WACAP Air, Snow and Vegetation Results: A Focus on SEKI, YOSE, and LAVO

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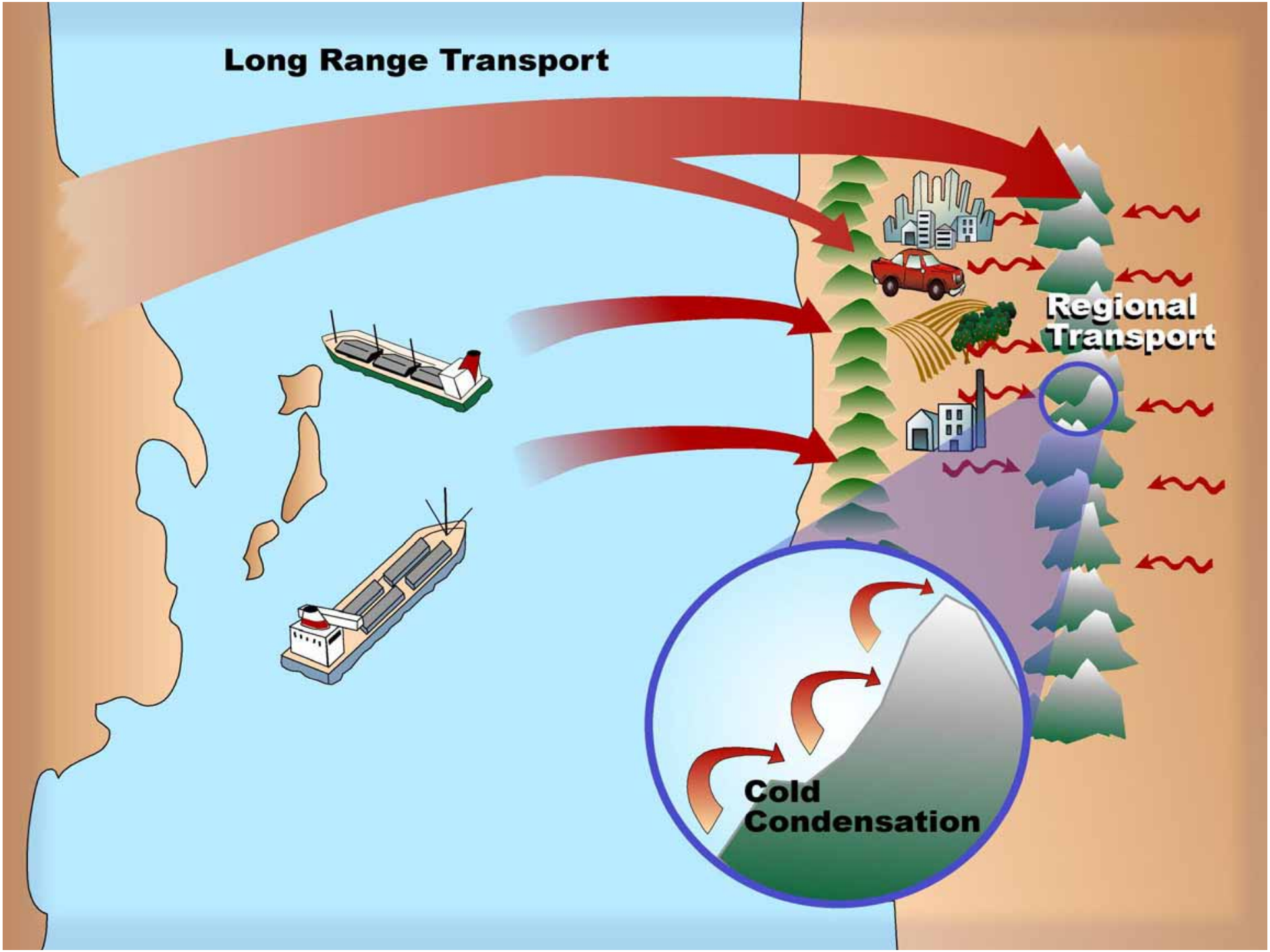

Long Range Transport
Regional Transport
Cold Condensation

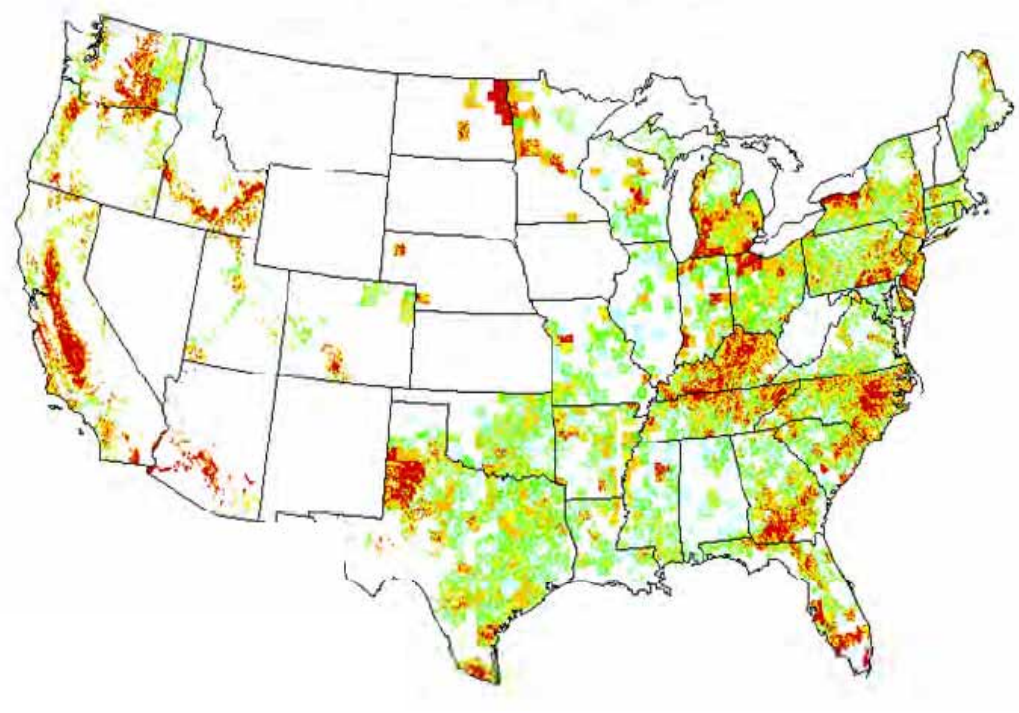
SELECTION of WACAP SEMI-VOLATILE ORGANIC COMPOUNDS (SOCs)

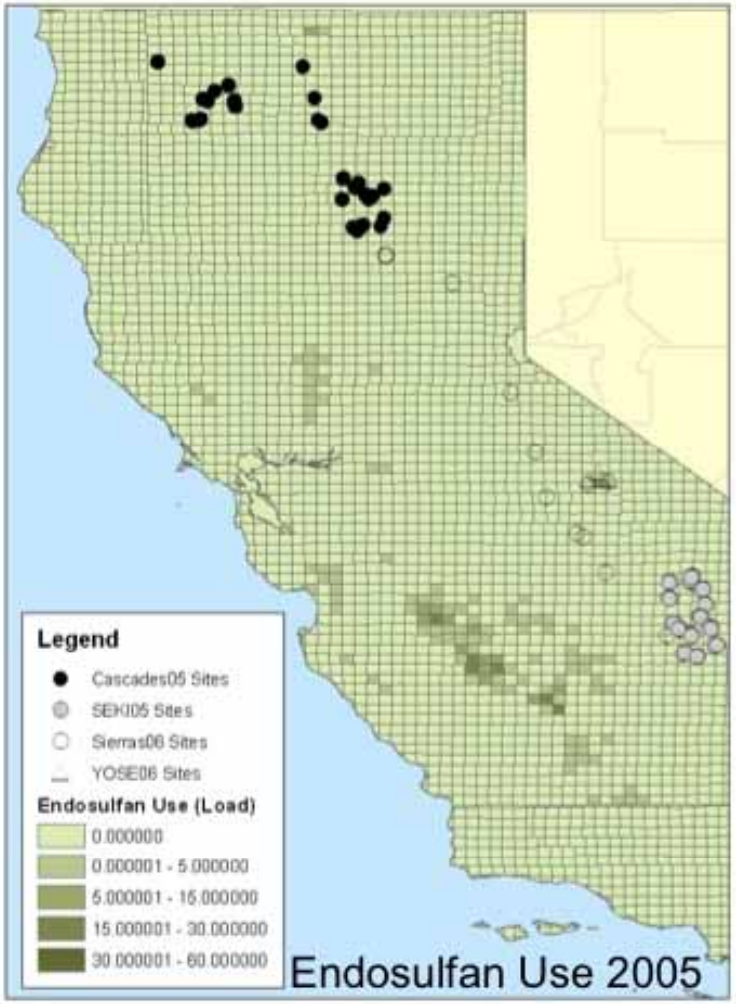
- Evidence of atmospheric long-range transport to high elevation or high latitude ecosystems
- Potential to accumulate in food webs
- Releases from combustion, agricultural, and industrial/urban sources
- Some currently used in the U.S. (current use pesticides, PBDEs, and PAHs) and some banned from use in the U.S. (historic use pesticides and PCBs)
- Some persistent organic pollutants (POPs) and persistent, bioaccumulative and toxic (PBTs)
- Likelihood of developing and validating analytical methods
- Same SOCs measured at Simonich NSF air sampling sites

SEMI-VOLATILE ORGANIC COMPOUNDS (SOCs) MEASURED

Electron Impact Ionization	Electron Capture Negative Ionization
PAHs: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene **Pesticides and degradation products:** o,p'-DDT*, p,p'-DDT, o,p'-DDD*, p,p'-DDD, o,p'-DDE, p,p'-DDE, Diazinon, Demeton S, Ethion, Etradiazole, Malathion*, Parathion and Methyl - Parathion, Phorate, Metolachlor*, Methoxychlor, Acetochlor*, Alachlor, Prometon, Pebulate, EPTC, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine **Surrogates:** d_{10}-Fluorene, d_{10}-Phenanthrene, d_{10}-Pyrene, d_{12}-Triphenylene, d_{12}-Benzo[a]pyrene, d_{12}-Benzo[ghi]perylene, d_{14}-EPTC, d_{10}-Phorate, d_5-Atrazine, d_{10}-Diazinon, d_7-Malathion, d_{10}-Parathion, d_8-p,p'-DDE, d_8-p,p'-DDT, d_6-Methyl Parathion, d_{13}-Alachlor, d_{11}-Acetochlor **Internal Standards:** d_{10}-Acenaphthene, d_{10}-Fluoranthene, d_{12}-Benzo[k]fluoranthene	**PCBs:** PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 118 (2,3',4,4',5-Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5'-Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl), PCB 183* (2,2',3,4,4',5',6-Heptachlorobiphenyl), and PCB 187 (2,2',3,4',5,5',6-Heptachlorobiphenyl) **Pesticides and degradation products:** Hexachlorocyclohexanes (HCH) - α*, β, γ-(lindane), and δ, Chlordanes – cis*, trans*, oxy*, Nonachlor – cis, trans, Heptachlor*, Heptachlor Epoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorothalonil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Triallate, Mirex **Polybrominated Diphenyl Ethers** **Surrogates:** $^{13}C_{12}$ PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), $^{13}C_{12}$ PCB 180 (2,2', 3,4,4',5,5'-Heptachlorobiphenyl), d_{10} - Chlorpyrifos, $^{13}C_6$-HCB, d_6-γ-HCH, d_4-Endosulfan I, d_4-Endosulfan II **Internal Standards:** d_{14}-Trifluralin

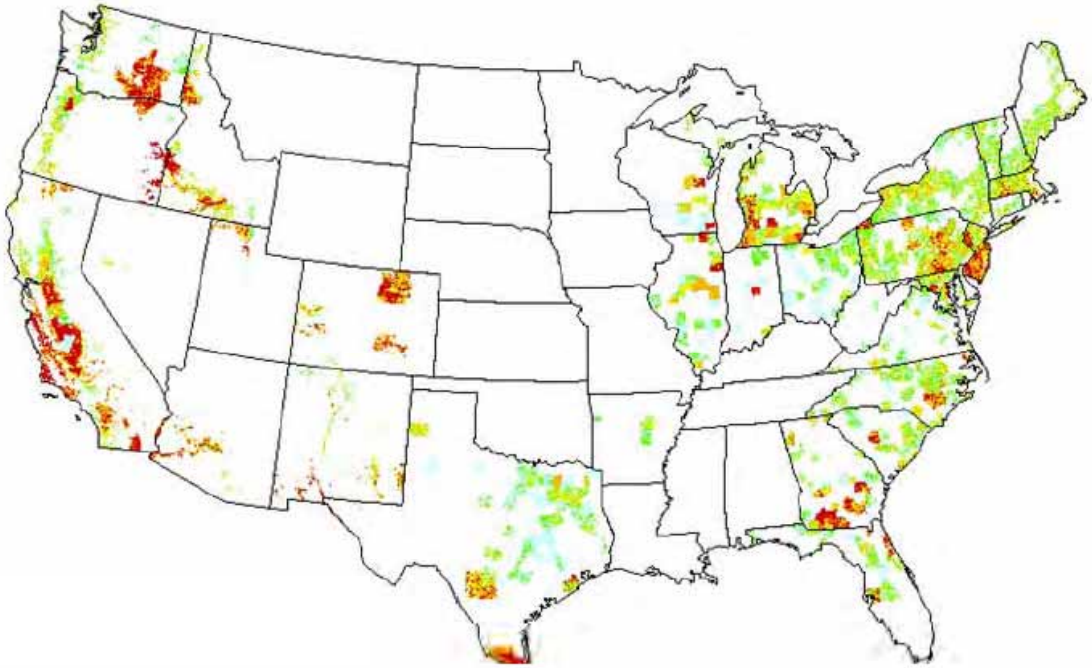
ENDOSULFAN

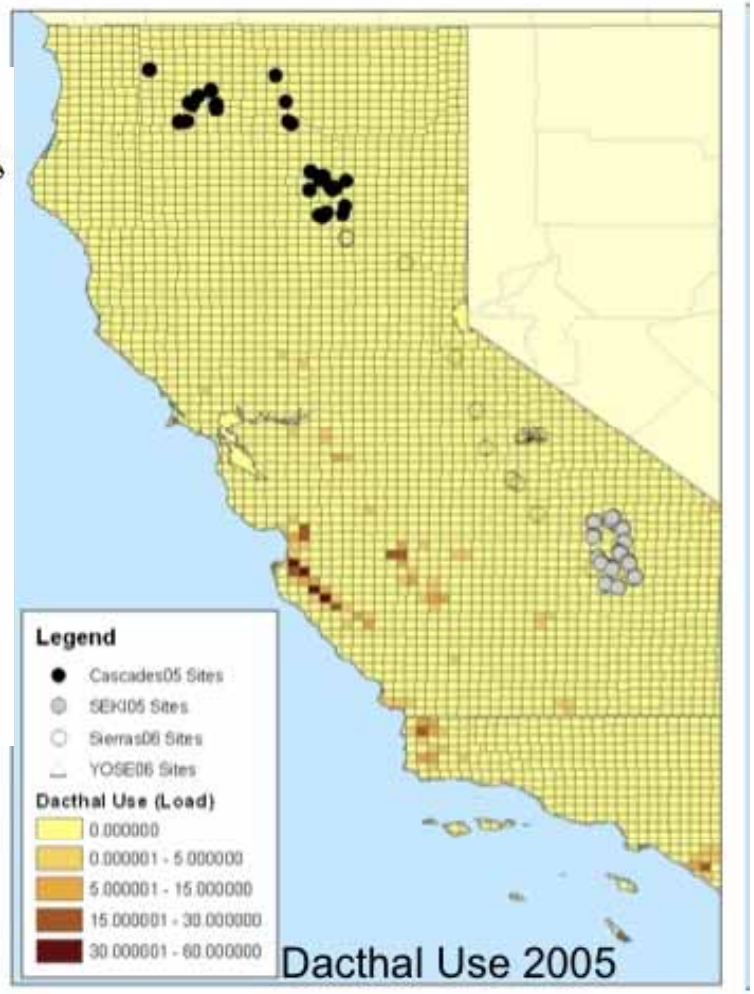




- Chlorinated Insecticide first used in 1954
- Nationwide Use: cotton, tomatoes, potatoes, apples, tobacco, pears, cucumbers, lettuce, green beans, squash

