

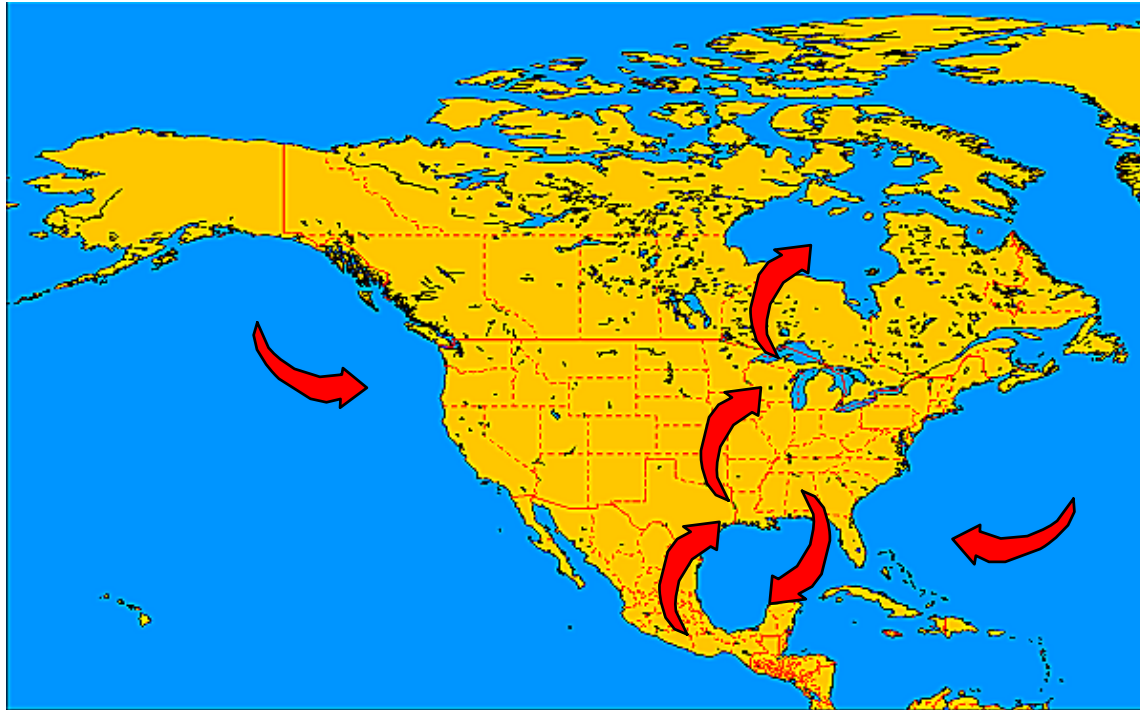
DDT in Great Lakes Air: Long-Range Transport or Home-Grown?

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New sources, old sources ...

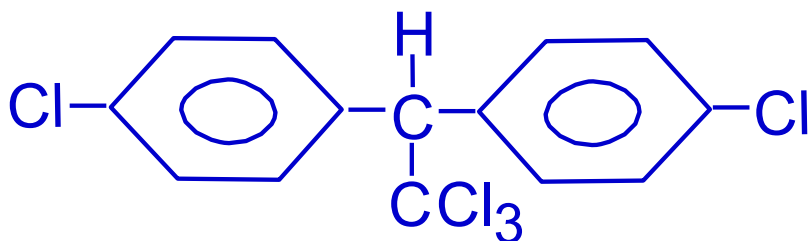


Legacy pesticides are still found in air and precipitation

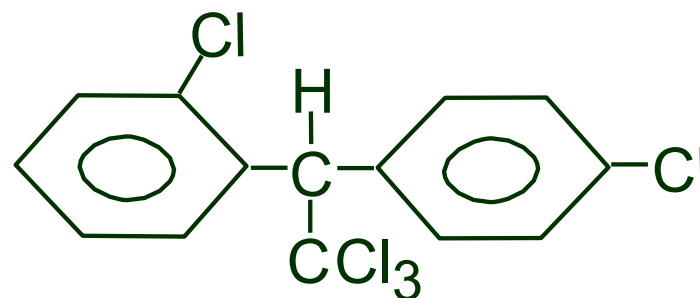
Potential Sources:

- Recent use in Mexico - Central America
- Emissions of "legacy" residues from soil and water
- Trans-oceanic

Technical DDT



p,p'-DDT ~77%



o,p'-DDT ~15-20%

- Used worldwide for disease vector control and agriculture since 1945.
- Total estimated global usage 2.4 megatonnes¹.
- Global elimination under Stockholm Convention, except for vector control.

1. Li et al., Sci. Total Environ., 2005

Use of DDT in North America¹

- United States used 590 kt for agriculture and 55 kt for public health between 1947-72. Deregistered in 1972.
- Phased out in Canada during mid-1970s and all remaining uses cancelled by 1985.
- Mexico used 180 kt for agriculture and 71 kt for malaria control between 1953-00. "Official" used stopped in 2000.

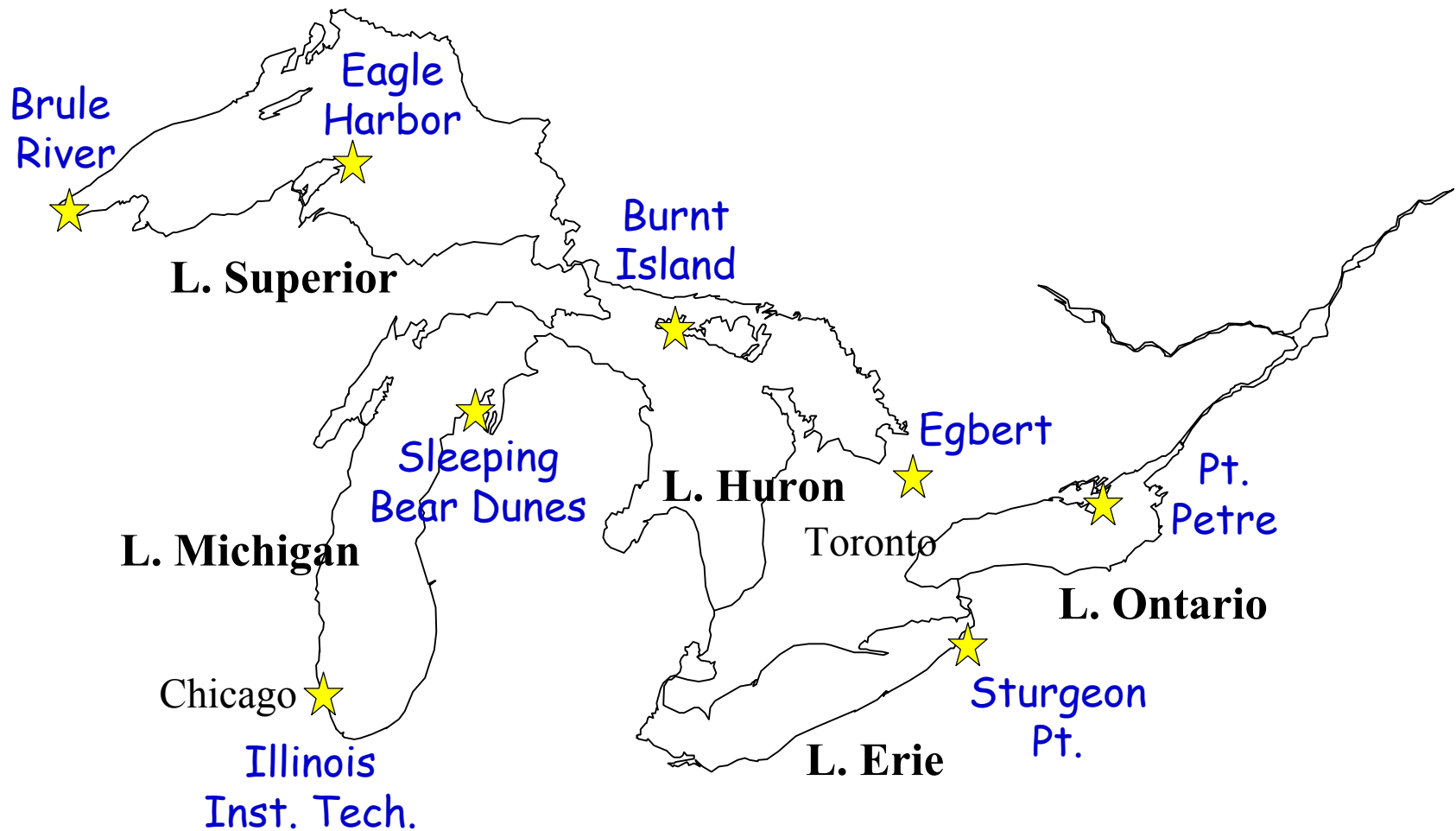
1. Li et al., Sci. Total Environ., 2005; N. Amer. Comm. Environ. Cooperation
http://www.cec.org/files/PDF/POLLUTANTS/HistoryDDTe_EN.PDF

