Volatile Organic Compounds in the Unsaturated Zone at the Amargosa Desert Research Site

Toxic Substances Hydrology Program, January 26-29, 2009

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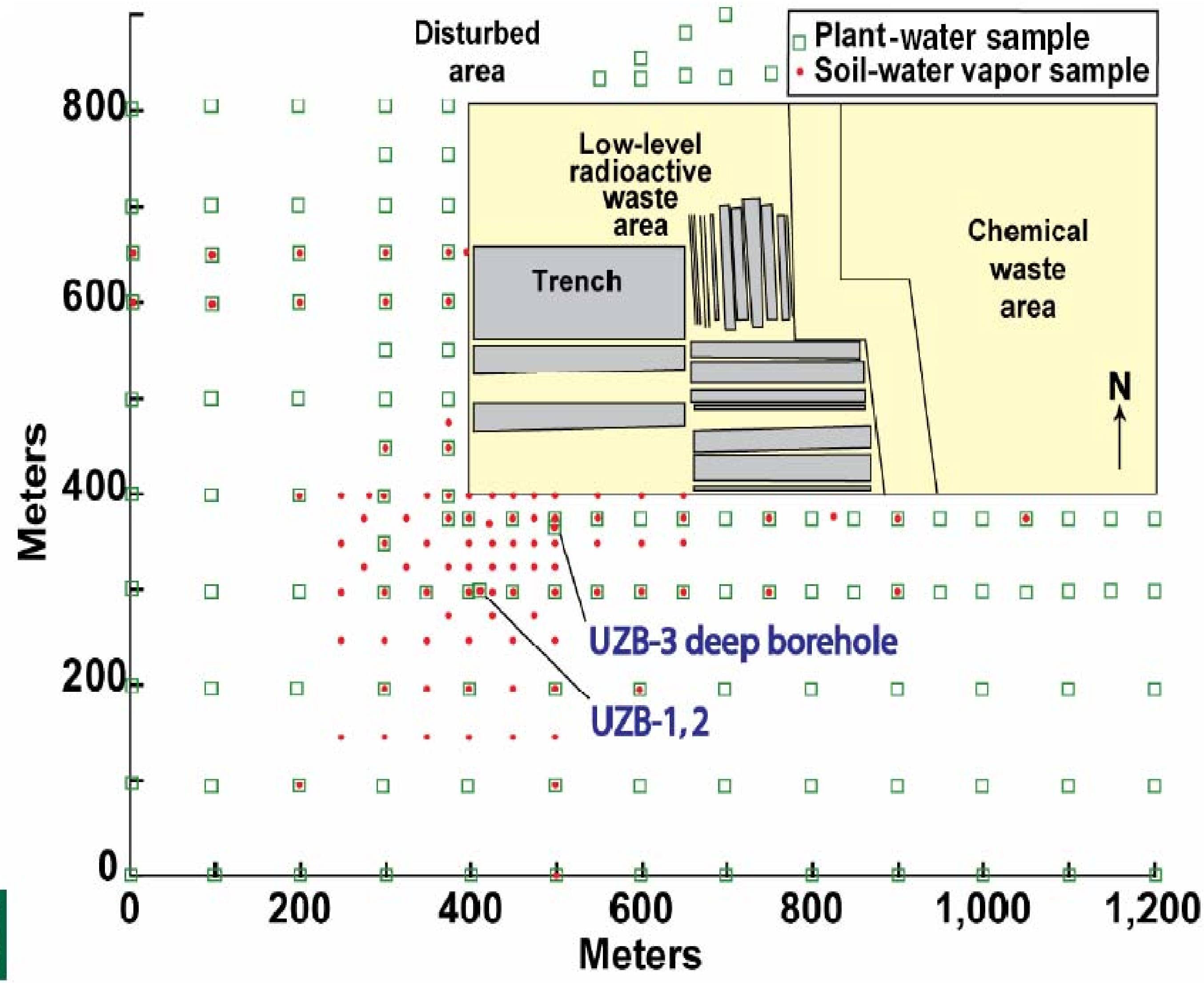
  - Relative Abundance
  - Aerial and Depth Distribution
  - Trends over Time
- Suggestions about VOC Transport

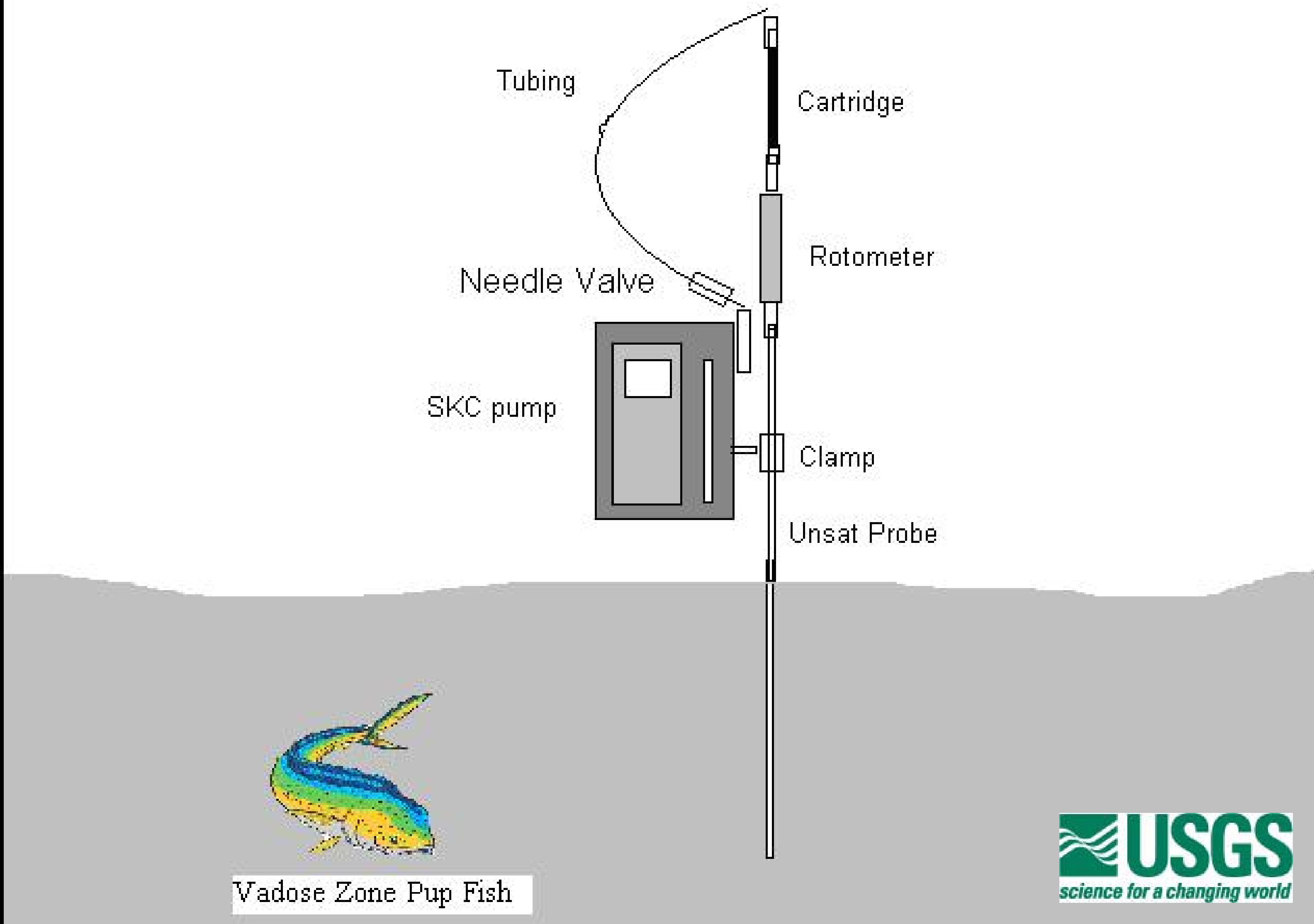
CONTAMINANT SAMPLING — Deep UZ, Soil, Plants



Data Collection Methods

- Unsaturated-vapor samples
  - "Cartridge" method
    - Activated carbon and synthetic polymers in a glass tube
    - About 1 liter of vapor pumped through tube at 40 mL/min, VOCs are adsorbed
    - VOCs are later thermally desorbed for GC/MS analysis
    - Method published by Pankow and others, ***Analytical Chemistry***, vol. 70, p. 5213-5221, (1998).