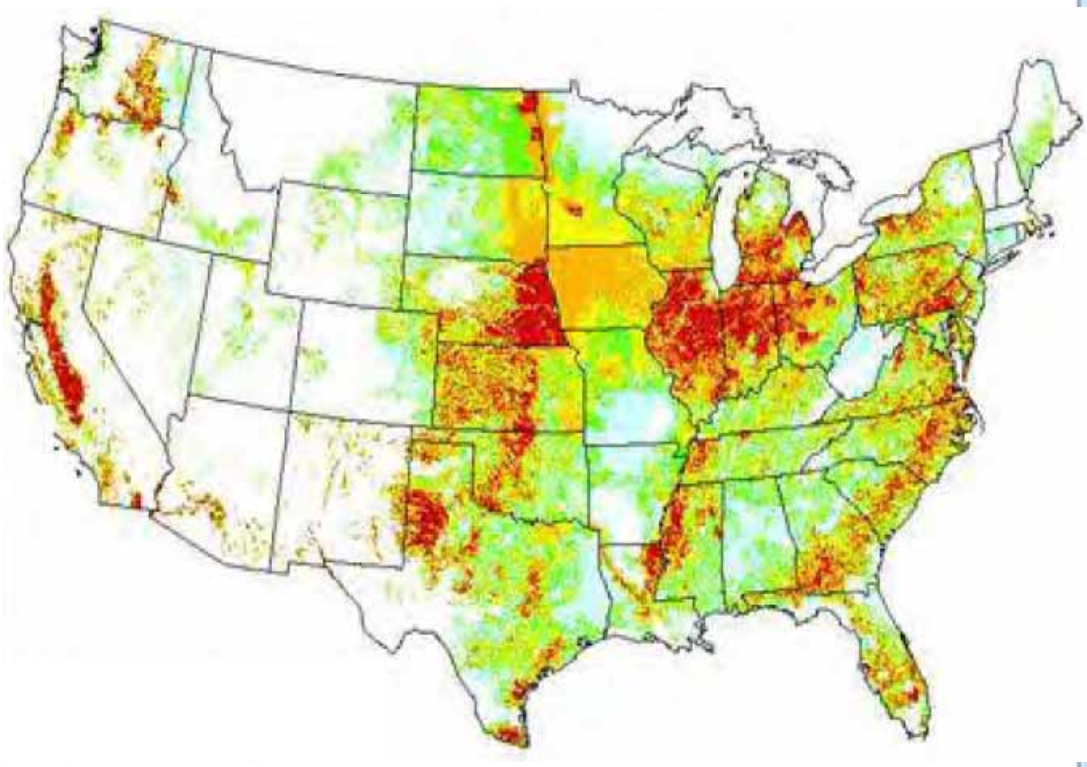
DACTHAL (DCPA)

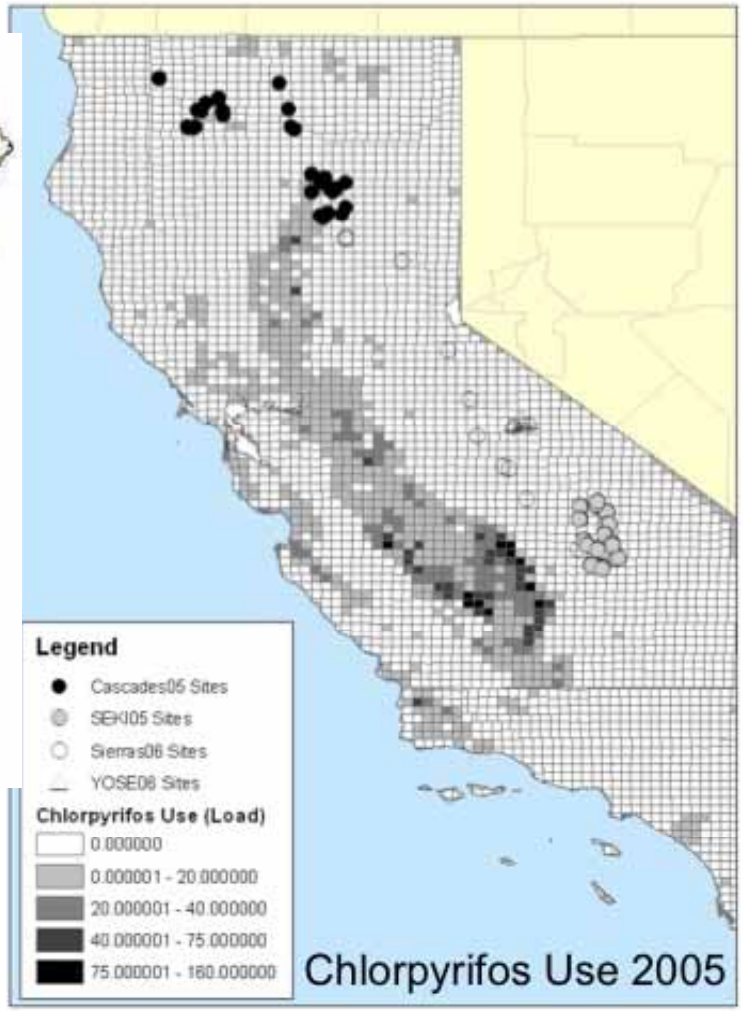




- Herbicide first used in 1955
- Nationwide Use: onions, broccoli, sod, cabbage, cauliflower, squash, collards, dry beans, strawberries

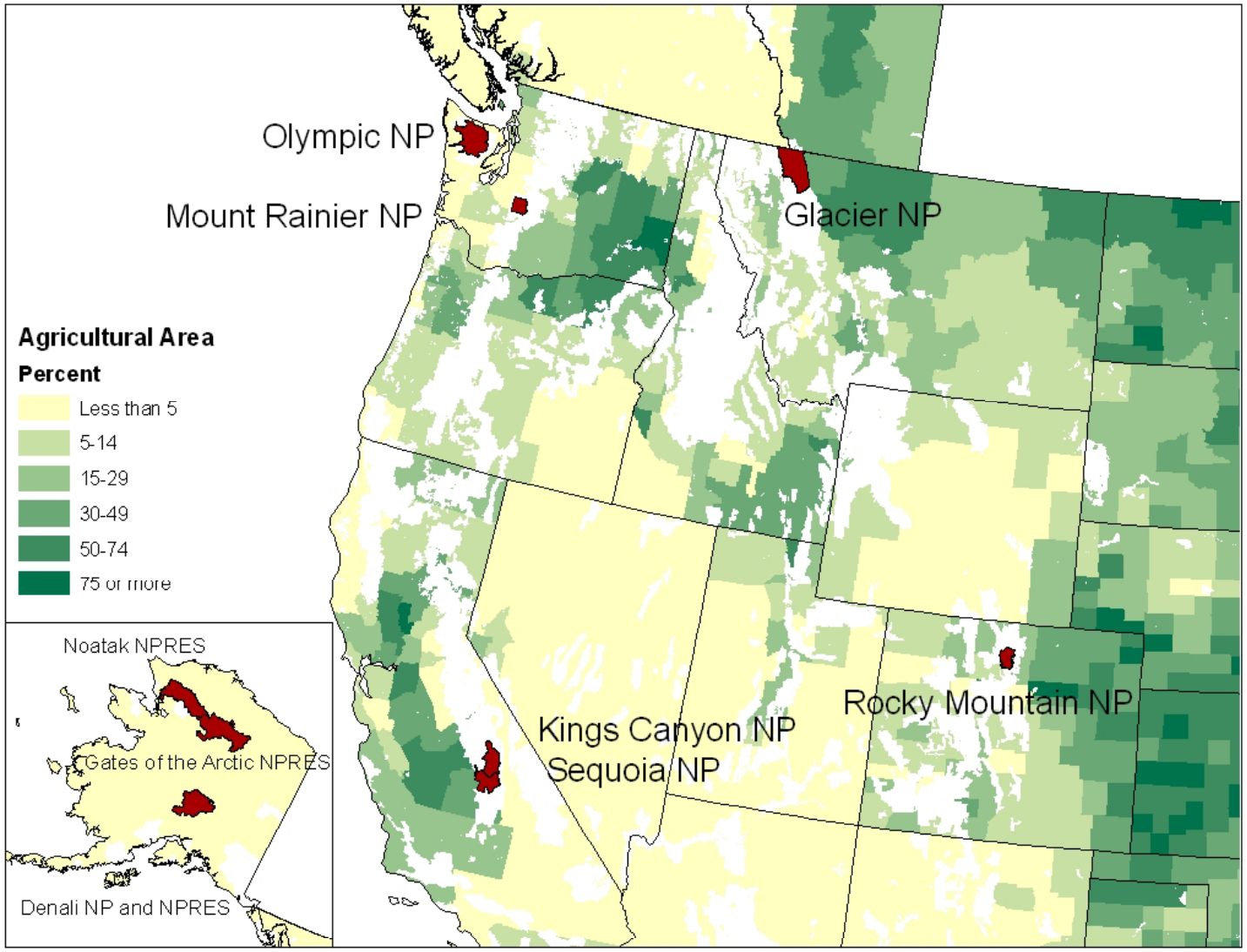
CHLORPYRIFOS





- Insecticide first used in 1965
- Nationwide Use: corn, cotton, hay, wheat, citrus, apples, peanuts, soybeans, pecans, tobacco

CROPLAND INTENSITY

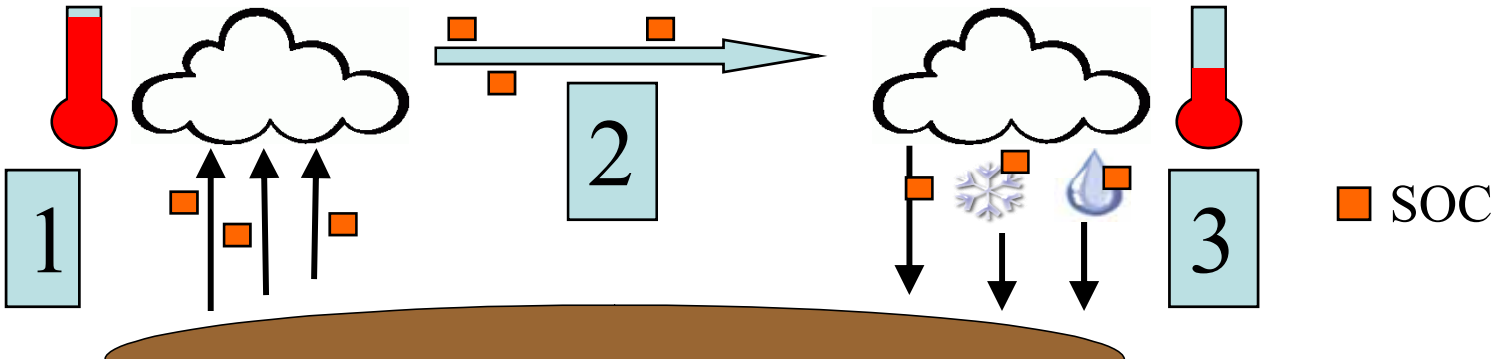


An indication of where historic use pesticides were used

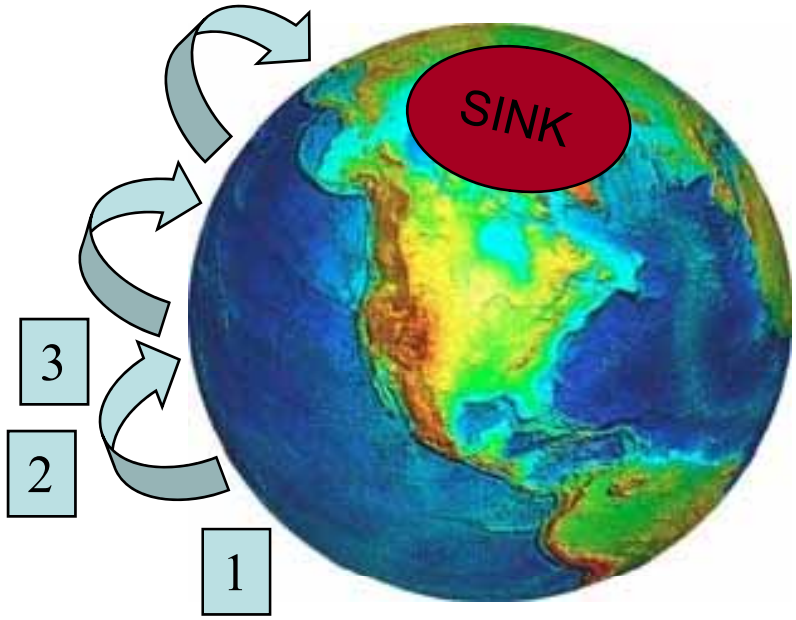
POPULATION DENSITY

An indication of where PAHs and PBDEs are emitted

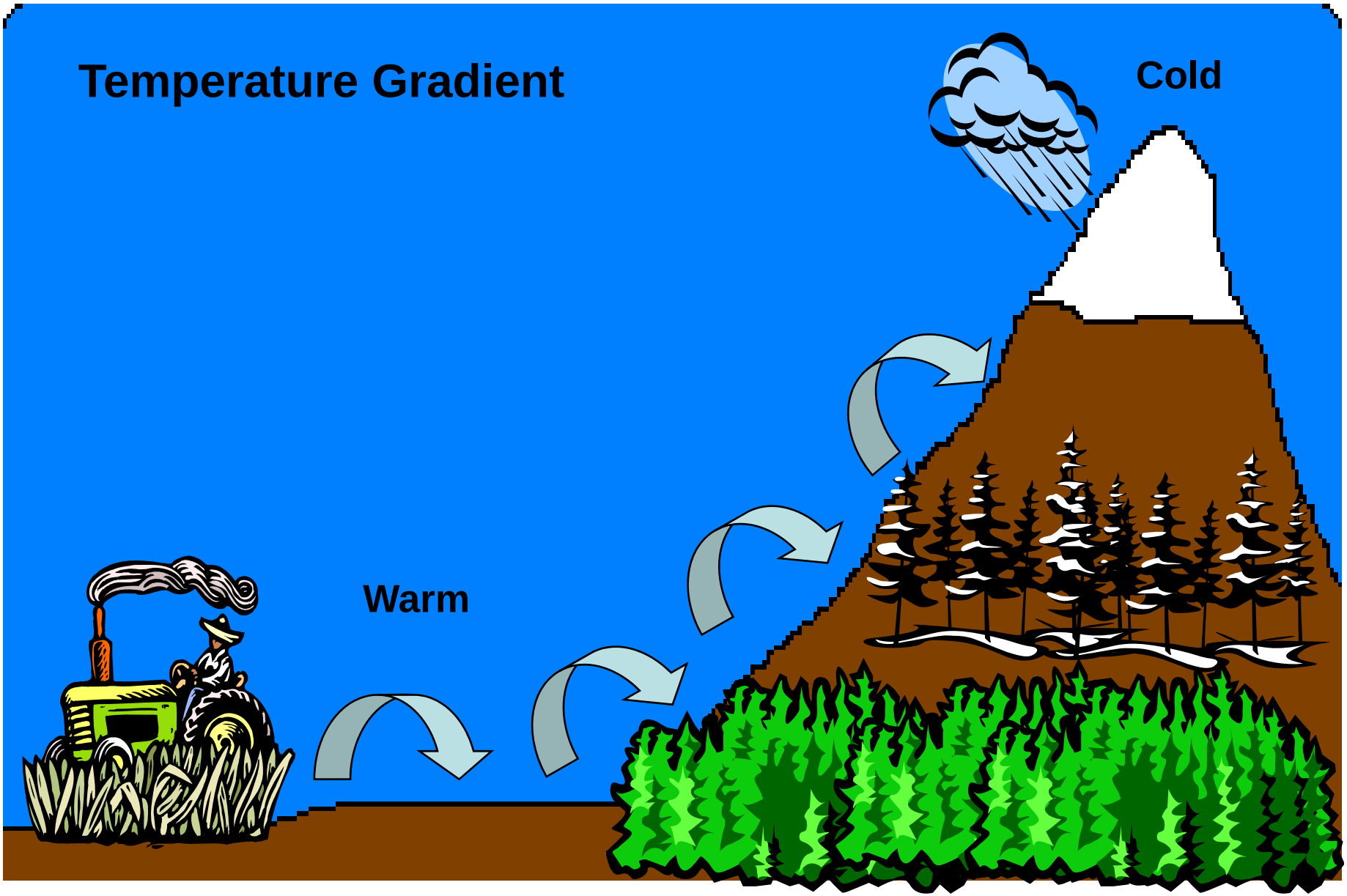
GLOBAL DISTILLATION or COLD CONDENSATION



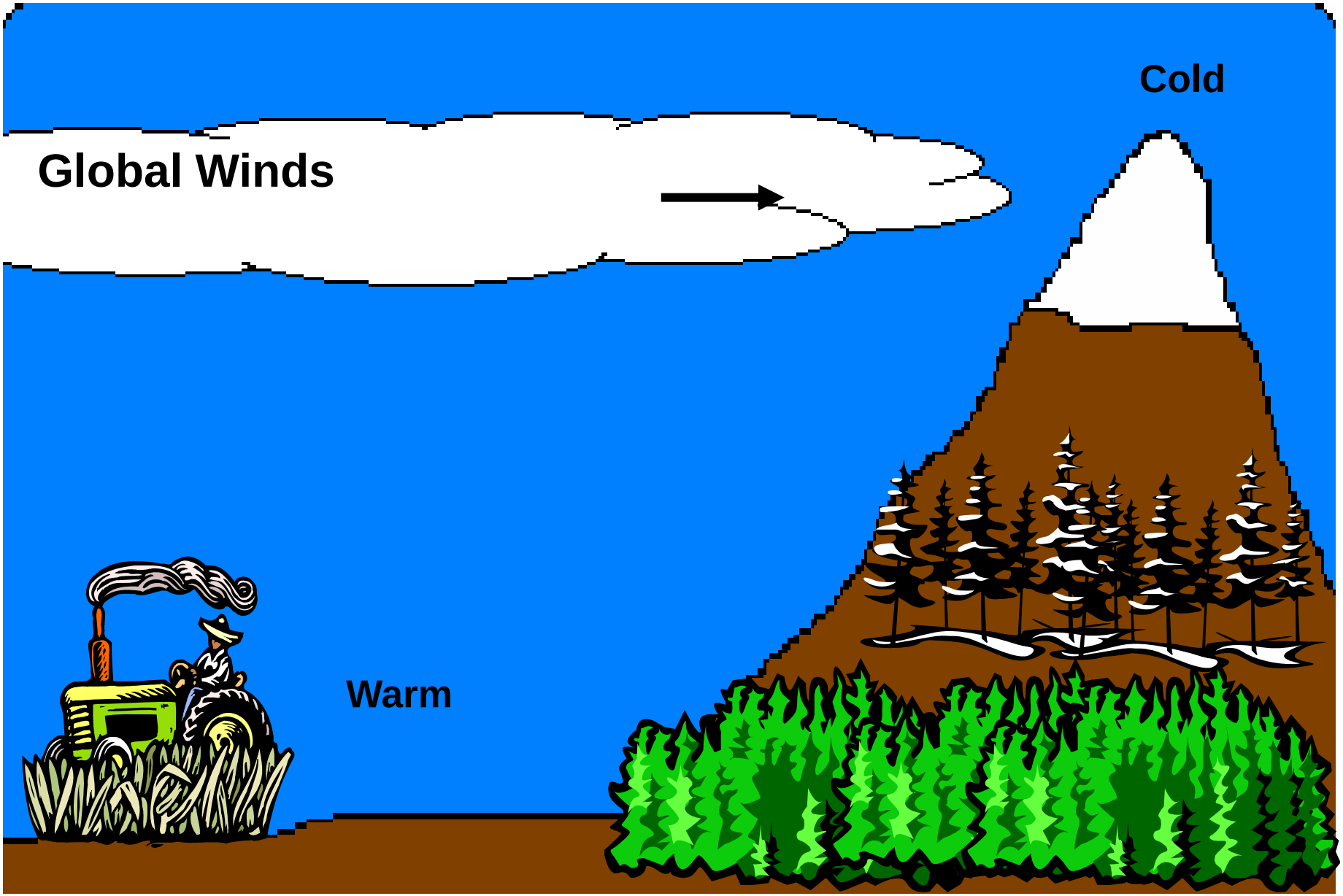
1. At warm temps, semi-volatile organic compounds (SOCs) volatilize into the atmosphere.
2. SOCs are transported in the atmosphere.
3. At cold temps, SOCs condense and undergo deposition.