Geopolitics of DDT

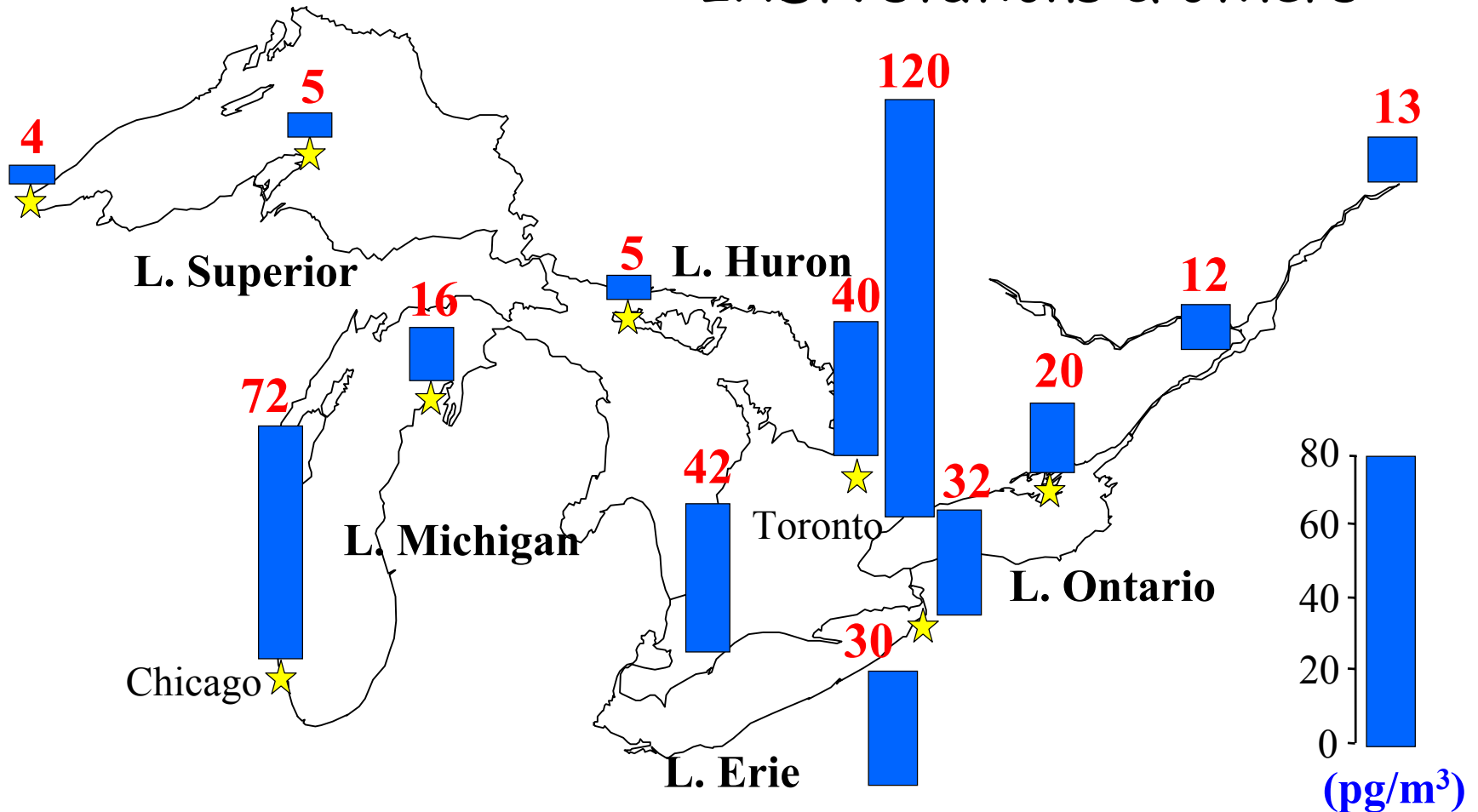
- Stockholm Convention permits production and use of DDT for disease vector control under World Health Organisation guidelines.
- Requires that DDT be used only when locally safe, effective and affordable alternatives are not available.
- WHO states¹: "It is anticipated that, for some time to come, there will continue to be a role for DDT in combating malaria, particularly in the poorest endemic countries."

1. World Health Organisation, 2005. WHO position on DDT use in disease vector control under the Stockholm Convention on POPs. WHO Roll Back Malaria Department, Geneva, Switzerland, WHO/HTM/RMB/2004.53.

Integrated Atmospheric Deposition Program (IADN) early-mid 1990s to present



Σ DDTs in air IADN stations & others



IADN data base, Motelay-Massei et al., ES&T 2005; Shen et al., ES&T 2005

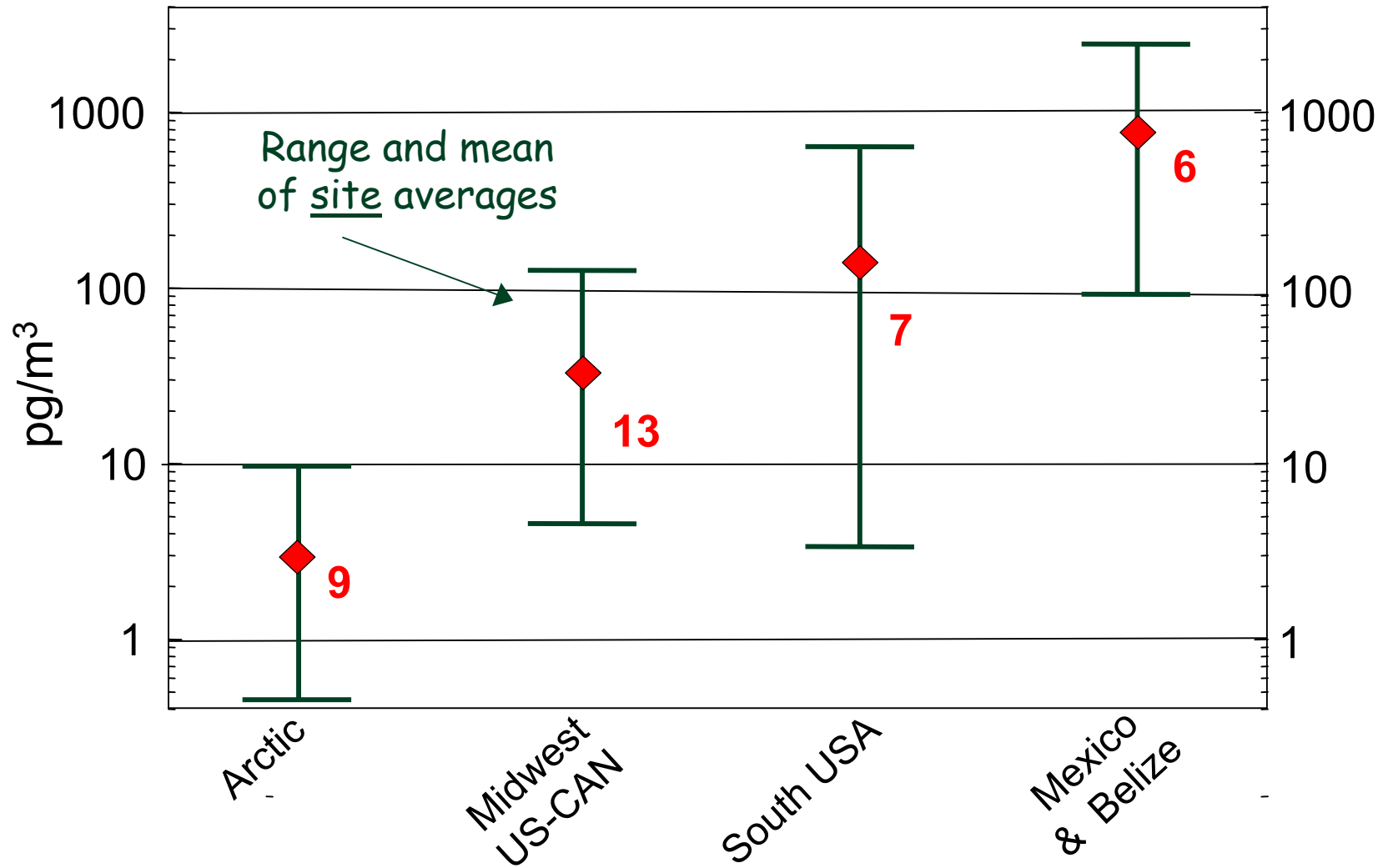
Air sampling in Mexico & Belize, 1995-2004



