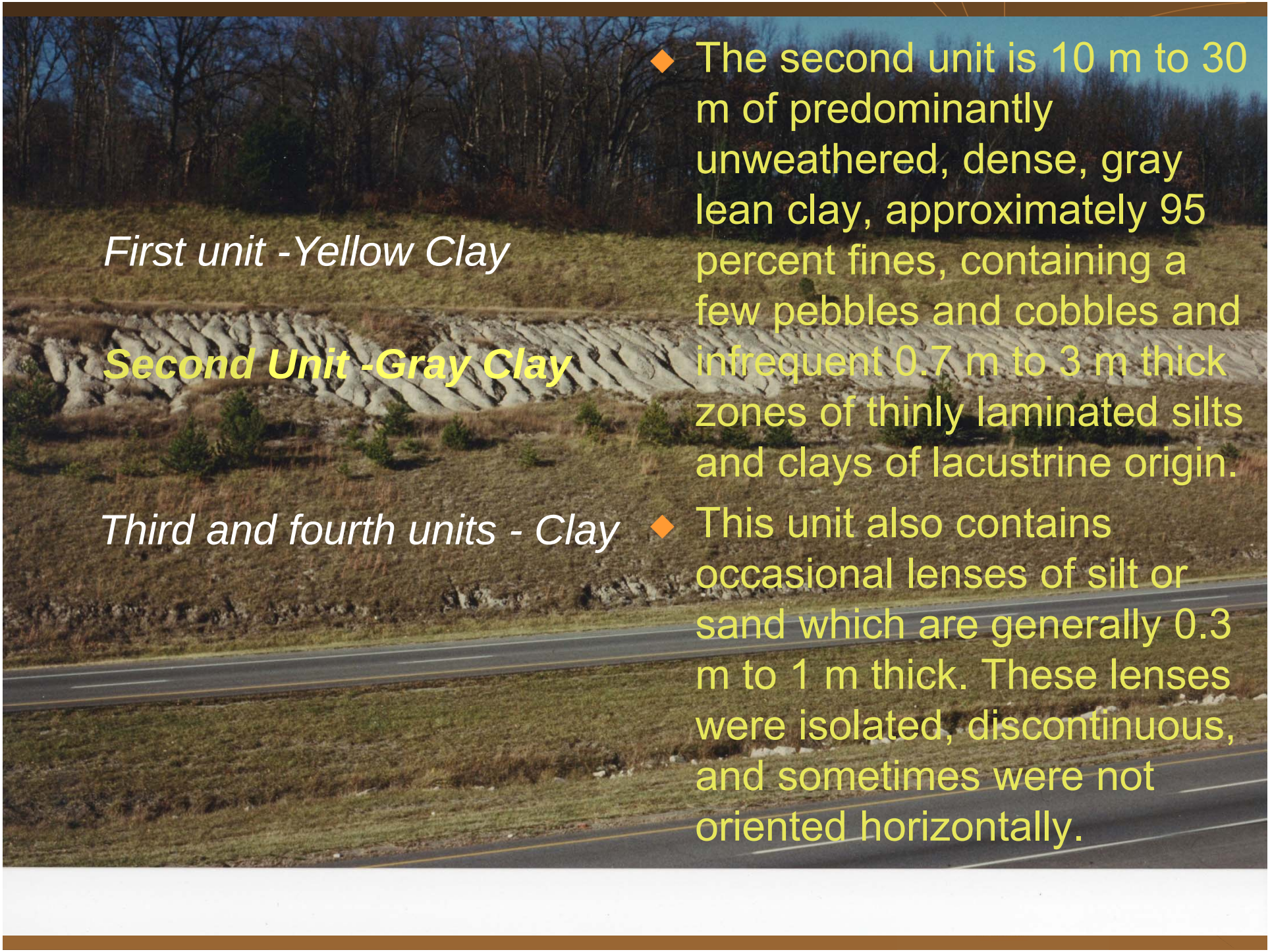
Second Unit -Gray Clay

Third and fourth units - Clay

- In-situ dry unit mass is about 1680 kg/m^3 .
- Measured particle average specific gravity is approximately 2.7.
- Petrographic analyses indicated about 5 to 25 percent vermiculite, 5 to 25 percent illite/mica, and 5 to 20 percent kaolinite, and minor traces of mixed-layer minerals.



- Laboratory measurement of hydraulic conductivities using intact core samples ranged from 2.8 x 10^{-8} cm/s to 8.6 x 10^{-8} cm/s.
- The upper three meters were desicated and exhibited a significant number of nearly vertical fractures.
- Six approximately 46-cm diameter surface infiltration tests were performed. Measured hydraulic conductivities ranged between 7 x 10^{-6} cm/s and 6 x 10^{-5} cm/s.

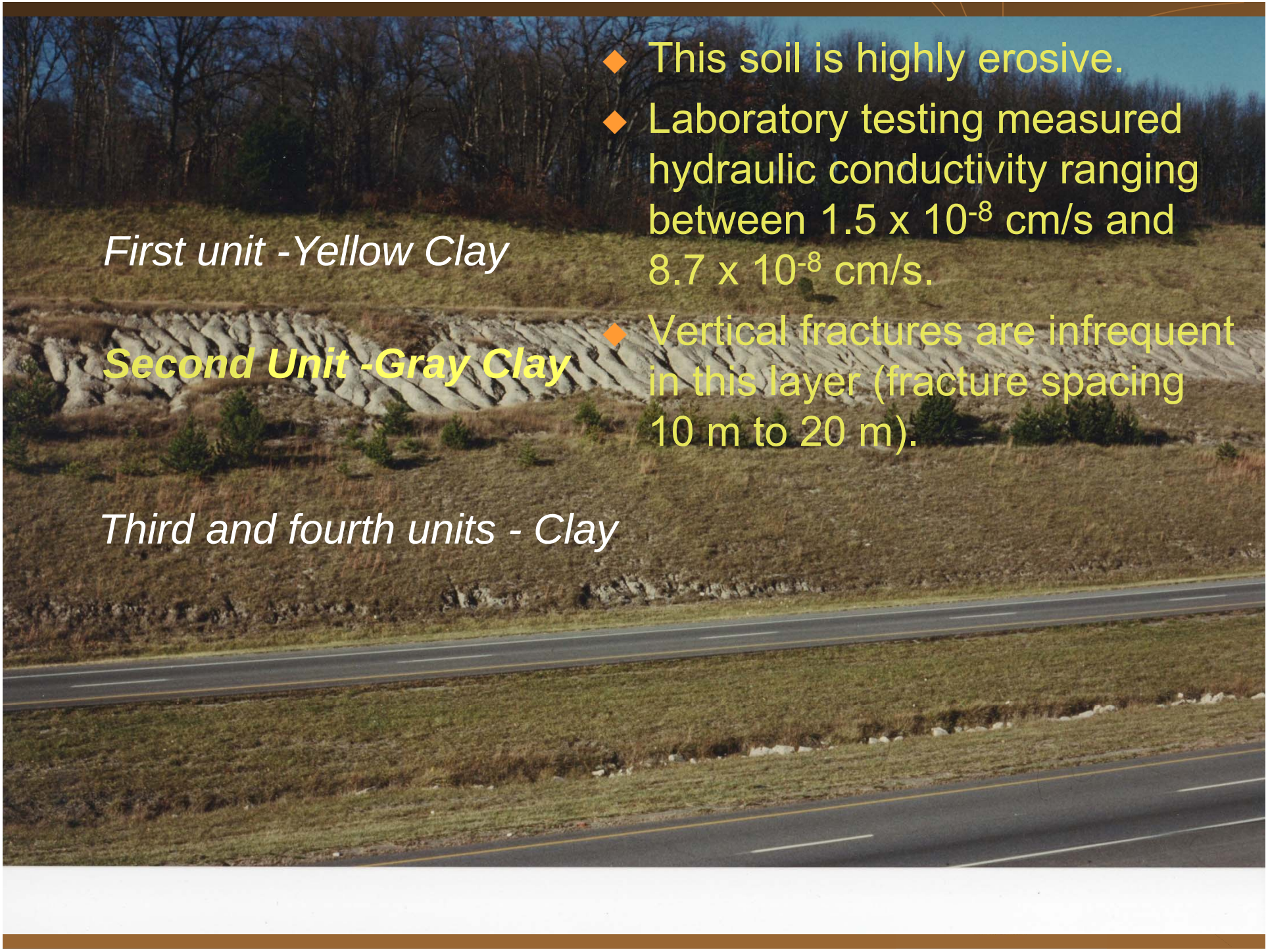


First unit -Yellow Clay

Second Unit -Gray Clay

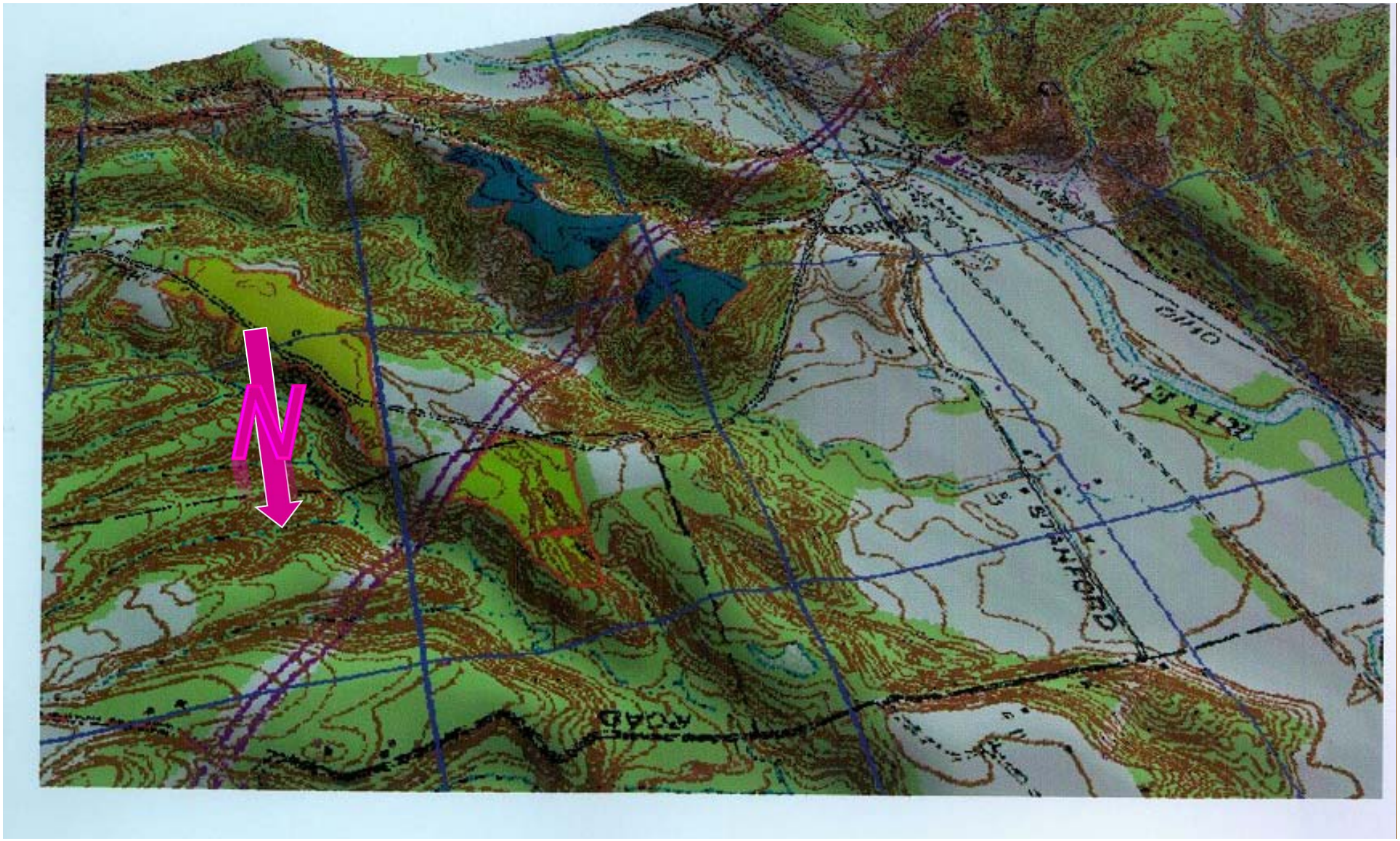
Third and fourth units - Clay

- The second unit is 10 m to 30 m of predominantly unweathered, dense, gray lean clay, approximately 95 percent fines, containing a few pebbles and cobbles and infrequent 0.7 m to 3 m thick zones of thinly laminated silts and clays of lacustrine origin.
- This unit also contains occasional lenses of silt or sand which are generally 0.3 m to 1 m thick. These lenses were isolated, discontinuous, and sometimes were not oriented horizontally.

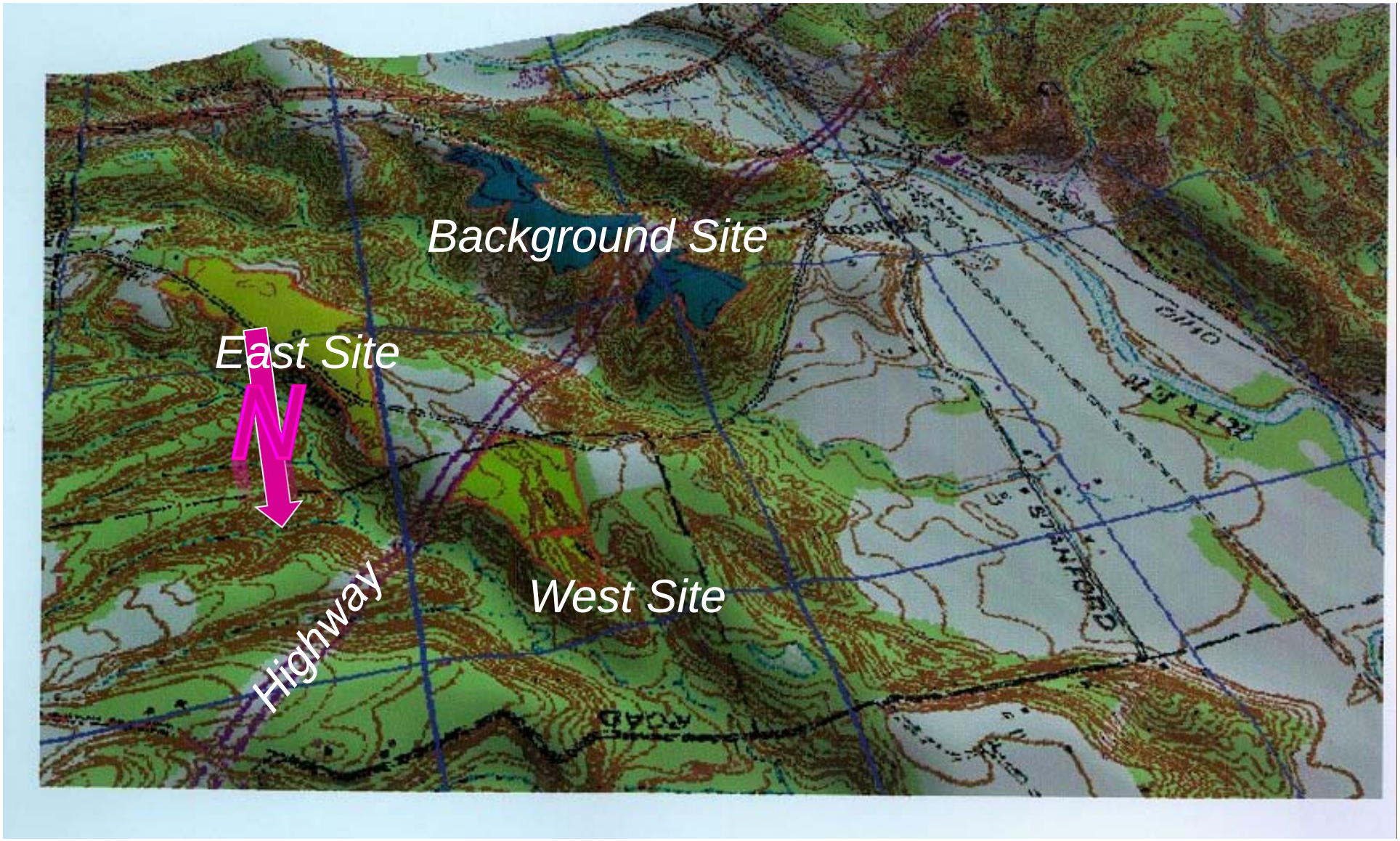


- This soil is highly erosive.
- Laboratory testing measured hydraulic conductivity ranging between 1.5×10^{-8} cm/s and 8.7×10^{-8} cm/s.
- Vertical fractures are infrequent in this layer (fracture spacing 10 m to 20 m).

Upper Paleolithic erosion created valleys and plateaus.



The site is generally located on a relatively flat plateau and is transected by a highway.