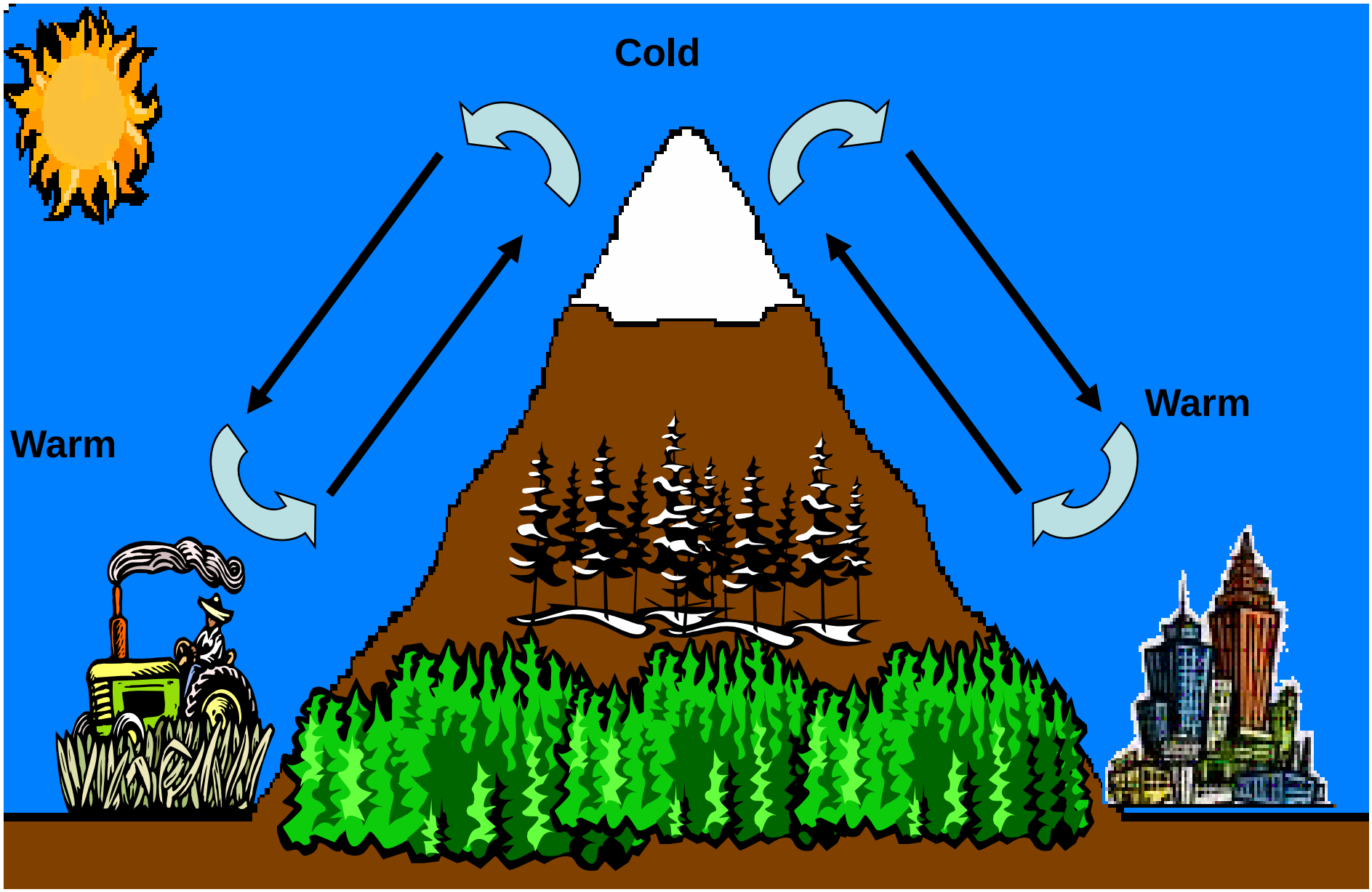
OROGRAPHIC COLD TRAPING



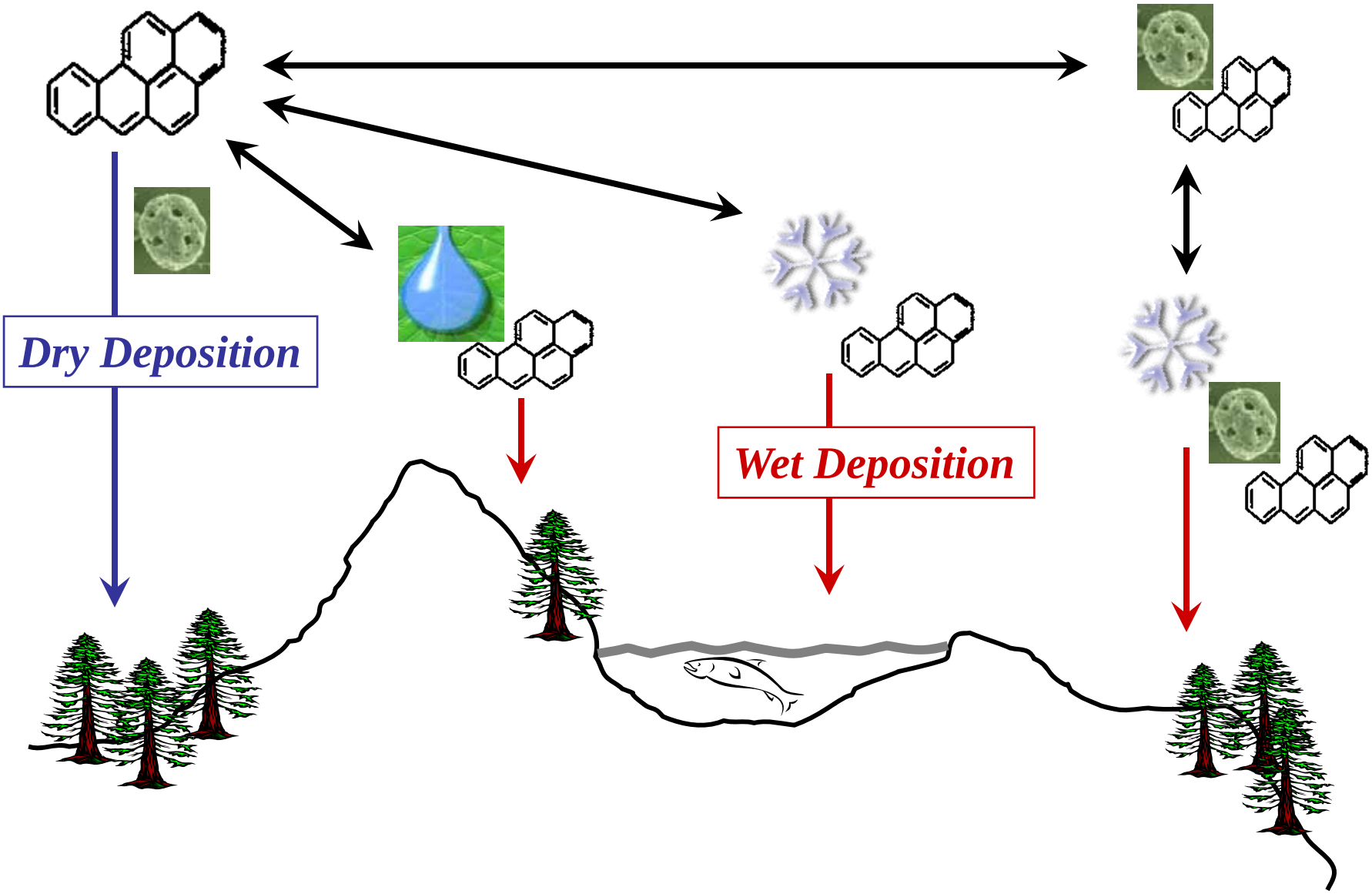
LONG-RANGE TRANSPORT AND DEPOSITION



REGIONAL/LOCAL TRANSPORT AND DEPOSITION



IMPORTANCE of SNOW in SCAVENGING POPs



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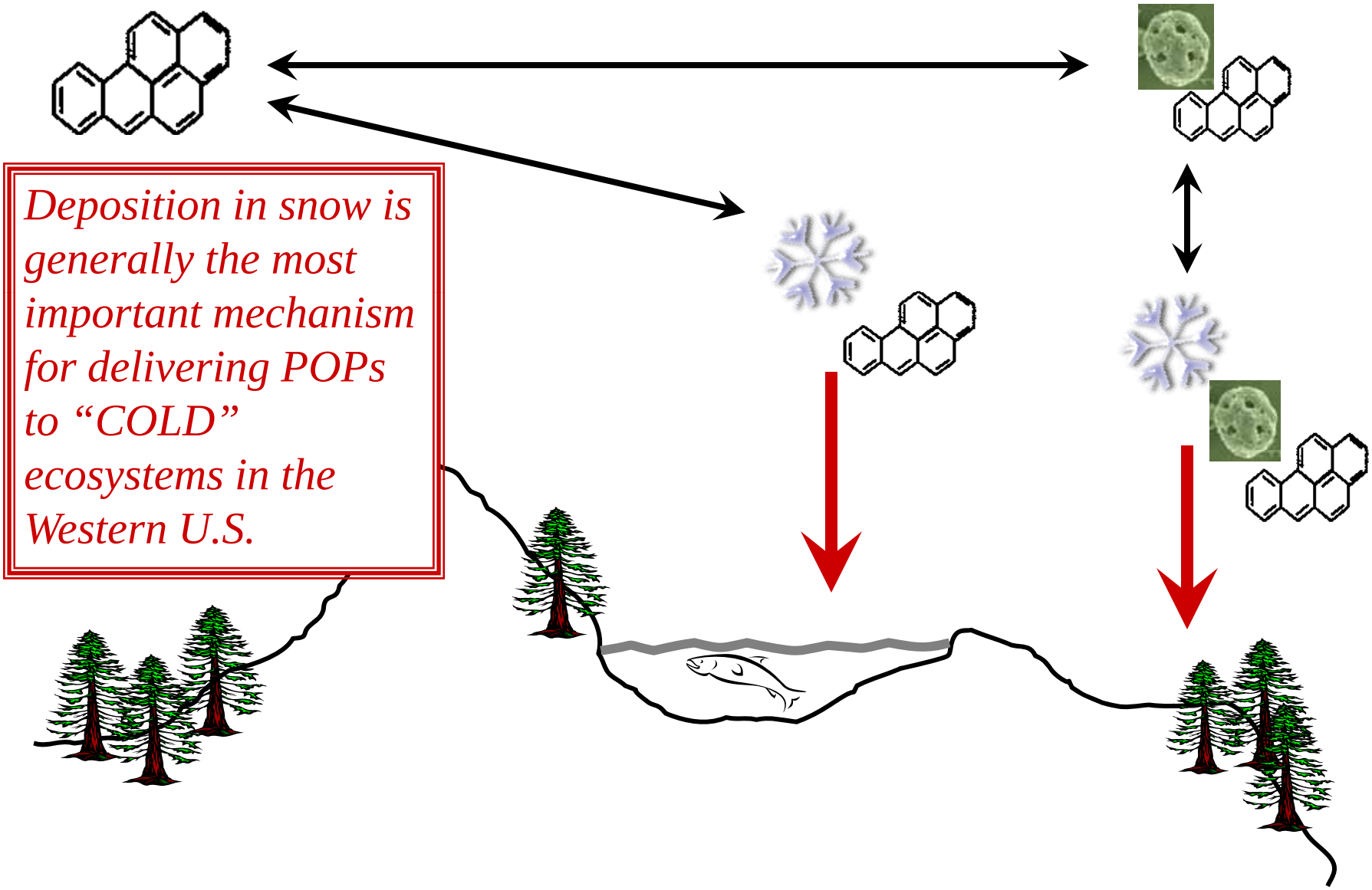
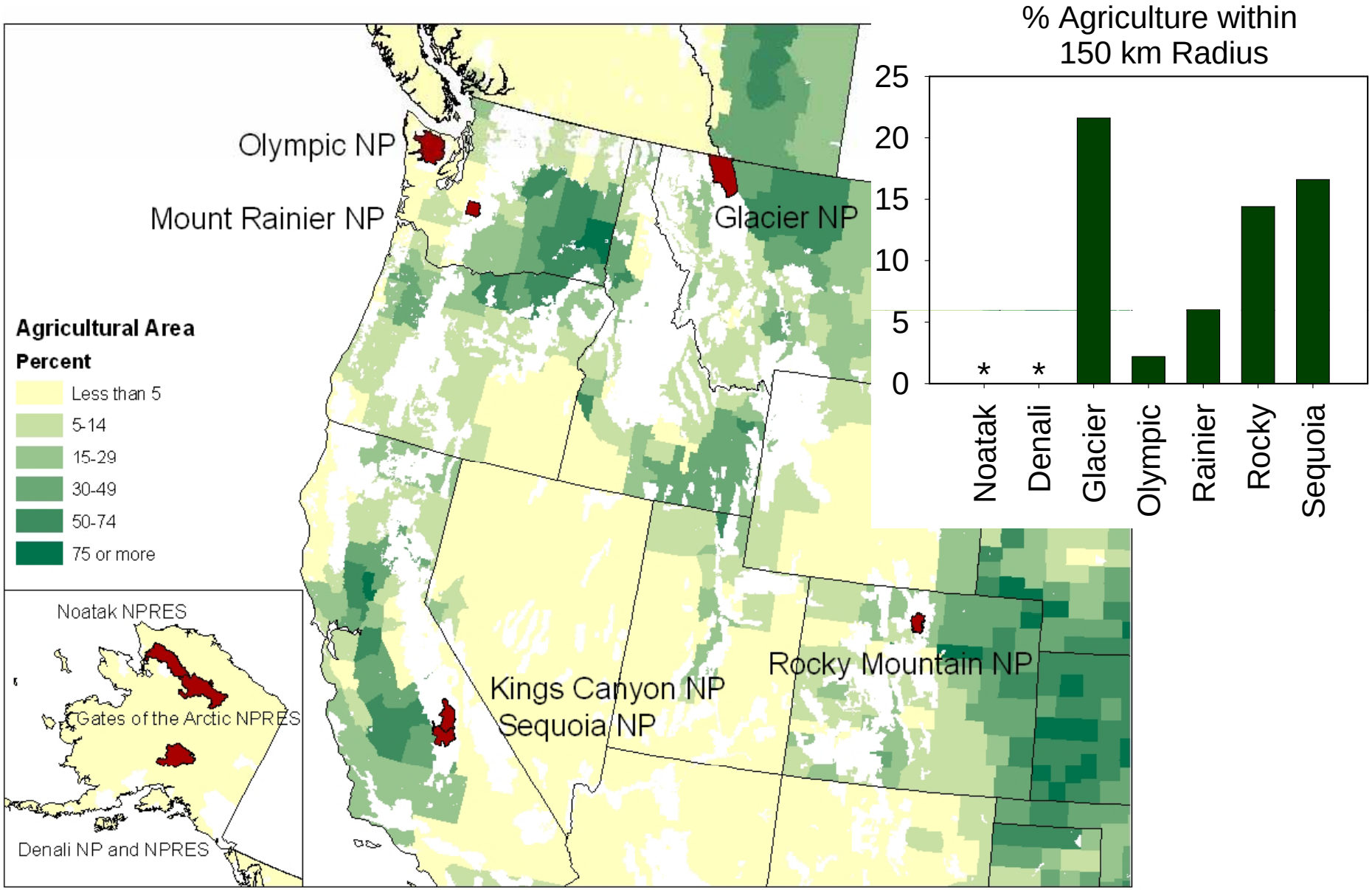
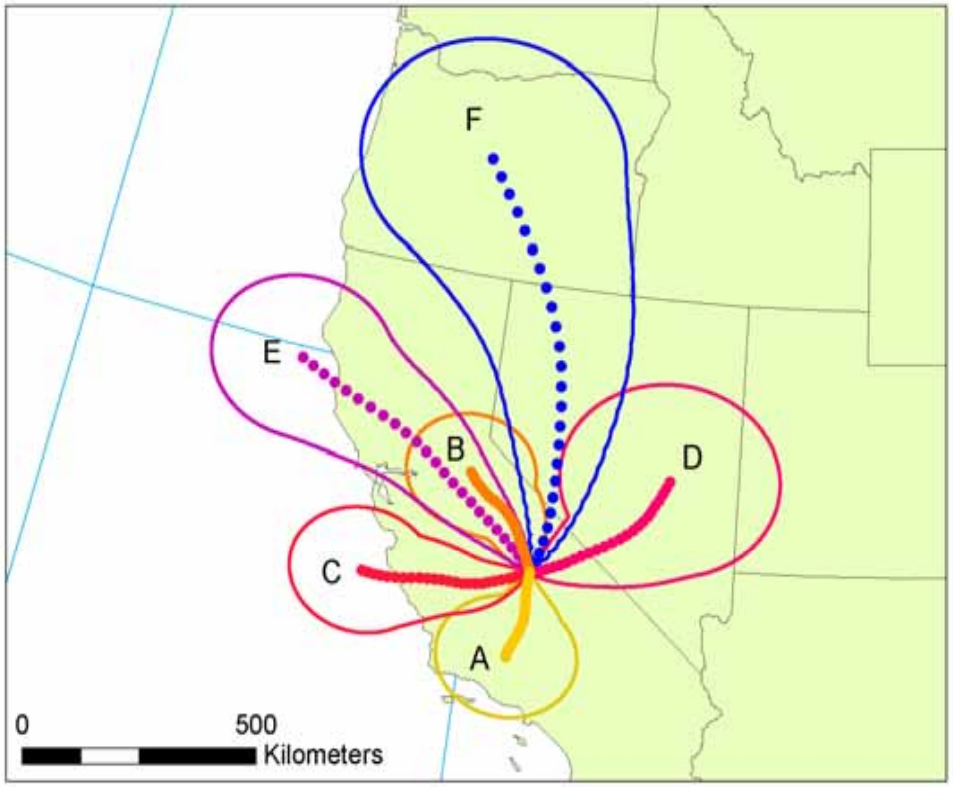
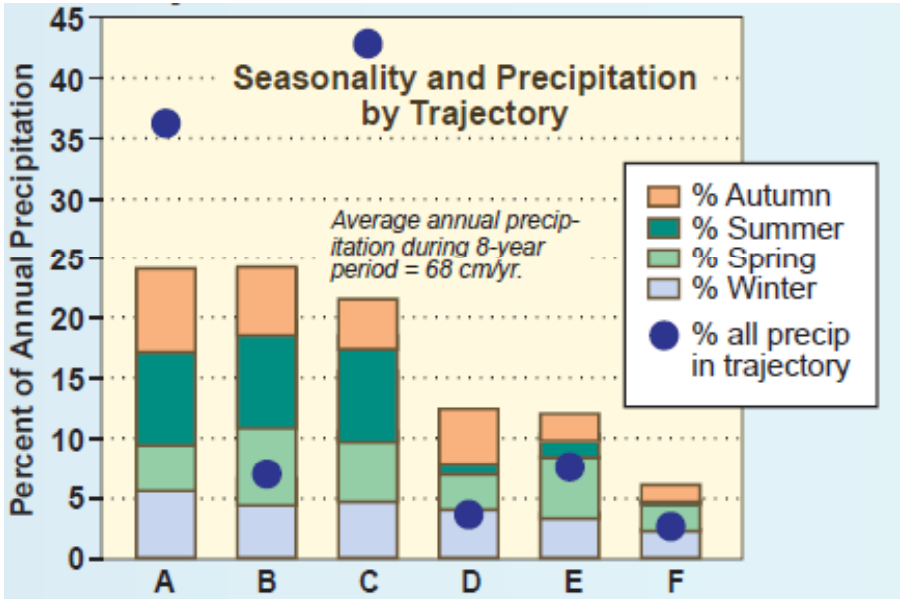