Unsaturated Zone Sampling: Setting the Flowrate



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Most Abundant VOC Compounds Among All Samples Collected

VOC Compound	Mean Conc.	Relative Conc.
1,1,2,-Trichloro-1,2,2-Trifluoroethane(CFC113)	2477.38	1.0000
Trichlorofluoromethane(CFC11)	1615.23	0.6521
Dichlorodifluoromethane(CFC12)	1038.63	0.4193
1,1-Dichloroethene	960.06	0.3876
Tetrachloroethene(PCE)	534.51	0.2158
1,1-Dichloroethane	500.54	0.2021
Chloroform	496.25	0.2003
Trichloroethene(TCE)	356.87	0.1441
Methylenechloride	147.10	0.0594
1,1-Dichloropropene	84.90	0.0343
Toluene	67.25	0.0271
1,1,1-Trichloroethane	38.08	0.0154
Chloroethene(Vinylchloride)	16.61	0.0067
2-Butanone(Methylethylketone)	13.93	0.0056
Carbontetrachloride	11.38	0.0046
2,2-Dichloropropane	10.95	0.0044

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Most Abundant VOC Compounds Among All Samples Collected

VOC Compound	Mean Conc.	Relative Conc.
Chloromethane	8.04	0.0032
Tetrahydrofran	6.03	0.0024
Bromodichloromathane	5.53	0.0022
Diethylether	3.99	0.0016
2-Hexanone(MBK)	2.64	0.0010
m,p-Xylene	2.57	0.0010
4-Methyl-2-pentanone(MIBK)	2.05	0.0008
cis-1,2-Dichloroethene	1.53	0.0006
Naphthalene	1.48	0.0005
1,2,4-Trimethylbenzene	1.24	0.0005
o-Xylene	1.09	0.0004
tert-Butylalcohol	1.09	0.0004
Bromomethane	0.72	0.0003
Methylacetate	0.69	0.0003
Ethylbenzene	0.66	0.0003
Ethenylbenzene(Styrene)	0.59	0.0002

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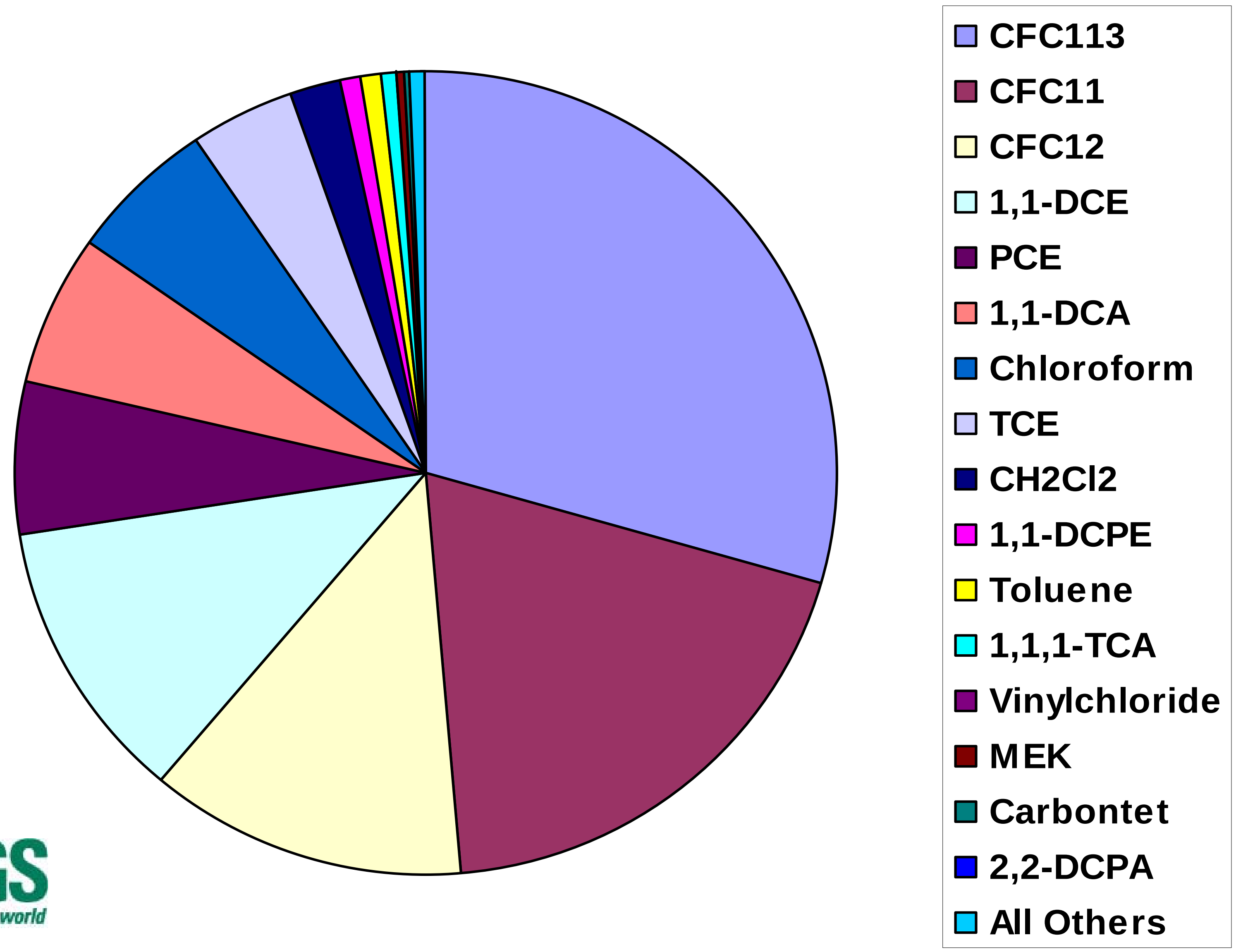
Relative Abundance of VOCs, mean of all samples collected