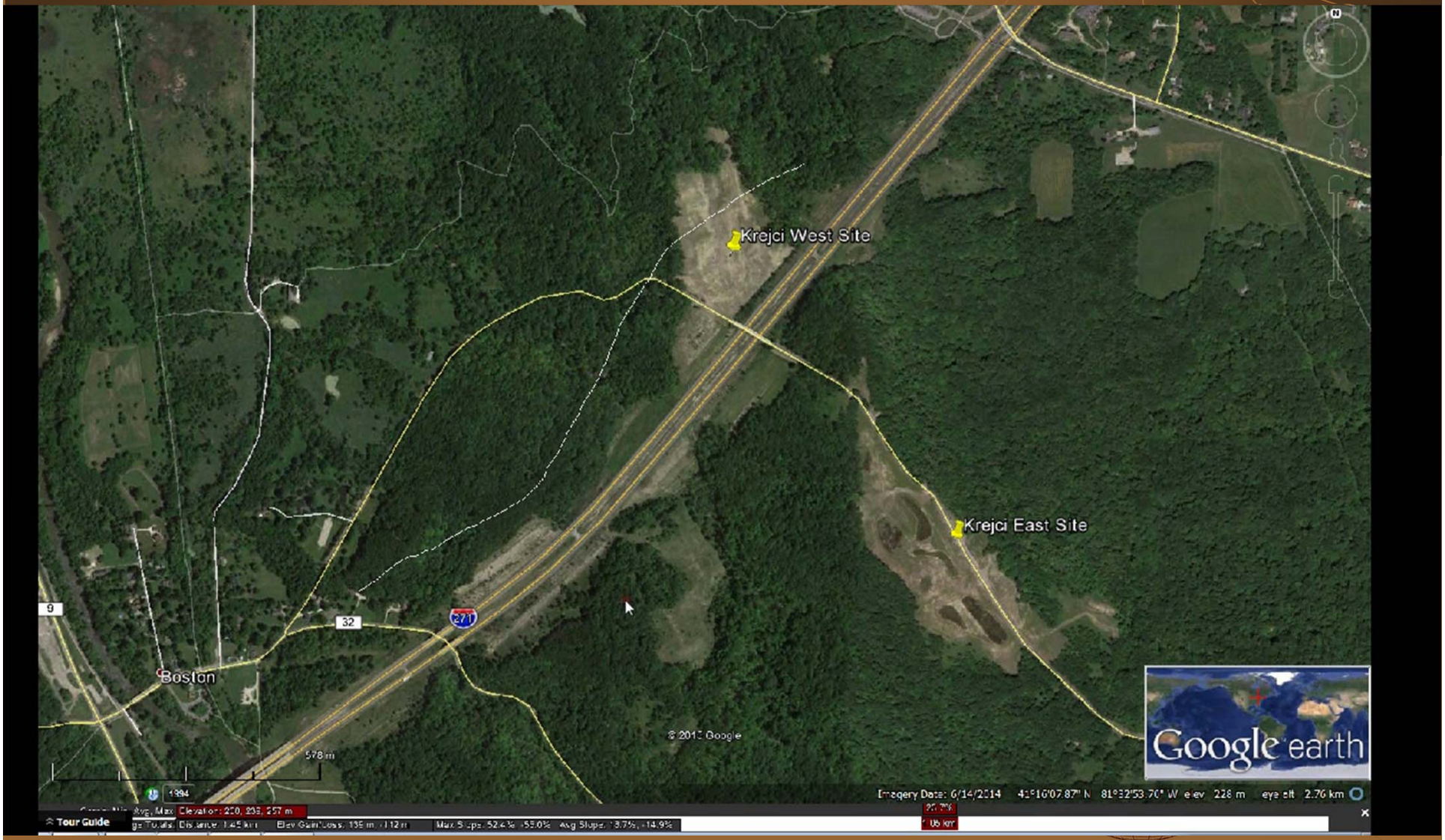


The West Site is the focus of this presentation and is located northwest of the Highway.

A parallel plateau located approximately 1 km southwest of the site was used for control and is called the Background Site.

The West Site includes a deep ravine that incised the 10 m thick upper till unit and cut an additional 10 m into the second till unit.

Looking North - A Cross-section of Background and West Site Reveals the 40 m to 50 m height of the plateaus and the location of the West Site Ravine.



Krejci Dump Site History

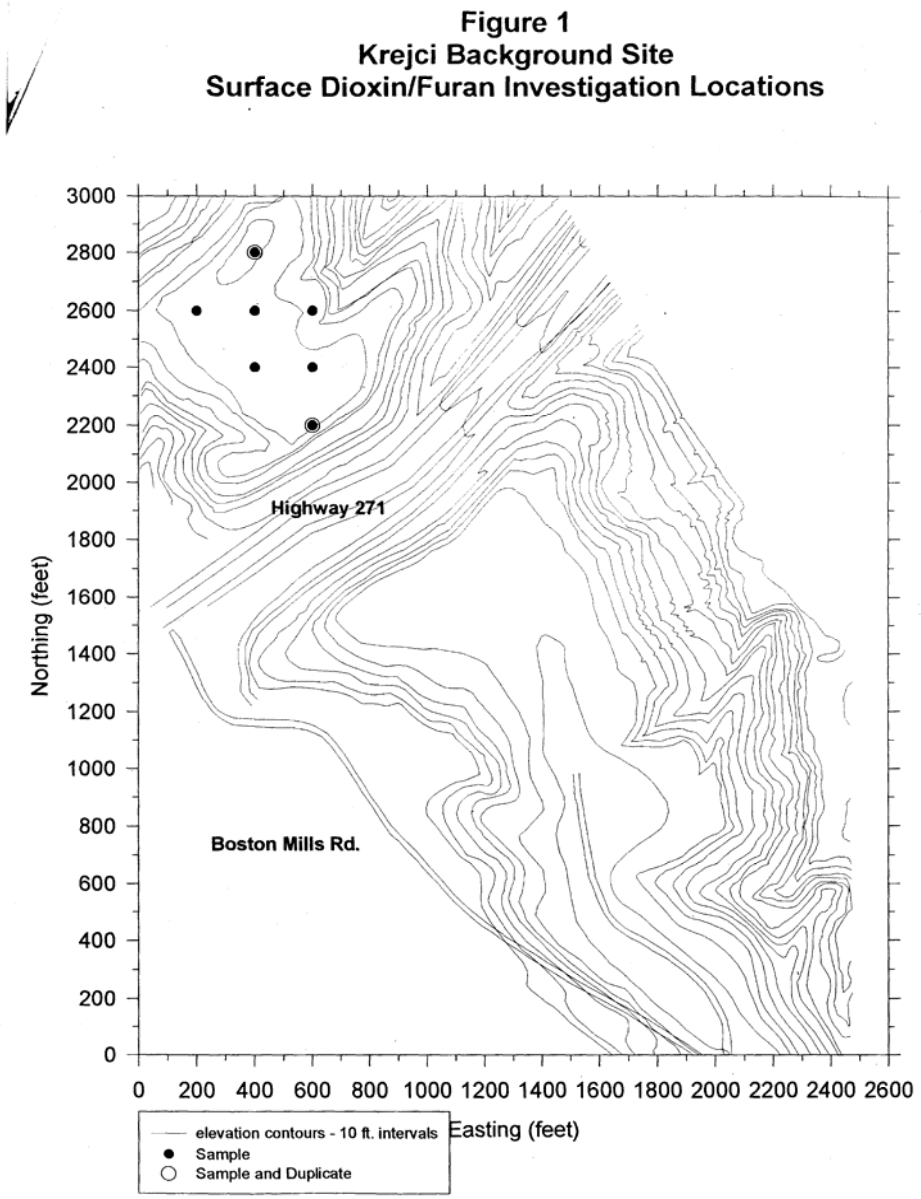
During the years of operation from approximately 1950 to 1980, large volumes of solid and liquid waste materials were brought to the dump, where significant quantities of hazardous substances were released to the environment as a result of open dumping, spills, leaking containers, and burning.

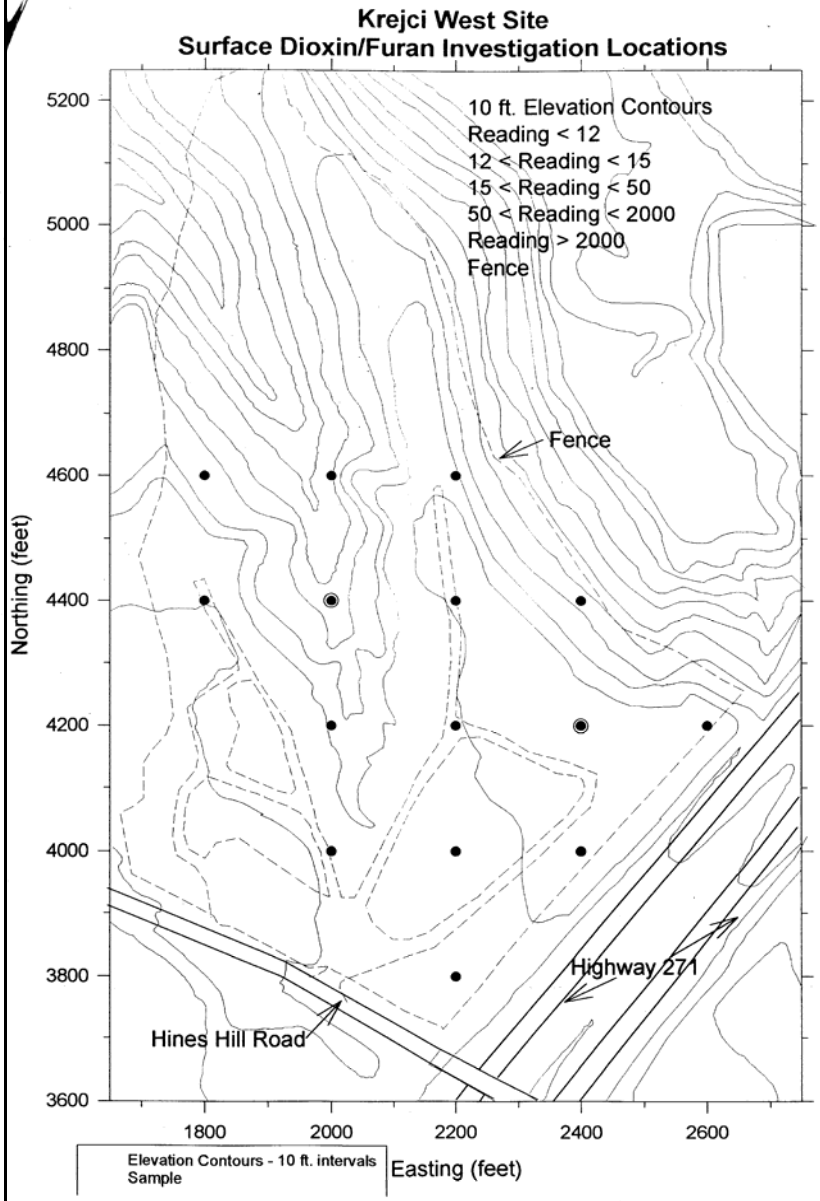

1987

The valley in the West Site was filled with debris and a fire smoldered for most of the dumps 30 years of operation.


1988-1992 Surface debris and unconsolidated waste were removed.

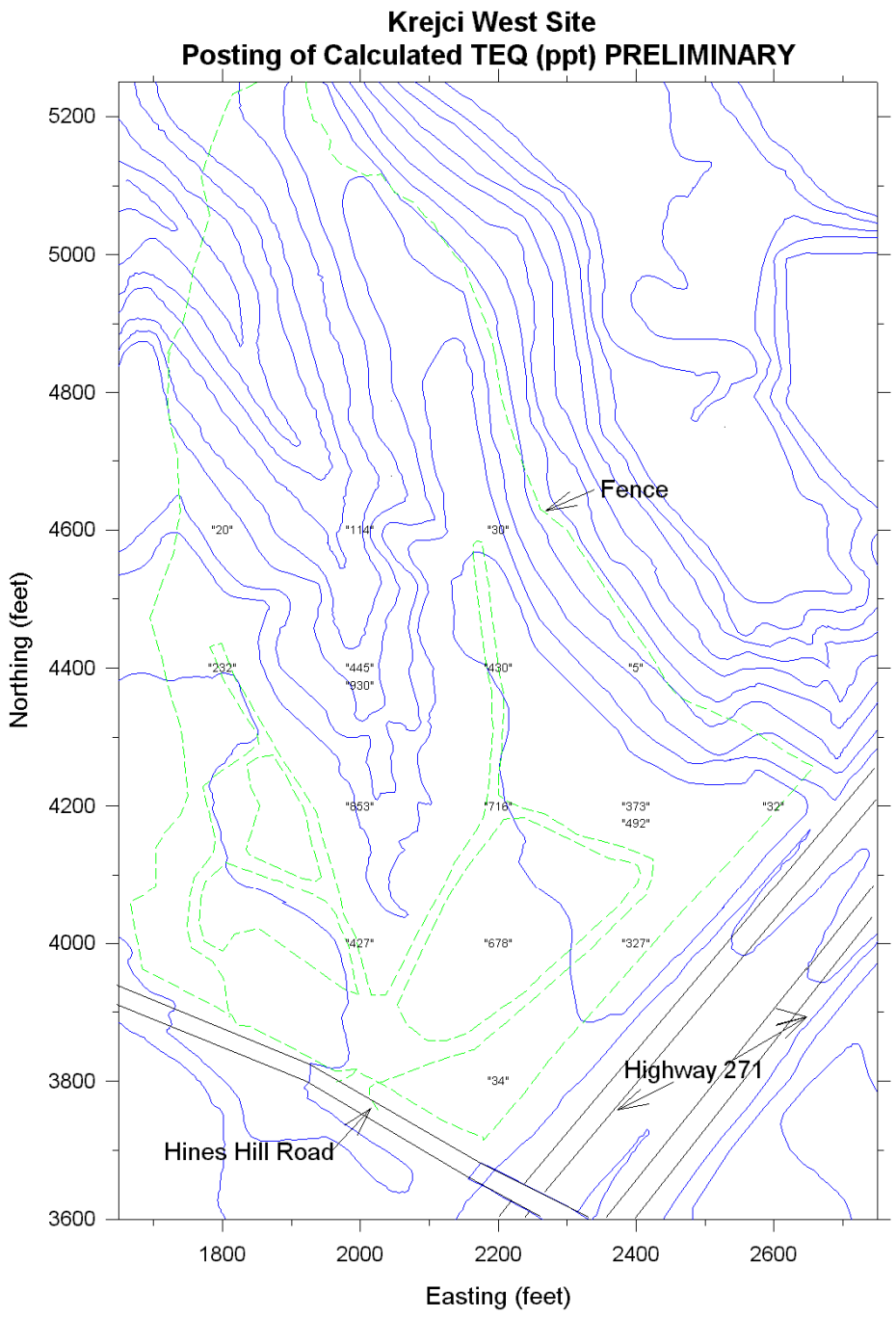

1994-1996
Remedial Investigation





1996 discrete sampling locations

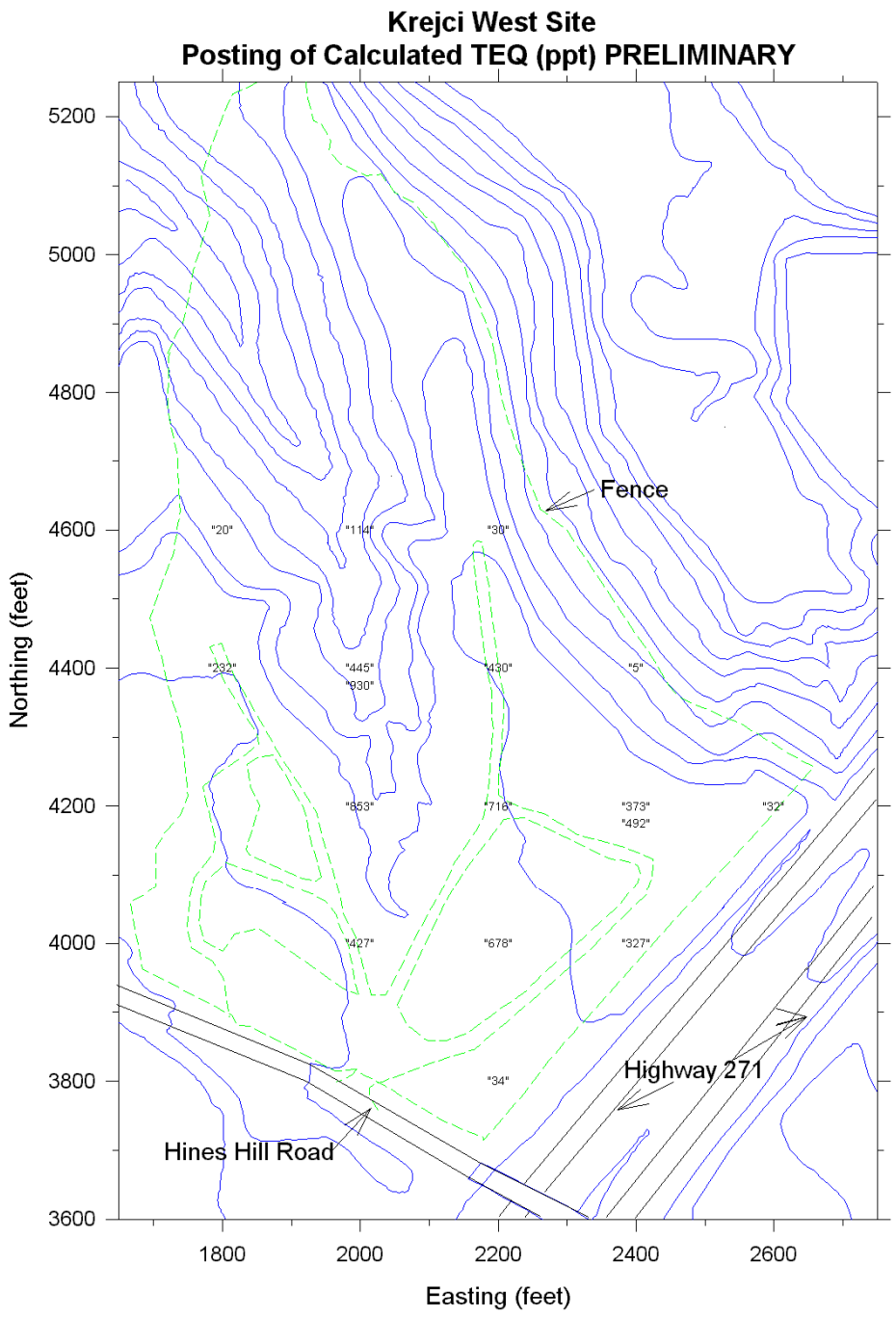
SW846 Method 8290



1996

TEQ was calculated.