Agricultural Lands in the Western US and Canada



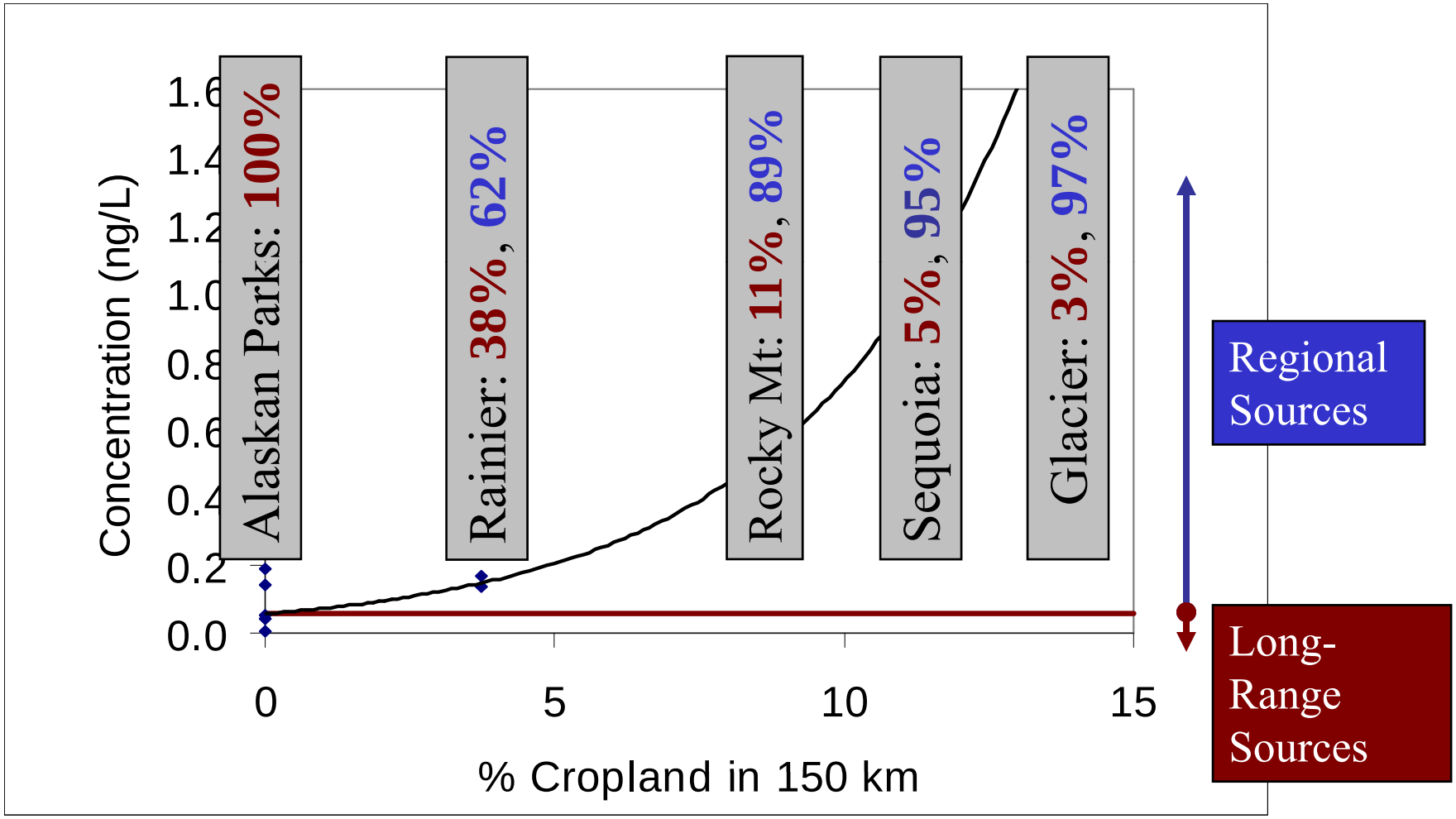
One day “Airshed” for Sequoia



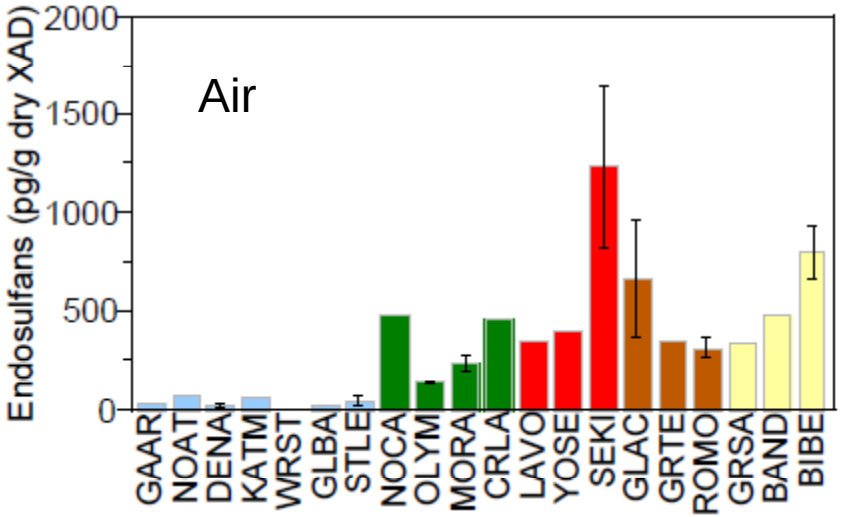


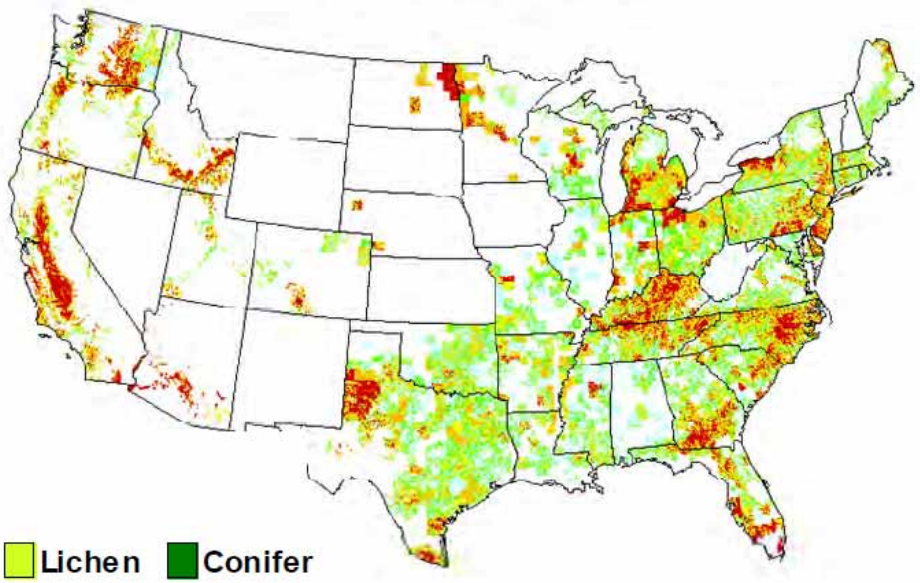
The “Airshed” for the primary WACAP parks were calculated for 1,5 and 10 days using the NOAA-HYSPLIT model based on the past 8 years of meteorological data. These airsheds show where the air has been within the specified number of days and give useful information on transport of regional pollutants with short lifetimes (e.g. PM 2.5 or haze; see Hafner et al., 2007)

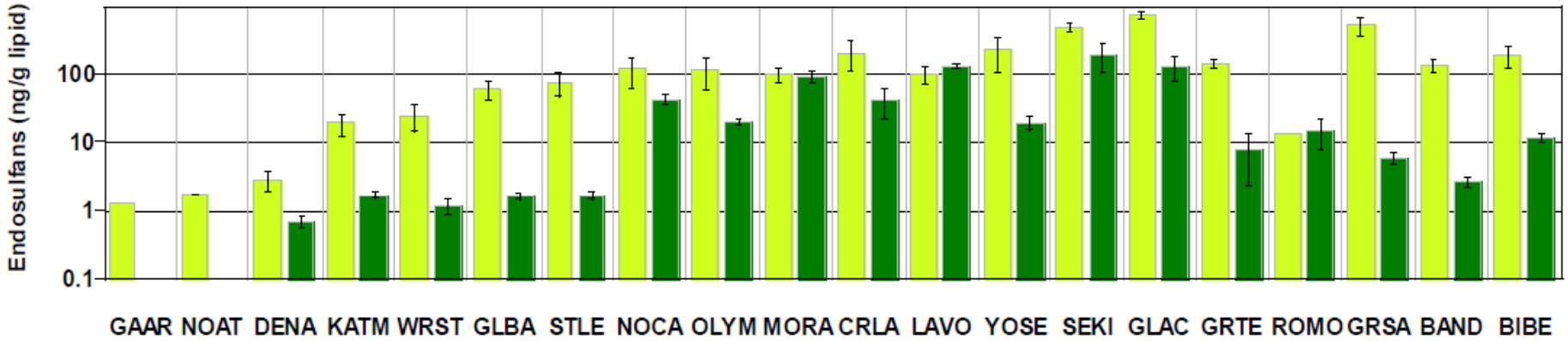
ENDOSULFANS – % Long Range vs. % Regional



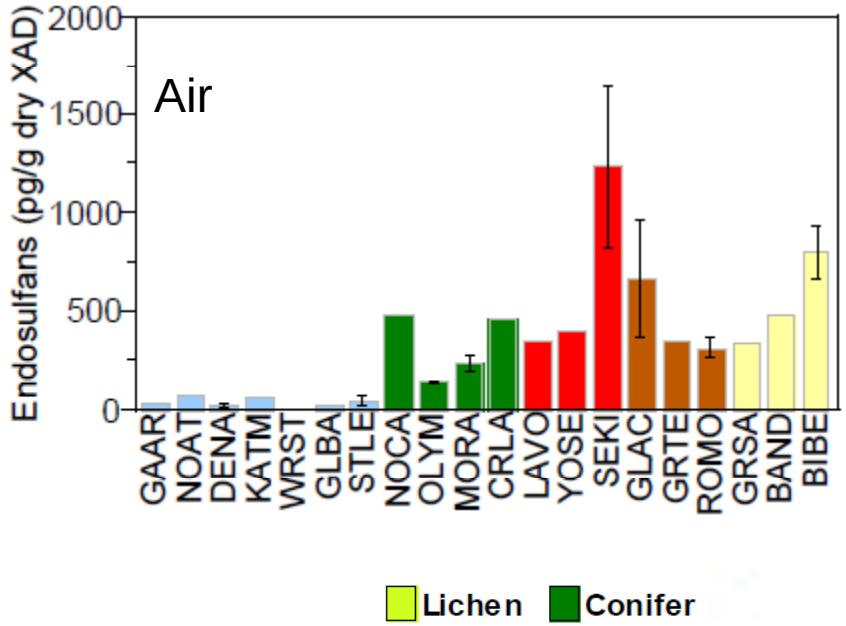
ENDOSULFAN


Air
Endosulfans (pg/g dry XAD)
2000
1500
1000
500
0
GAAR
NOAT
DENA
KATM
WRST
GLBA
STLE
NOCA
OLYM
MORA
CRLA
LAVO
YOSE
SEKI
GLAC
GRTE
ROMO
GRSA
BAND
BIBE


Lichen
Conifer


Endosulfans (ng/g lipid)
100
10
1
0.1
GAAR NOAT DENA KATM WRST GLBA STLE NOCA OLYM MORA CRLA LAVO YOSE SEKI GLAC GRTE ROMO GRSA BAND BIBE