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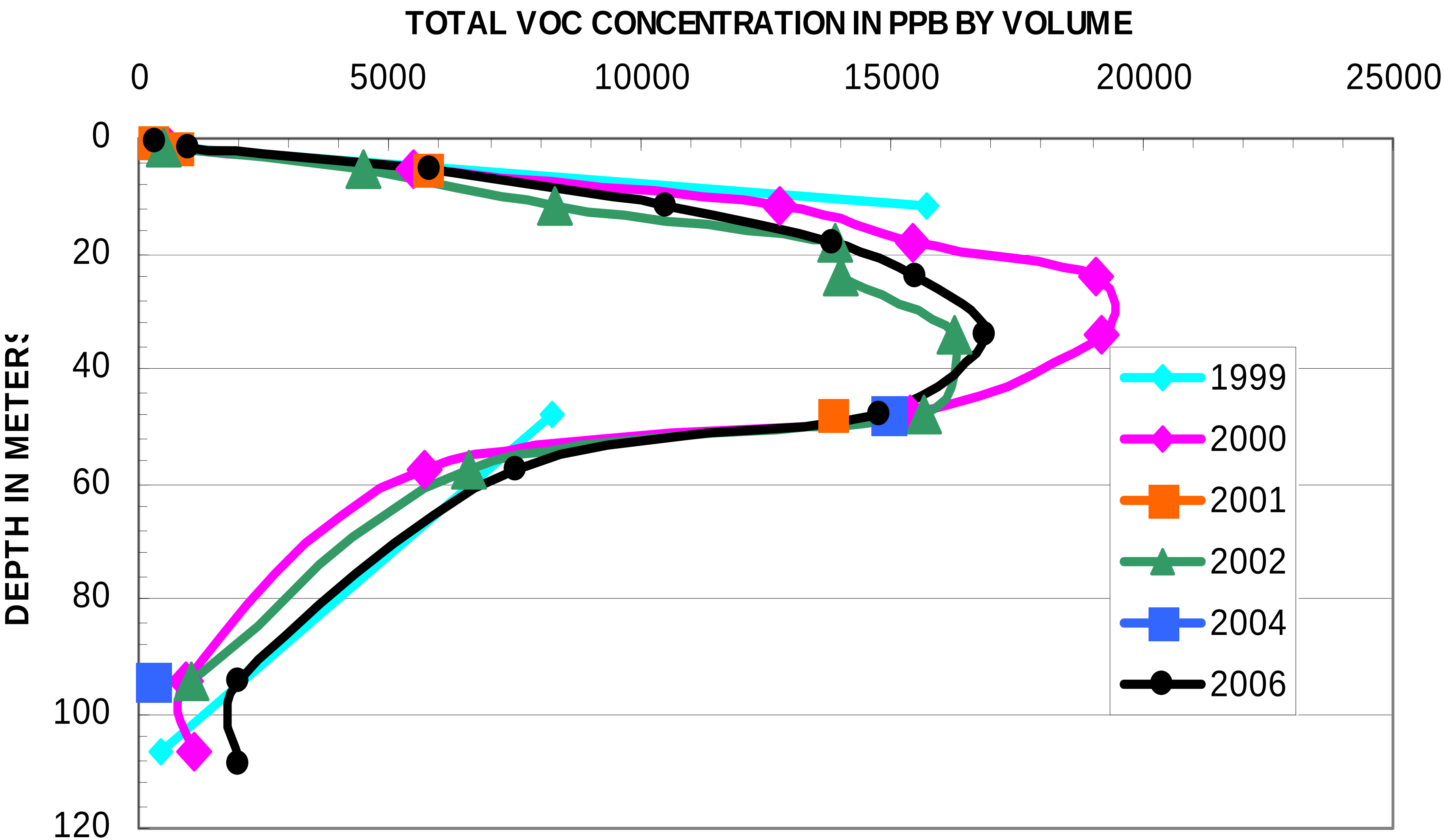
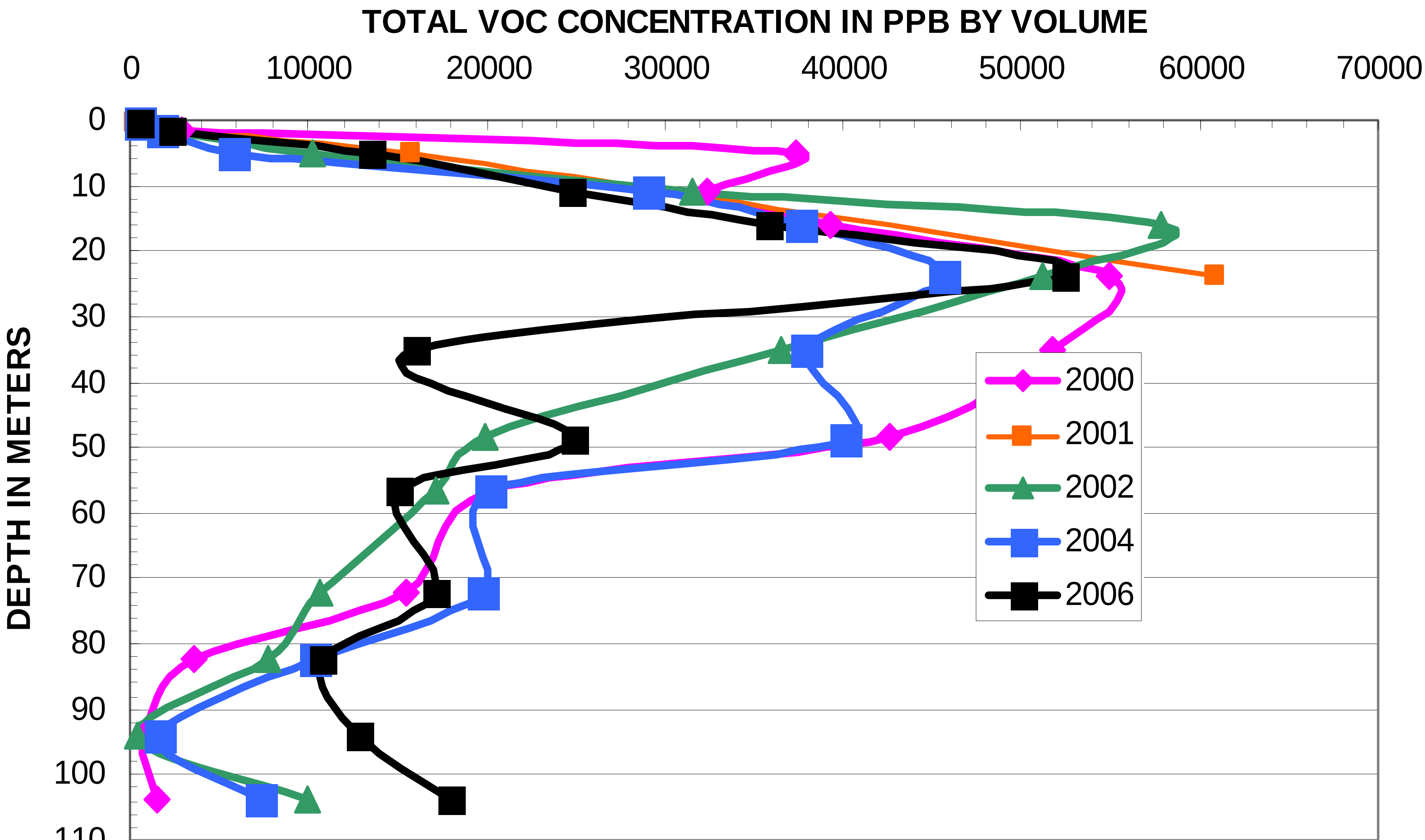
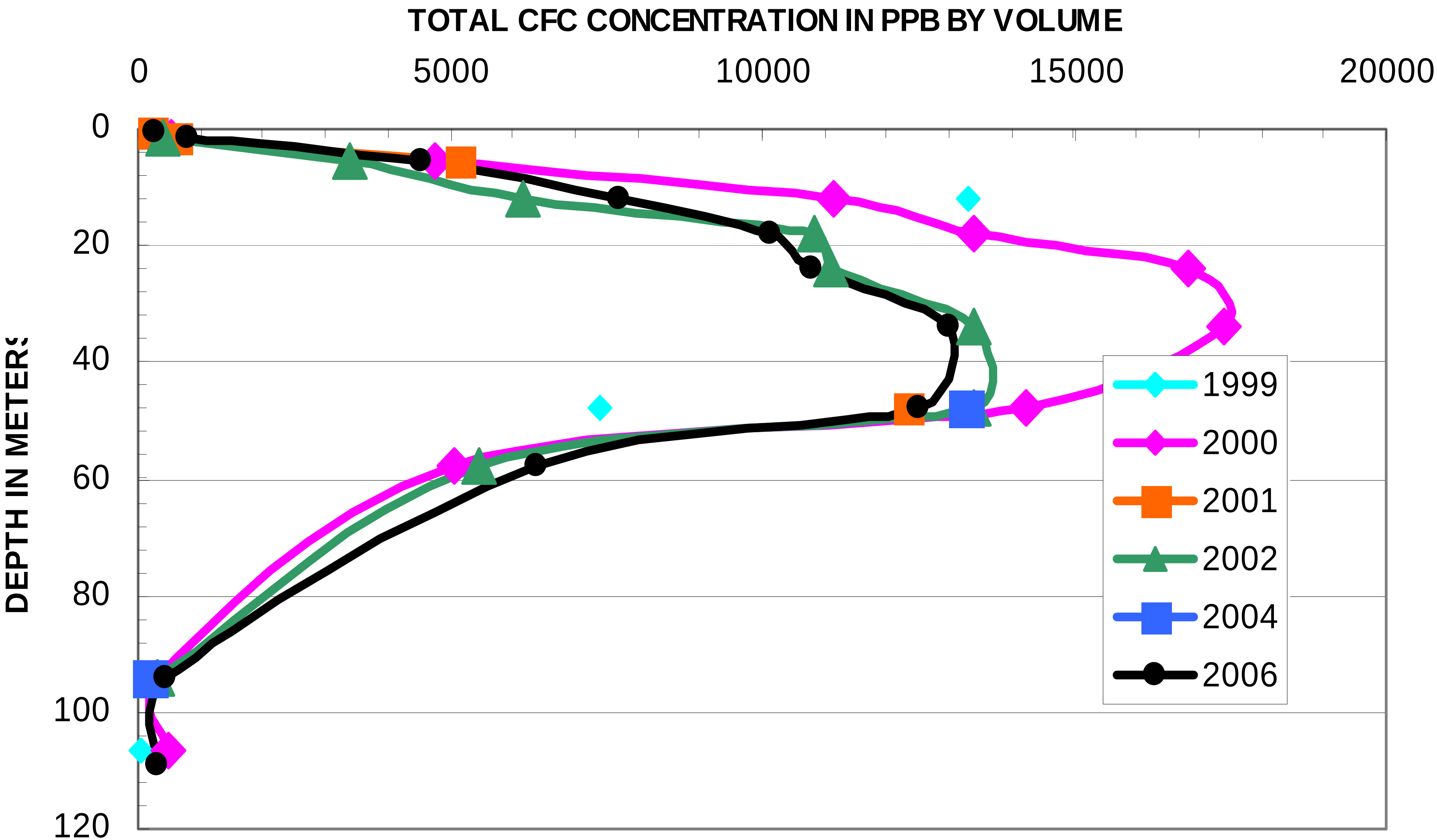
Total VOC Concentrations of Vapor Samples From UZB-2, 1999-2006