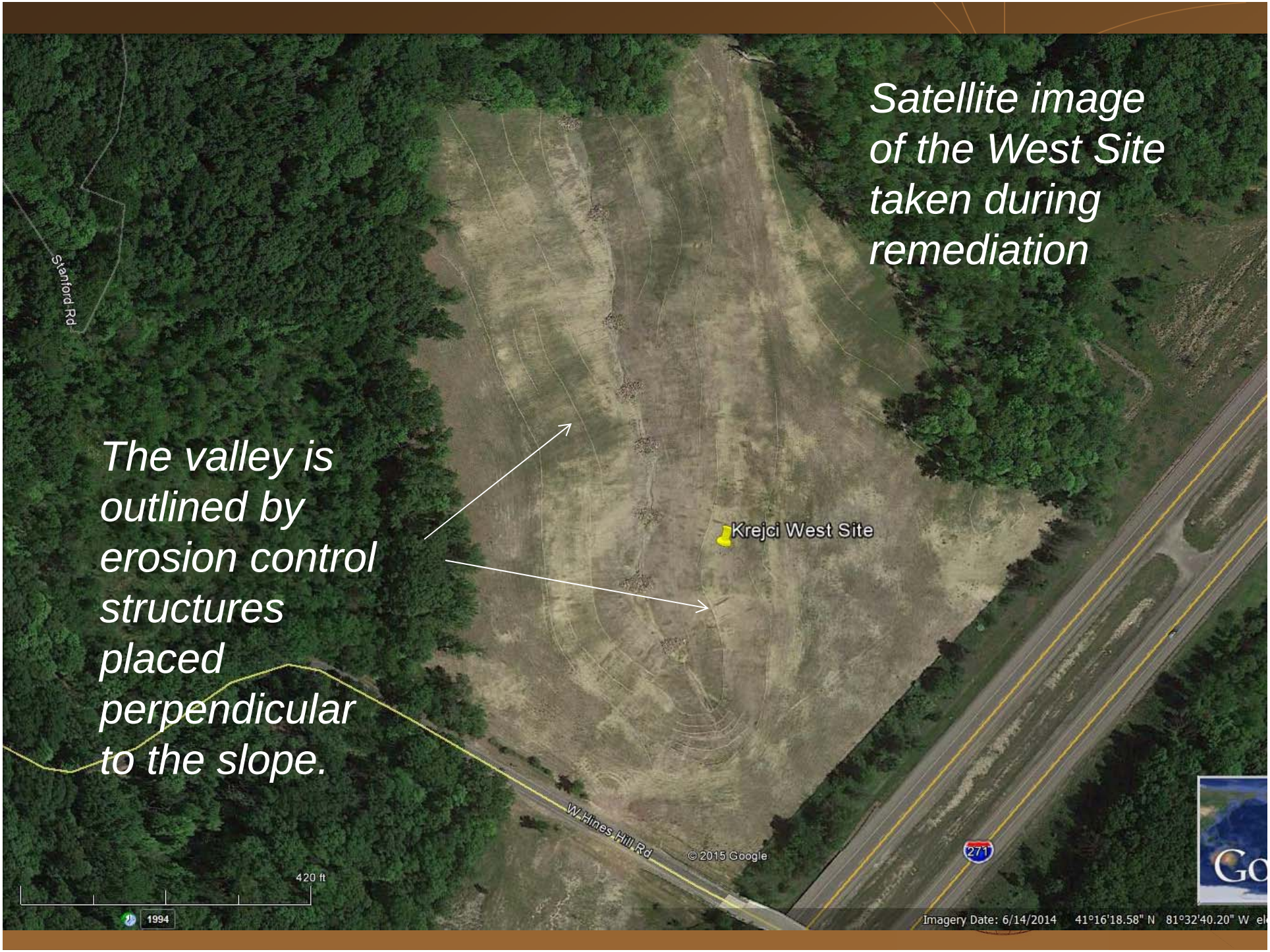
Estimating Exposure to Dioxin-Like Compounds. U.S. Environmental Protection Agency, Washington, D.C., EPA/600/6-88/005B

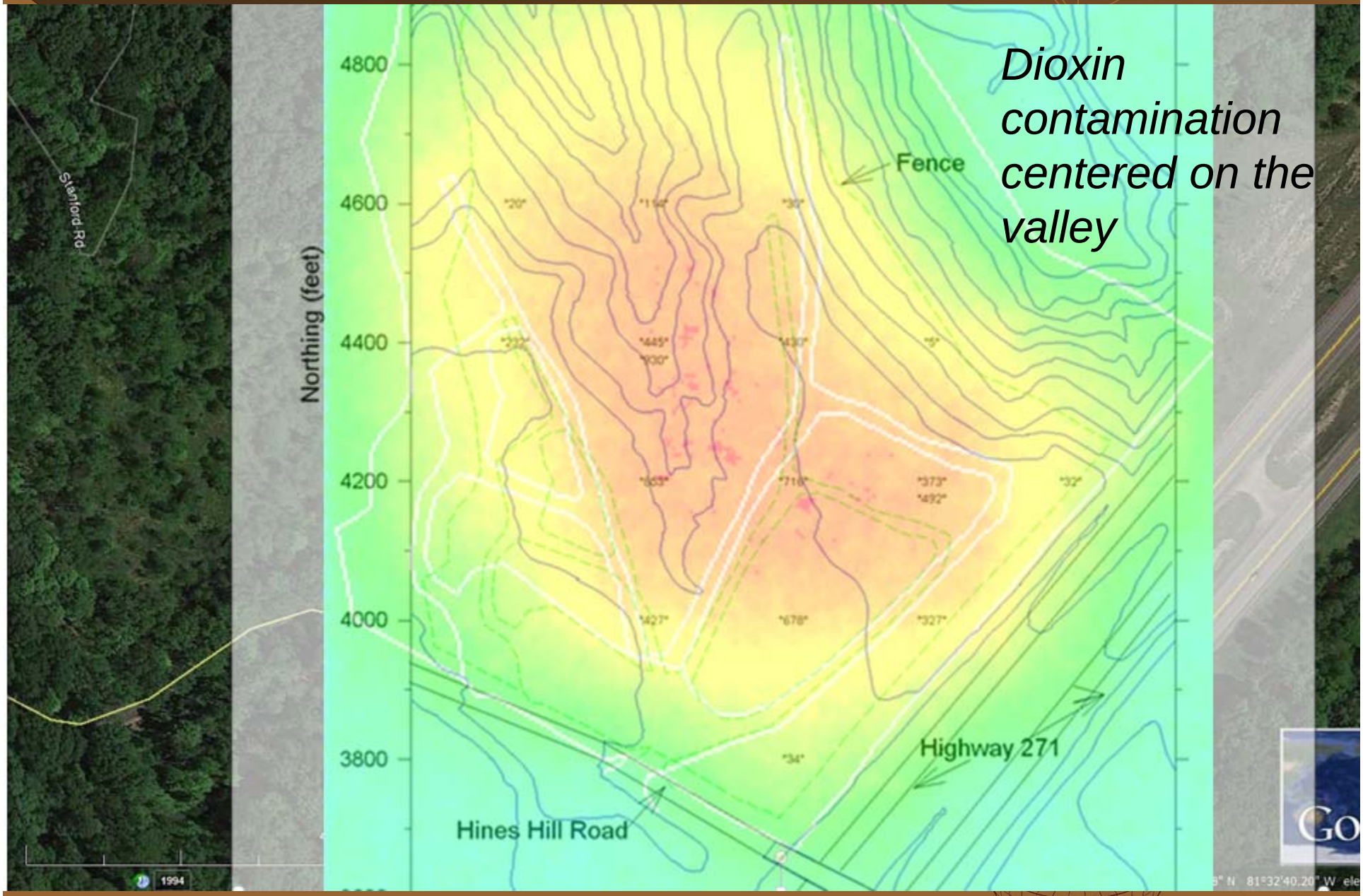


1996

All 17 congeners investigated were found on Site.

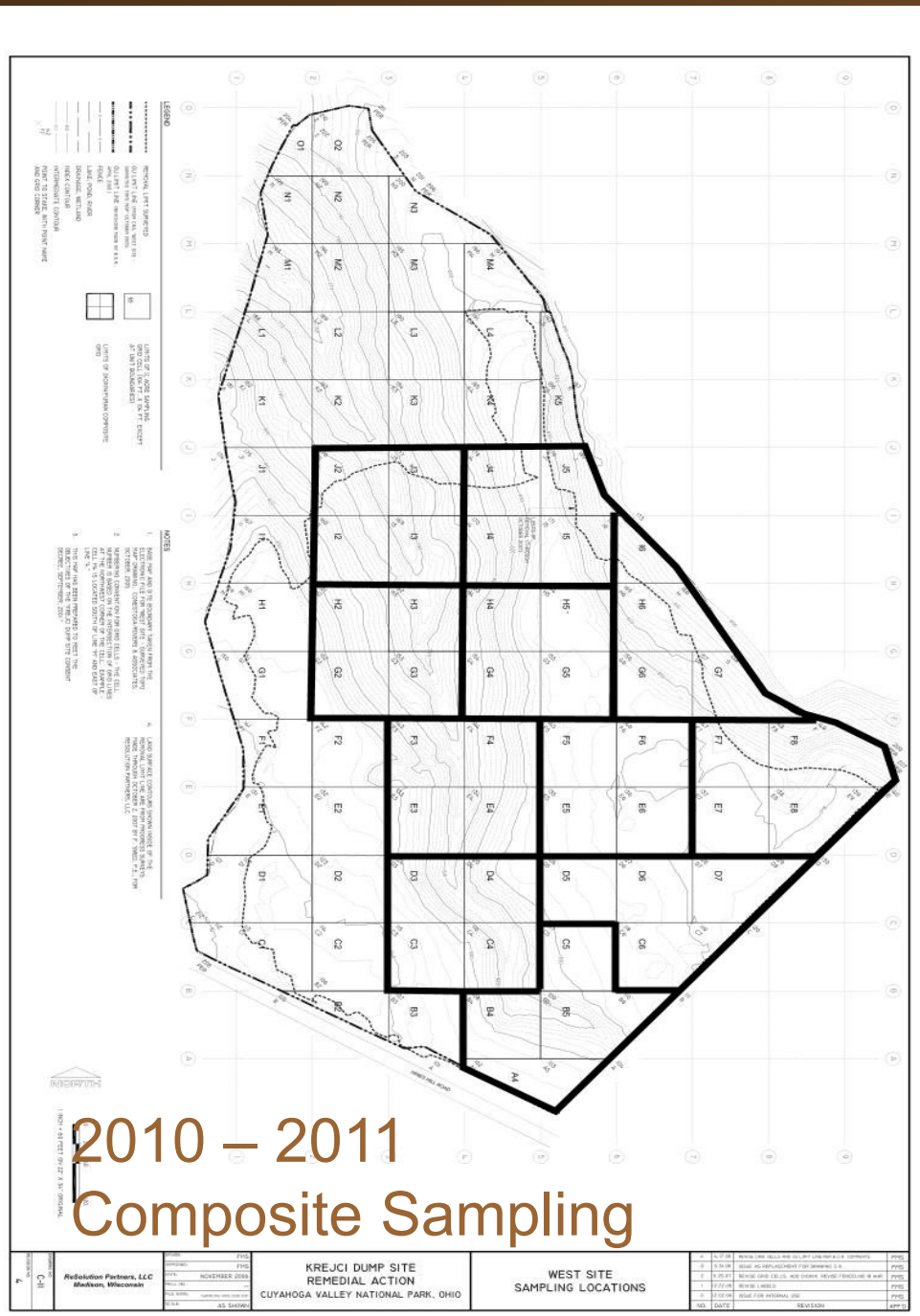
However, only 2,3,7,8 TCDF, 1,2,3,4,6,7,8-HpCDD, and OCDD were discovered on the Background plateau.


Satellite image of the West Site taken during remediation
The valley is outlined by erosion control structures placed perpendicular to the slope.
Stanford Rd
Krejci West Site
W Hines Hill Rd
© 2015 Google
271
420 ft
1994
Imagery Date: 6/14/2014 41°16'18.58" N 81°32'40.20" W


Dioxin contamination centered on the valley
Fence
Highway 271
Hines Hill Road
Northing (feet)
4800
4600
4400
4200
4000
3800
Stanford Rd
1994

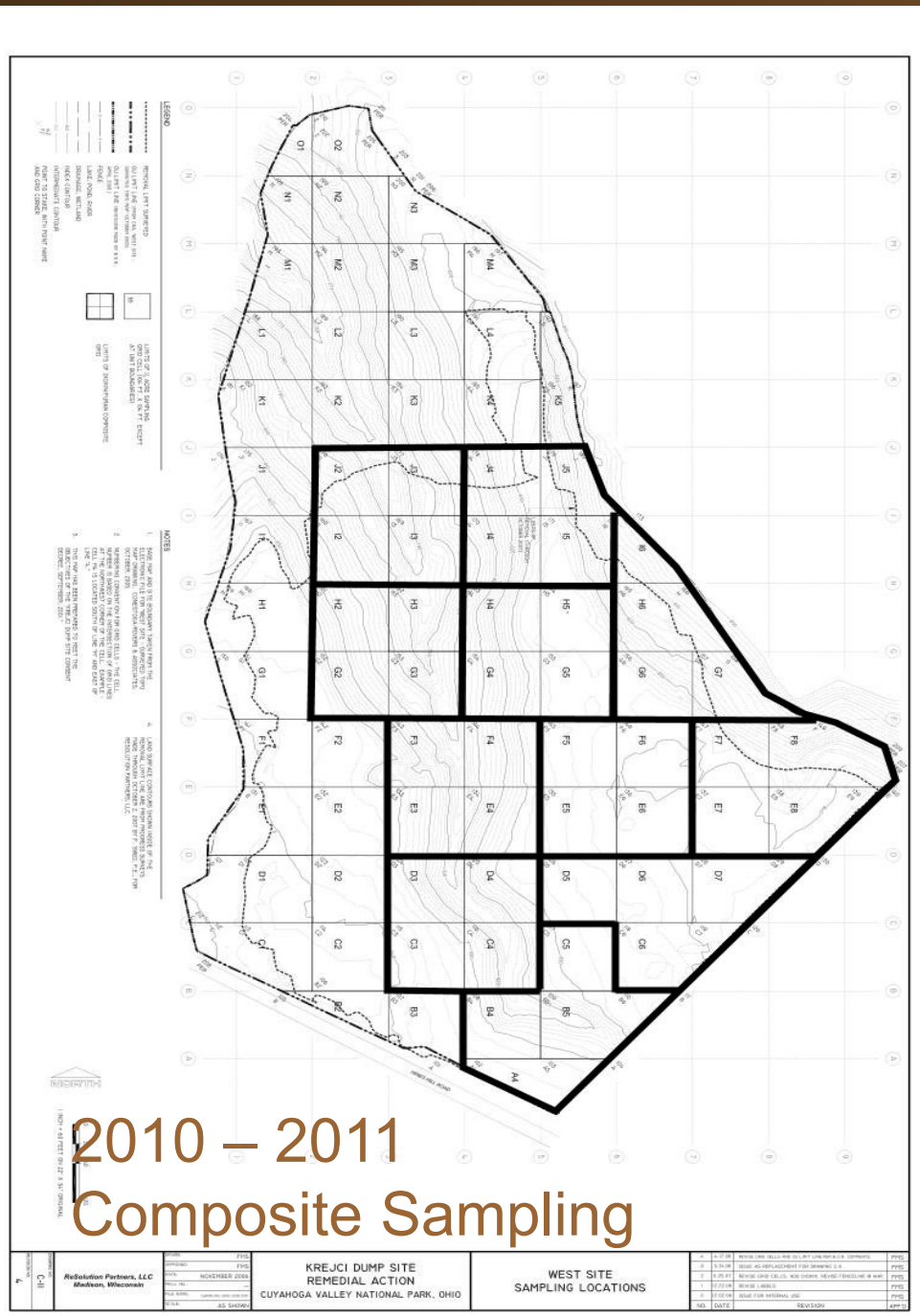
Remediation and Cleanup Verification

- The remediation required excavation and removal of soil to achieve calculated TEQ's less than 3 pg/g.
- Composite samples were used to represent 4000 m^2 areas.
- Any 4000 m^2 area having a composite sample with TEQ equal or exceeding 3 pg/g was excavated a minimum of 15 cm.
- This process was iterated until all areas exhibited composite sample concentrations less than 3 pg/g.



2010 – 2011
Composite Sampling

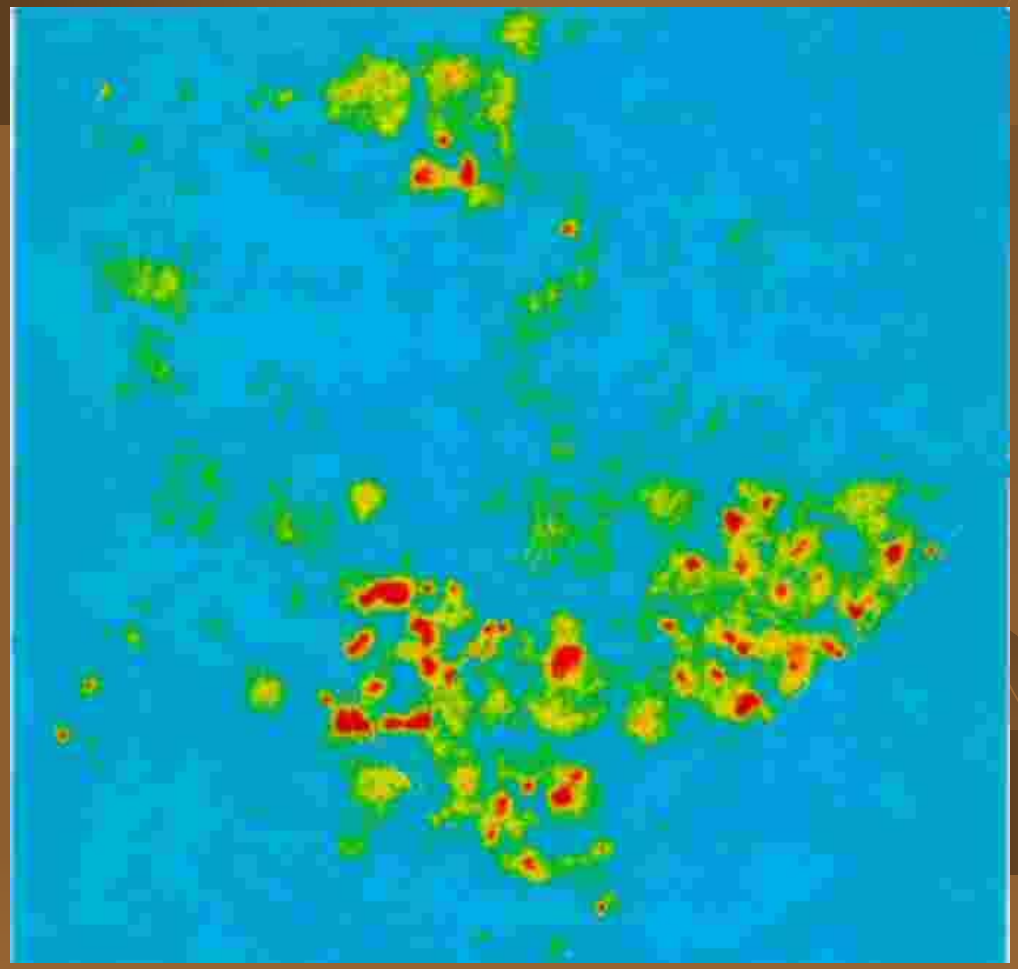
4000 m² represented the approximate size of exposure areas that had been used in human health risk assessment.