ENDOSULFAN


Air
Endosulfans (pg/g dry XAD)
2000
1500
1000
500
0
GAAR
NOAT
DENA
KATM
WRST
GLBA
STLE
NOCA
OLYM
MORA
CRLA
LAVO
YOSE
SEKI
GLAC
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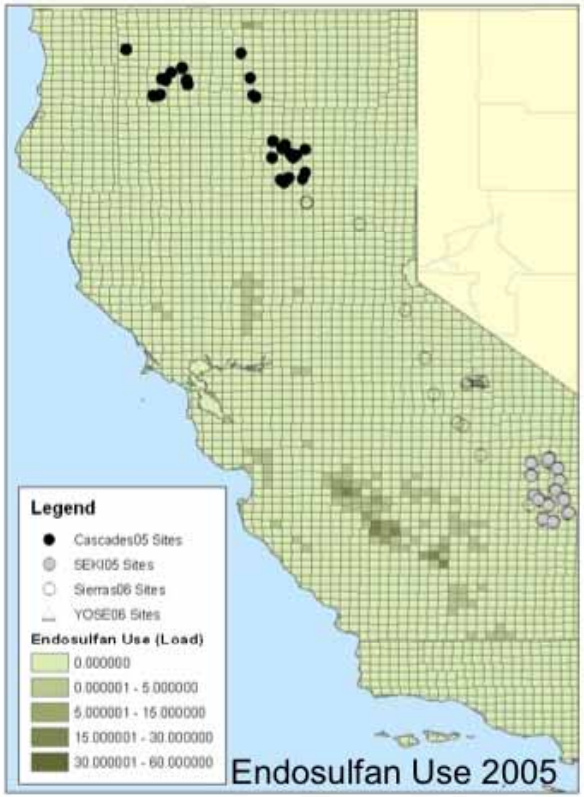
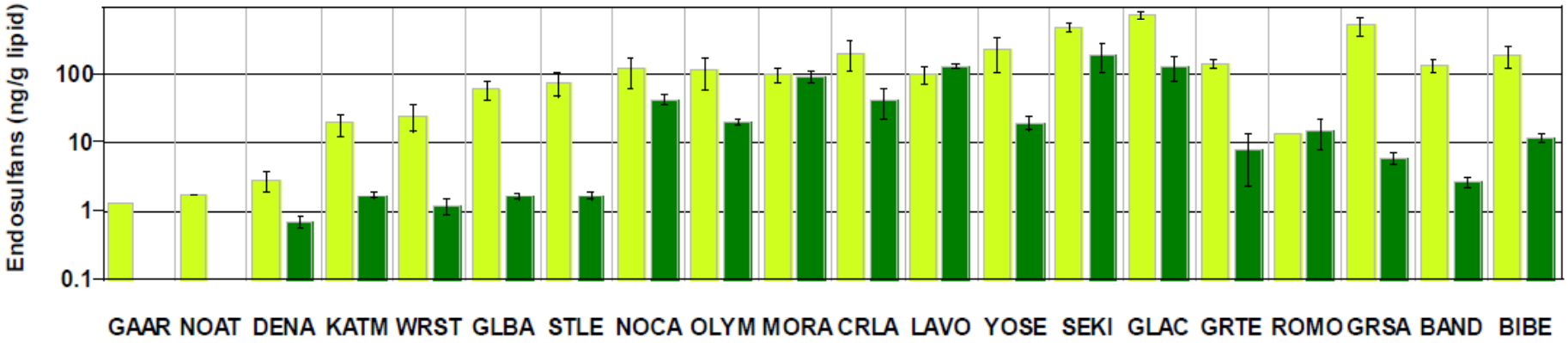
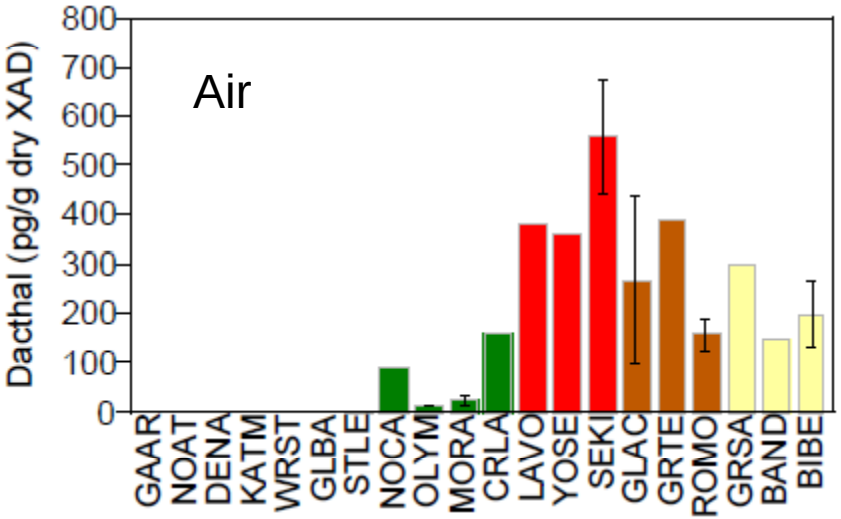
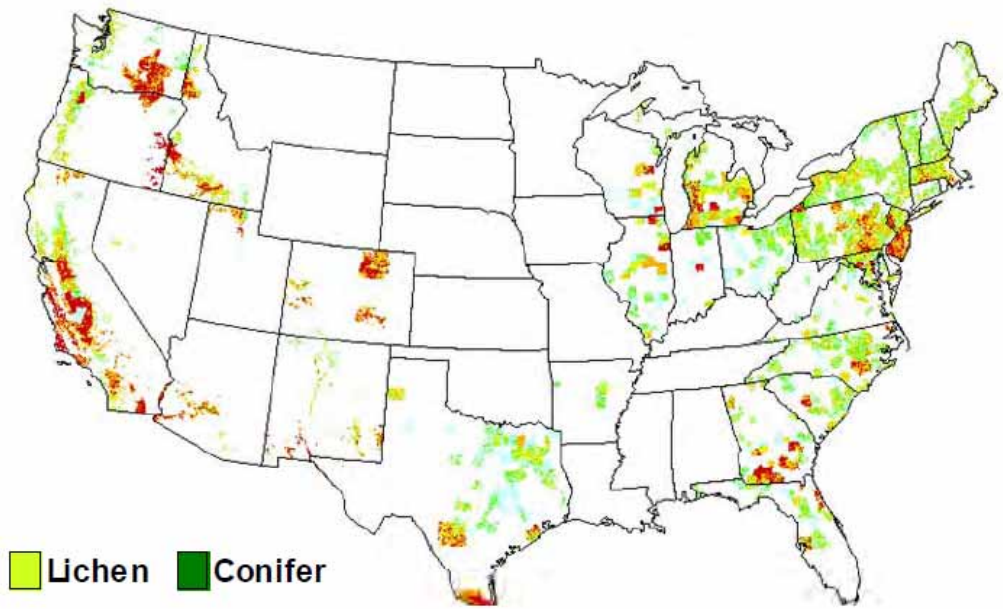
ROMO
GRSA
BAND
BIBE
Lichen
Conifer

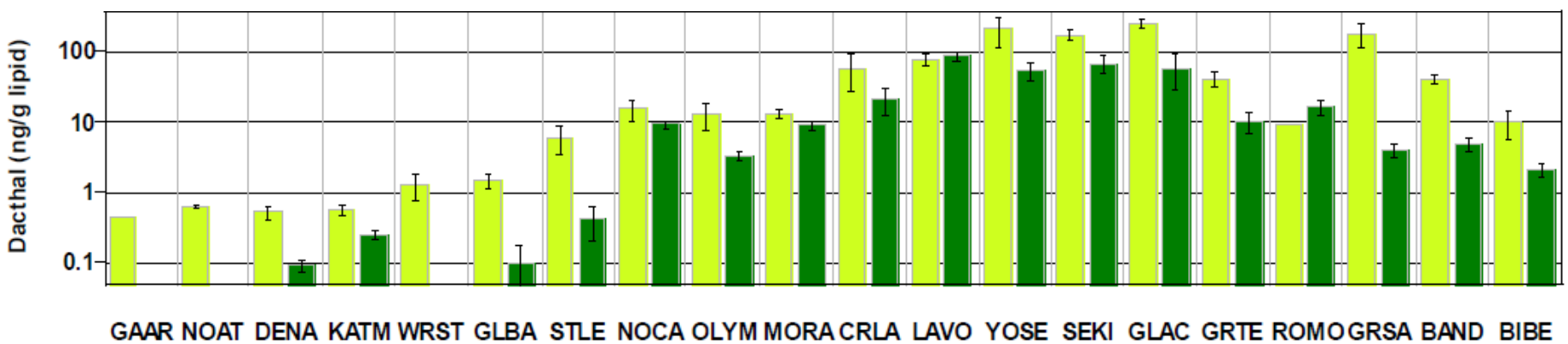

Legend
Cascades05 Sites
SEKI05 Sites
Sierras06 Sites
YOSE06 Sites
Endosulfan Use (Load)
0.000000
0.000001 - 5.000000
5.000001 - 15.000000
15.000001 - 30.000000
30.000001 - 60.000000
Endosulfan Use 2005


Endosulfans (ng/g lipid)
100
10
1
0.1
GAAR NOAT DENA KATM WRST GLBA STLE NOCA OLYM MORA CRLA LAVO YOSE SEKI GLAC GRTE ROMO GRSA BAND BIBE

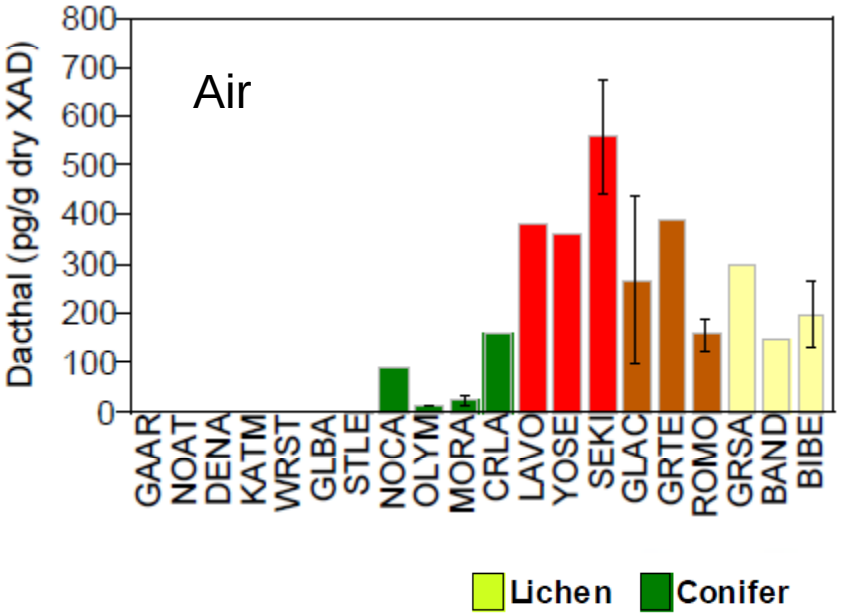
DACTHAL (DCPA)

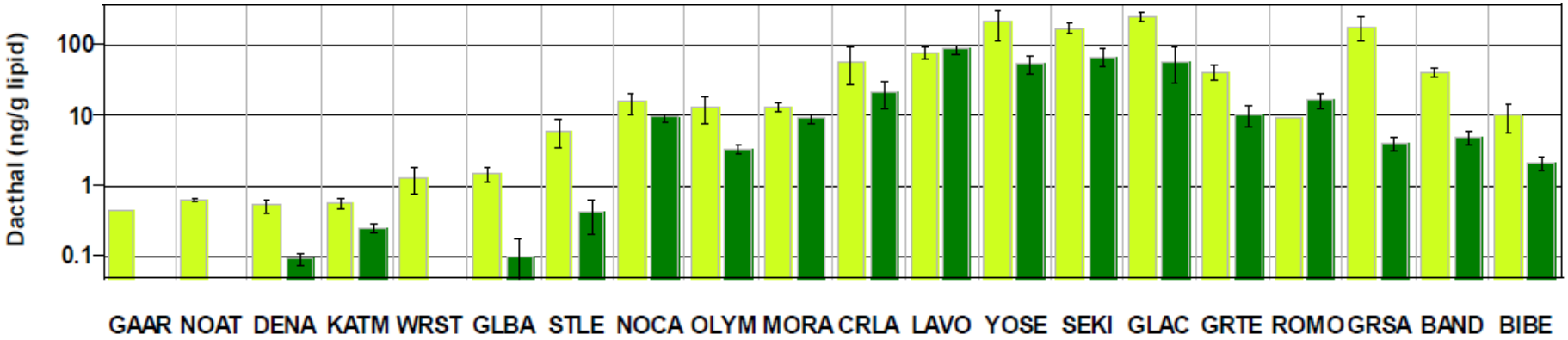




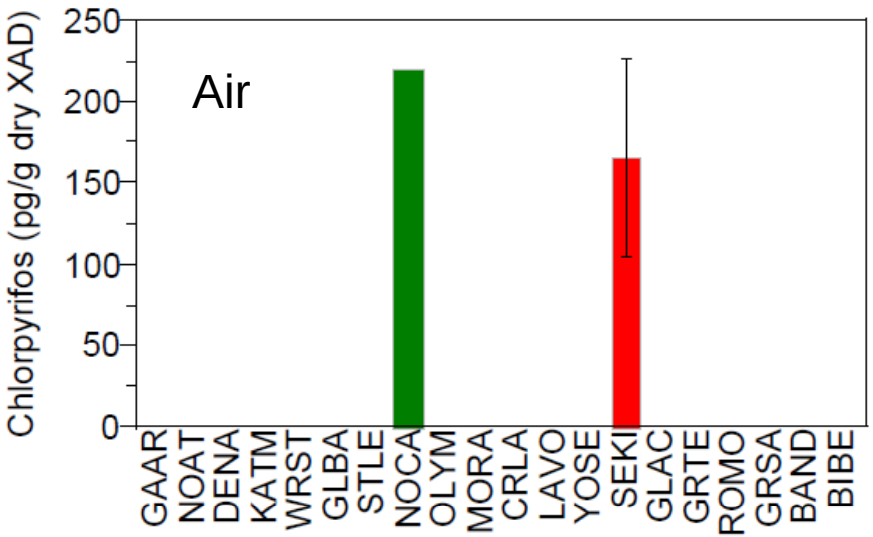


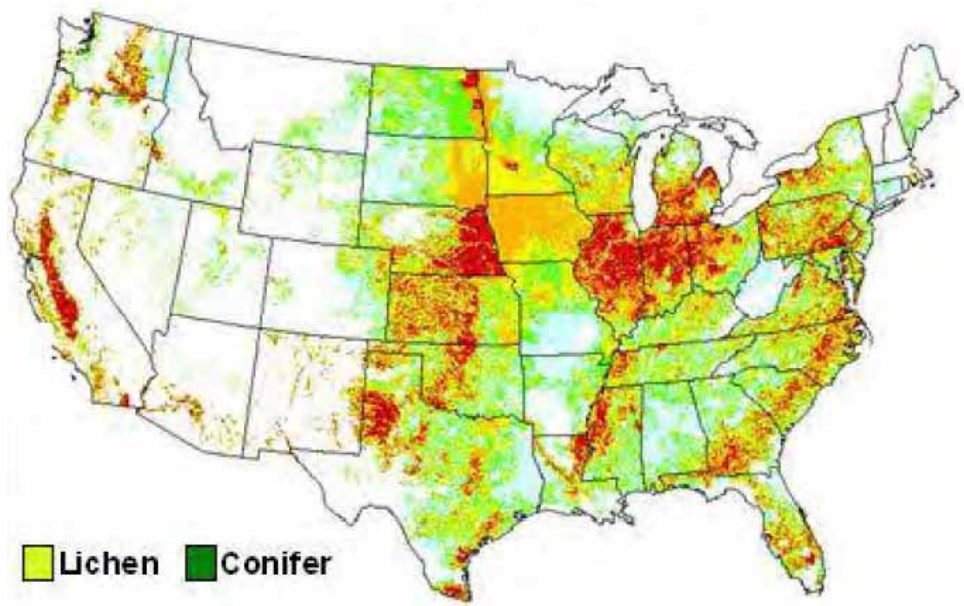
DACTHAL (DCPA)