© 1992 Magellan GeographixSM Santa Barbara, CA (800) 929-4627

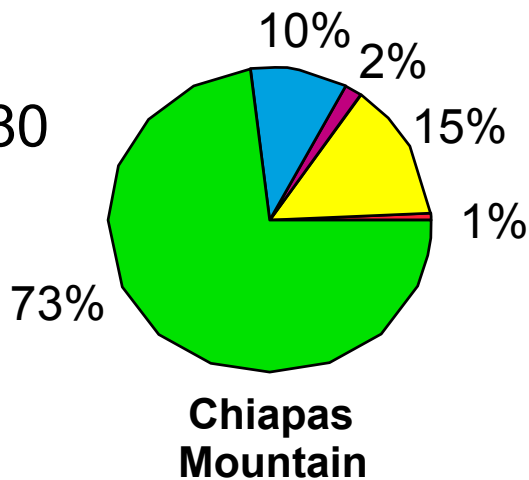
Alegria et al., ES&T 2000; Environ. Pollut., 2006,
Shen et al., ES&T 2005; Wong, Alegria, et al., DIOXIN-05

Total DDTs in air are higher in southern Mexico- Belize

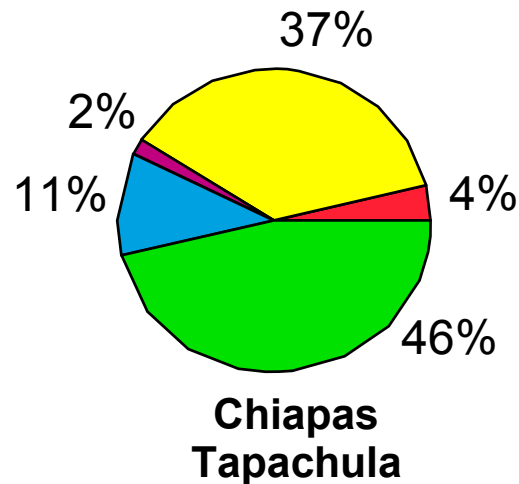


DDTs (pg m⁻³) in Mexican air, 2002-04

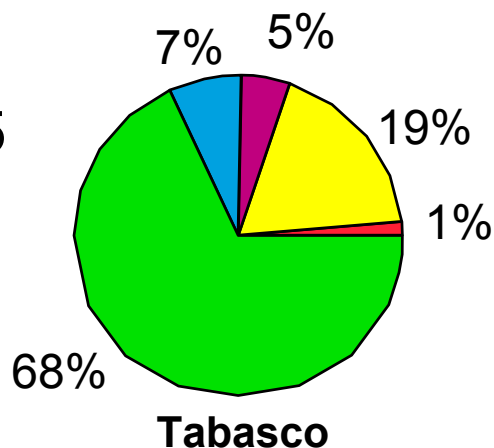
Σ DDT
2300 $\pm$ 780



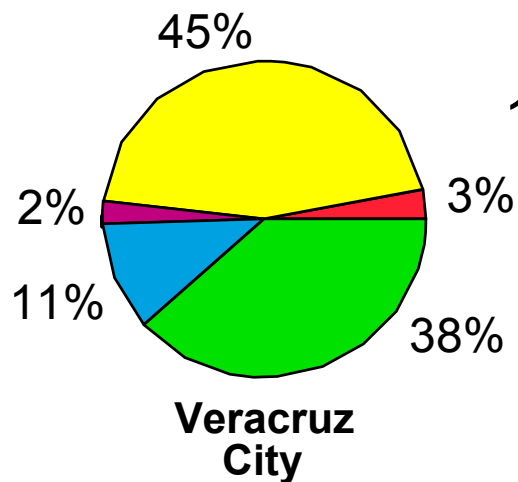
Σ DDT
520 $\pm$ 190



Σ DDT
240 $\pm$ 245



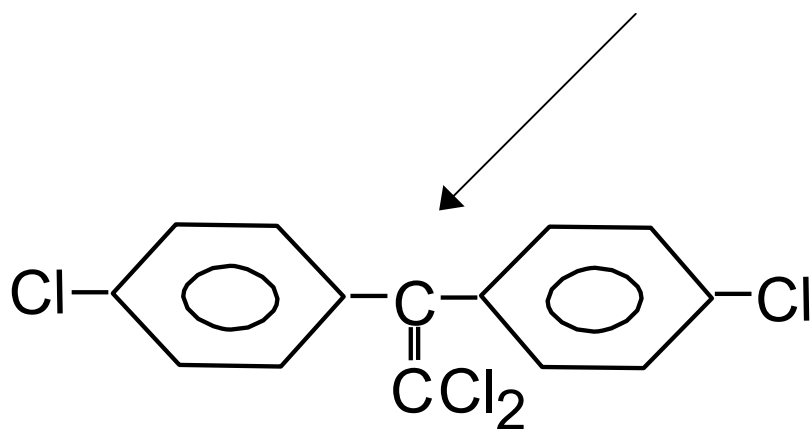
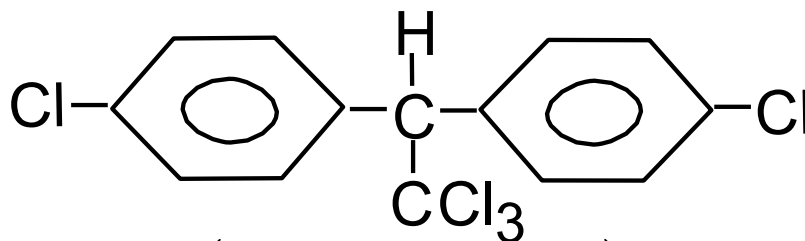
Σ DDT
1200 $\pm$ 490



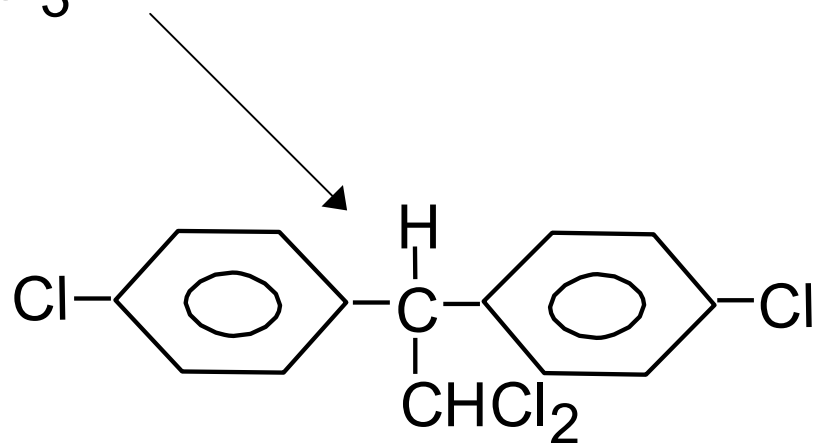
■ o,p'-DDE ■ p,p'-DDE ■ p,p'-DDD ■ o,p'-DDT ■ p,p'-DDT

DDTs are metabolised to DDEs and DDDs

p,p'-DDT



p,p'-DDE



p,p'-DDD

Similarly for o,p'-DDT

Ratio of DDT/DDE roughly indicates age of residues

High DDT/DDE
Newer



Low DDT/DDE
Older

Problems:

- Metabolism rates in soils differ greatly.