2010 – 2011
Composite Sampling

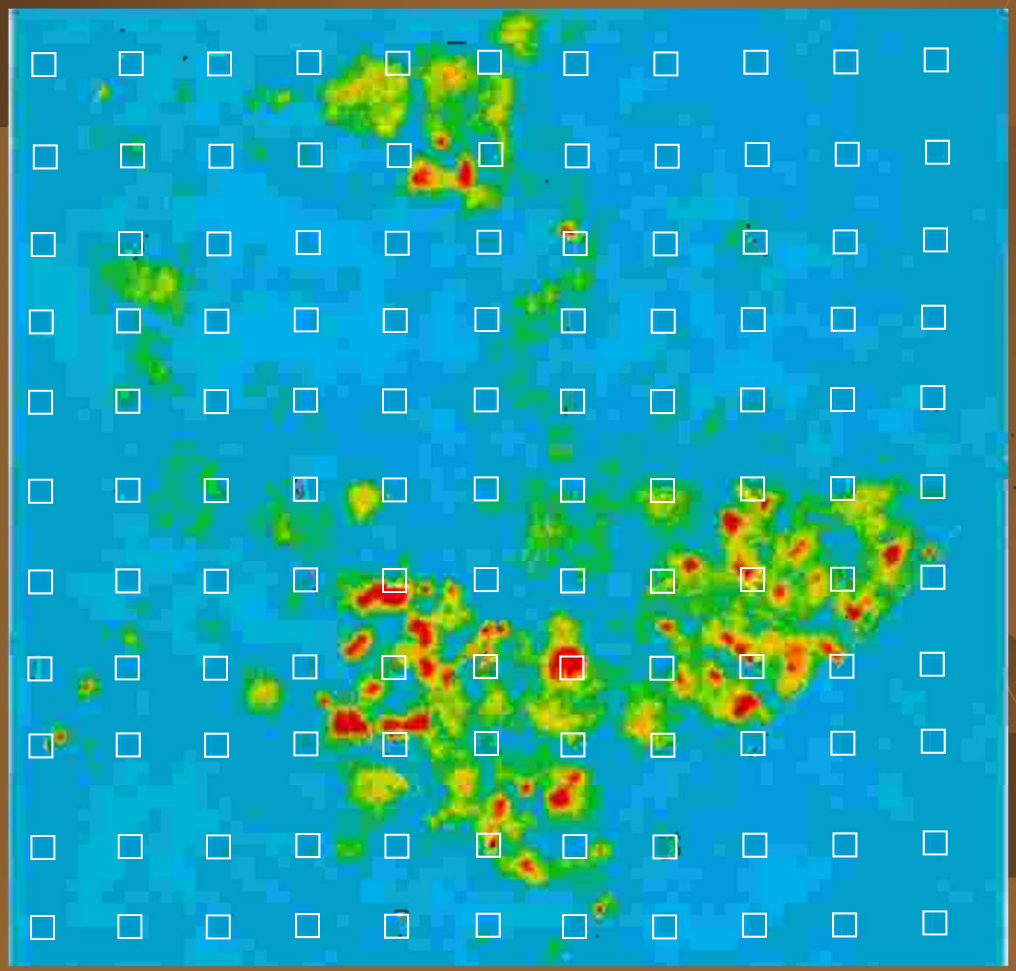
Ultimately, the areas were subdivided and composite samples were created to represent 1000 m^2 subareas.

Composite Sample Design



To aid in explaining the composite sample plan design. Assume the image represents the contamination distribution in a 4000 m^2 area following an episode of excavation.

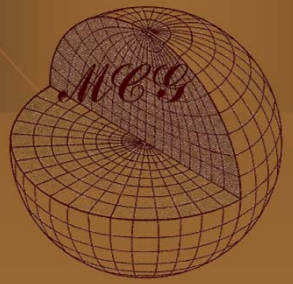
Composite Sample Design



The locations shown here represent an 11x11, 121-specimen collection grid

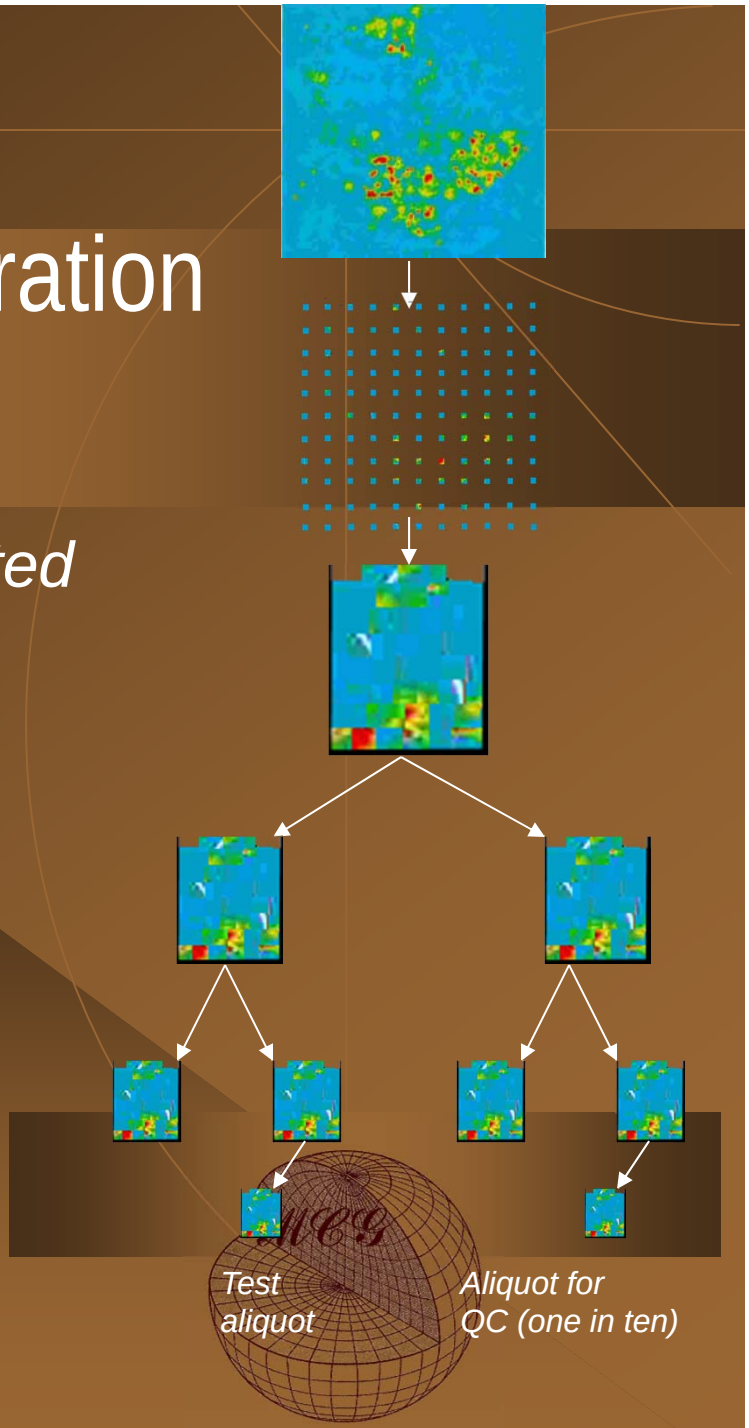
Collect Specimens from the Area of Concern

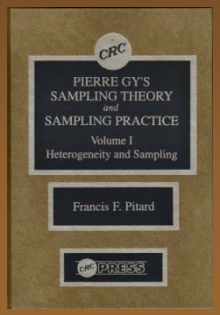
Equal mass specimens are placed in a single sample container



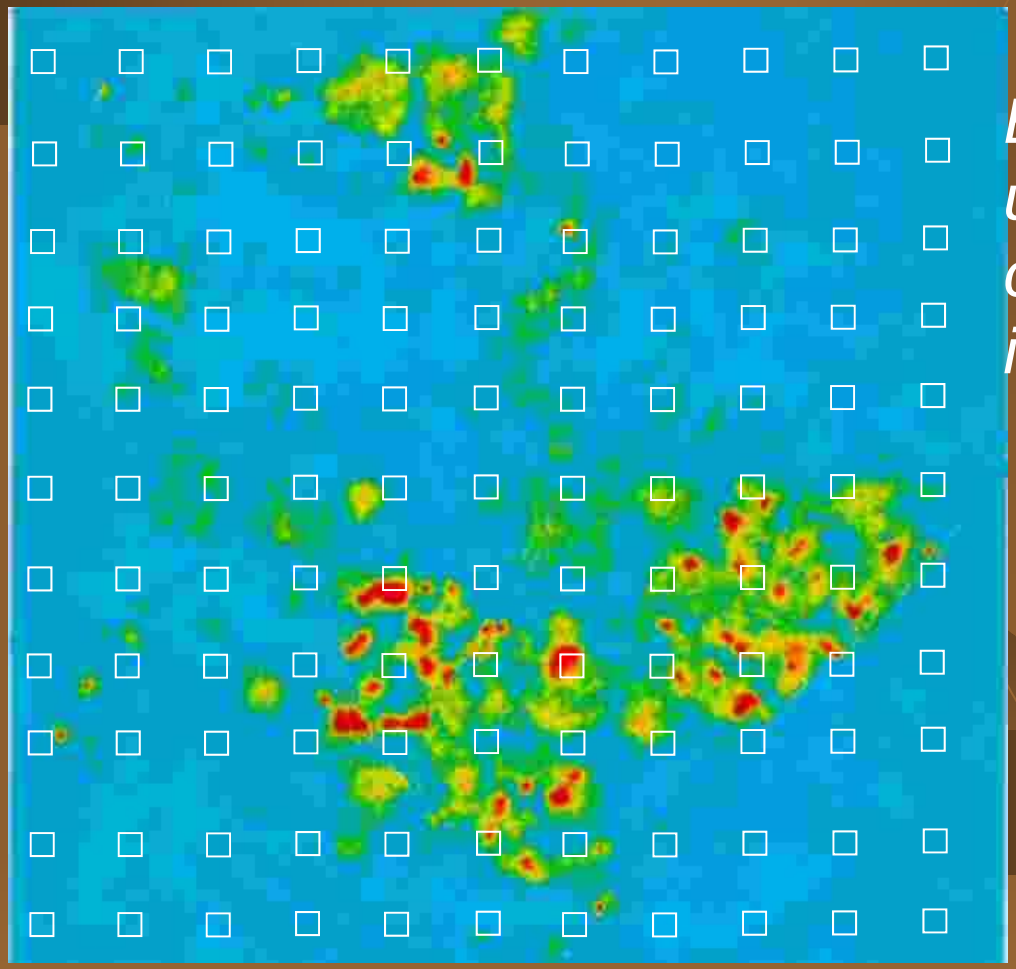
The Area is Represented Throughout the Aliquot Preparation Process

The sample is reduced in size by repeated Grinding-and-Splitting operations



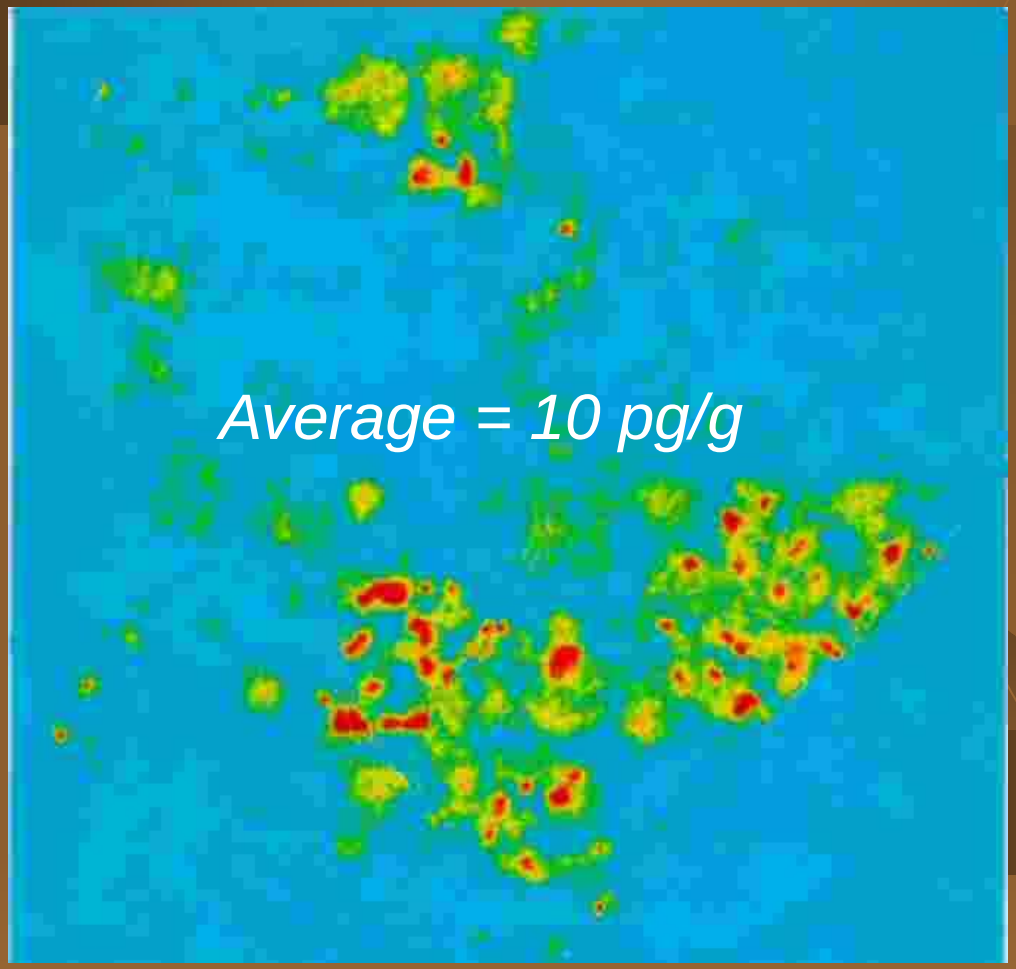


How Many Soil Specimens are Needed?



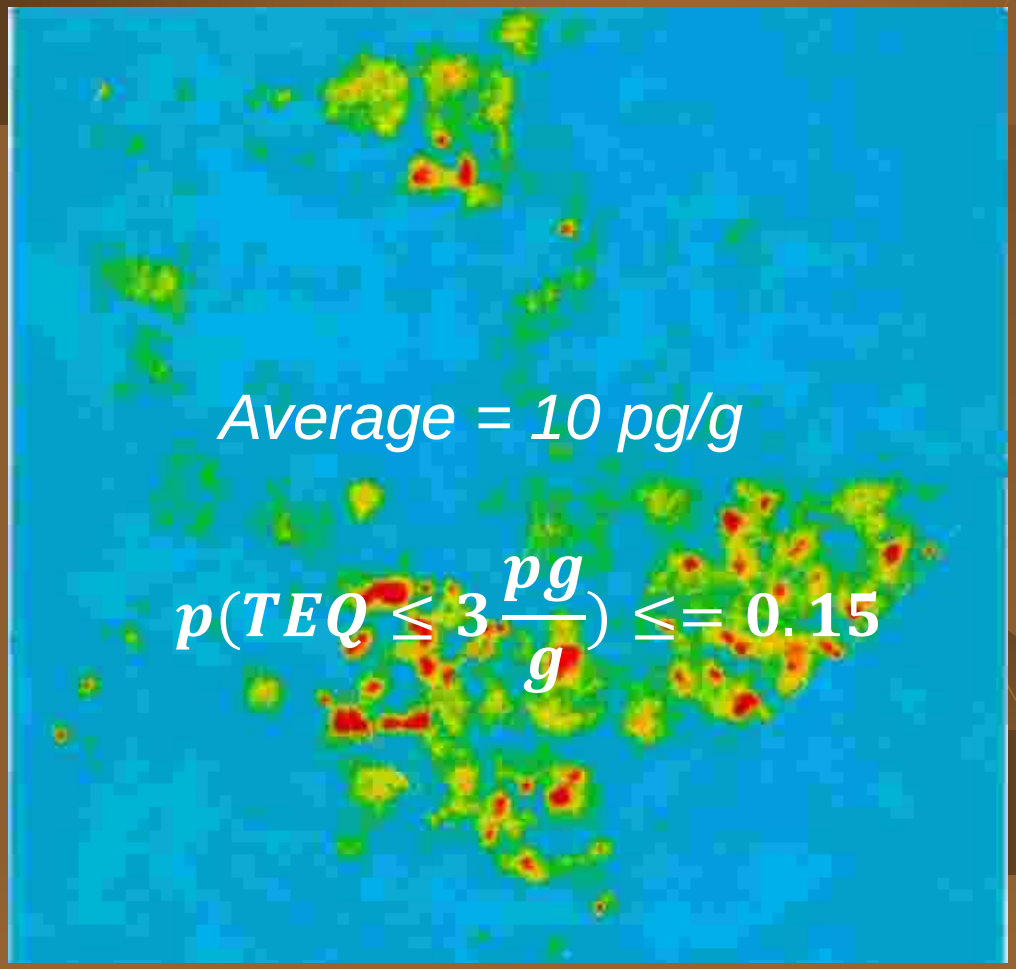
Enough to assure that underrepresented contamination is inconsequential.