Total VOC Concentrations of Vapor Samples From UZB-3, 2000-2006



Total CFC Concentrations of Vapor Samples From UZB-2, 1999-2006



Total CFC Concentrations of Vapor Samples From UZB-3, 2000-2006

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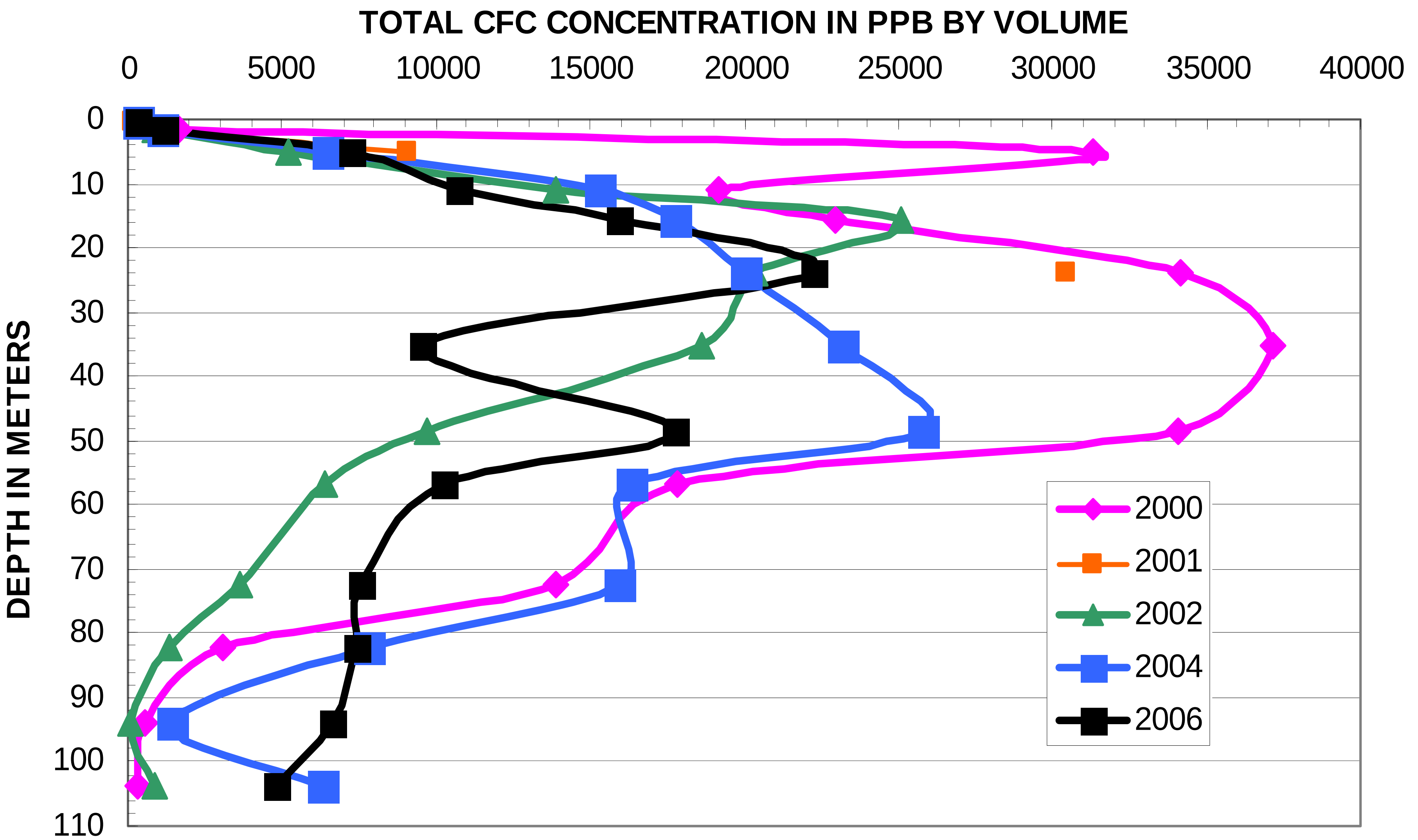
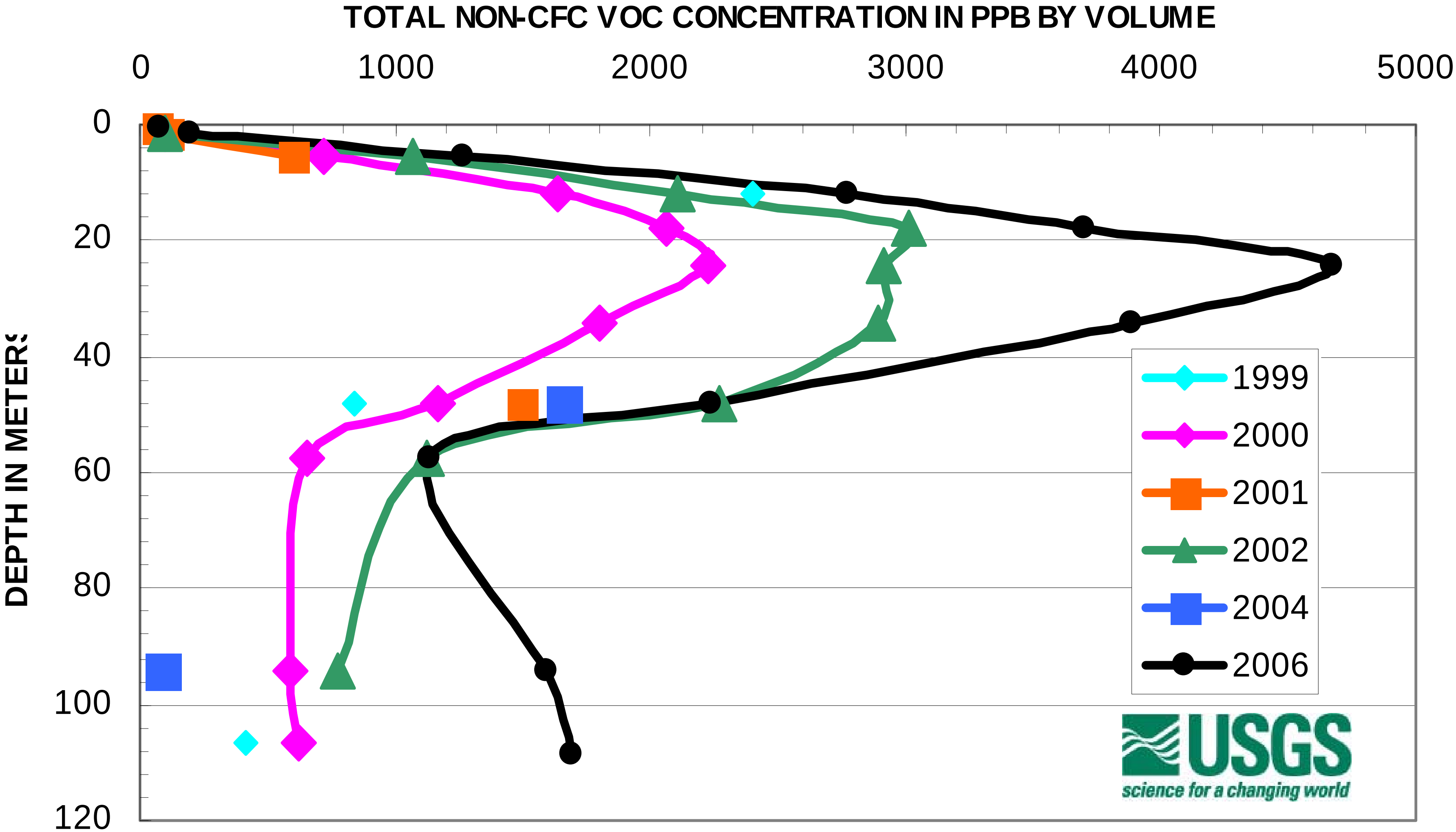
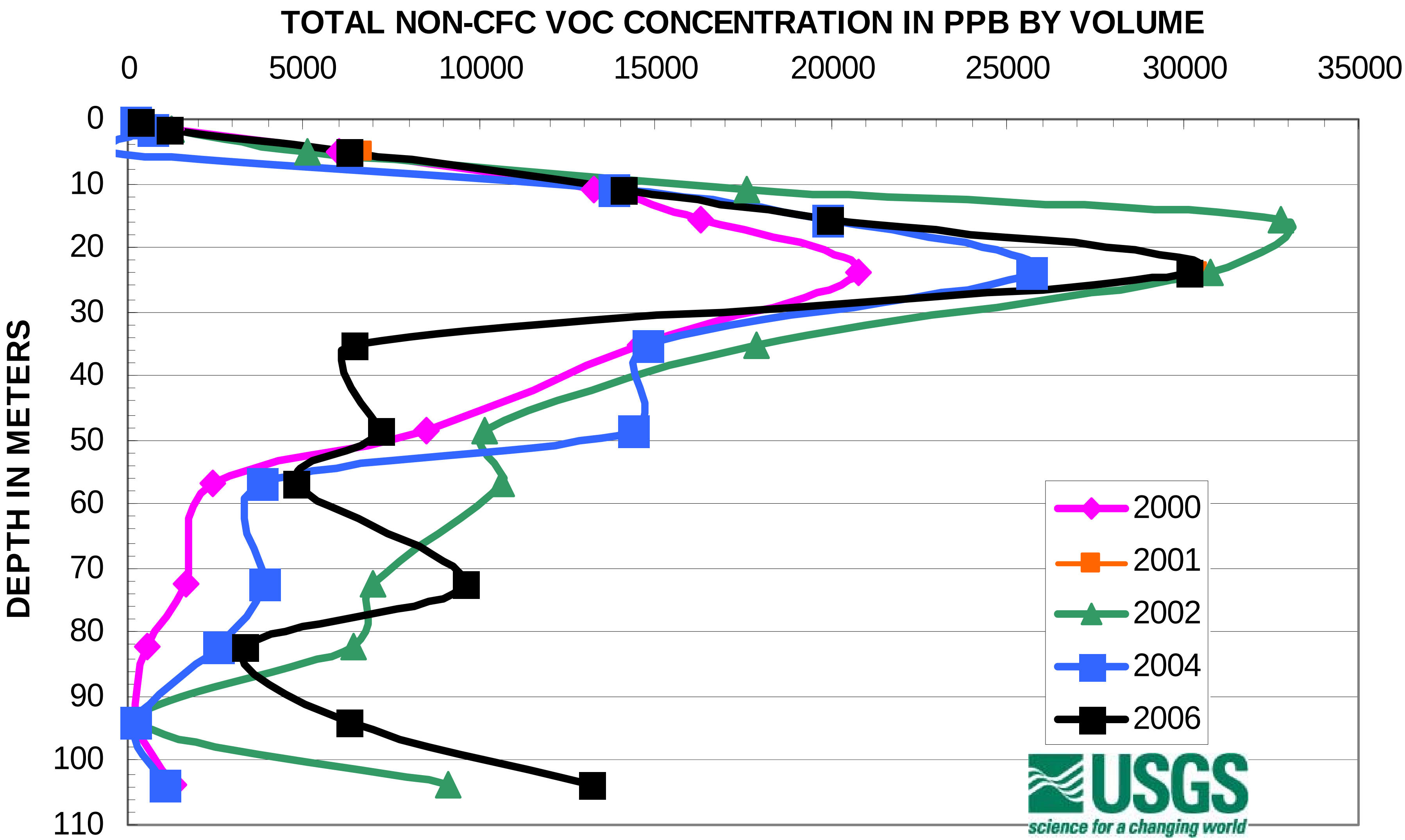