Ratio of DDT/DDE roughly indicates age of residues

High DDT/DDE
Newer

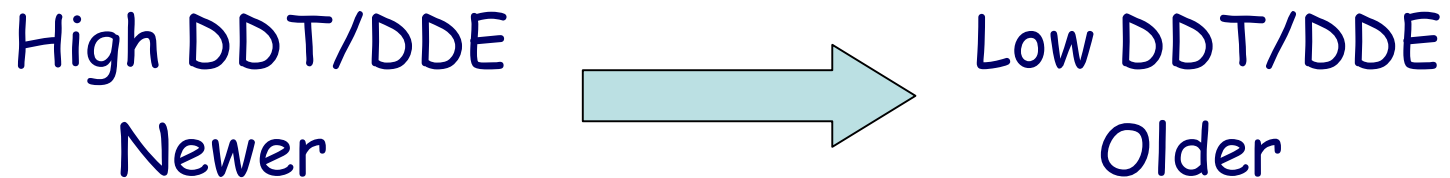


Low DDT/DDE
Older

Problems:

- Metabolism rates in soils differ greatly.
- Limits on ratios: >1 = "new" and <1 = "old"?

Ratio of DDT/DDE roughly indicates age of residues



Problems:

- Metabolism rates in soils differ greatly.
- Limits on ratios: >1 = "old" and < 1 = "new"?
- DDT and DDE have different volatilities; fractionation from soil to air.

Expressing proportions of DDT and DDE

- Ratios easy to understand, difficult to average.

$$R_{DDTE} = p,p'\text{-DDT}/p,p'\text{-DDE}$$

- Fractions preferred to ratios for statistics¹.

- Results expressed as F_{DDTE} :

$$F_{DDTE} = p,p'\text{-DDT}/(p,p'\text{-DDT} + p,p'\text{-DDE})$$

$$F_{DDTE} = R_{DDTE}/(R_{DDTE} + 1)$$

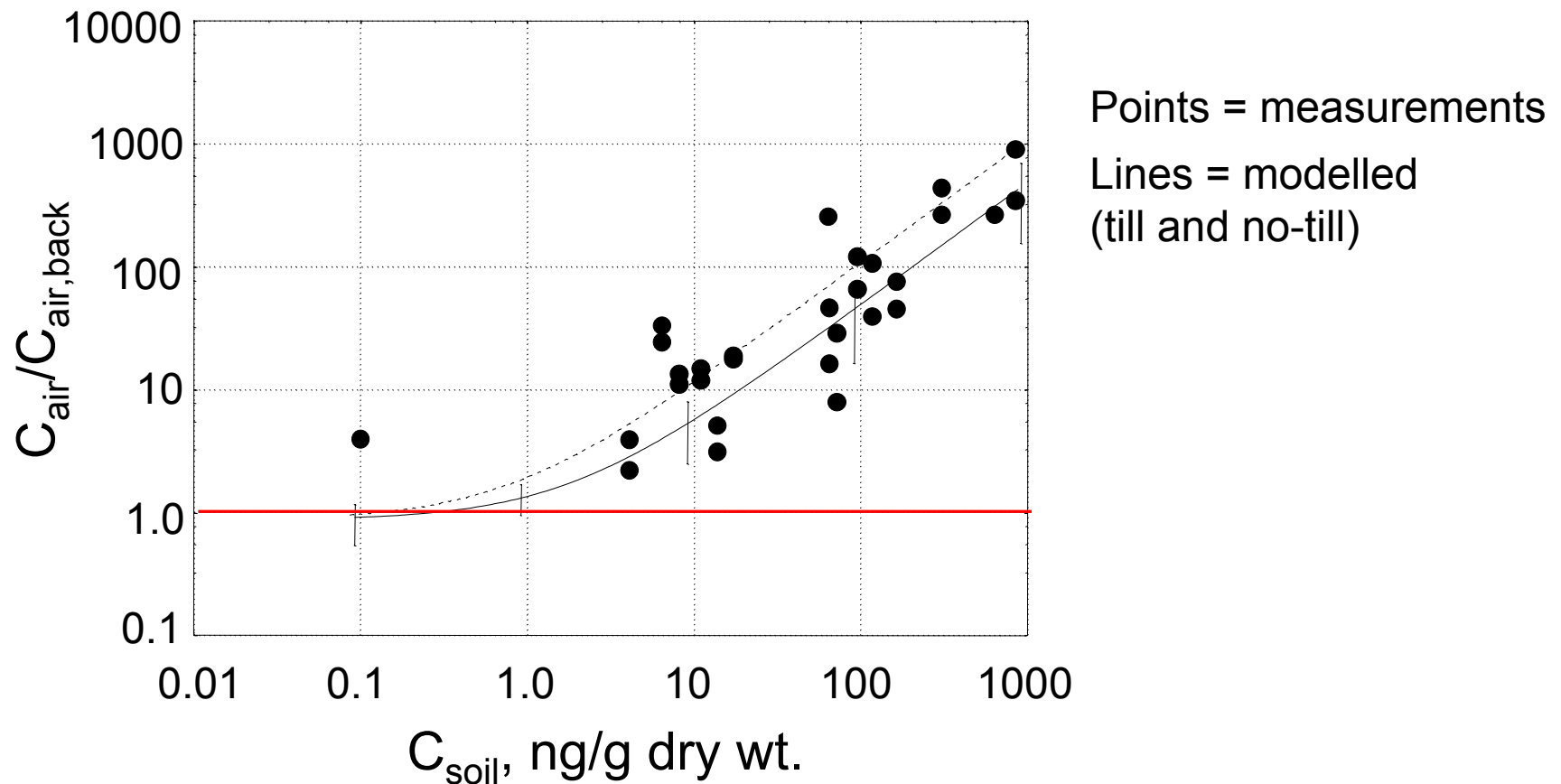
1. Harner et al., ES&T
2000; Ulrich et al.,
Chemosphere 2003

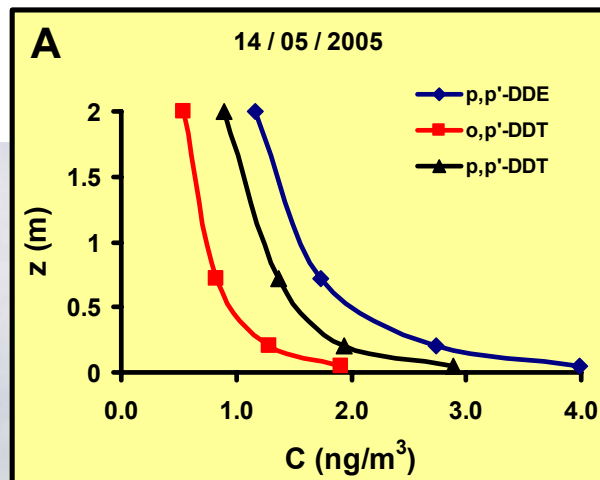
R_{DDTE}	F_{DDTE}
0.25	0.20
1.00	0.50
4.00	0.80

Are old residues emitted from soils?

p,p'-DDE in air sampled 40 cm above farm soils in the southern U.S.A.