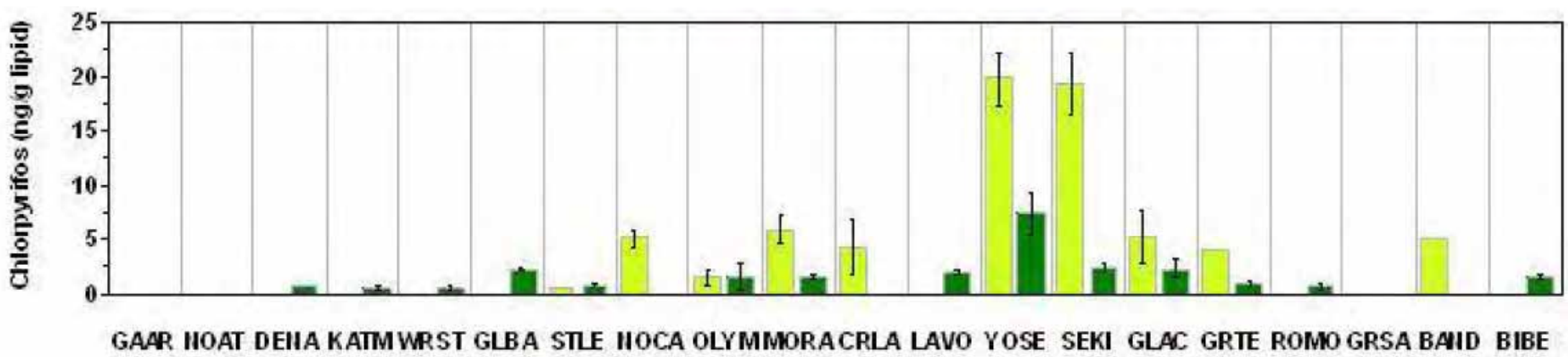




CHLORPYRIFOS







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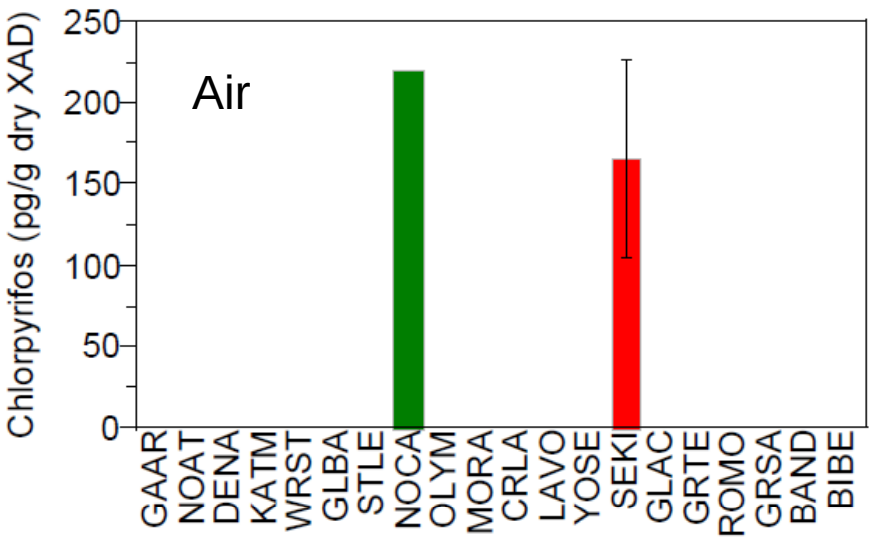
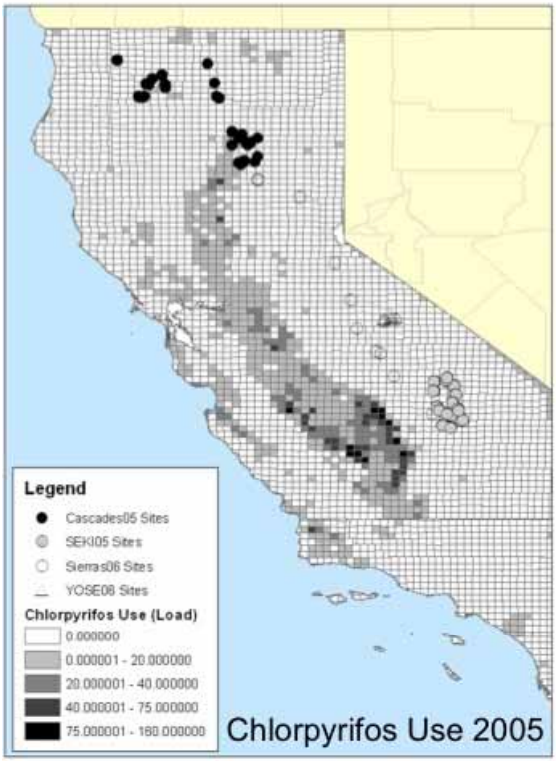
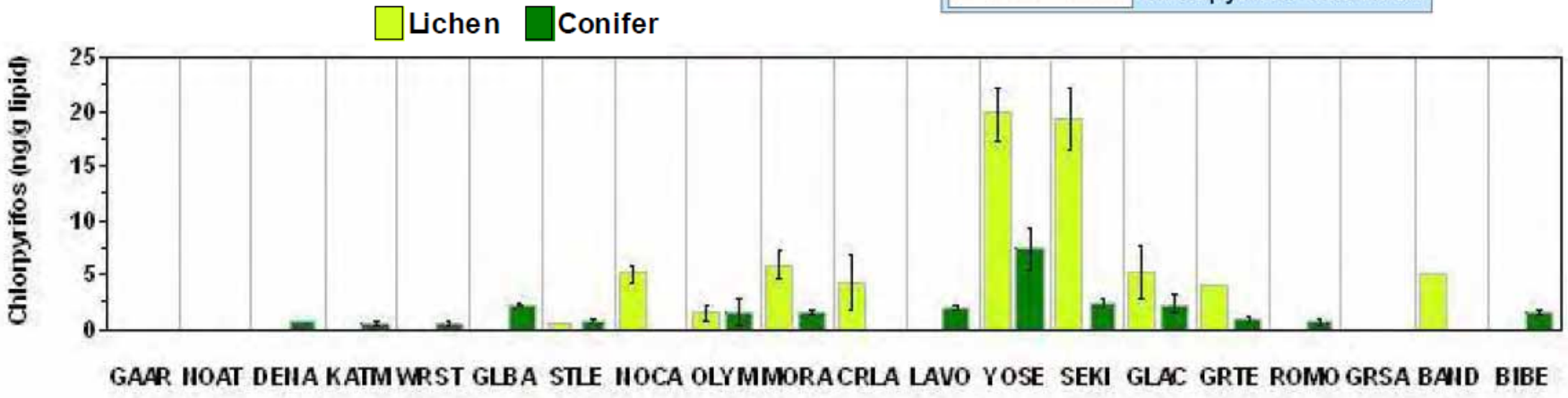
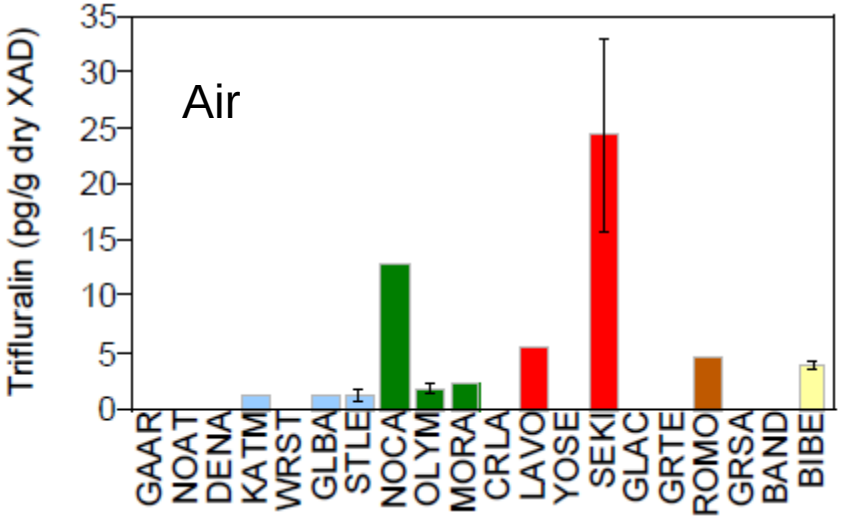
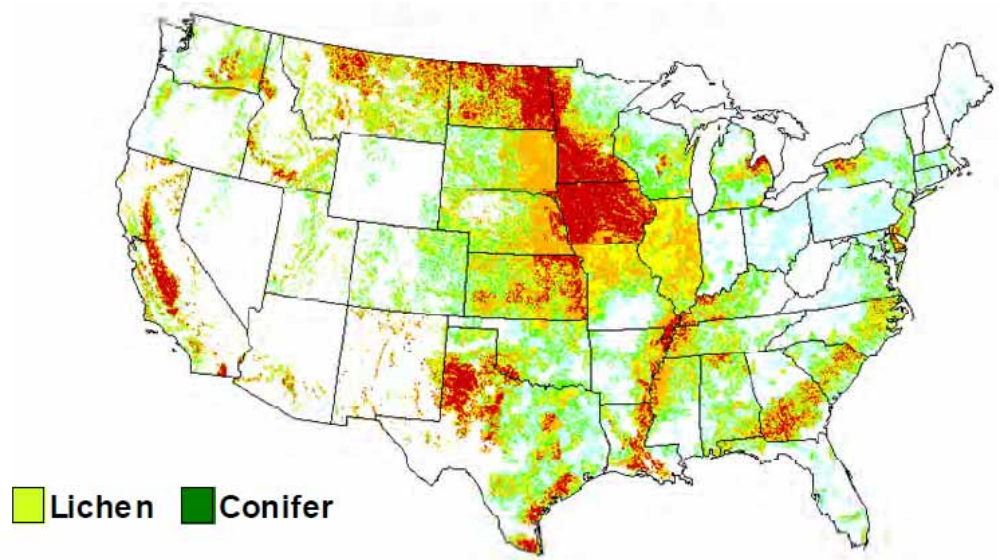


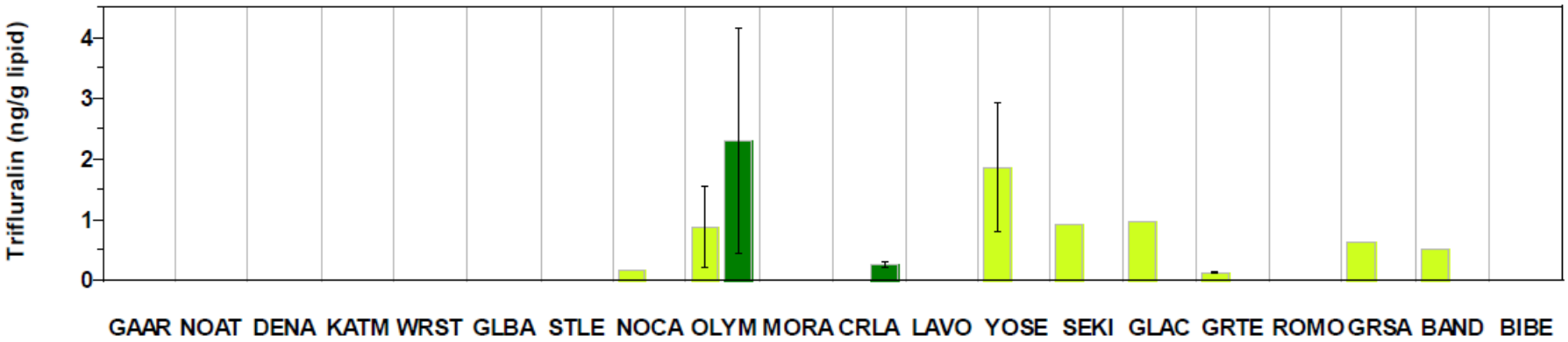




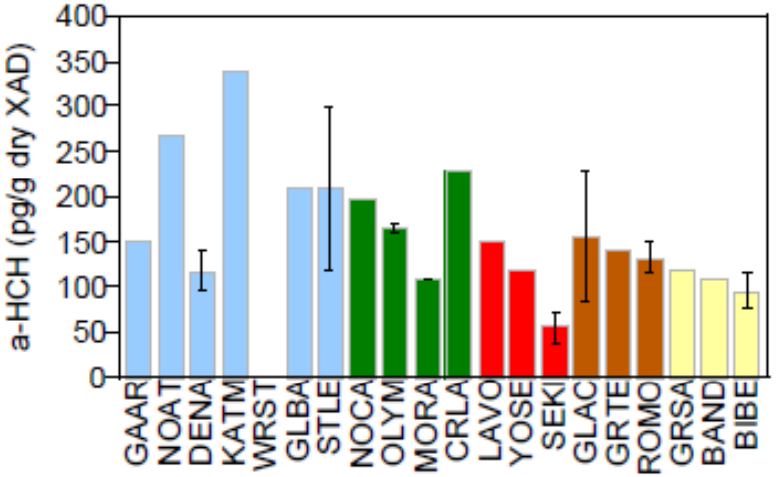
TRIFLURALIN

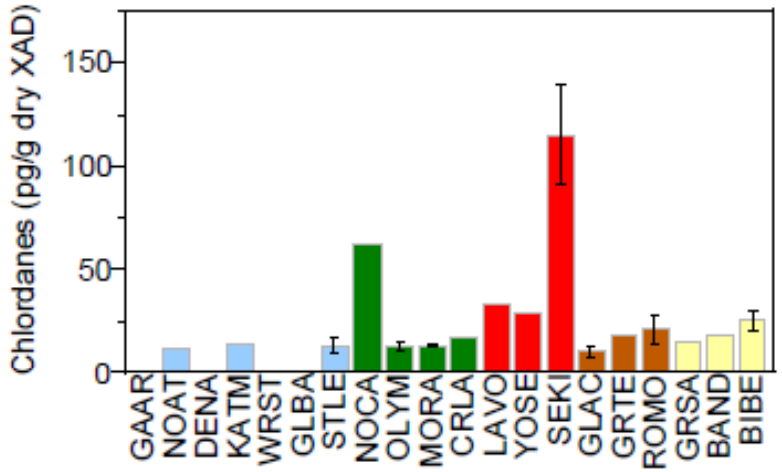






HUPs in AIR


a-HCH (pg/g dry XAD)
400
350
300
250
200
150
100
50
0
GAAR
NOAT
DENA
KATM
WRST
GLBA
STLE
NOCA
OLYM
MORA
CRLA
LAVO
YOSE
SEKI
GLAC
GRTE
ROMO
GRSA
BAND
BIBE


Chlordanes (pg/g dry XAD)
150
100
50
0
GAAR
NOAT
DENA
KATM
WRST
GLBA
STLE
NOCA
OLYM
MORA
CRLA
LAVO
YOSE
SEKI
GLAC
GRTE
ROMO
GRSA
BAND
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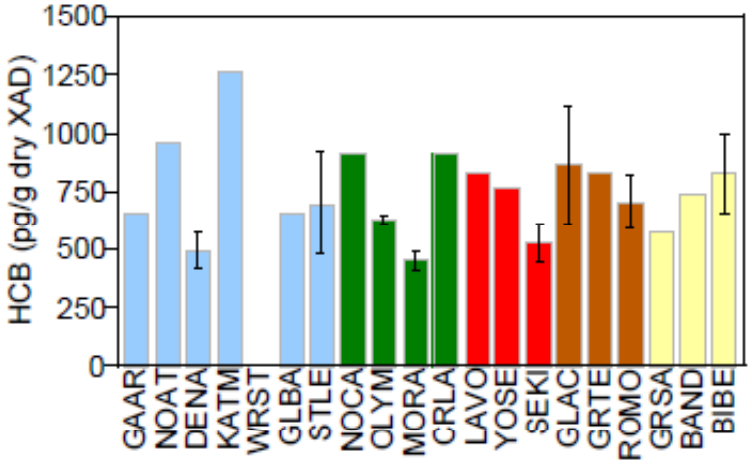
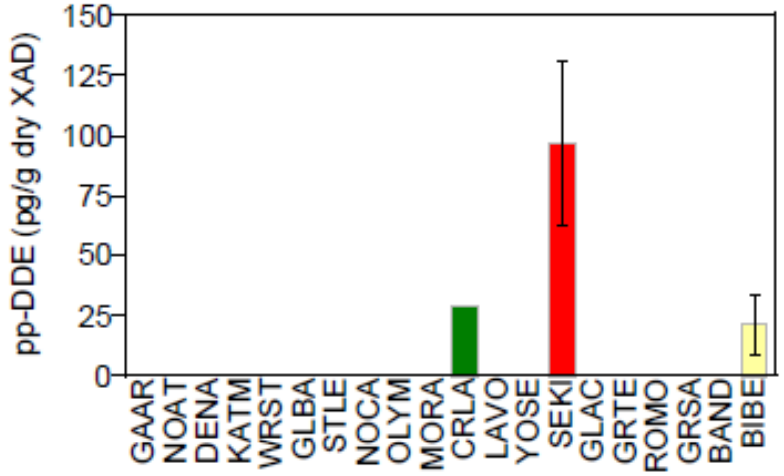
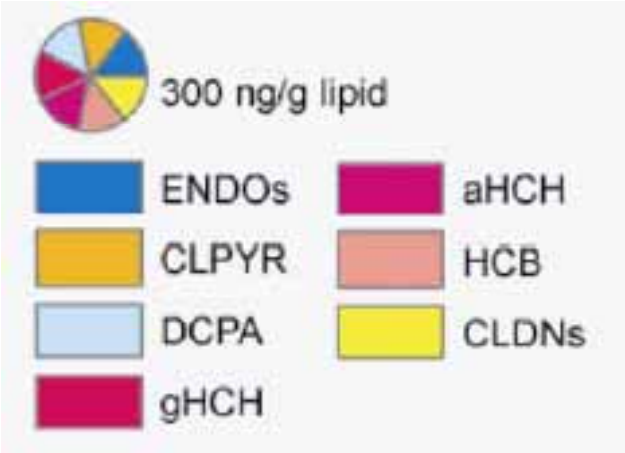
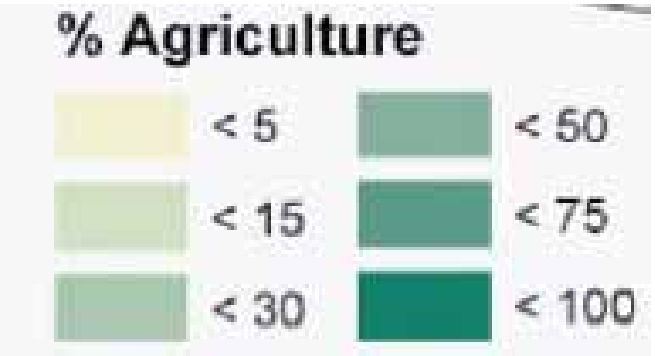
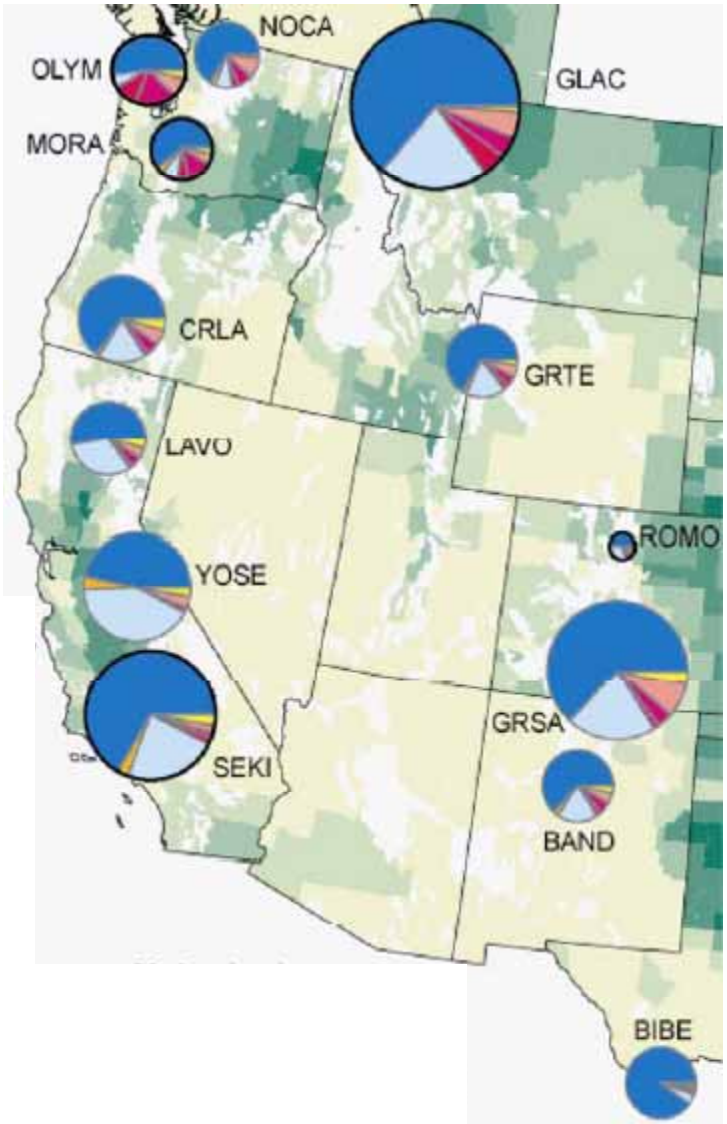