Total Non-CFC VOC Concentrations of Vapor Samples From UZB-2, 1999-2006

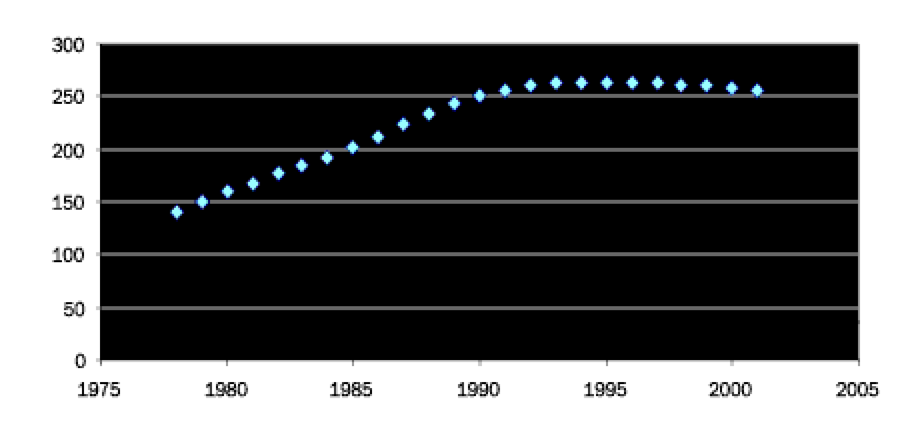


Total NON-CFC VOC Conc. of Vapor Samples From UZB-3, 2000-2006

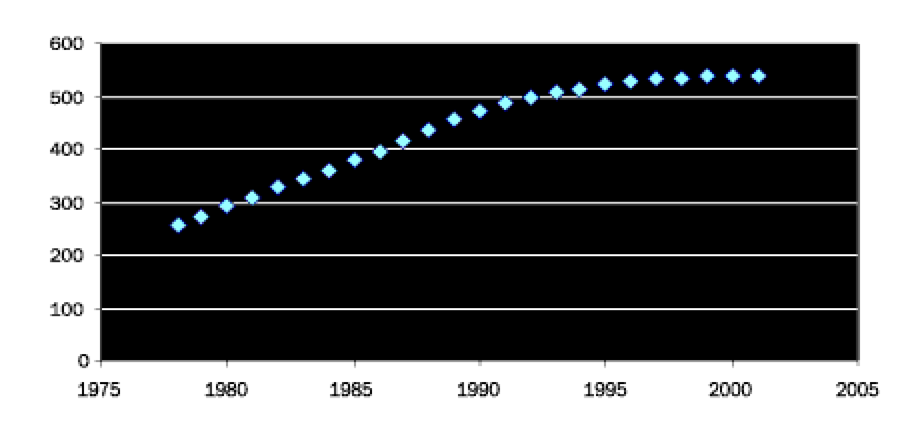


Atmospheric CFC Concentrations Over Time at Cape Grim, Tasmania (ppt, V/V)