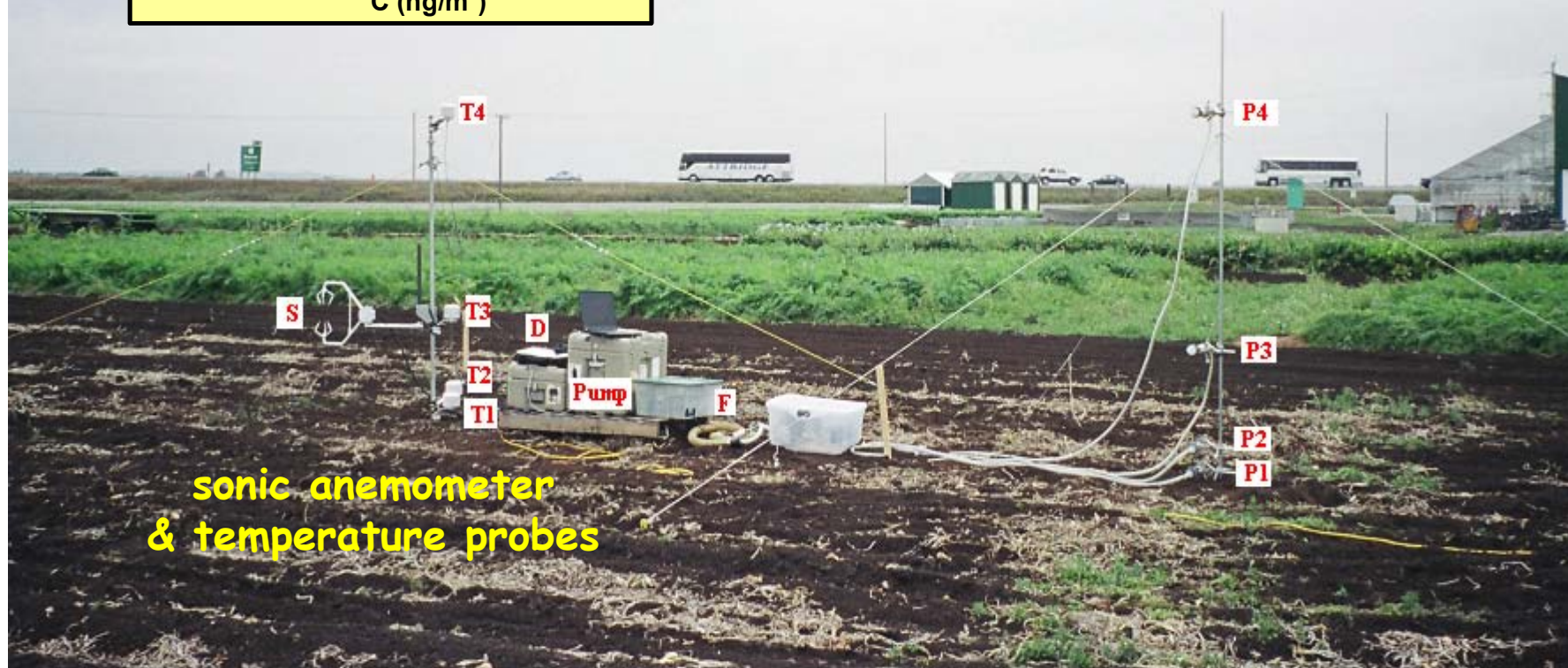
Ratio of C_{air} over soil to background air, $C_{\text{air,back}} = 28 \text{ pg/m}^3$





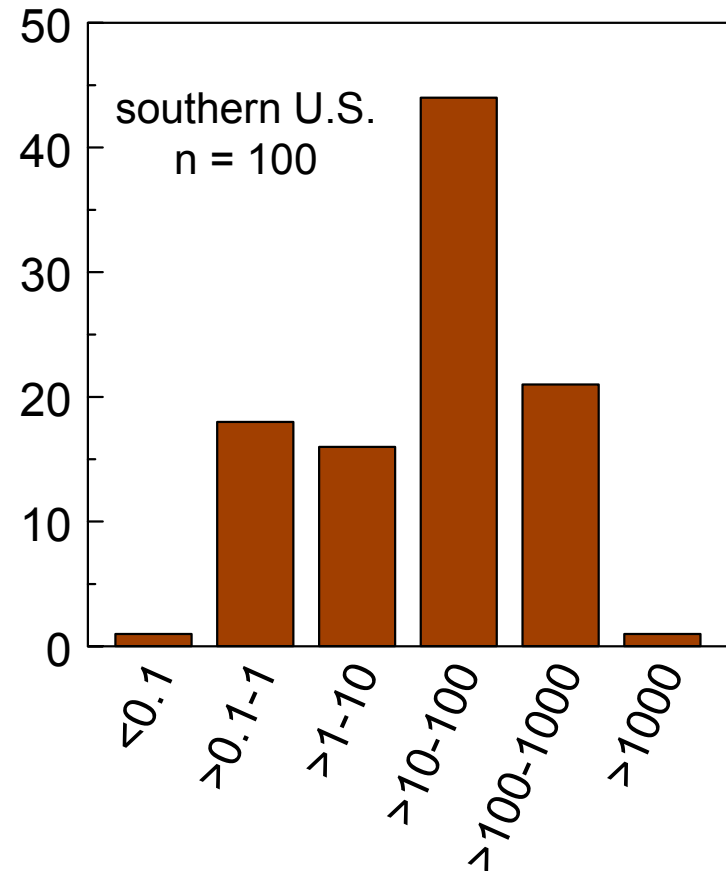
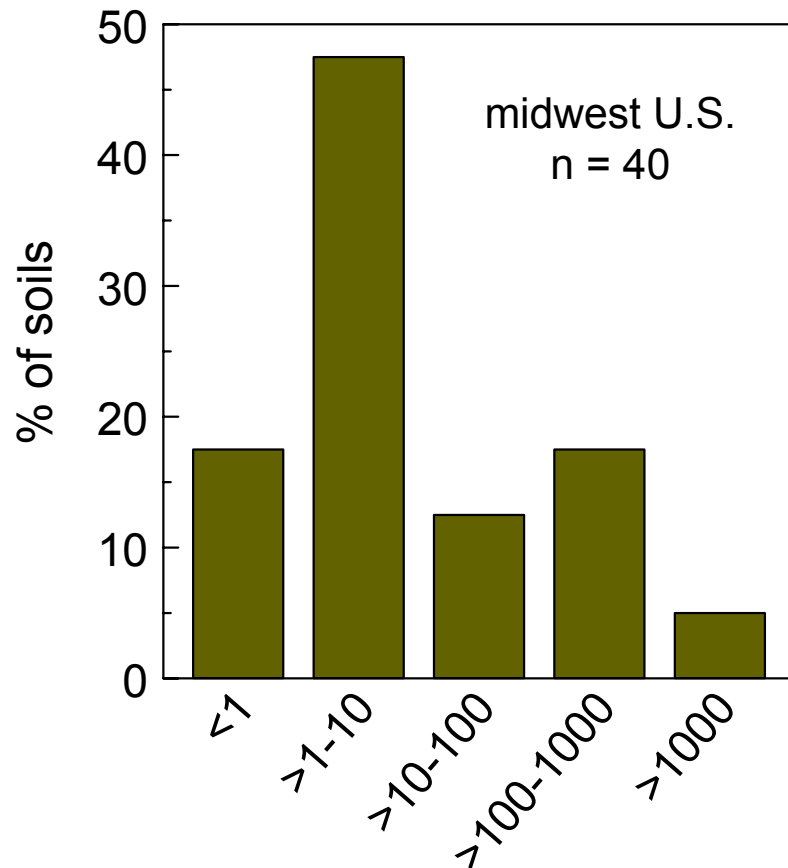
Soil-air fluxes of DDTs in southern Ontario (Kurt-Karakus et al., submitted)