Composite Sample Design



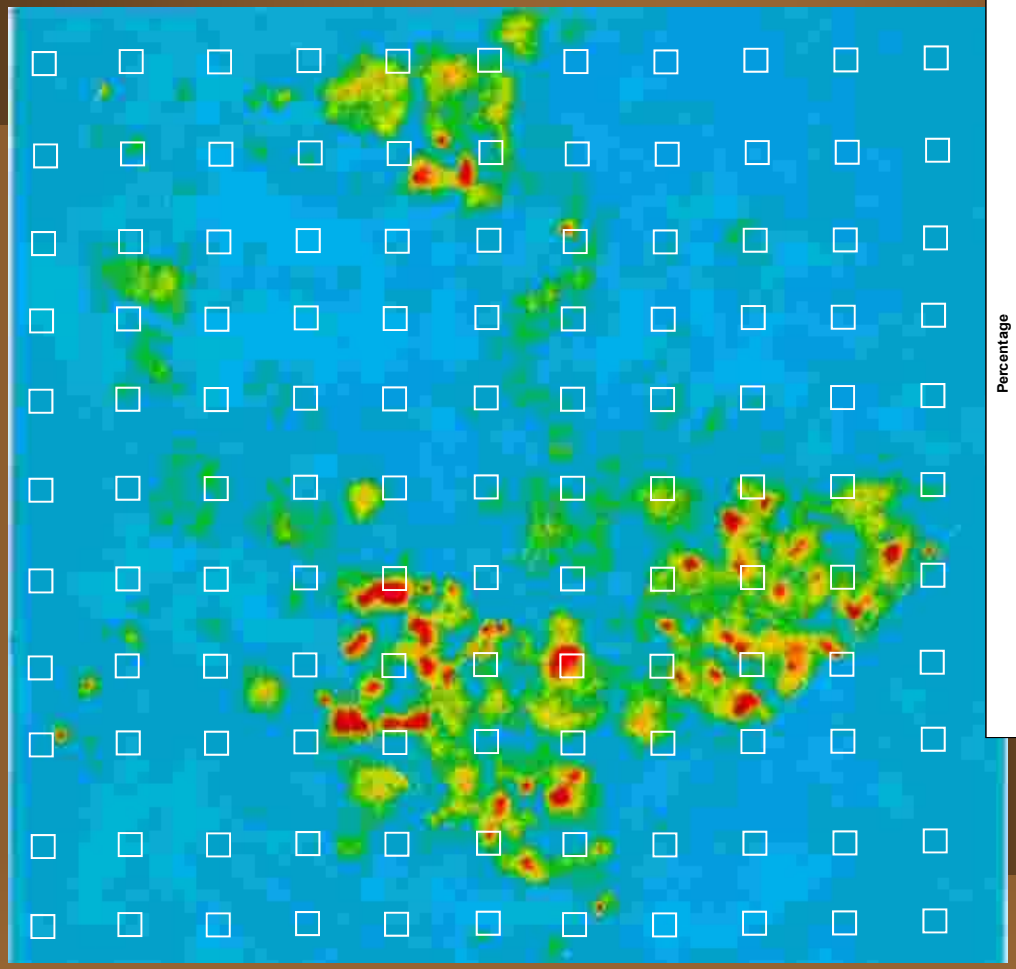
Now consider the contamination distribution shown represents the smallest footprint expected following remediation and that could exhibit a marginally acceptable average TEQ of 10 pg/g.

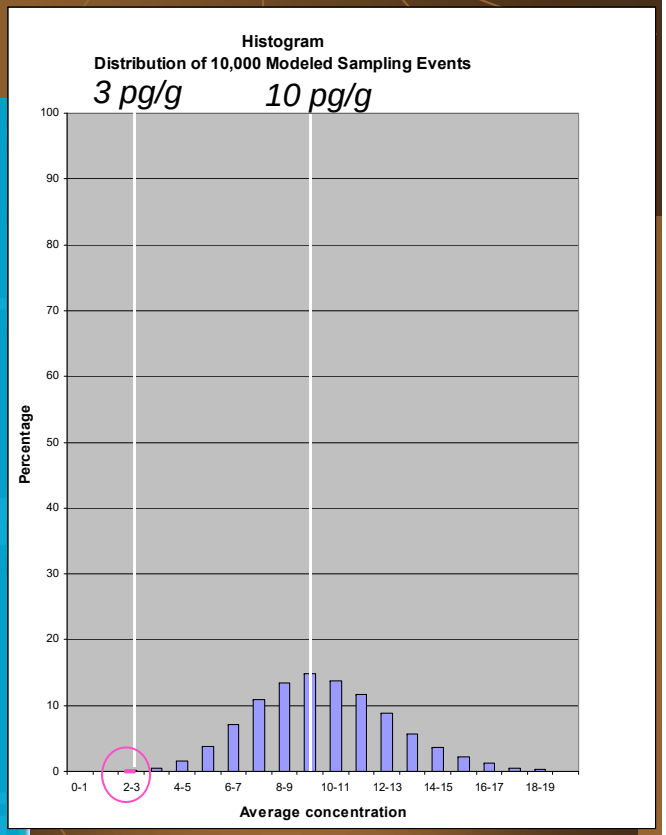
Composite Sample Design



It is desired that there be less than a 15 percent chance a composite sample will have an average TEQ less than 3 pg/g.

Example: 10000 simulations of a 121-Specimen Random Sampling Event.

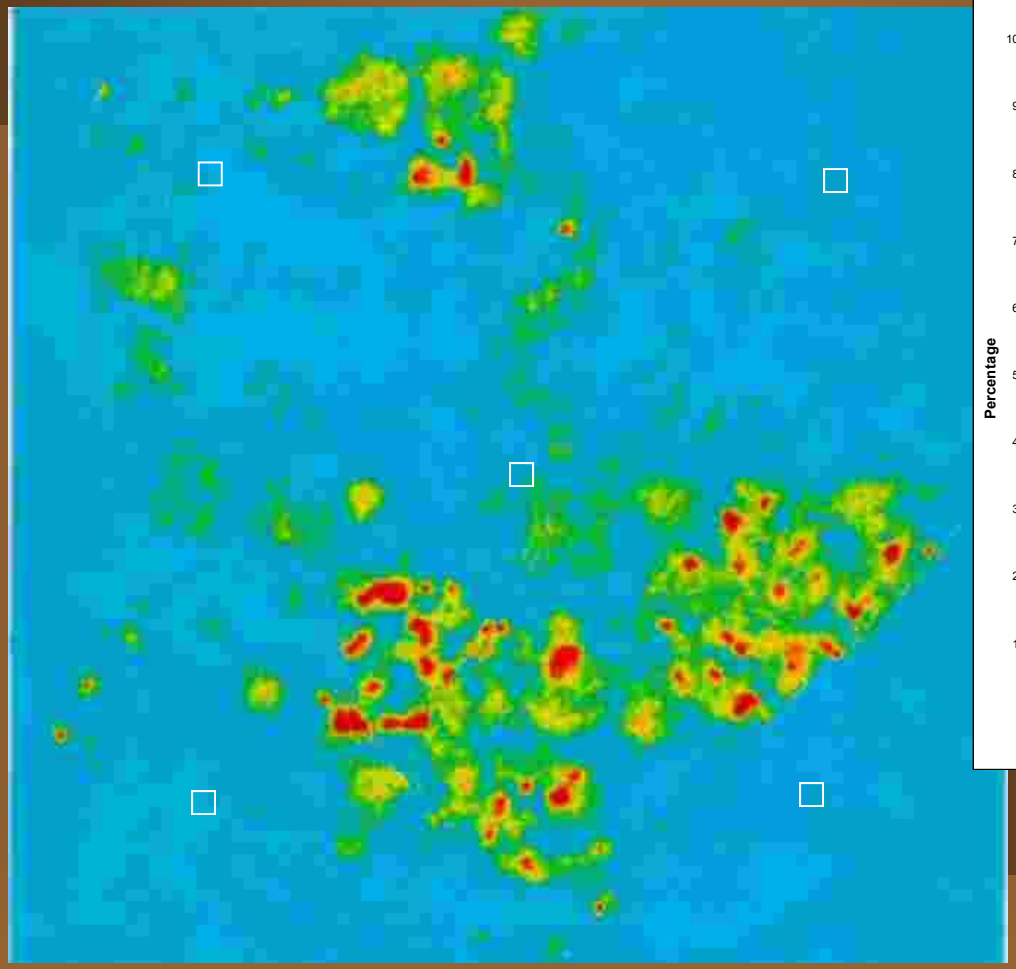


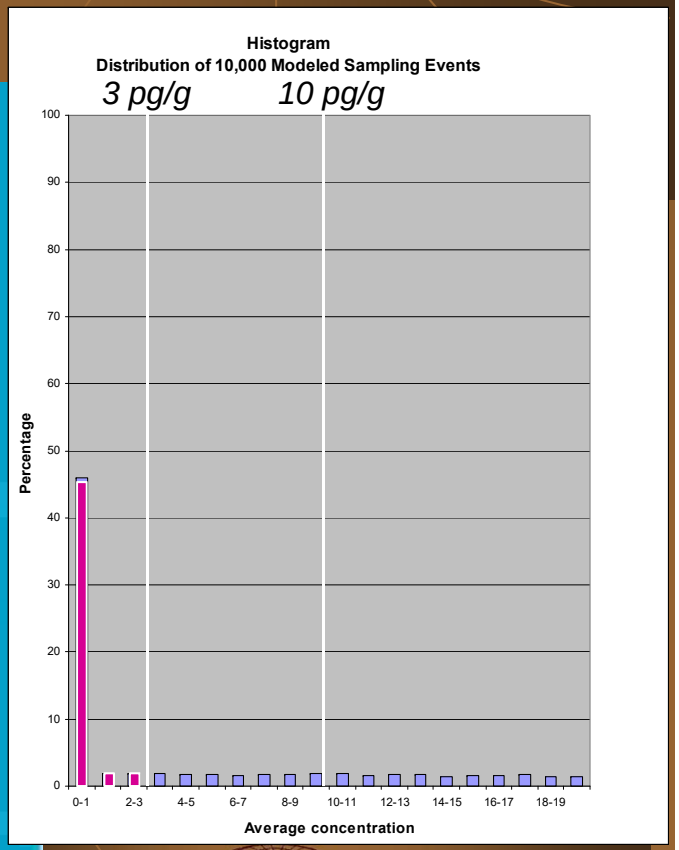


Distribution of Sample Concentrations

More than 99 percent of the modeled events result in the composite having a TEQ greater than 3 pg/g.

Example: 10000 Iterations of a 5-specimen Random Sampling Event.

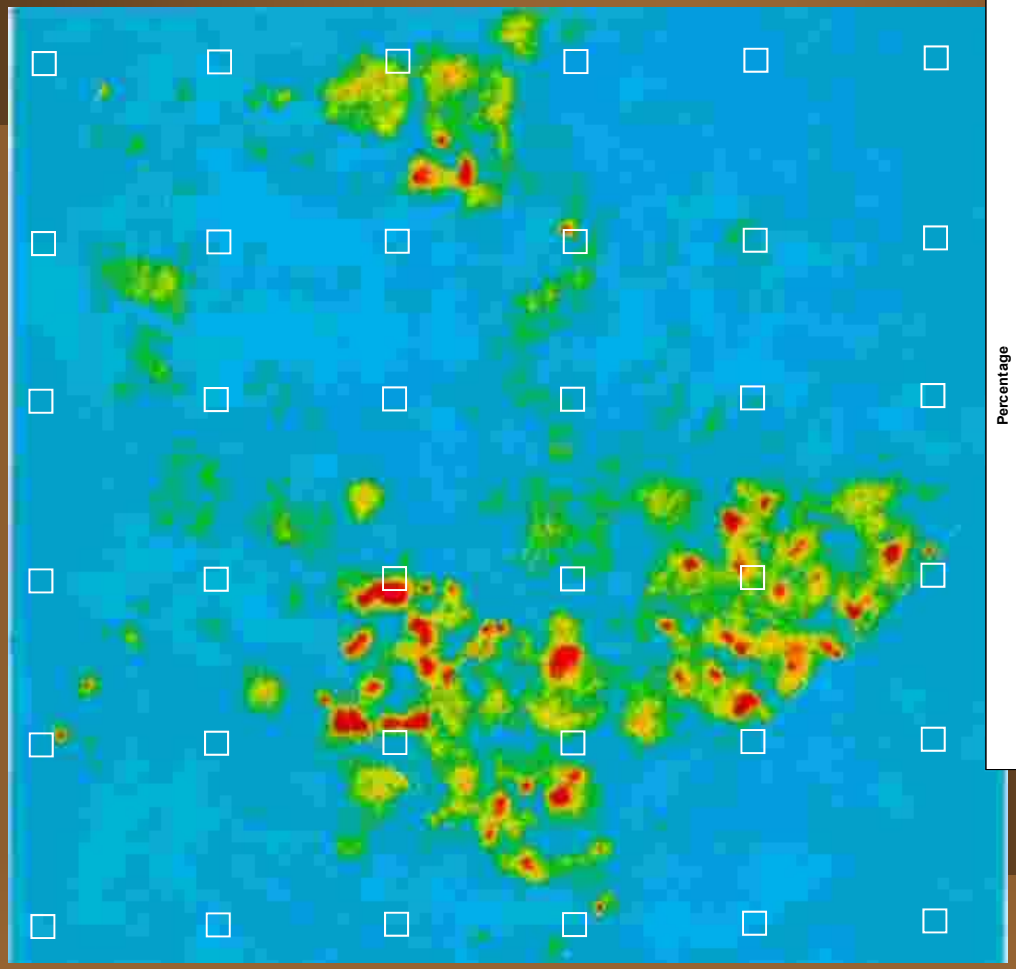


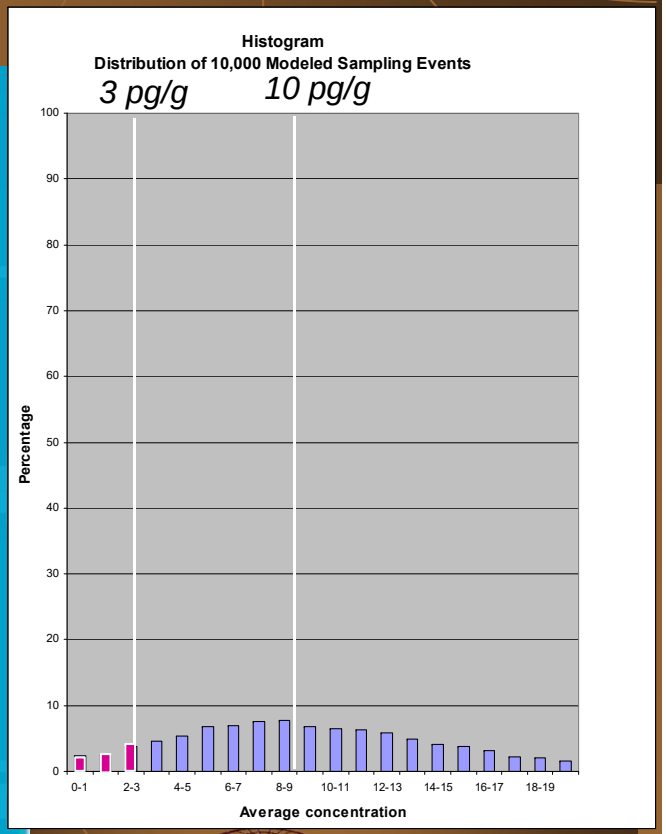


Distribution of Sample Concentrations

More than 50 percent of the modeled events result in the composite having a TEQ less than 3 pg/g.

Example: 10000 Iterations of a 36-Specimen Random Sampling Event.





Distribution of Sample Concentrations

About 80 percent of the modeled events result in the composite having a TEQ greater than 3 pg/g.