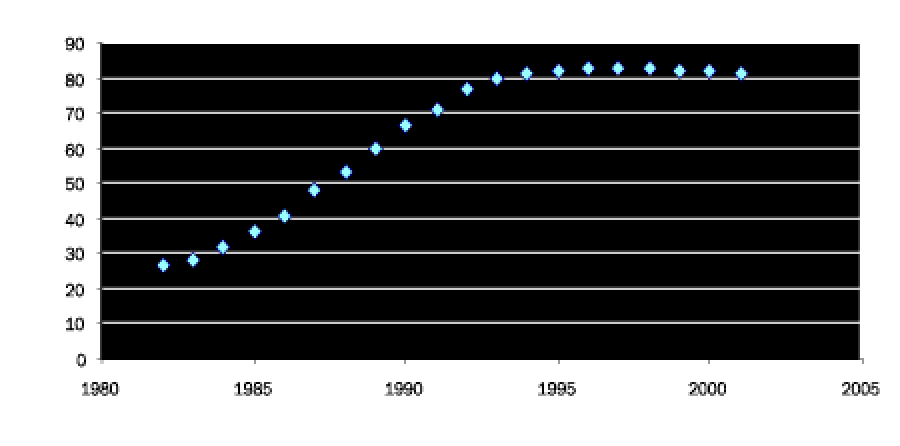
CFC11



CFC12



CFC113



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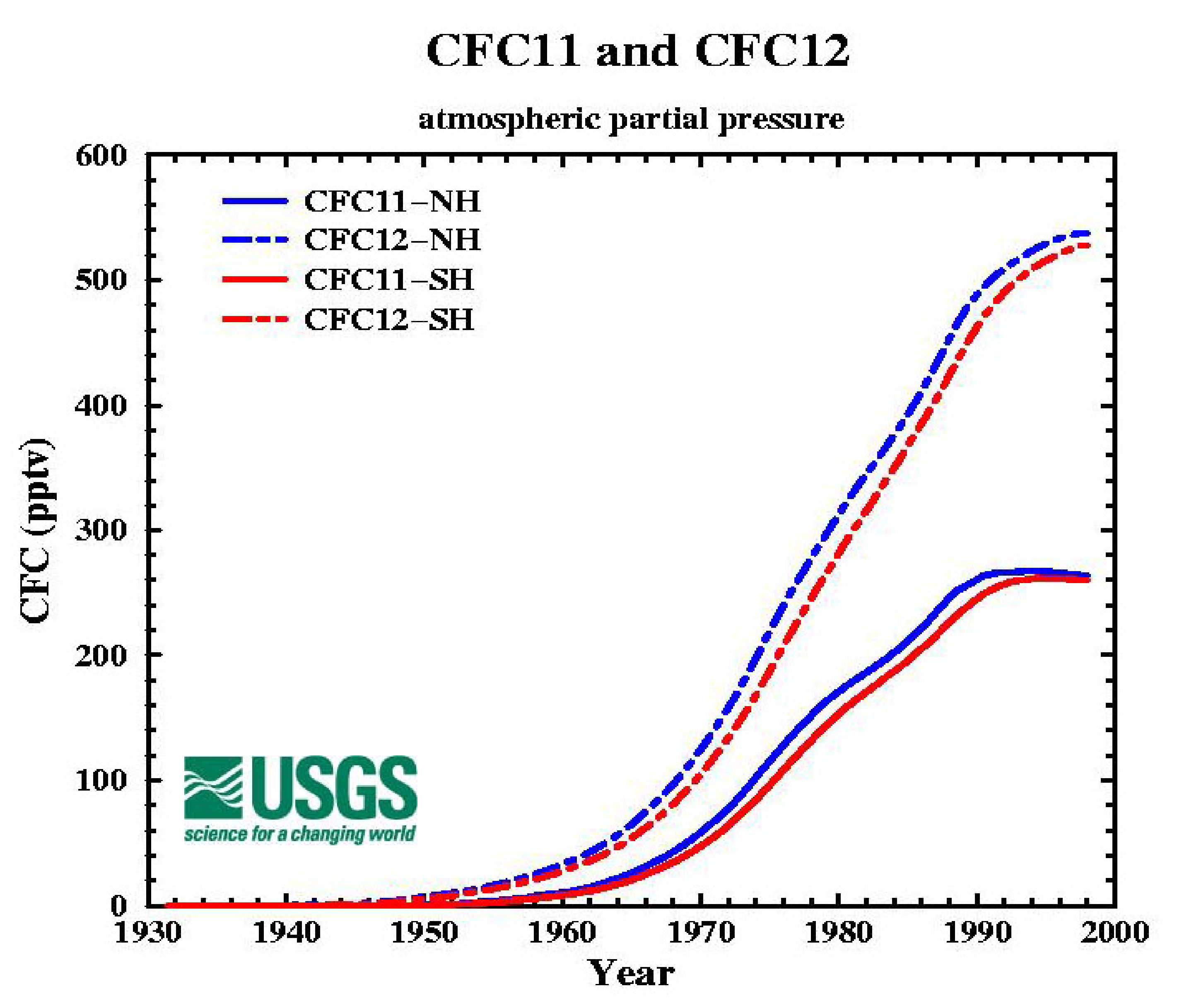
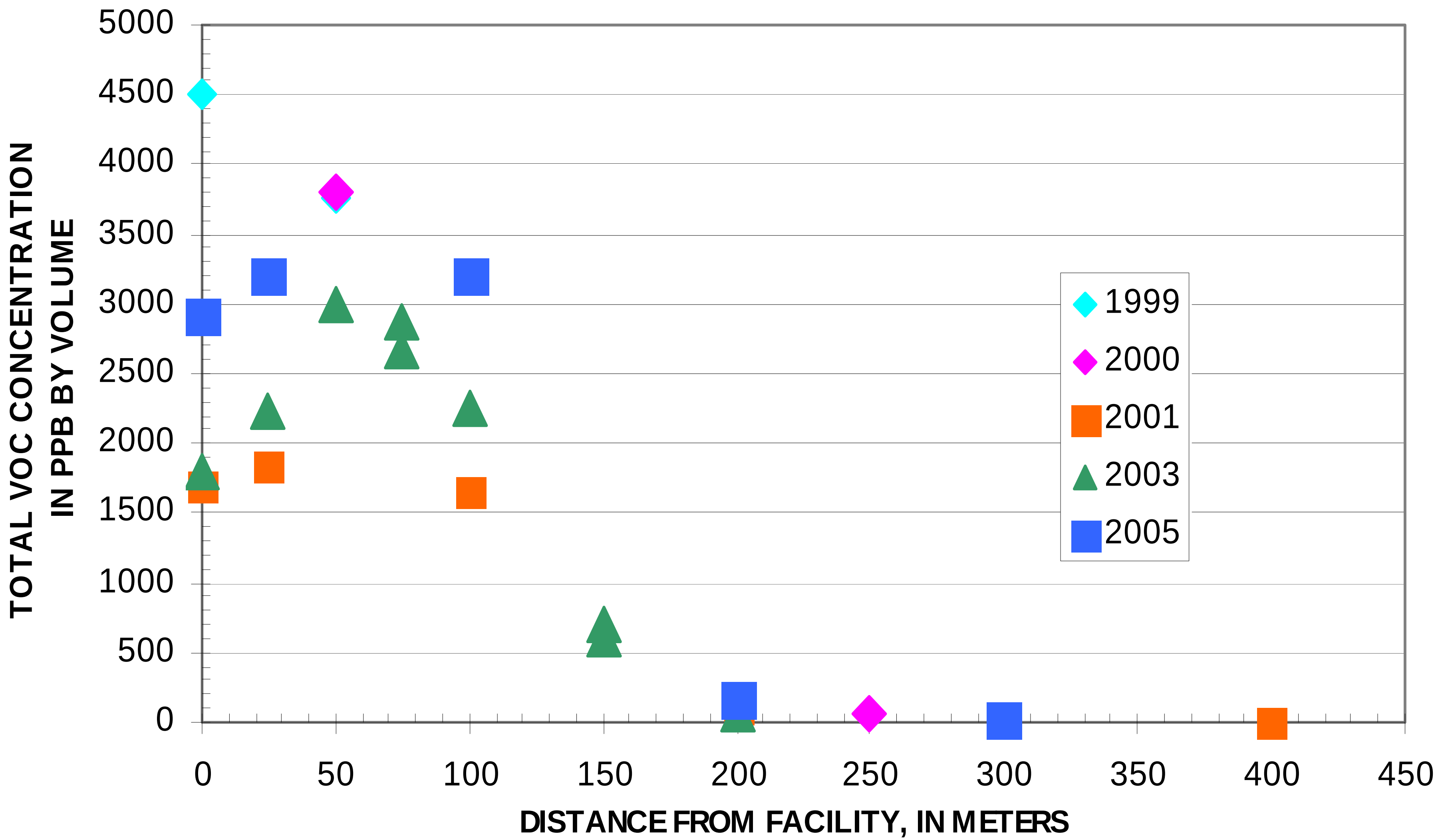
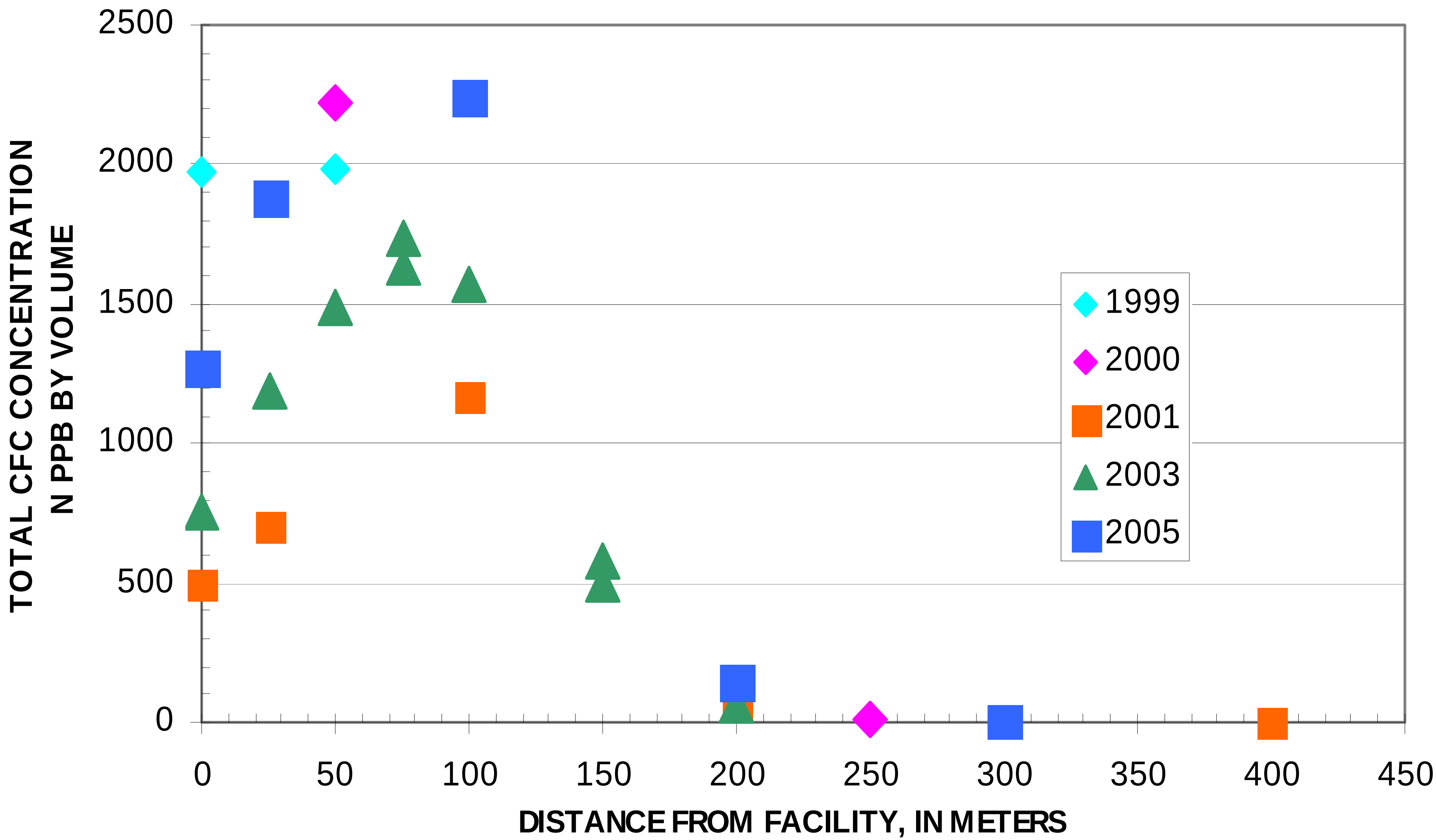