HCB (pg/g dry XAD)
1500
1250
1000
750
500
250
0
GAAR
NOAT
DENA
KATM
WRST
GLBA
STLE
NOCA
OLYM
MORA
CRLA
LAVO
YOSE
SEKI
GLAC
GRTE
ROMO
GRSA
BAND
BIBE


pp-DDE (pg/g dry XAD)
150
125
100
75
50
25
0
GAAR
NOAT
DENA
KATM
WRST
GLBA
STLE
NOCA
OLYM
MORA
CRLA
LAVO
YOSE
SEKI
GLAC
GRTE
ROMO
GRSA
BAND
BIBE

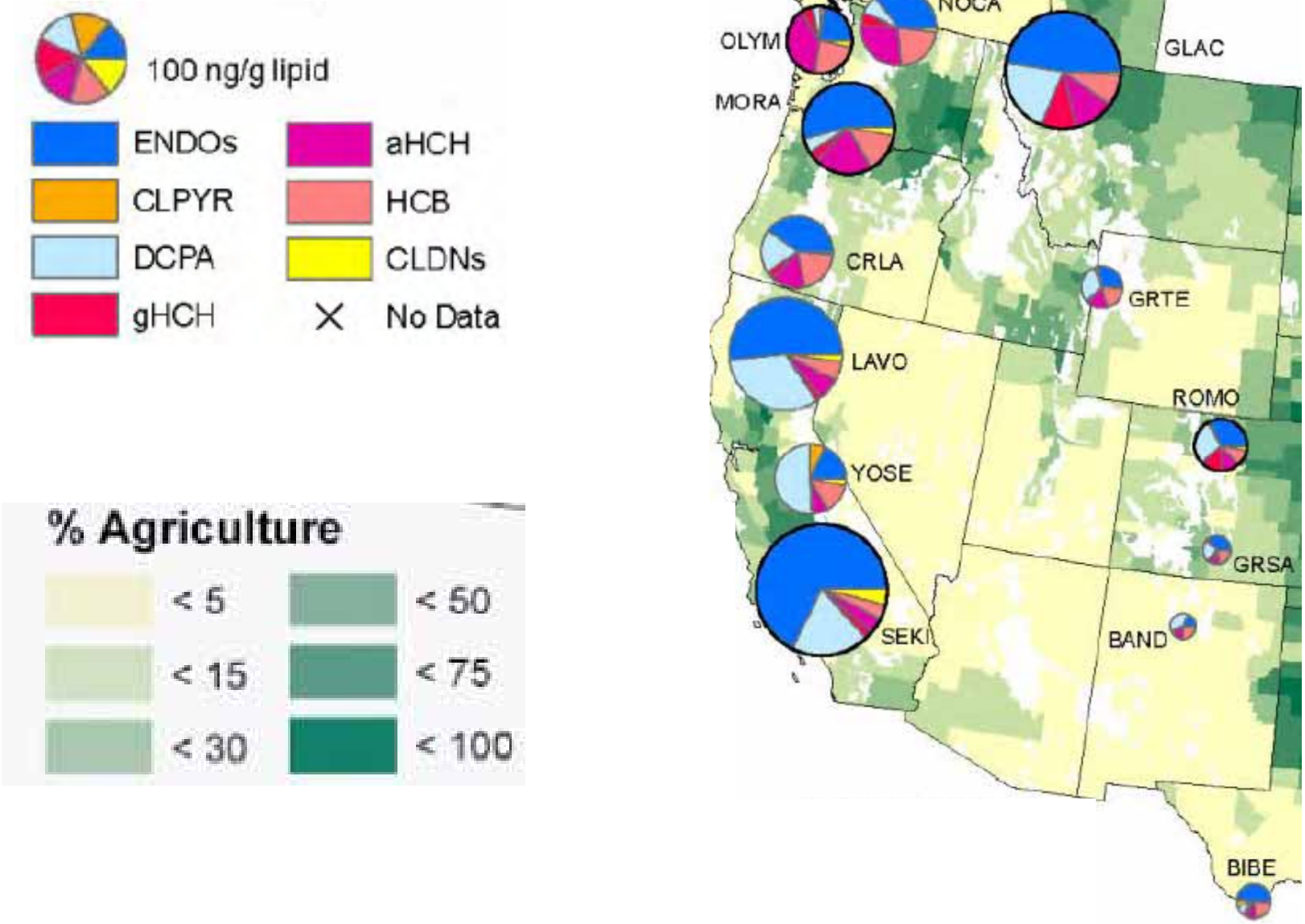
PESTICIDES in LICHEN







PESTICIDES in CONIFER

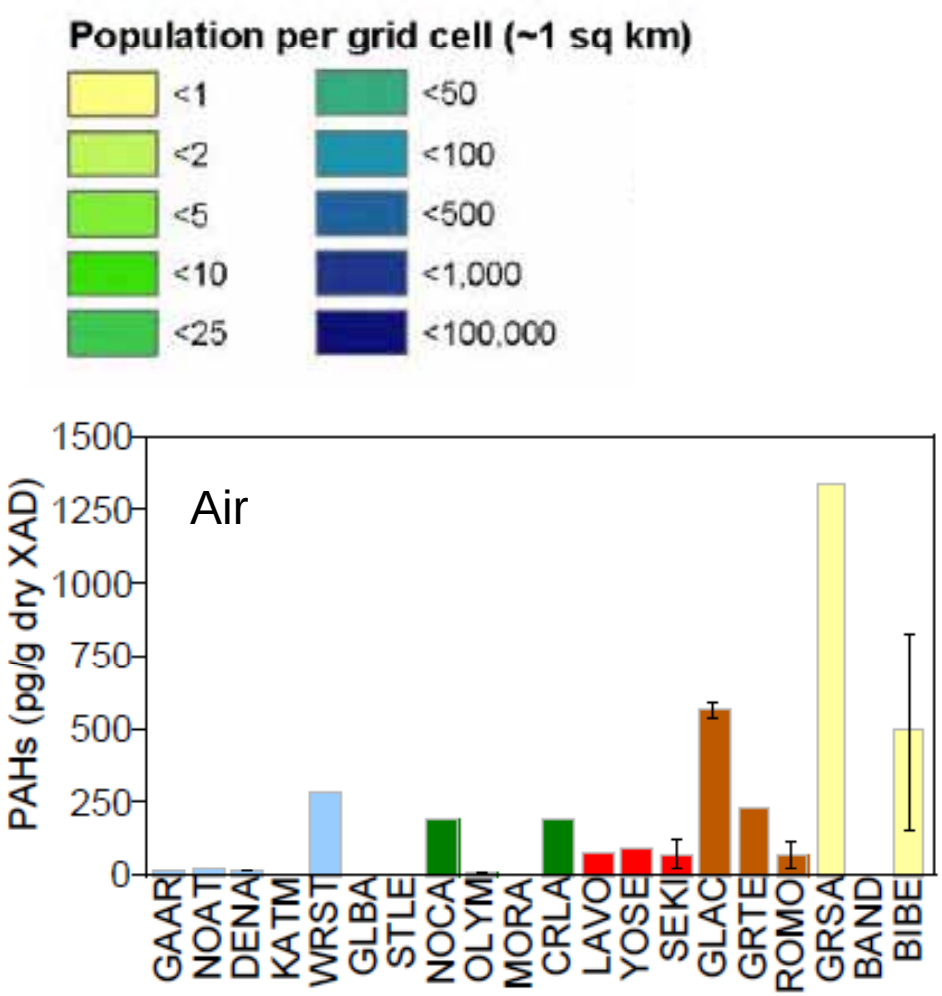


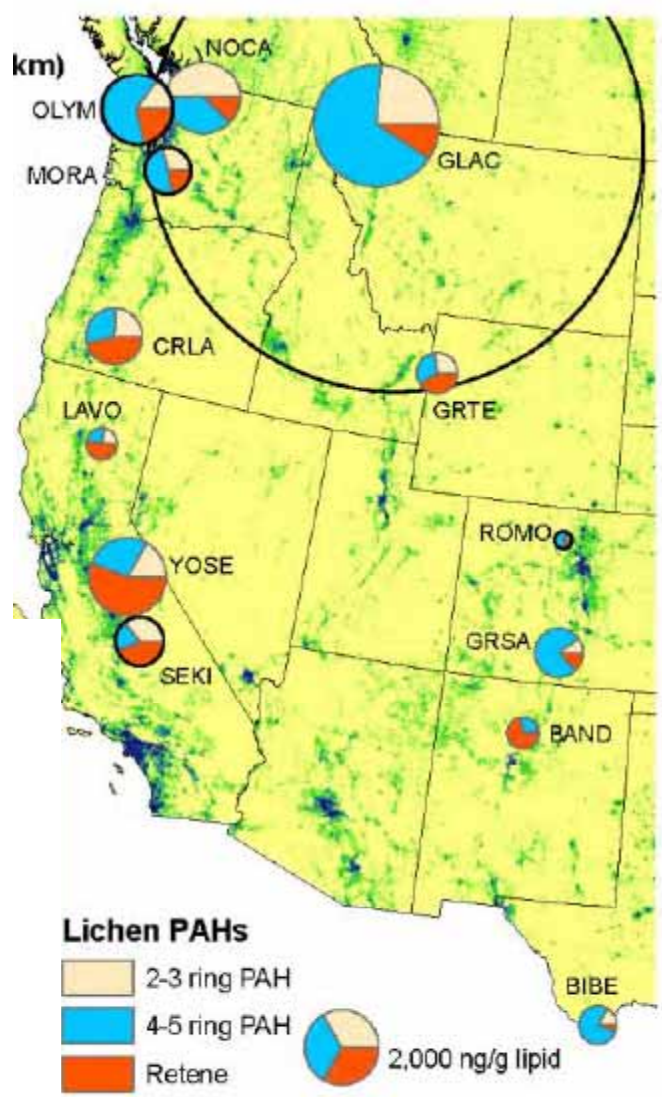
ACCUMULATION OF PESTICIDES in FORESTS

	Endosulfans Accumulated in Second-Year Conifer Needles (g/ha)*		
Forest location	**Low Productivity Forest**	**Average Productivity Forest**	**High Productivity Forest**
Remote	0.0016	0.010	0.080
Near Source	0.0091	0.058	0.45
2002 US Endosulfan Application Rates**	**(g/ha)****		
Not applied	0		
Lowest	0.0085 to 0.049		
Low	0.05 to 0.15		
Medium	0.16 to 0.55		
Highest	0.55 to 2.19		
Highest	≥ 2.20		

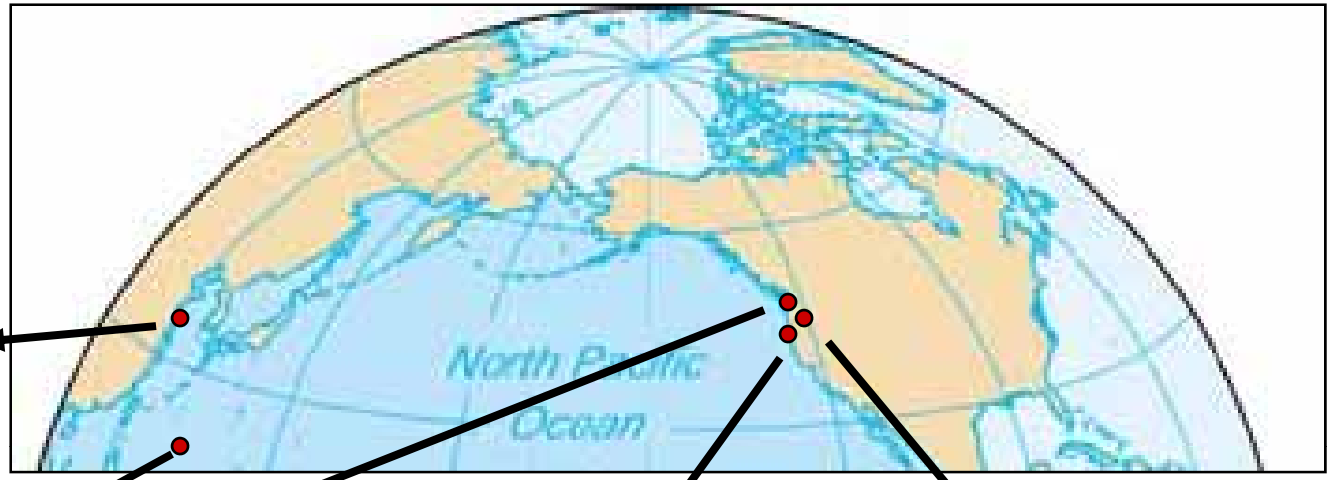
Comparable to low to medium application rates on crops

POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)





Atmospheric Transport from Asia to the U.S.