Excavation commenced in 2005

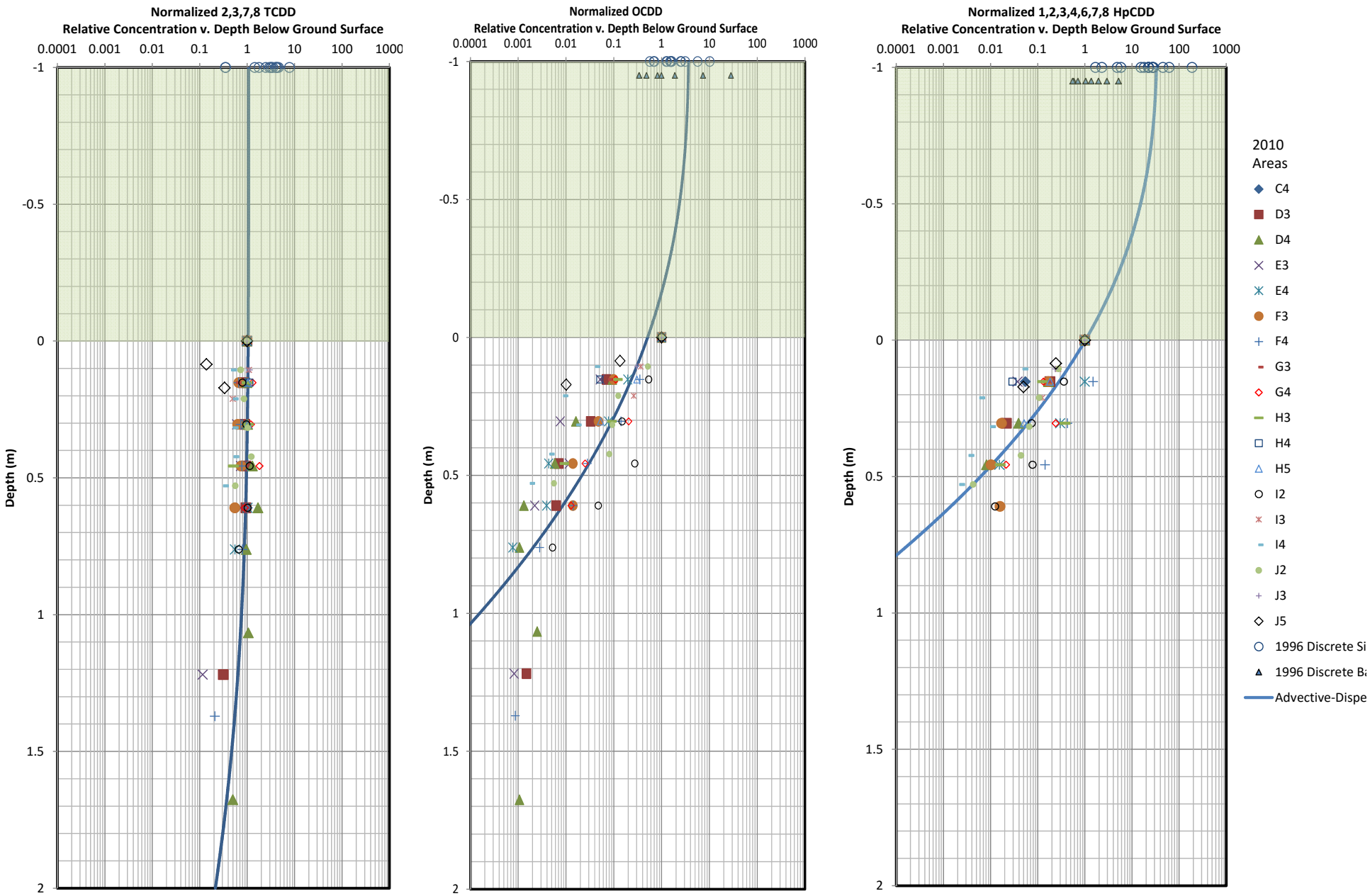
- Individual grids were excavated to remove visible signs of contamination and soil that had been altered by burning.
- It is estimated that approximately 1 m of soil was removed in this process.

Excavation commenced in 2005

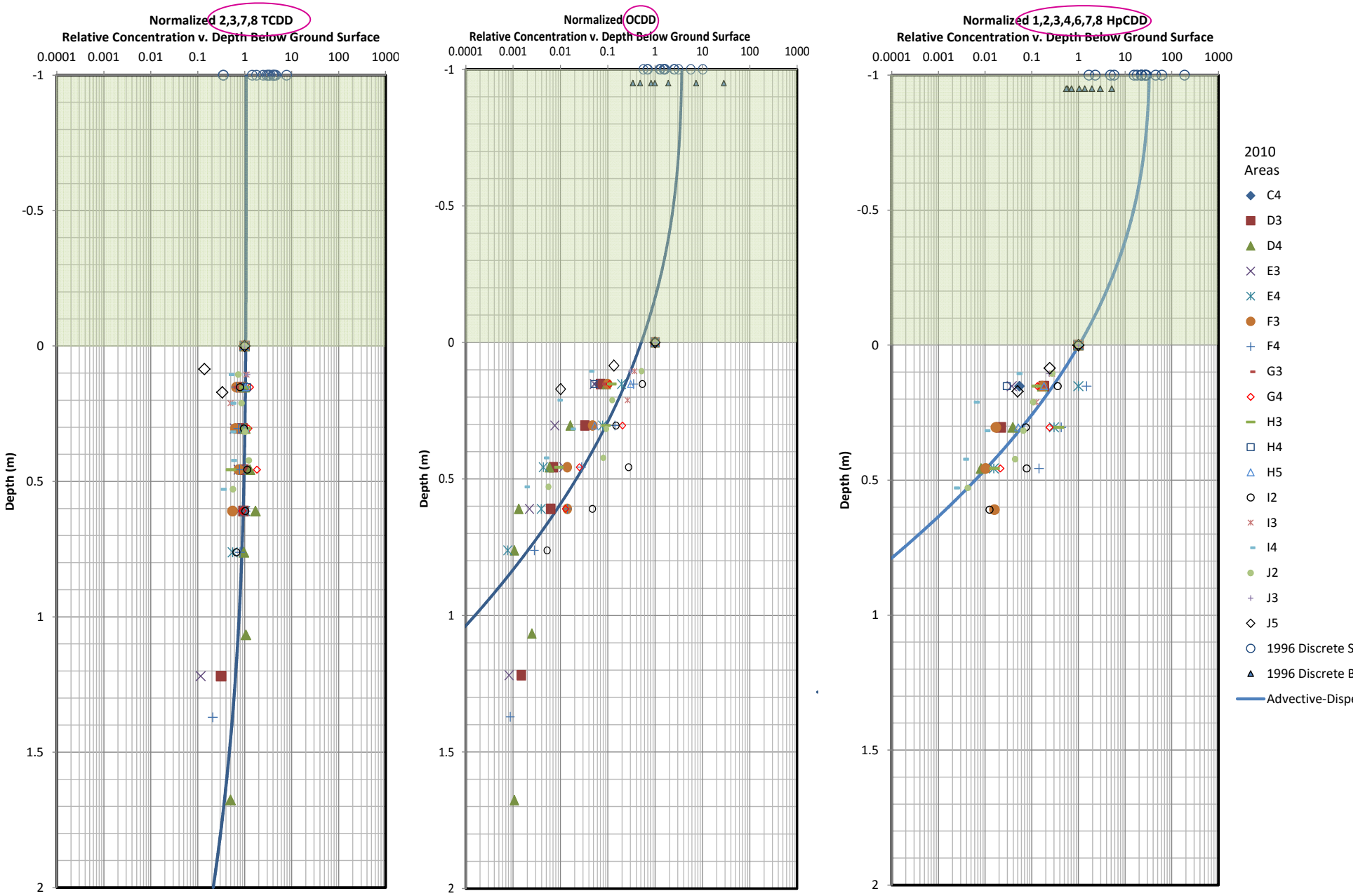
- Individual 1000 m^2 grids exceeding 3.0 pg/g TEQ were then excavated a minimum of 15 cm.
- A composite sample was collected from the exposed surface of each excavated grid.
- This process was iterated


Some of the areas and subareas are discernable in this satellite image.
W Hines Hill Rd
© 2012 Google
381 ft
Google earth

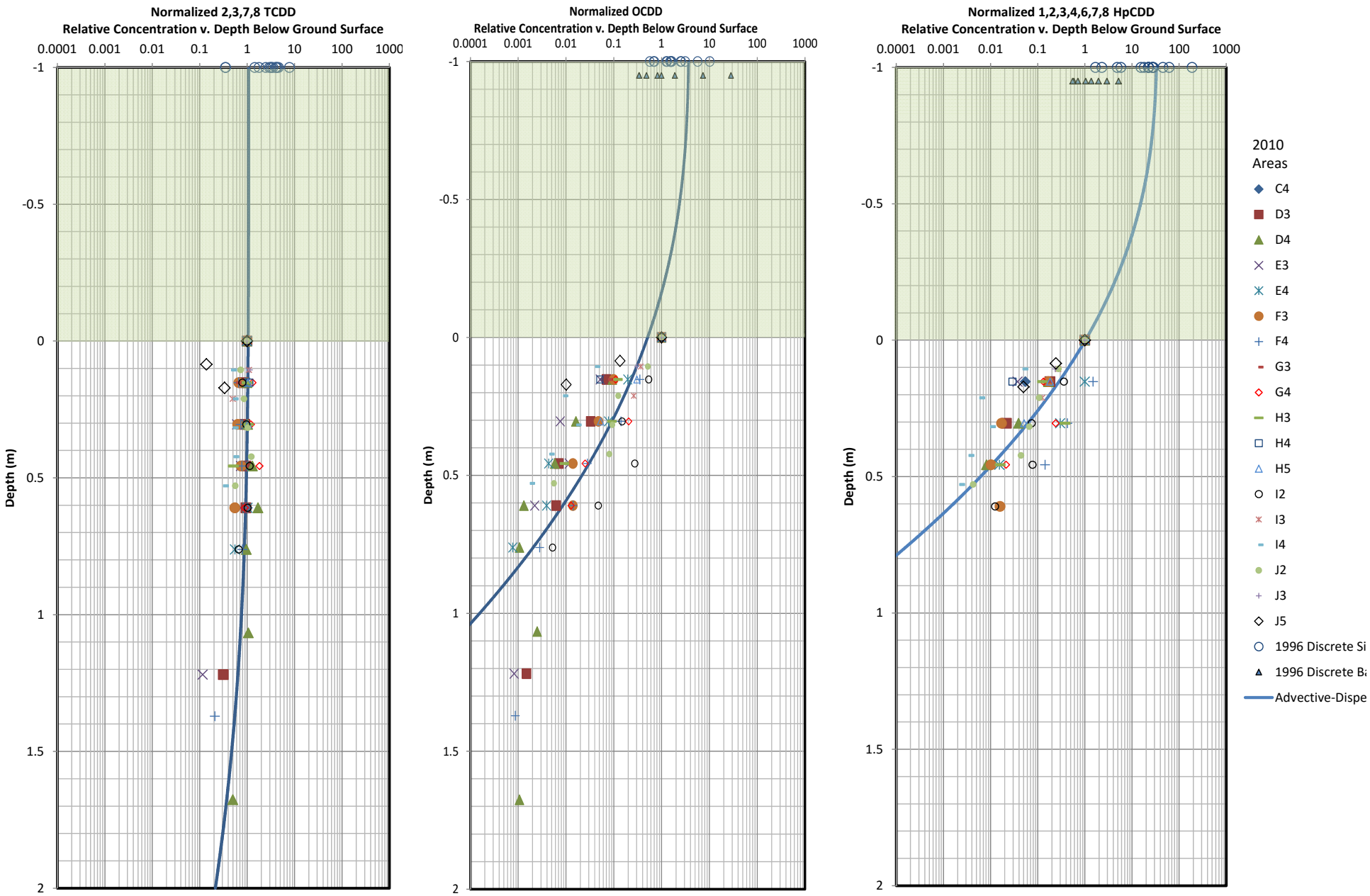
The resulting measurements demonstrate the separation of three dioxin congeners with increasing depth.



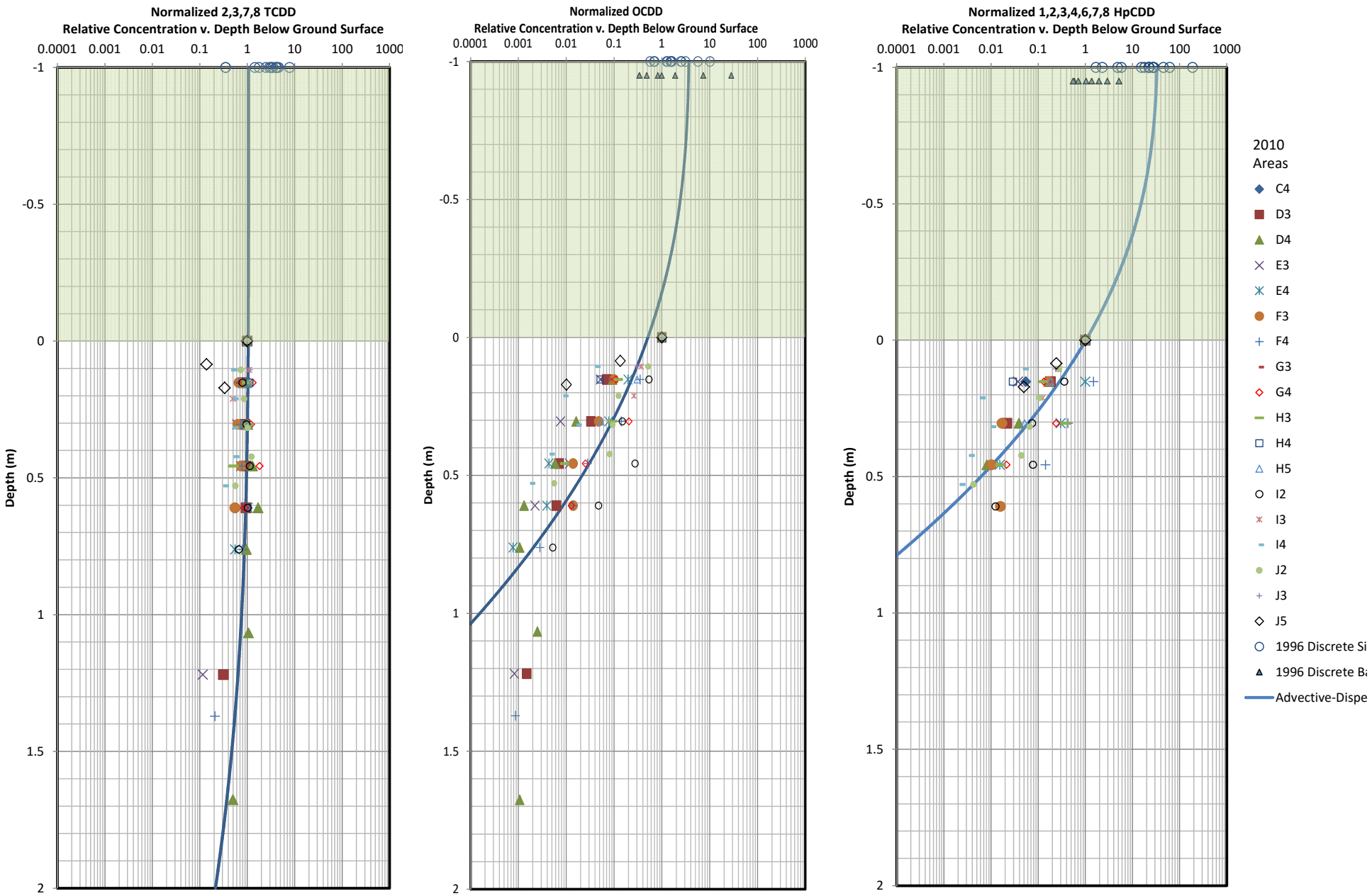
Three Congeners had measureable concentrations.



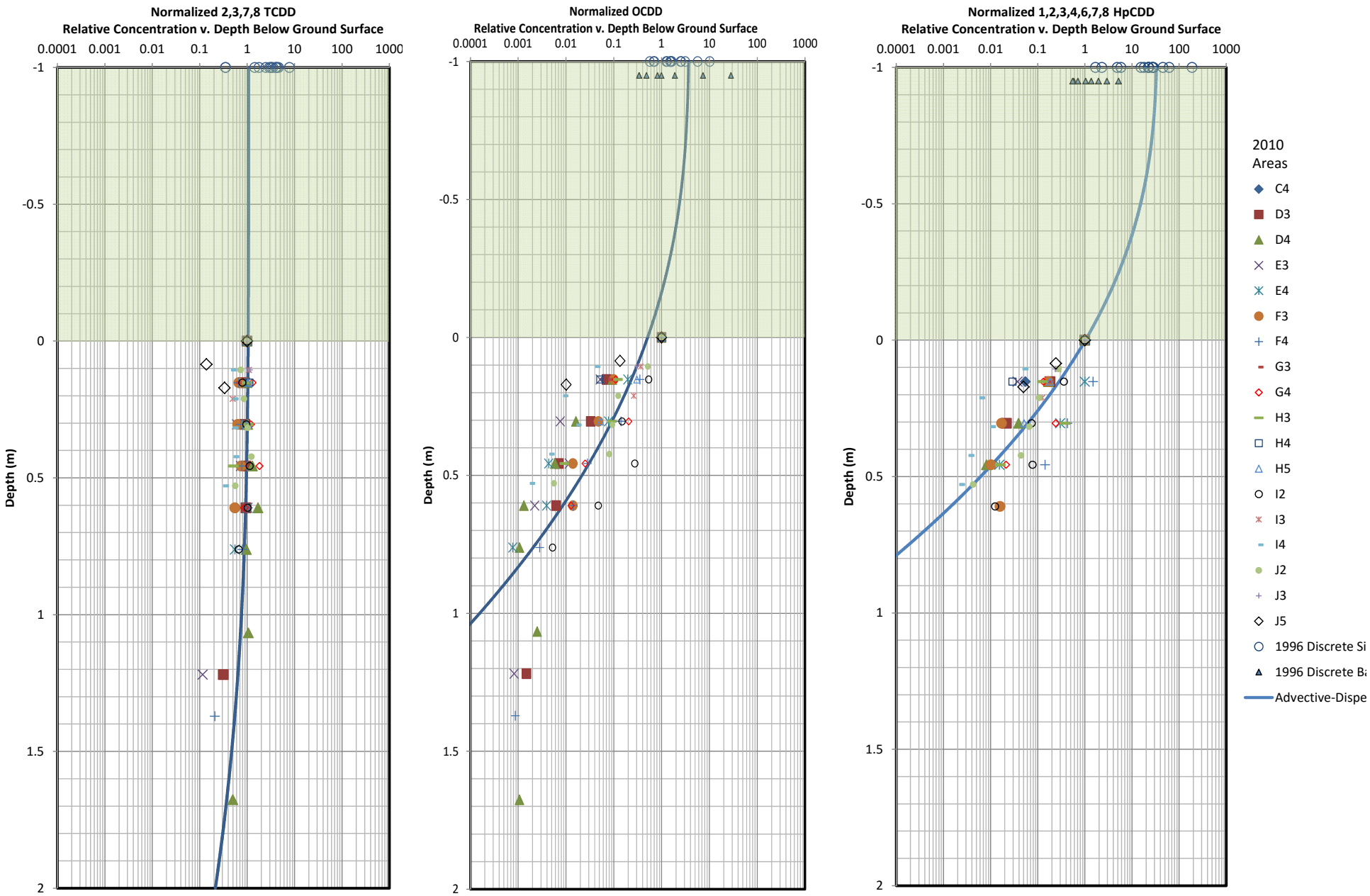
These are 2,3,7,8 TCDD, OCDD and 1,2,3,4,6,7,8 HpCDD