Walker et al., ***2000***, ***JGR*** 105: 14285-14296

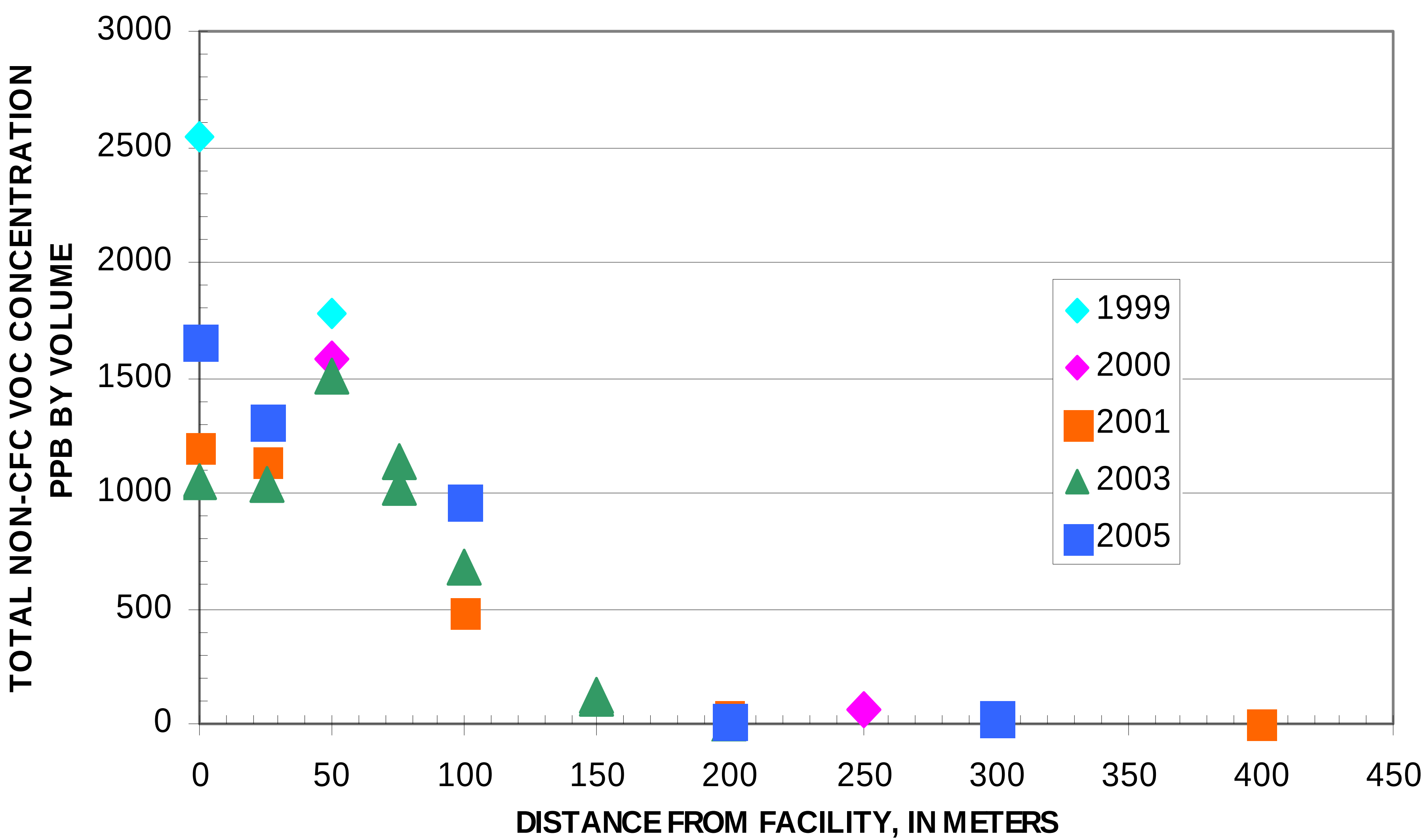
Total VOC Concentrations of Vapor Samples "A-Line", 1999-2005



Total CFC Concentrations of Vapor Samples "A-Line", 1999-2005



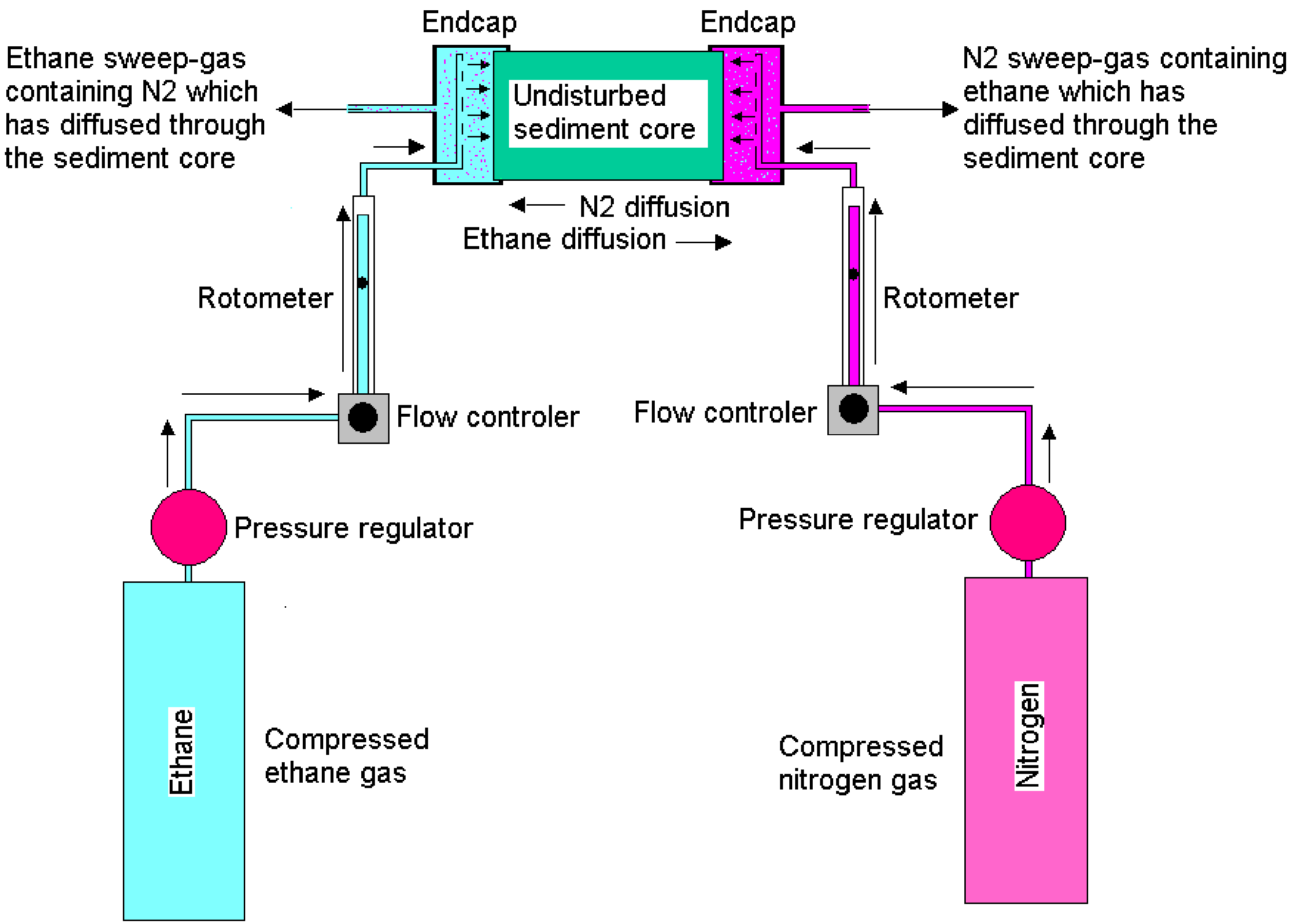
Total Non-CFC VOC Concentrations of Vapor Samples "A-Line", 1999-2005



Question: Is a substantial amount of VOC mass being lost by diffusive transport through the surface to the atmosphere?

- Determine diffusion constant of a vapor species (ethane or nitrogen) in undisturbed cores from ADRS
- Calculate diffusion constants of VOCs from that of ethane or nitrogen
- Determine the gradient of VOC concentration as a function of depth
- Apply Fick's Law to calculate vertical fluxes of VOCs at sampling locations at ADRS

Apparatus for determining diffusion constants in undisturbed sediment cores



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Counter-current diffusion of ethane and nitrogen is measured in the apparatus shown. The Steffan-Maxwell equation is applied:

$$\frac{dE}{dz} = \frac{1}{CD_{EN}} \left(E \frac{J_N}{w_N} - N \frac{J_E}{w_E}\right), \quad N = 1 - E$$

N and E (mole fractions of N_2 and ethane): measured by GC

J_N and J_E (fluxes of N_2 and ethane): calculated from E, N, and gas flow rates

w_N and w_E (Molecular weights of N_2 and ethane): literature values

C (vapor-phase molar density) : 4.46 10-5 mol/cm^3 at standard temperature and pressure

D_{EN} (effective diffusion constant of ethane in nitrogen in the core): determined using an interactive Fortran program (Arthur Baehr, unpublished) that contains an analytical solution to the Steffan-Maxwell equation.

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Determining diffusion constants of VOCs at ADRS from the diffusion constant of ethane in undisturbed cores

D_{OA} (effective diffusion constant of contaminant "O" in air in the core):
$D_{OA} = (D_{EN})(D^b_{OA})/(D^b_{EN})$
where D^b_{OA} and D^b_{EN} are binary bulk diffusion constants calculated from molecular structures

D_{OA} Diffusion constants in cores taken from 3.2 and 23 meter depths:
$D_{OA} = 0.021 \pm 0.006$ g/cm²/sec for VOCs detected at ADRS.
No significant difference observed between two depths.