filter-PUF
samplers



sonic anemometer
& temperature probes

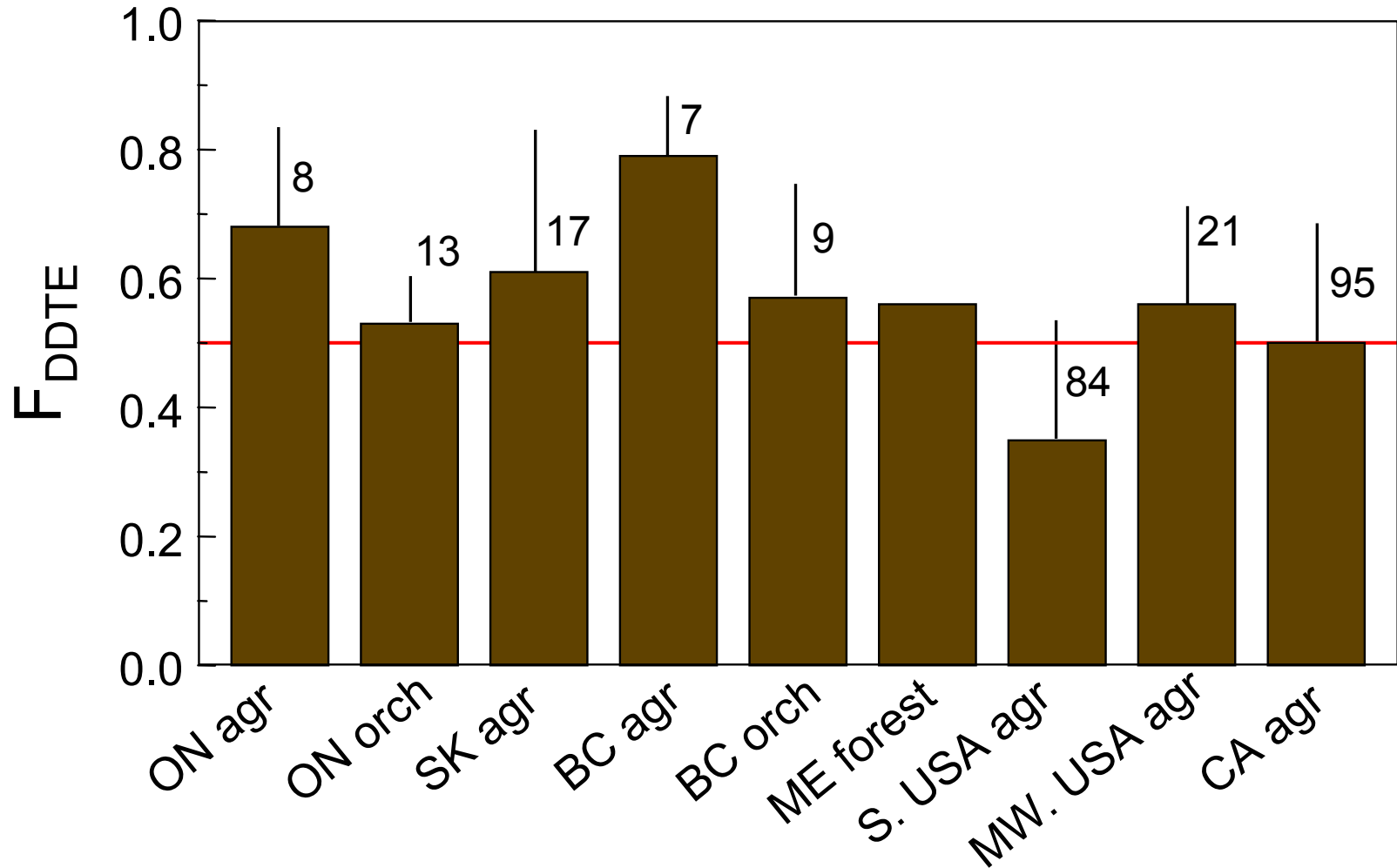
Σ DDTs in agricultural soils, ng/g dry weight



Aigner et al., ES&T 1998; Bidleman & Leone, Environ. Pollut., 2004;
Kannan et al., Arch. Env. Contam. Tox., 2003

F_{DDTE} in North American soils, 1985 - 2005

— $F_{DDTE} = 0.5$, $R_{DDTE} = 1$



DDTs in soil emissions

Assume volatilisation from soil is related to liquid-phase vapour pressure (VP)

VP¹ at 20°C:

p,p'-DDT: 0.00026 Pa,

p,p'-DDE: 0.0018 Pa

$$VP_{\text{DDT}}/VP_{\text{DDE}} = 0.14$$

$$(R_{\text{DDTE}})_{\text{air}} = (R_{\text{DDTE}})_{\text{soil}} \times VP_{\text{DDT}}/VP_{\text{DDE}}$$

Does this work?

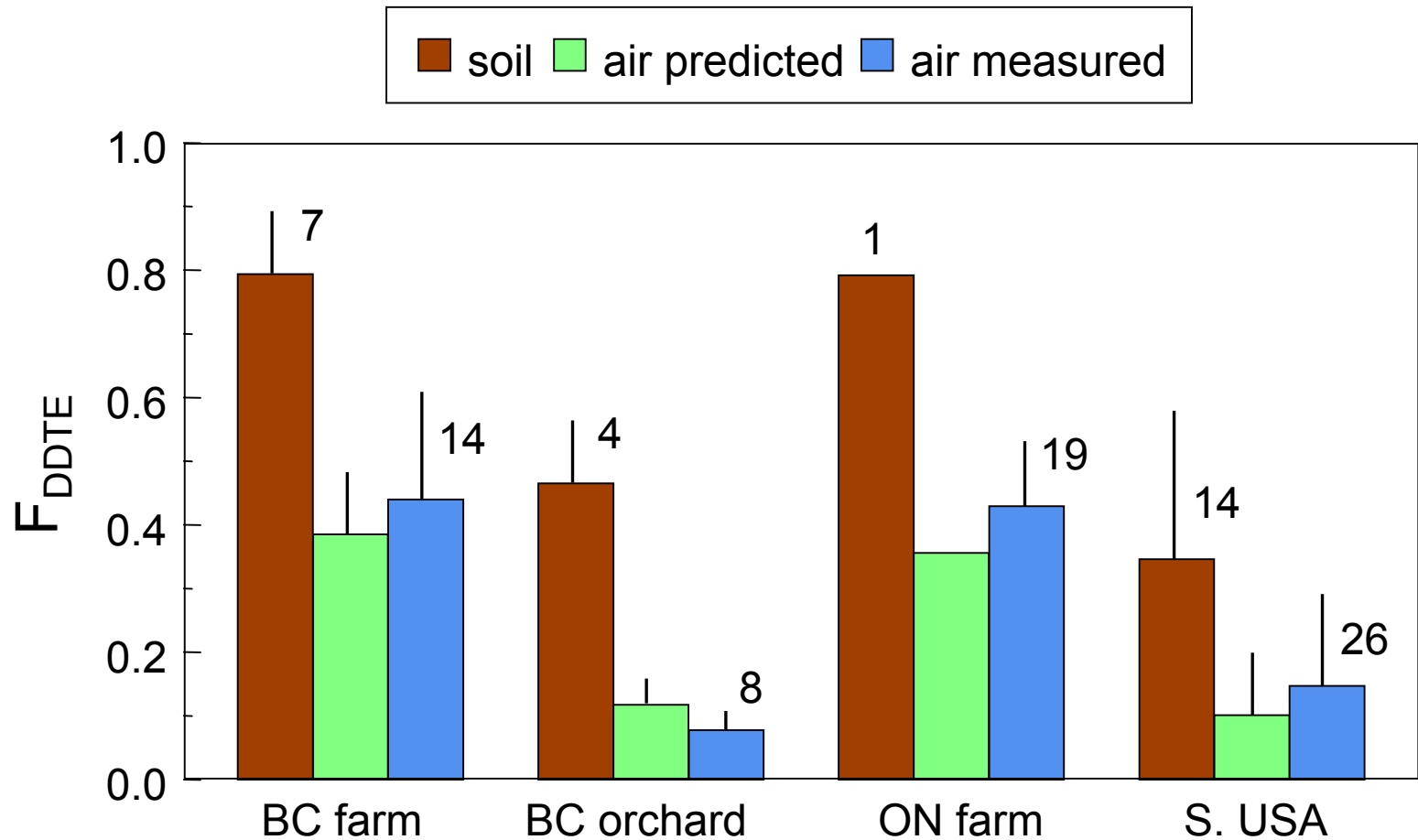
1. VPs from Hinckley et al., J. Chem. Eng. Data, 1990