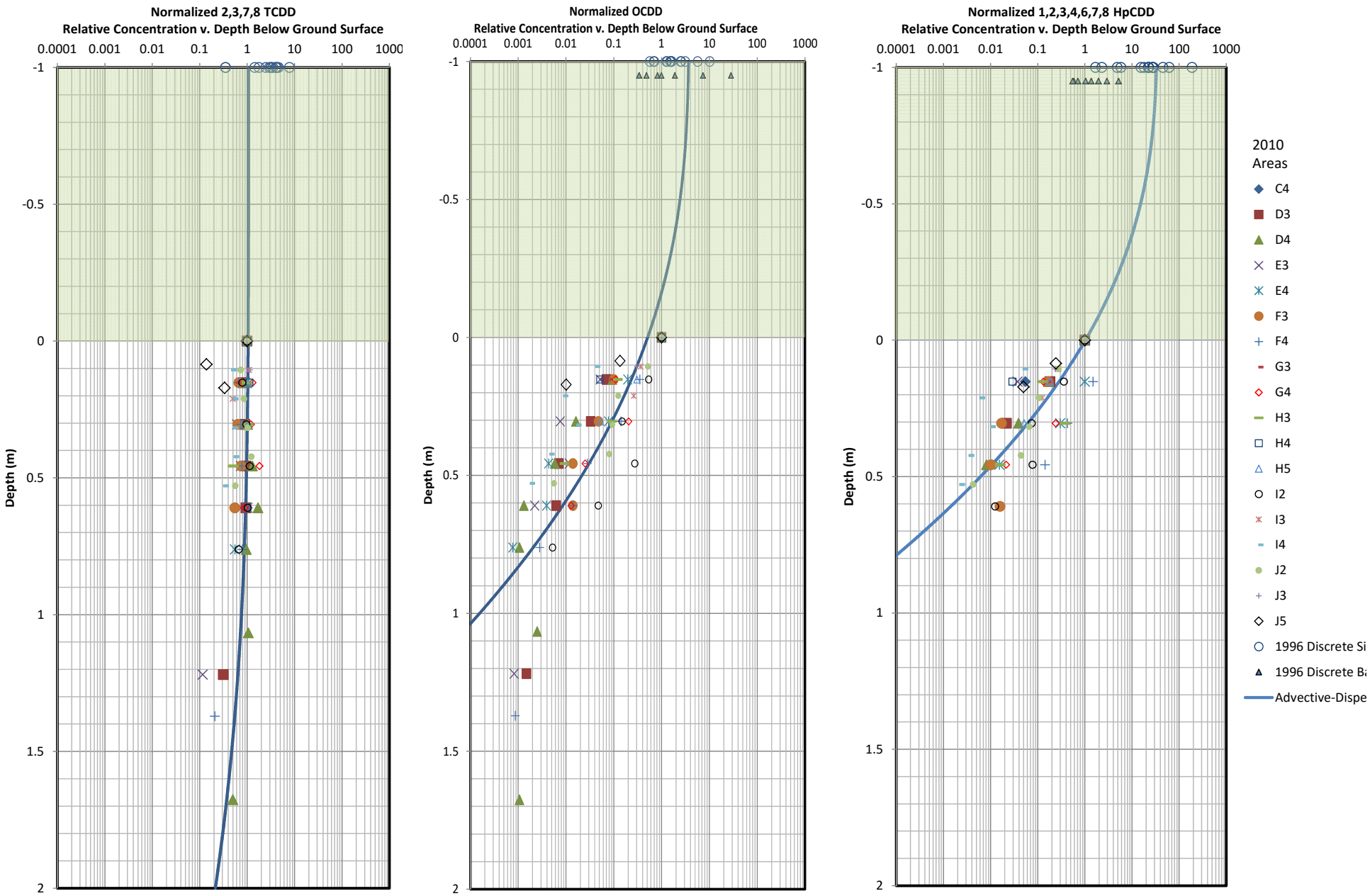
Charts present depth v normalized concentration (C/C_o)



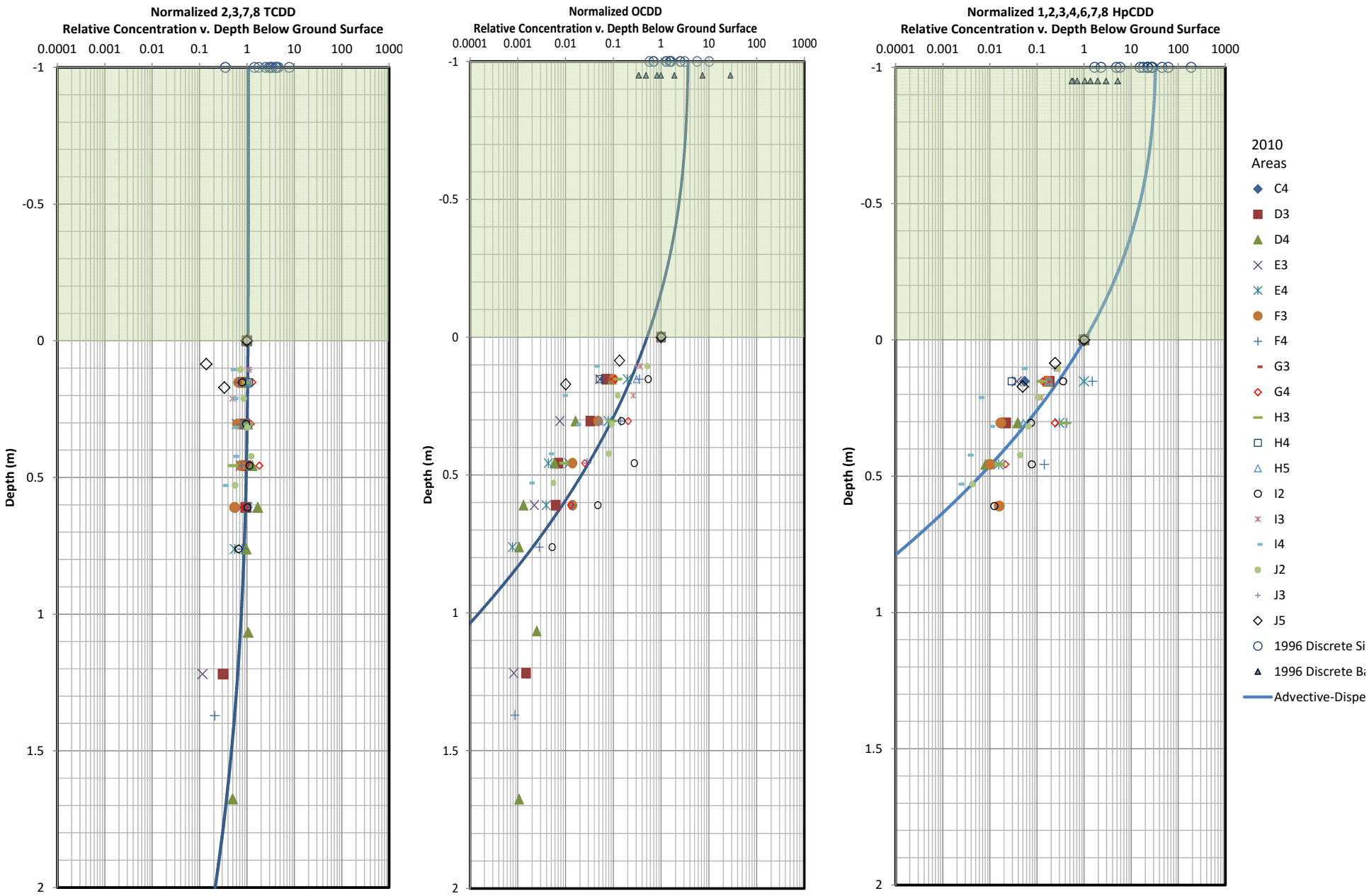
C_o *is the concentration on the surface following the initial excavation*



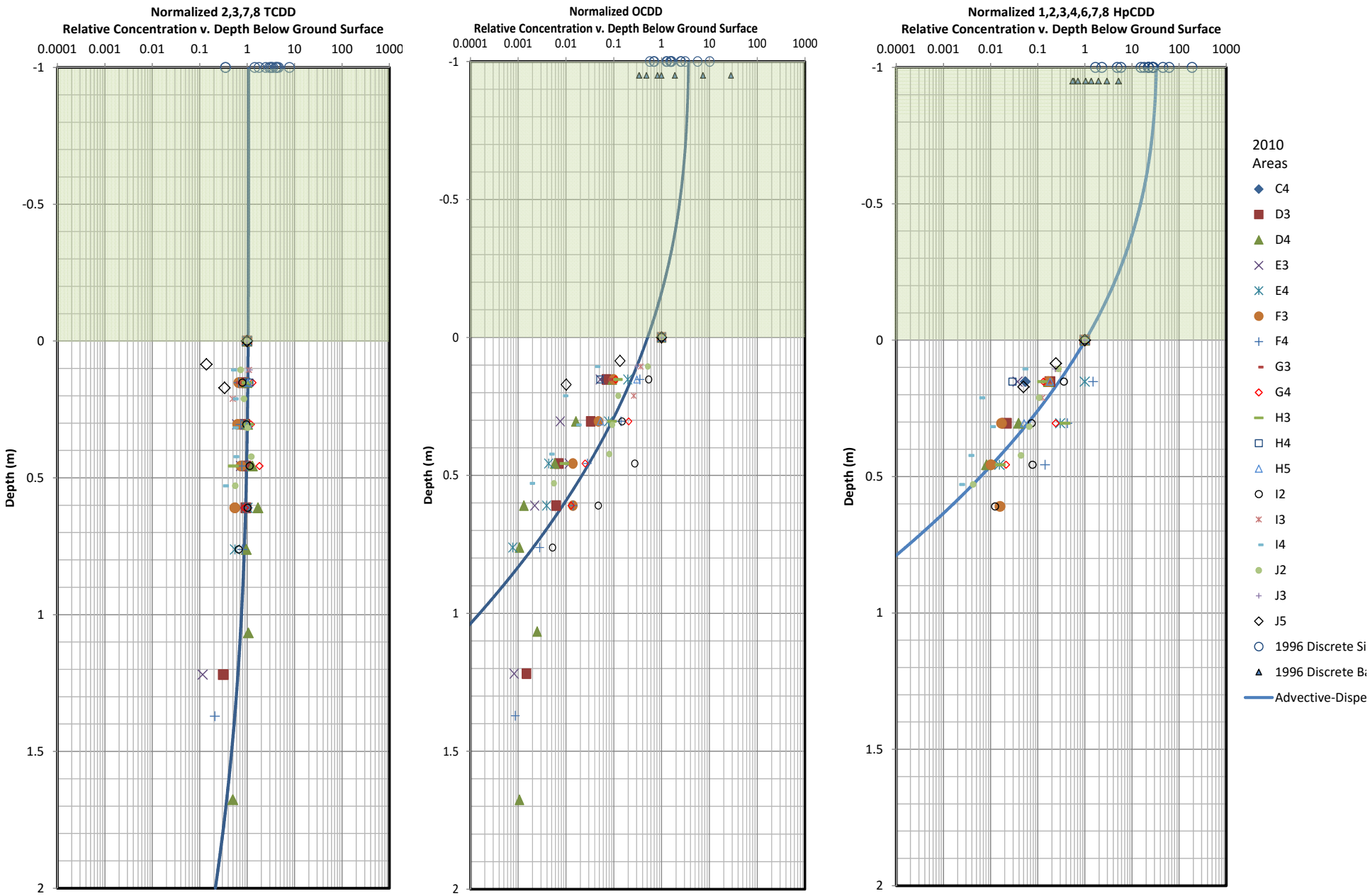
Depth is the distance from the surface following the initial excavation



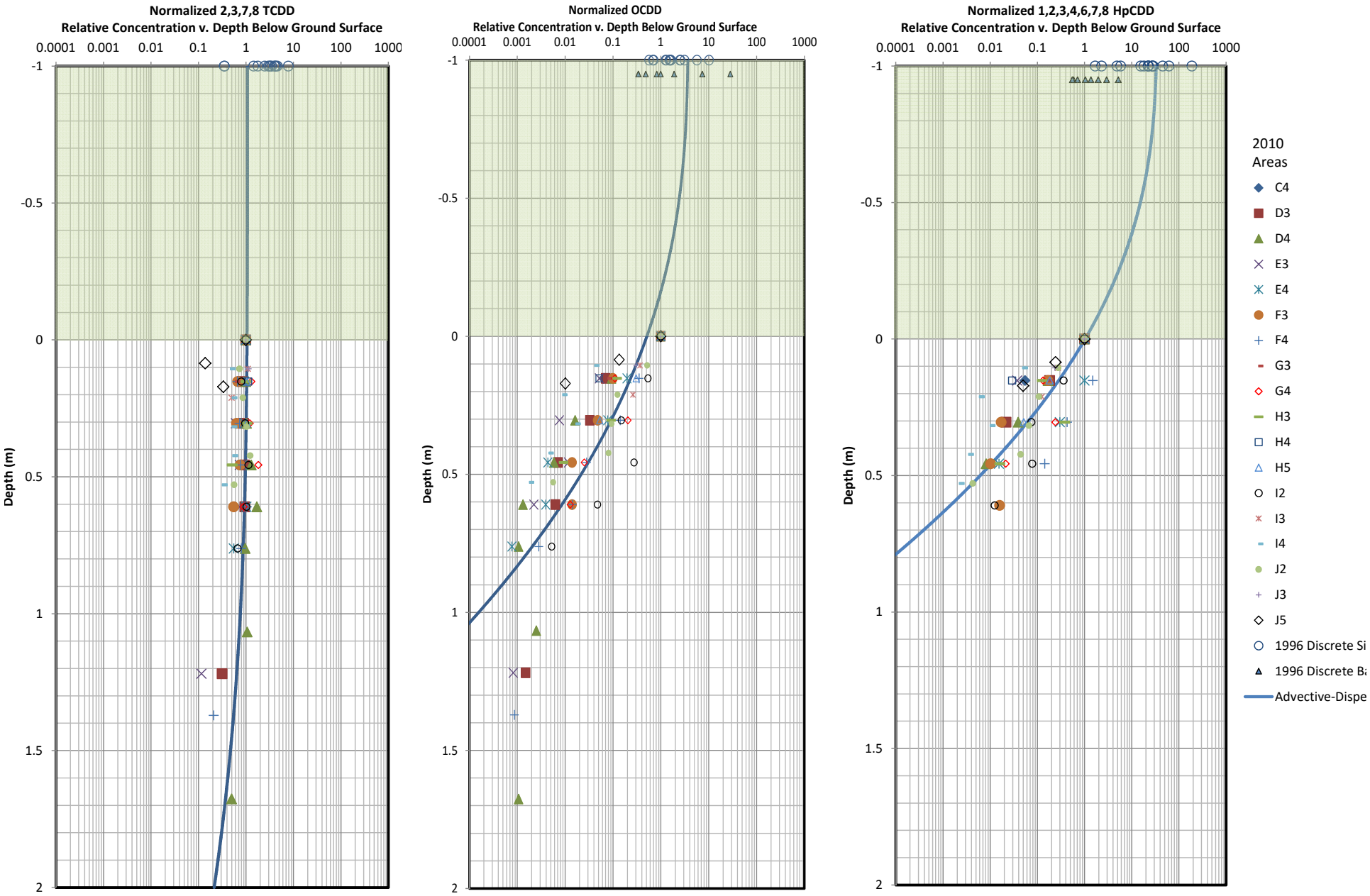
It is presumed that the initial excavation removed 1 m of soil.