Diffusion Constants of VOCs in Air and in Undisturbed Cores from ADRS

Compound	Diff. Const. In air (1 bar, 20 C (cm^2/sec)	Diff. Const. In sediment (1 bar, 20 C) (cm^2/sec)
Dichlorodifluoromethane (CFC12)	0.0852	0.0138
Chloromethane	0.1261	0.0205
Chloroethene (Vinyl chloride)	0.1079	0.0175
Bromomethane	0.1140	0.0185
Chloroethane	0.1043	0.0169
Bromoethene (Vinyl bromide)	0.1000	0.0162
Trichlorofluoromethane (CFC11)	0.0818	0.0133
1,1,2,-Trichloro-1,2,2-Trifluoroethane (CFC113)	0.0675	0.0110
Acetone	0.1040	0.0169
Diethyl ether	0.0880	0.0143
1,1-Dichloroethene	0.0912	0.0148
tert-Butyl alcohol	0.0880	0.0143
2-Propenenitrile (Acrylonitrile)	0.1114	0.0181
Methylene chloride	0.1015	0.0165

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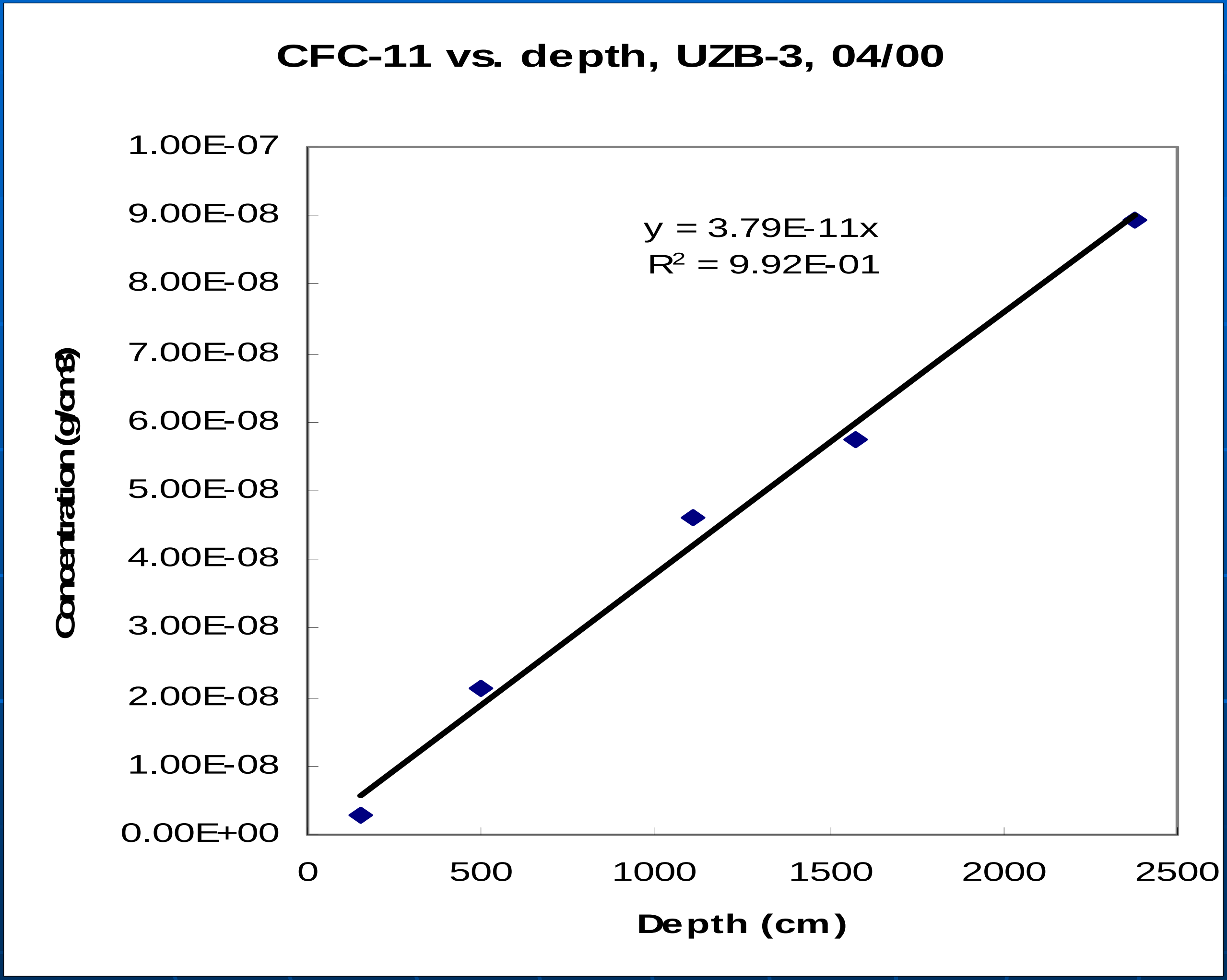
Example of a Linear Concentration Profile with Depth that can be Used to Estimate Vertical Flux: CFC-11 in UZB-3



Fick's Law:

Flux is proportional to concentration gradient

J=D(effective)*dC/dX

D(i,air) = 8.182E-02

Tortuosity = 2.00E-01

D(effective) = 5.40E-03

slope (dc/dx)=3.79E-11

J (g/cm2-s) = 2.05E-13

J (g/m2-y) = 6.45E-02

Example of Flux Valued Determined from 0.5 and 1.5 Meter Depth Samples: CFC-11 in the A Transect

Molecular Weight	137.37					
Bulk diffusion constant in air	0.0818					
Effective diffusion constant at ADRS	0.0132					
	------------------------Vertical Flux (g/cm2-s) -------------------------					
Location	A1	A2	A5	A9	A13	A17
	8.40E-14	1.4E-13	1.77E-13	4.34E-15	1.22E-16	1.18E-17

Planned and Ongoing Work

- Identification of additional VOC compounds in chromatograms (Wentai Luo)
- Test of whether substantial amounts of VOCs are removed from vapor when water is removed by cold trapping (Results: vapor VOC concentrations are virtually unchanged, trapped water contains little VOC mass)
- Transport simulation as per mercury and CO2

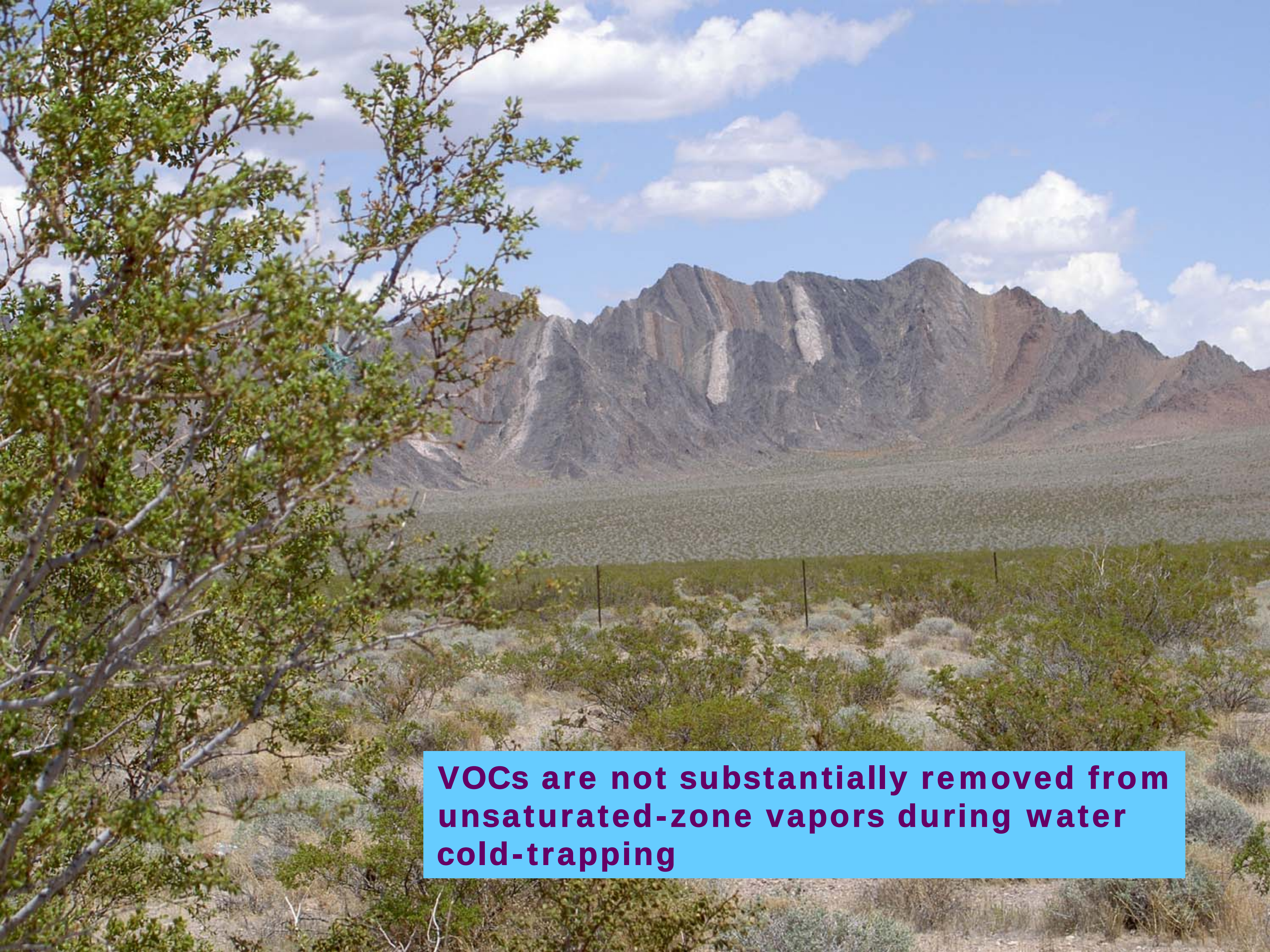
Conclusions to this point:

1. Significant concentrations of a variety of VOCs are present in the unsaturated zone as far as 200 meters from the source

2. No strong temporal trends have been noted over 8 years of sampling

3. CFCs dominate the list of VOCs present, and are present at levels up to 1,000,000 x atmospheric levels at 30-40 meter depths

There is likely loss of VOCs to the atmosphere by diffusion through the surface based on vertical gradients observed


VOCs are not substantially removed from unsaturated-zone vapors during water cold-trapping