Soil-Air Exchange Experiments, 2000-05

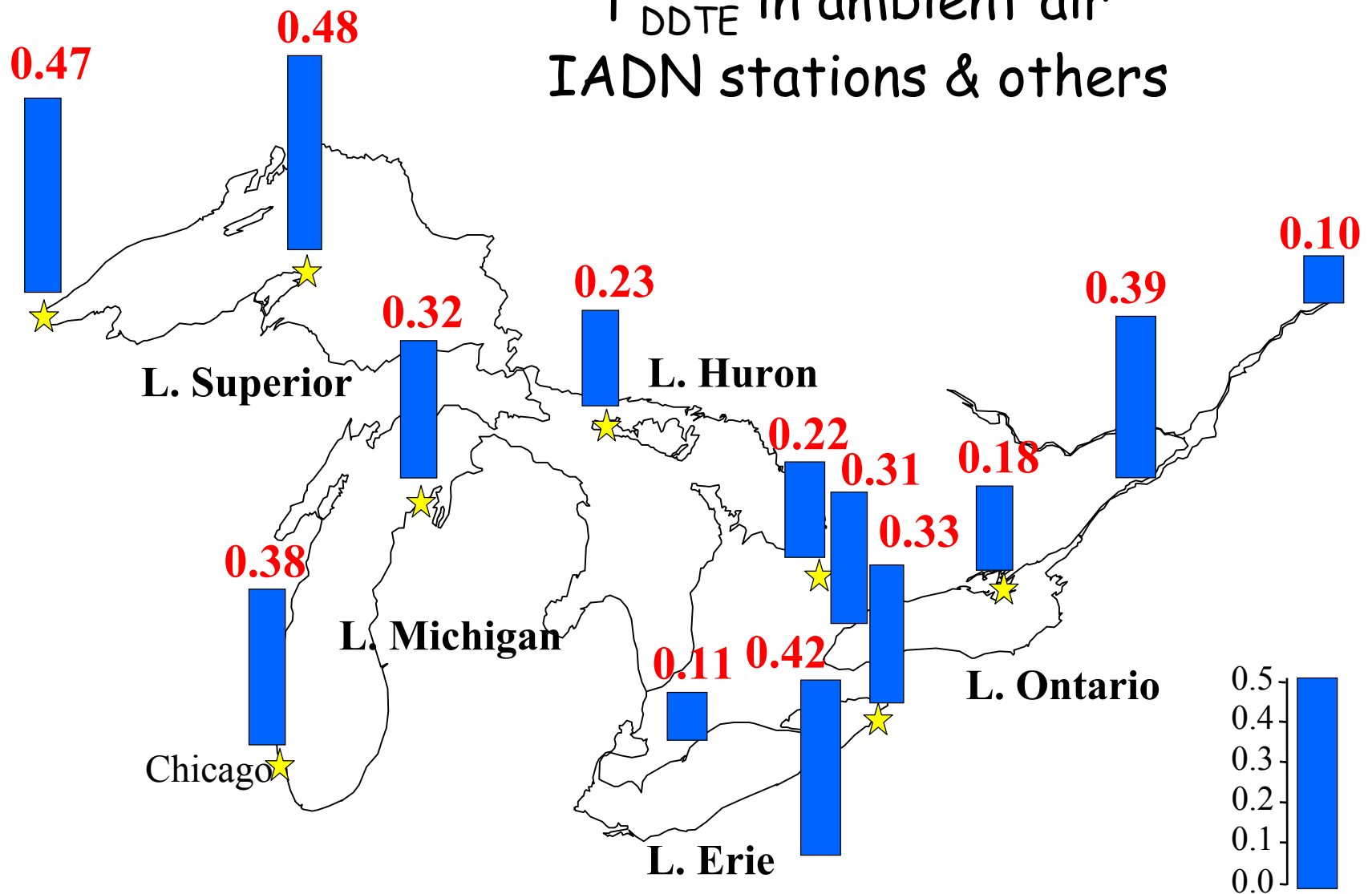
- Soil samples collected from farm fields.
- R_{DDTE} in air predicted from soil residues using VP ratios.
- Converted to F_{DDTE} .
- Air samples collected over the soil (5-40 cm) and F_{DDTE} compared to predictions.

Bidleman & Leone, Environ. Pollut., 2004;
Bidleman et al., ET&C, in press; Kurt-Karakus et al., submitted