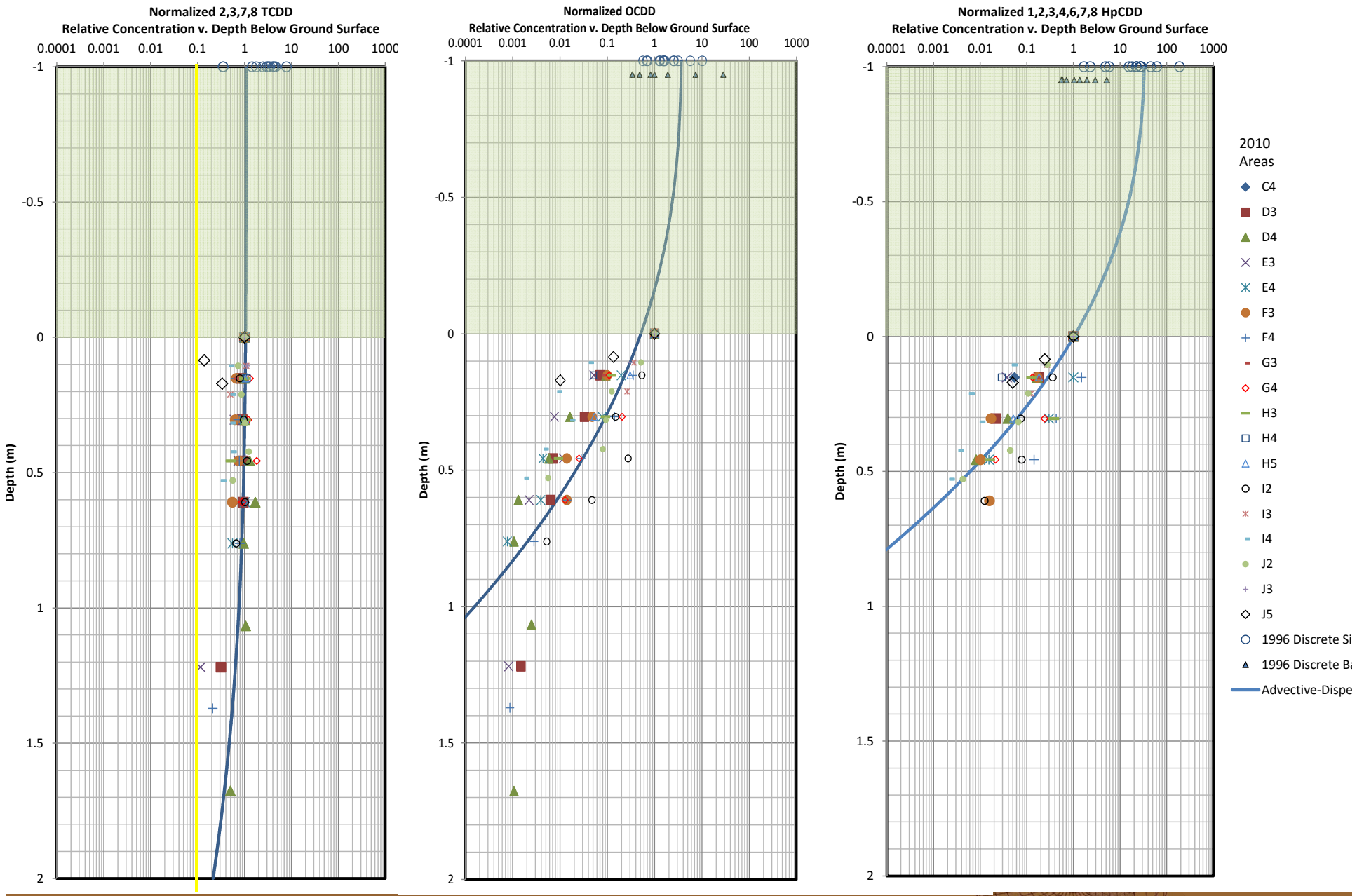
The 1996 site measurements, circles, are shown at a depth of -1 m.



The 1996 background measurements, triangles, are offset for clarity.



2,3,7,8 TCDD was not detected on background.



C/Co = 0.1 approximates the reporting limit for 2,3,7,8 TCDD .

One-Dimensional Advective-Dispersive Transport Equation for Reactive Solutes

$$\frac{\partial c}{\partial t} = \frac{D}{R_d}\frac{\partial^2 c}{\partial x^2} - \frac{v_s}{R_d}\frac{\partial c}{\partial x}$$

c = concentration

t = time

x = distance

R_d = retardation factor = v_s/v_c

v_s = seepage velocity

v_c = solute velocity at $c/c_o = 0.5$

D = coefficient of hydrodynamic dispersion

All variables were held constant except R_d and the initial Concentration C_o.

$$R_d \propto K_{ow}$$

For purposes of this presentation the expected ratios of R_d are estimated as ratios of K_{ow}

Therefore the expected approximate ratios of Rd's are:

$$\frac{R_{d(HpCDD)}}{R_{d(TCDD)}} = \frac{10^8}{10^7} = 10$$

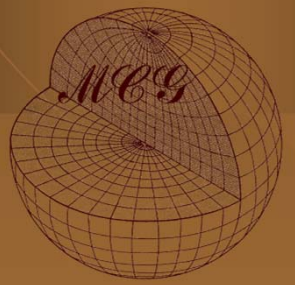
$$\frac{R_{d(TCDD)}}{R_{d(TCDD)}} = \frac{10^7}{10^7} = 1$$

$$\frac{R_{d(OCDD)}}{R_{d(TCDD)}} = \frac{10^8}{10^7} = 10$$

Common values of K_{ow}

2,3,7,8 TCDD	10^7
HpCDD	10^8
OCDD	10^8

USEPA Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds National Academy Sciences (NAS) Review Draft, Volume 2, Chapter 2, 2003. http://www.epa.gov/ncea/pdfs/dioxin/nas-review/



Therefore the expected approximate ratios of R_d's are:

$\frac{R_{d(HpCDD)}}{R_{d(TCDD)}} = \frac{10^8}{10^7} = 10$

$\frac{R_{d(TCDD)}}{R_{d(TCDD)}} = \frac{10^7}{10^7} = 1$

$\frac{R_{d(OCDD)}}{R_{d(TCDD)}} = \frac{10^8}{10^7} = 10$

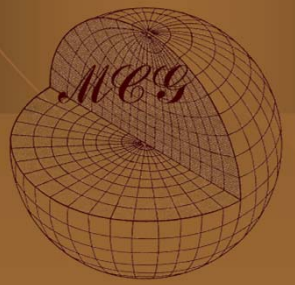
Best-fit ratios:

$\frac{R_{d(HpCDD)}}{R_{d(TCDD)}} = 6$

$\frac{R_{d(TCDD)}}{R_{d(TCDD)}} = 1$

$\frac{R_{d(OCDD)}}{R_{d(TCDD)}} = 3.5$

The difference between observed and expected ratios are reasonable considering that each congener's approximate K_{ow} may vary by a factor of 10 or more.

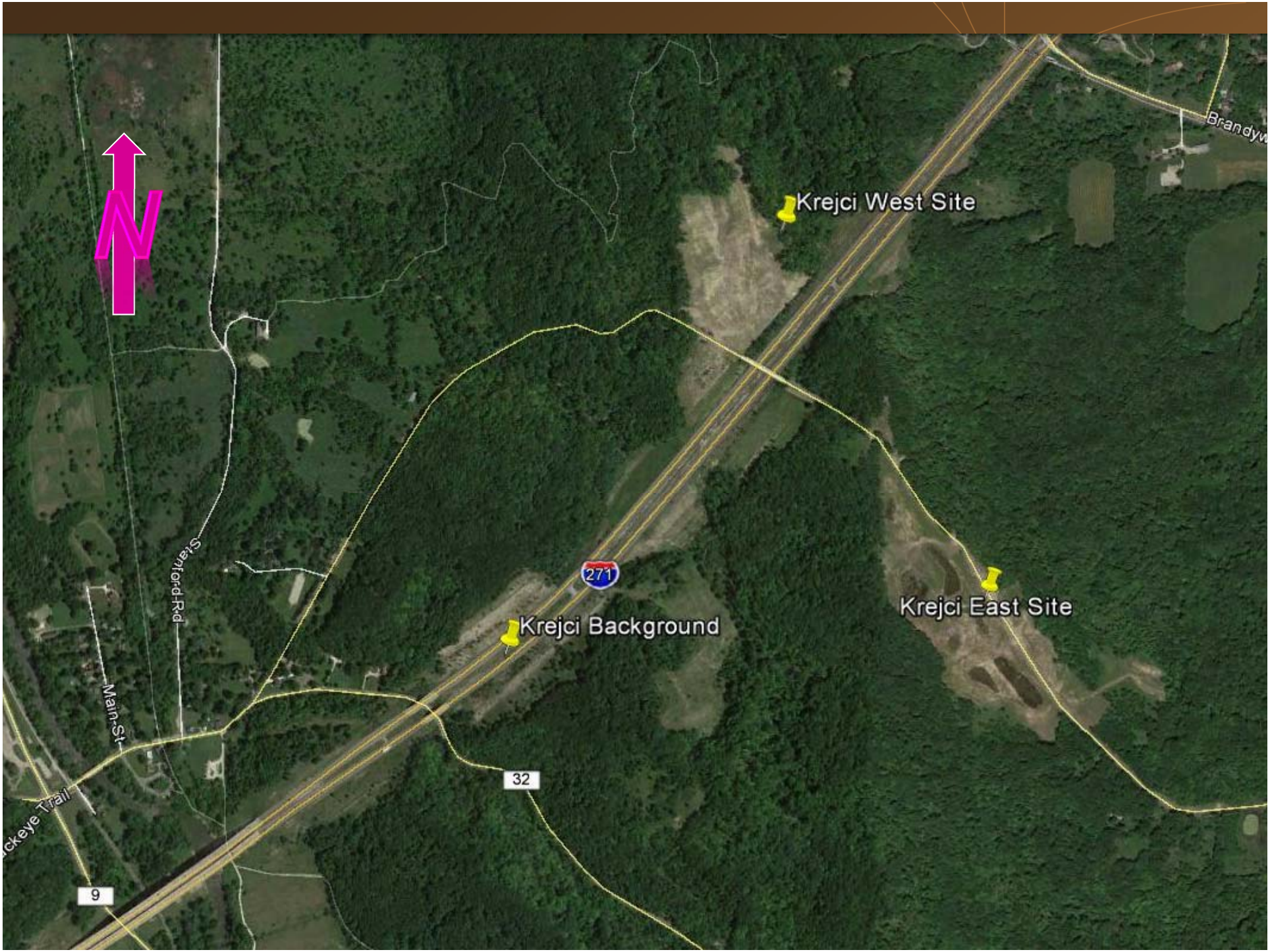


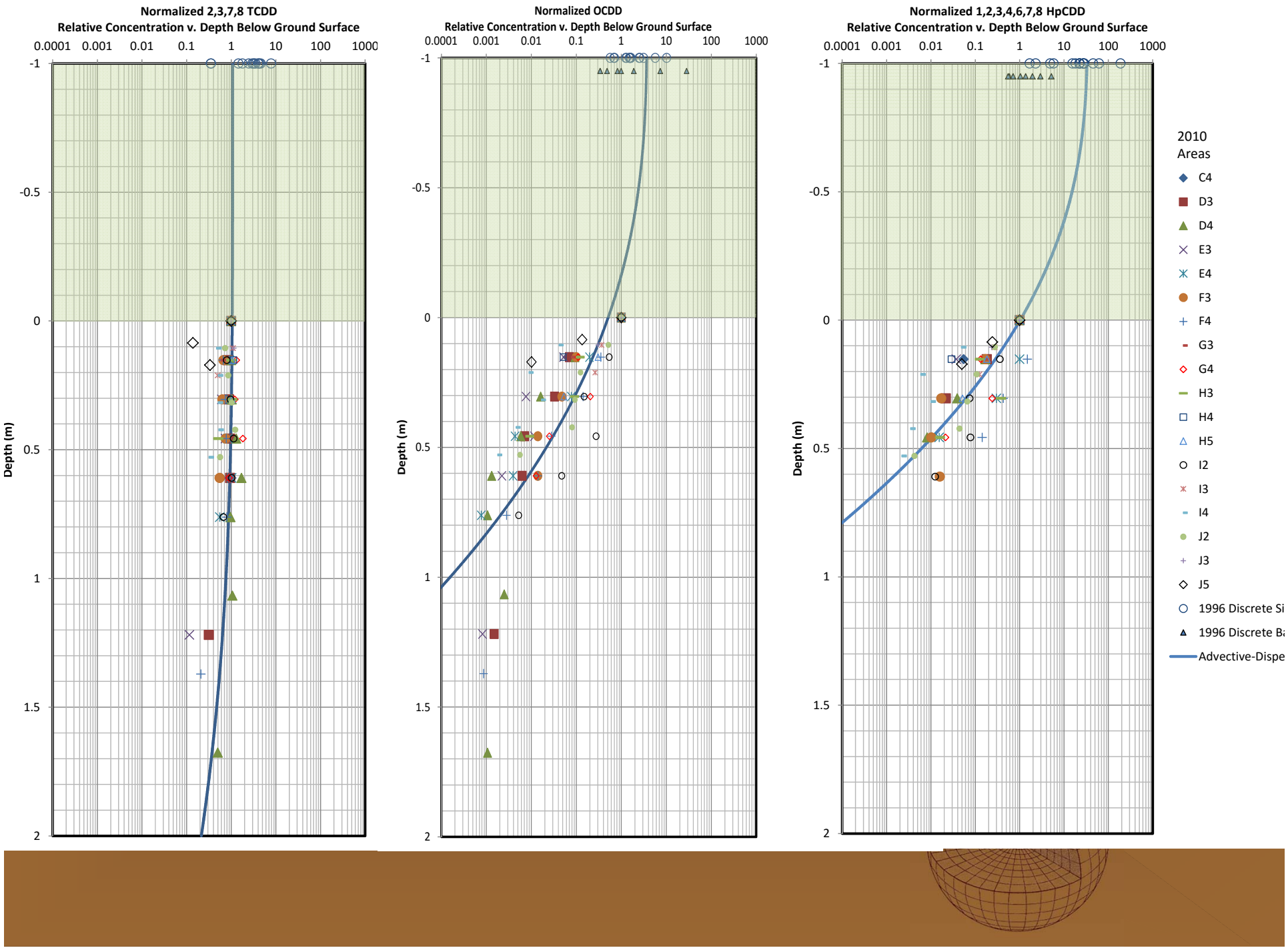
Importance of uncertainty in decision making

- The question at this site was: How deep must the soil be excavated to achieve 3 pg/g TEQ?
- The calculation is imprecise:
  - The estimate of seepage velocity (v_s) may be wrong by an order of magnitude or more.
  - The estimate of retardation factor (R_d) may be wrong by an order of magnitude or more.
- So initial estimates of the required excavation depth ranged between 10 cm and 10 m.
- Failure to investigate further resulted in many costly iterations of excavation.

Questions?

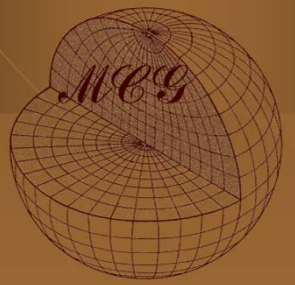
The data related reports may be downloaded at:
http://www.mcggeotechnical.com/


N
Krejci West Site
Krejci Background
Krejci East Site
271
32
9
Main St
Stanford Rd


Normalized 2,3,7,8 TCDD
Relative Concentration v. Depth Below Ground Surface
Normalized OCDD
Relative Concentration v. Depth Below Ground Surface
Normalized 1,2,3,4,6,7,8 HpCDD
Relative Concentration v. Depth Below Ground Surface
0.0001 0.001 0.01 0.1 1 10 100 1000
Depth (m)
-1 -0.5 0 0.5 1 1.5 2
2010 Areas
C4
D3
D4
E3
E4
F3
F4
G3
G4
H3
H4
H5
I2
I3
I4
J2
J3
J5
1996 Discrete Si
1996 Discrete Ba
Advective-Dispe

- The soil concentration C equals the mass of solute in pore space water per unit mass of soil (q) plus the mass of adsorbed solute per unit mass of solids (m).
- Show that the soil concentration ratio (C/C_o) is the same as the solute concentration ratio (c/c_o) for homogeneous conditions and linear adsorption.

- Both c and c_o are solute concentrations with units of mass per unit volume
- Both C and Co are soil concentrations with units of mass of solute per mass of soil solids.
- The mass of solute adsorbed to soil per unit mass of solids, termed q, is presumed linearly proportional to the solute concentration.
- $q=K_pc$ and $q_o=K_pc_o$
- The mass of solute in solution per unit mass of solids, termed m, is:
- $m=V_vc/m_s$ and $m_o=V_vc_o/m_s$:Where V_v is the volume of void space per unit mass of soil
- Void ratio $e=V_v/V_s$ and $m_s = \rho_s V_s$: Where ρ_s is the mass density of solids
- so
- substituting
- $m=eV_sc/m_s$ and $m_o=eV_sc_o/m_s$
- substituting
- $m=e(m_s/\rho_s)c/m_s$ and $m_o=e(m_s/\rho_s)c_o/m_s$
- $m=ce/\rho_s$ and $m_o=c_oe/\rho_s$
- $C=q+m$ and $C_o=q_o+m_o$
- susbstituting
- $C=K_pc+ce/\rho_s$ and $C_o=K_pc_o+c_oe/\rho_s$
- Rearranging
- $C=c(K_p+e/\rho_s)$ and $C_o=c_o(K_p+e/\rho_s)$
- Therefore $C/C_0 = c/c_o$



Relationship between Rd, Kp, Koc and Kow

- For simplicity let
  - $K_{oc} \cong K_{ow}$
  - $K_p \cong K_{oc} f_{oc}$
  - $R_d \cong 1 + A \times K_p$
  - where *A* = constant
- Then for large K_{ow}
  - $R_d \propto K_{ow}$

Common values of K_{ow}

2,3,7,8 TCDD	10^7
HpCDD	10^8
OCDD	10^8

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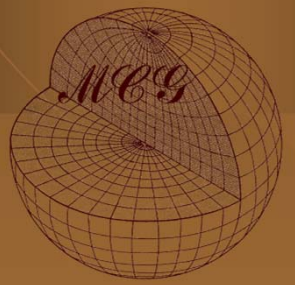
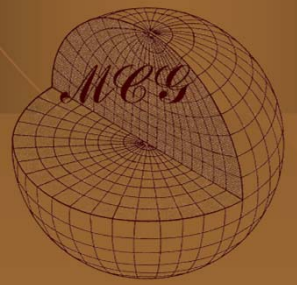


General Solution (Ogatta 1961)

$$\frac{c}{c_o} = \frac{1}{2}\{\mathrm{erfc}(z_1) + \exp(z_2)(\mathrm{erfc}(z_3)\}$$

Where

- $v_R = \frac{v_s}{R_d}$
- $D_R = \frac{D}{R_d}$
- $z_1 = \frac{x - v_R t}{2\sqrt{D_R t}}$
- $z_2 = \frac{v_R}{D_R}$
- $z_3 = \frac{x + v_R t}{2\sqrt{D_R t}}$



The Area is Represented Throughout the Aliquot Preparation Process

The sample is reduced in size by repeated Grinding-and-Splitting operations

In each step of the splitting operation, the split from the previous step is ground so that the ratio of the mass of the largest particle to the mass of the sample remains constant (1/3% ~ FE=17%).

Iterations of Grinding-and-Splitting are repeated until the test aliquot mass is obtained.