F_{DDTE} in air measured over soil and predicted from soil residues

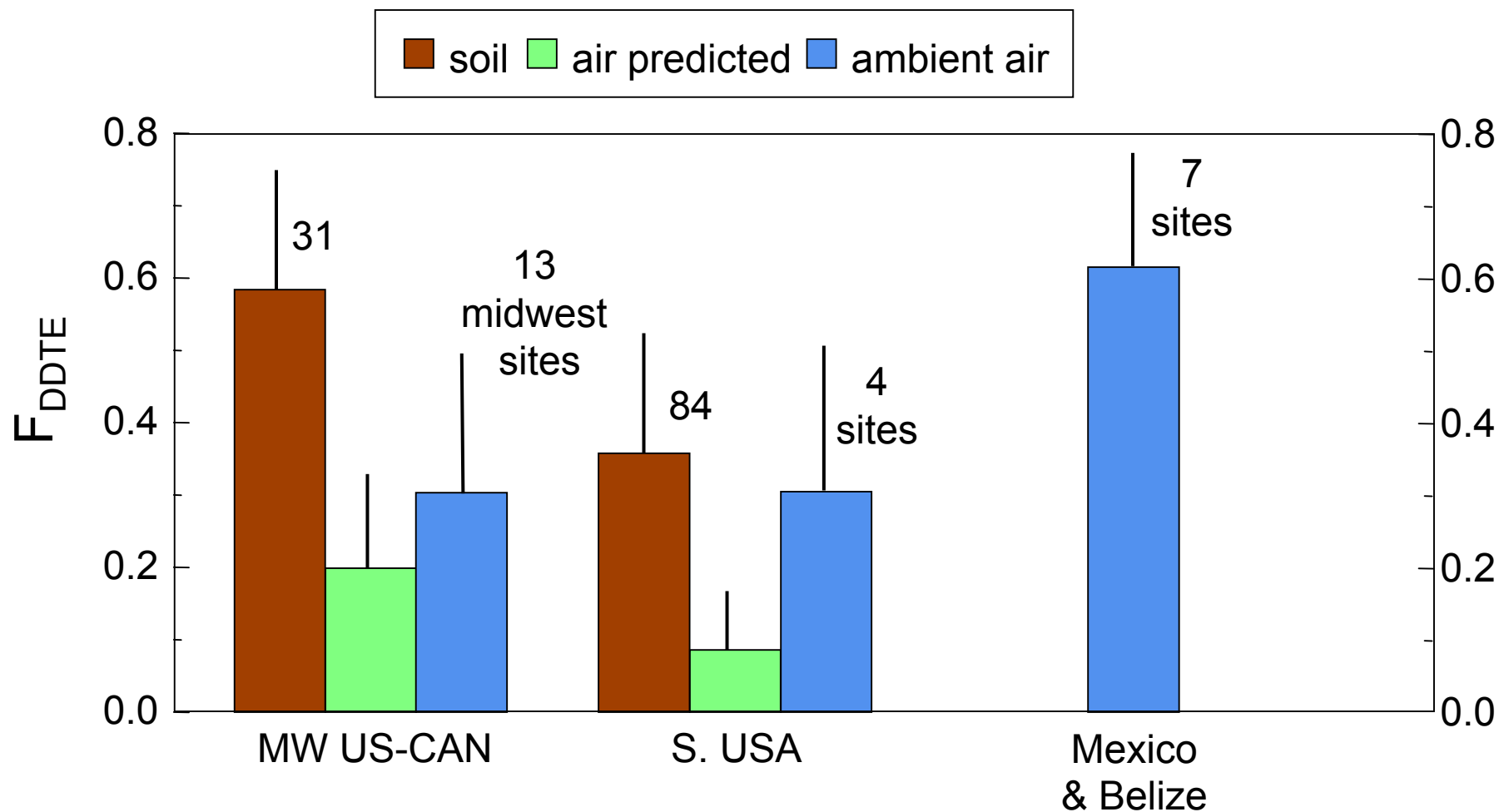


F_{DDTE} in ambient air IADN stations & others

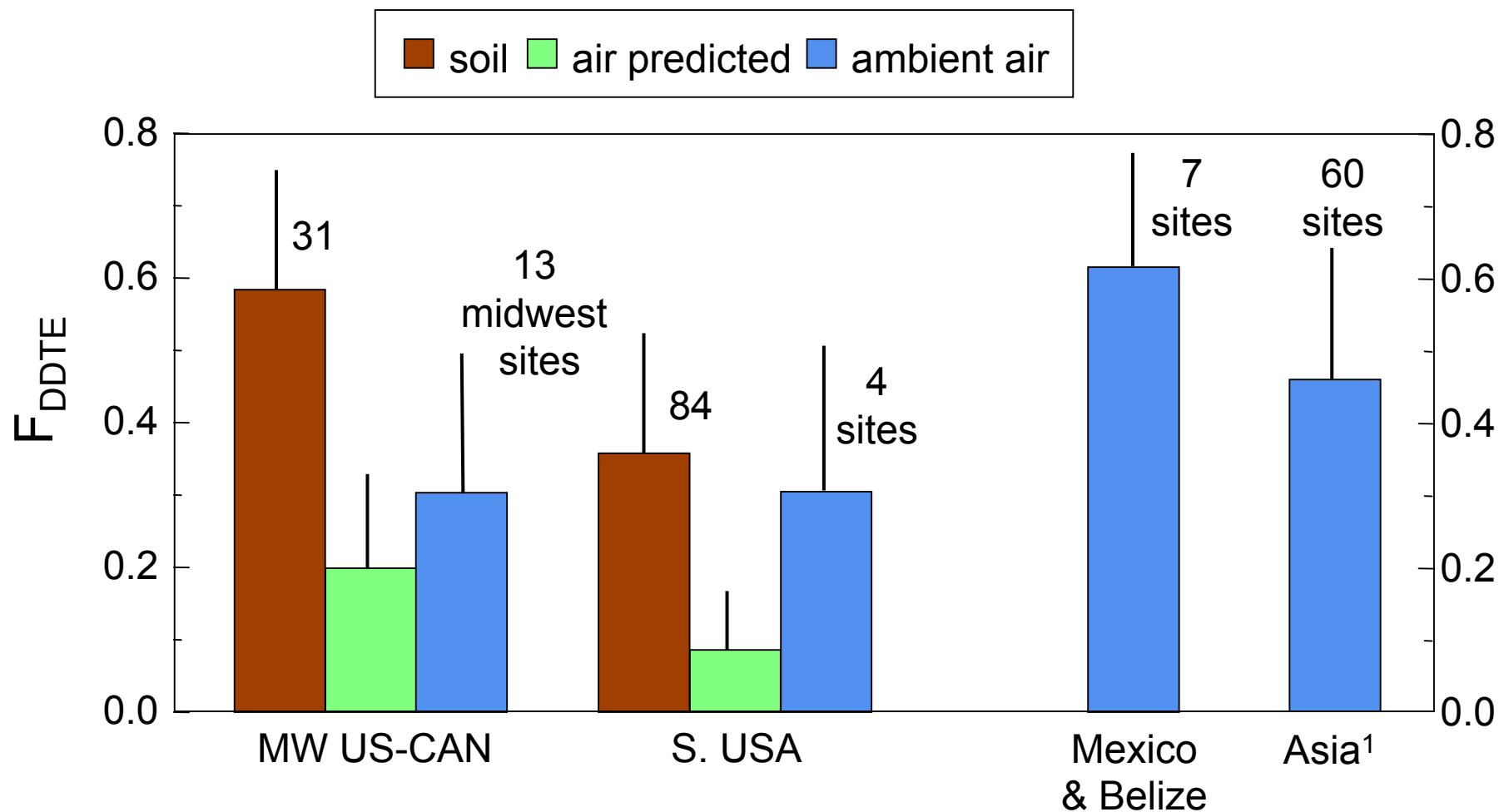


IADN data base, Motelay-Massei et al., ES&T 2005; Shen et al., ES&T 2005

F_{DDTE} in ambient air and predicted from soil emissions



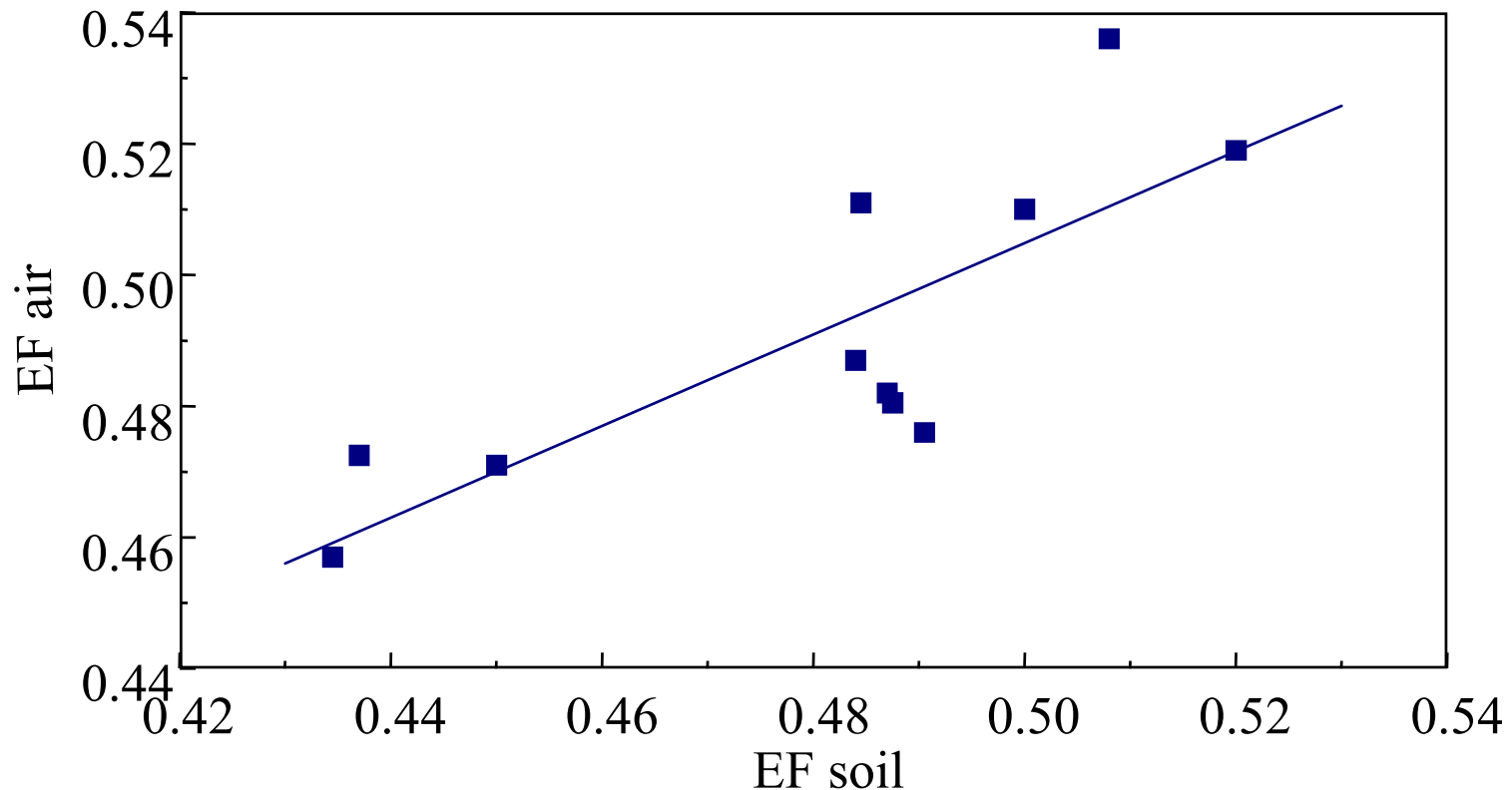
F_{DDTE} in ambient air and predicted from soil emissions



1. China, Japan, Korea, Singapore: Jaward et al., ES&T 2005

Enantiomer fractions (EFs) of o,p'-DDT in southern U.S. agricultural soil and overlying air at 40 cm

(Bidleman & Leone, Environ. Pollut., 2004)



Ambient air shows (+) degradation (EF ~0.47) in Canada & U.S., racemic (EF = 0.50) in Mexico - C.A. (Shen et al., ES&T 2005)

Summary

- Fractionation of p,p'-DDT and p,p'-DDE between soil and air is well predicted from relative VP.
- F_{DDTE} in ambient air of Great Lakes - midwest is similar, but slightly greater, than predicted from soil emissions.
- Discrepancy is greater in southern U.S., although small air data set.
- LRT from Mexico-Central America?

Final Words

- Soil emissions place limits on “old” F_{DDTE} in air.
- Compare with ambient air signals to judge possible “new” DDT input.
- Useful in N. America, and also countries which have recently stopped, or are still using, DDT.

Continuing passive campaign, 2003-present