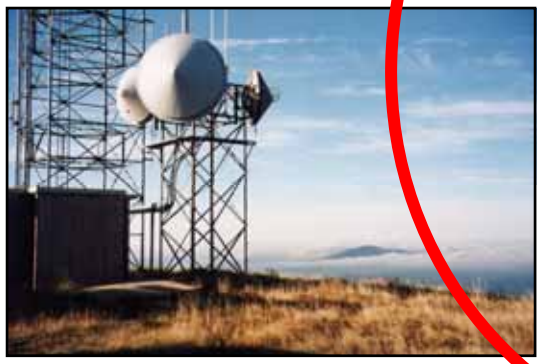


Beijing, China
45 m

Okinawa, Japan
60 m

Cheeka Peak Observatory
Tip of Olympic Peninsula
500 m

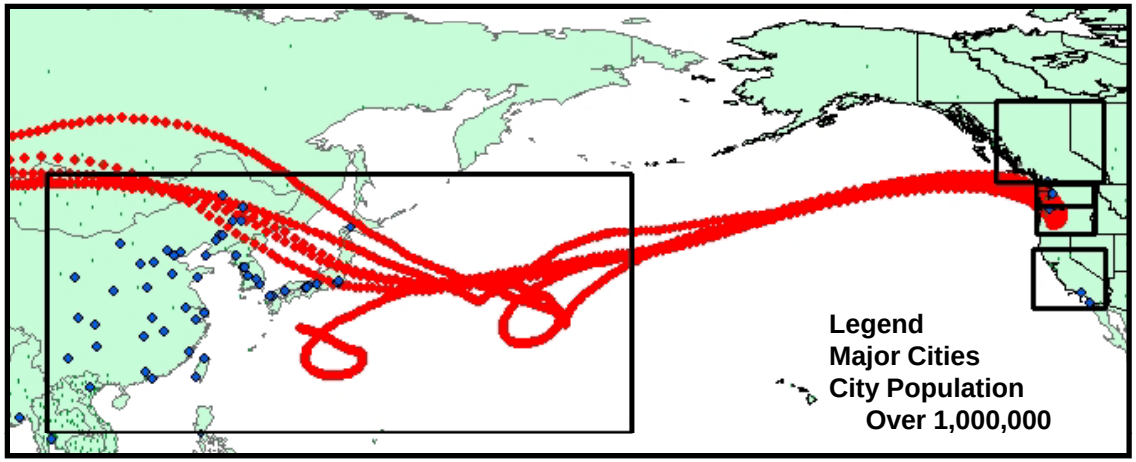
Marys Peak
Oregon Coast Range
1250 m



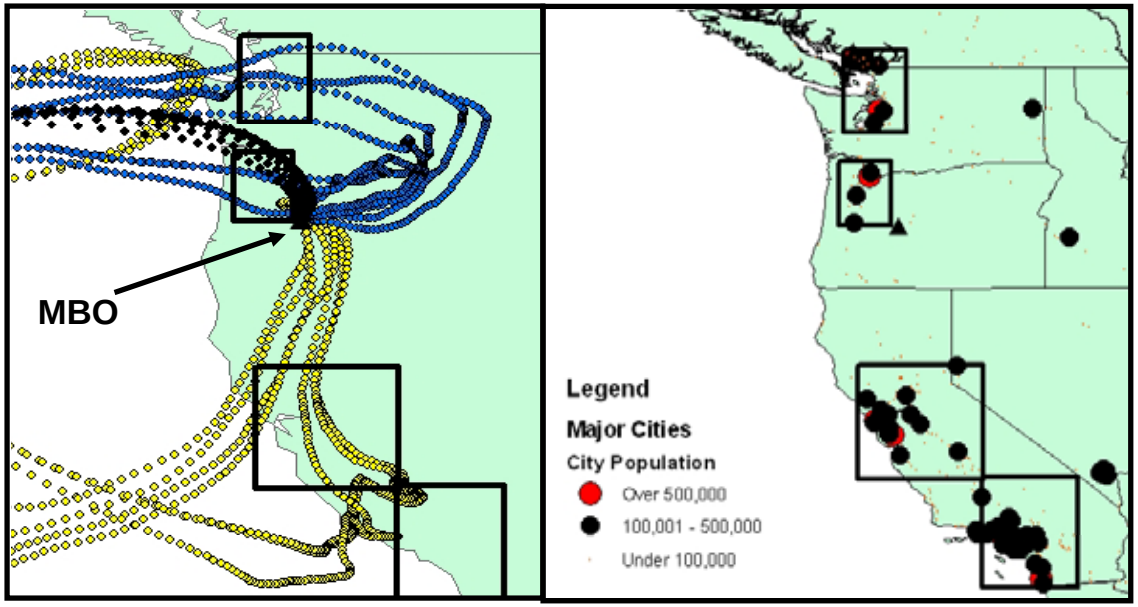
2004-2006

Mt. Bachelor
Oregon Cascade Range
2700 m

Mt. Bachelor Source Regions



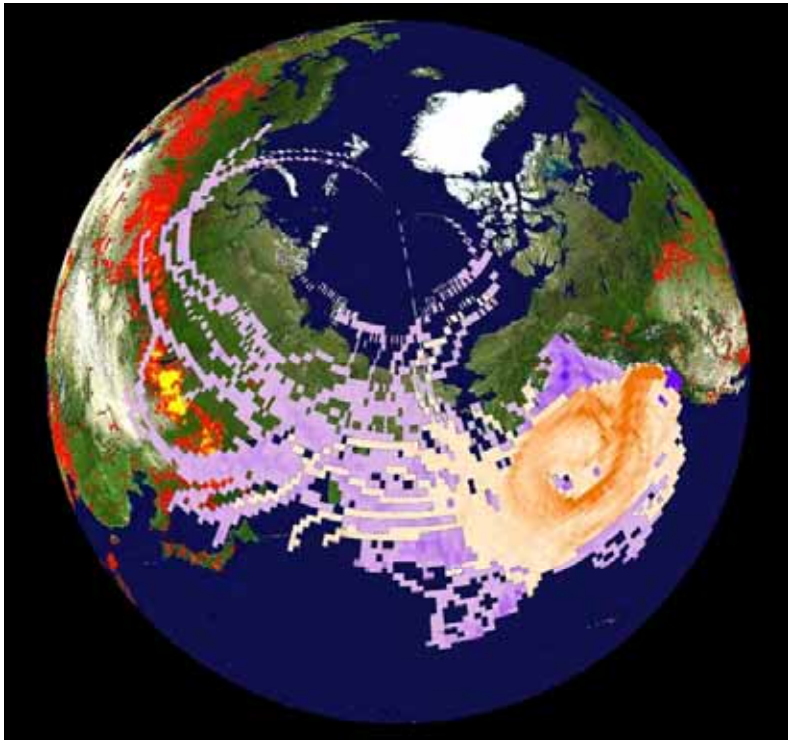
Asian and North American Source Regions



Western U.S. Urban Source Regions

Primbs and Simonich et al, *Environ. Sci. Technol.* **2008**, 6385-6391.

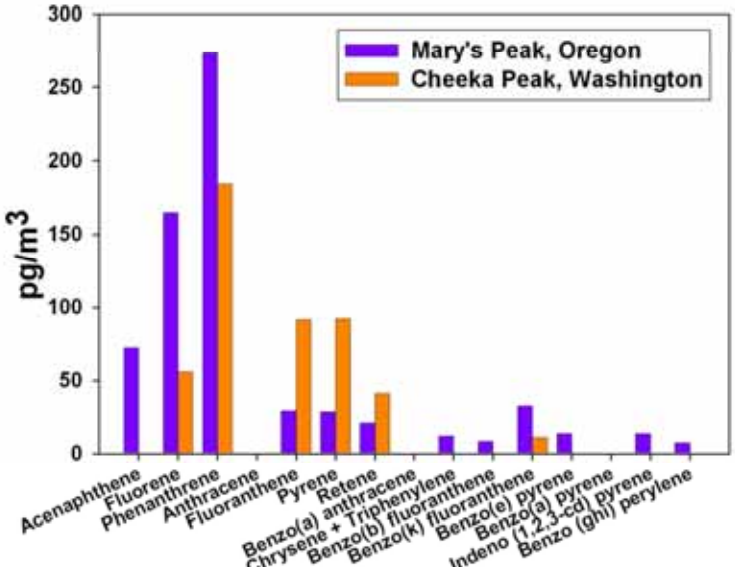
SOC Re-emission from Siberian Fires

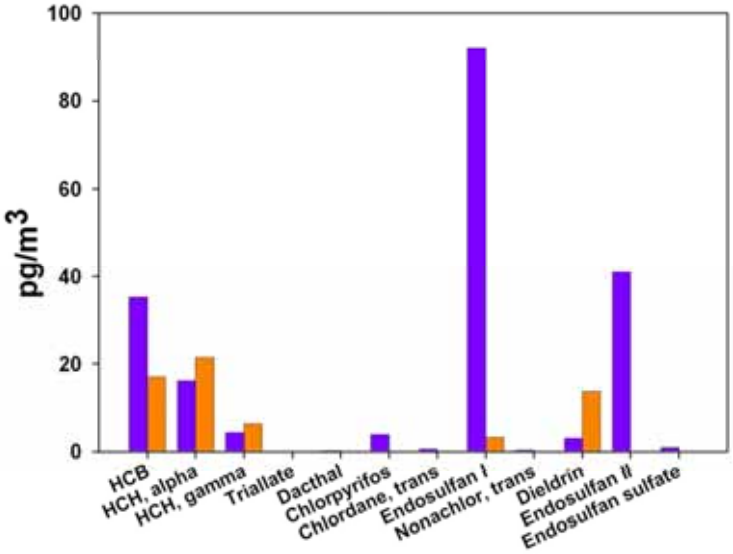


June 2, 2003

10-day Air Mass Back Trajectories

Marys Peak and Cheeka Peak



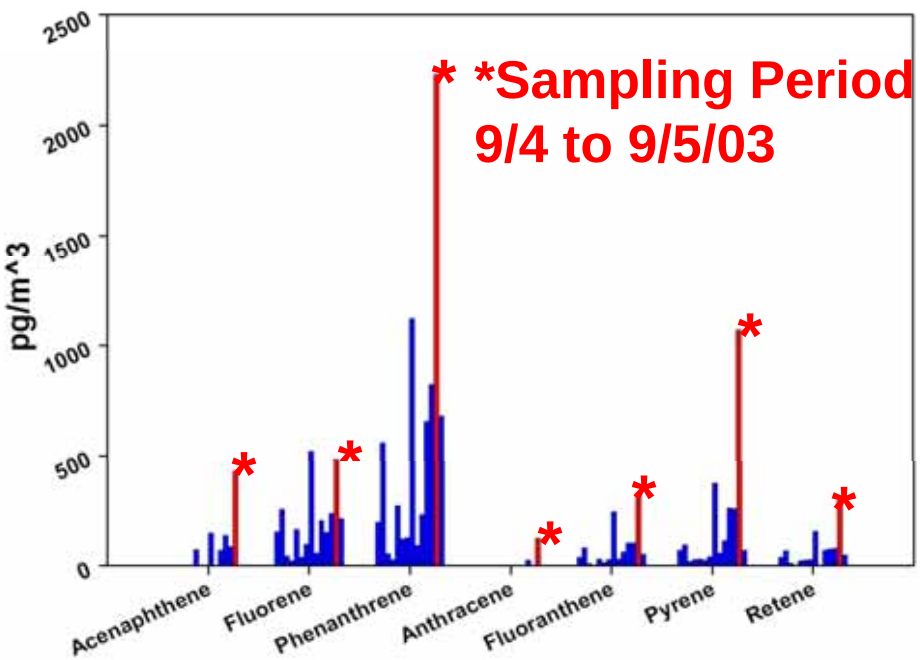


Genualdi and Simonich et al, *Environ. Sci. Technol.* **2009**, ASAP on-line

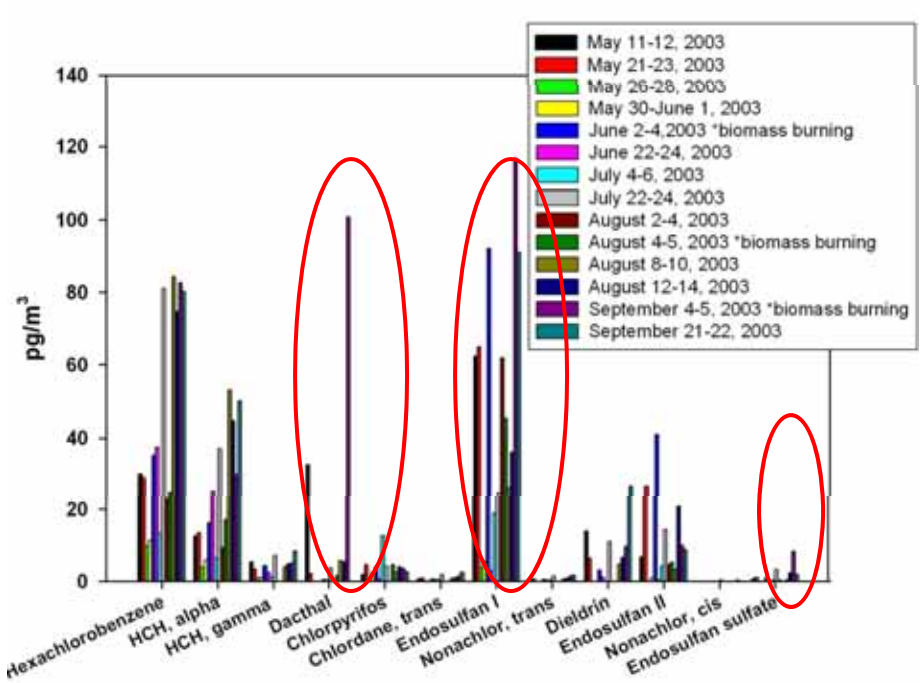
B & B Complex Fire
September 4-5, 2003

Marys Peak

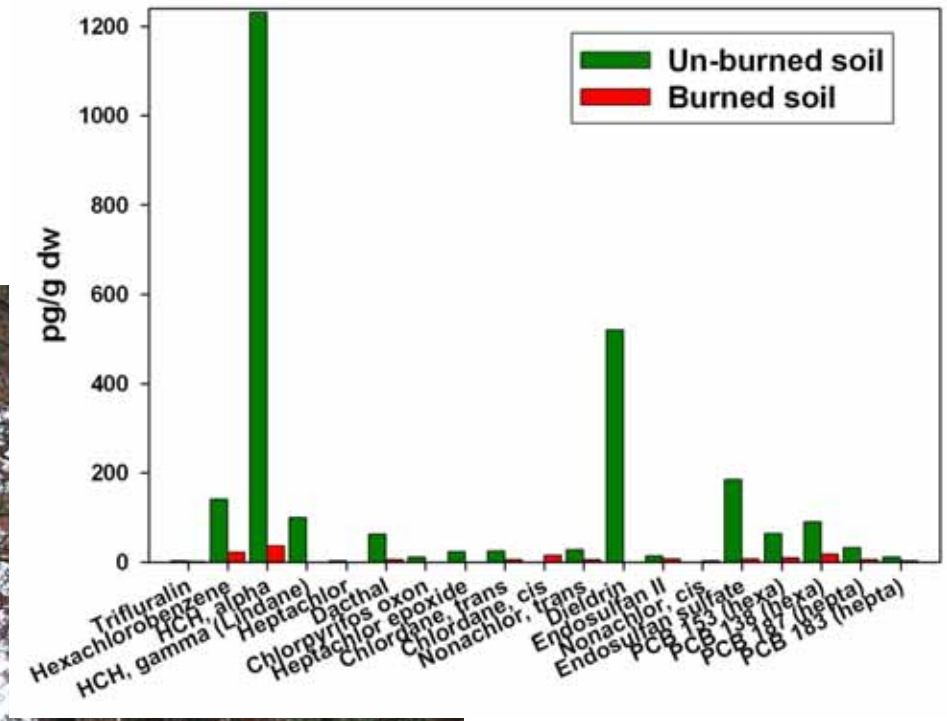
PAHs

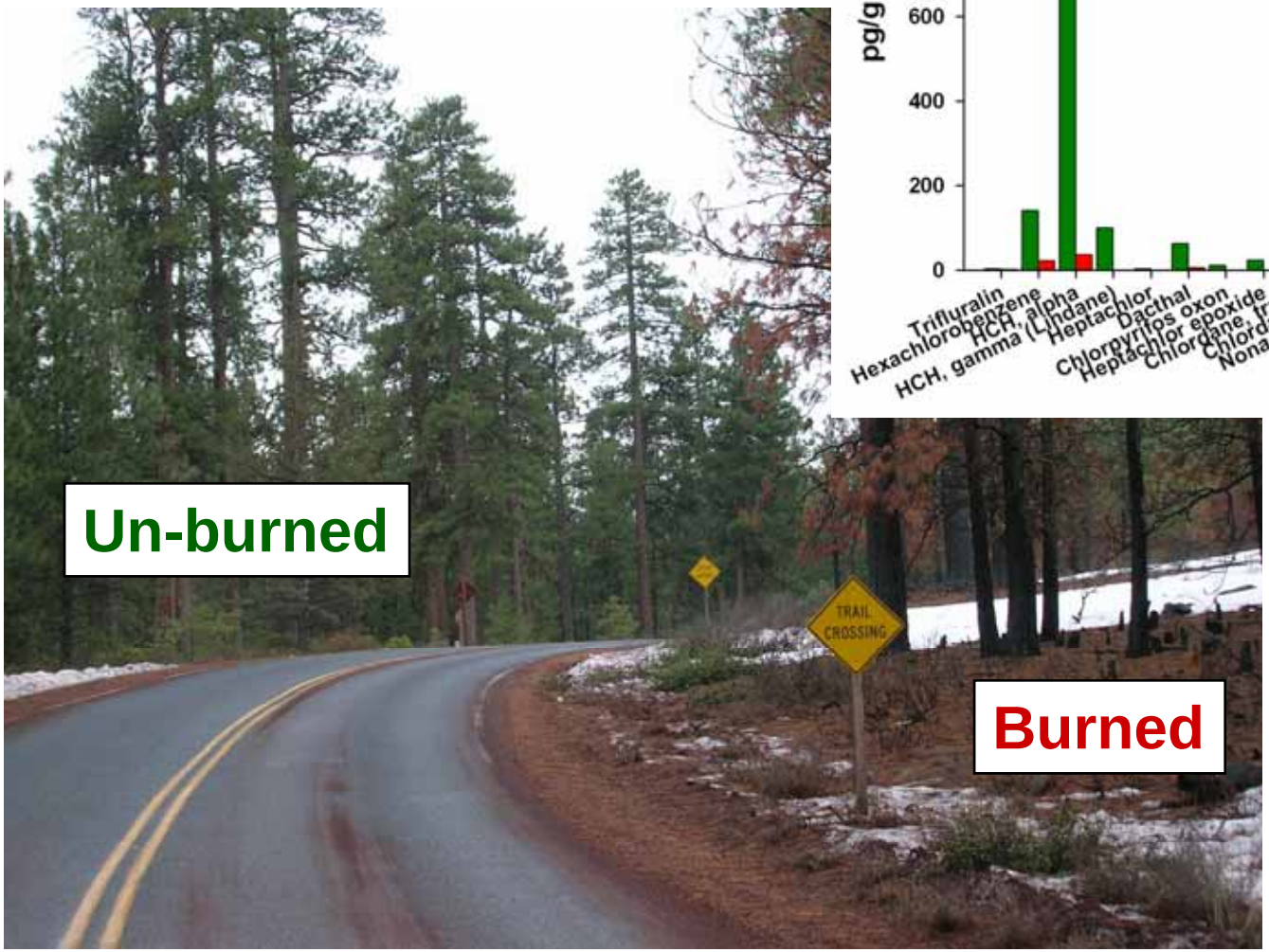


Pesticides



Soil from B & B complex fire





Genualdi and Simonich et al, *Environ. Sci. Technol.* **2009**, ASAP on-line

CONCLUSIONS

- Pesticide Concentrations: SEKI > GLAC > ROMO and SEKI > YOSE = LAVO

- CUPs – regional use > long range transport: Endosulfan, Dacthal, and Chlorpyrifos

- HUPs – past regional use > long range transport: Dieldrin, Chlordane, and DDE

- Significant long term accumulation of pesticides in forest ecosystems and potential for re-release during forest fires

SIMONICH LAB WACAP PUBLICATIONS TO DATE

K.J. Hageman, W.D. Hafner, D.H. Campbell, D.A. Jaffe, D.H. Landers, S.L. Massey Simonich. **2009**. "Variability in Pesticide Deposition and Source Contributions to Snowpack in Western U.S. National Parks", *Environmental Science and Technology,* in review.

L. Ackerman, A Schwindt, D. Koch, G. Wilson, S.L. Simonich. **2008**. "Measurement of PBDEs, Pesticides, PCBs, and PAHs in Western US National Park Fish: Concentrations and Consumption Guidelines", *Environmental Science and Technology*, 42(7), 2334-2341.

S. Usenko, D. Landers, P. Appleby, S.L. Simonich. **2007**. "Current and Historical Deposition of PBDEs, Pesticides, PCBs, and PAHs to Rocky Mountain National Park, USA: Does the Continental Divide Make a Difference?", *Environmental Science and Technology*, 41, 7235-7241.

K.J. Hageman, S.L. Simonich, D.H. Campbell, G.R. Wilson, D.H. Landers. **2006**. "Atmospheric Deposition of Current-Use and Historic-Use Pesticides in Snow at National Parks in the Western United States", *Environmental Science and Technology,* 40, 3174-3180.

S. Usenko, K.J. Hageman, D.W. Schmedding, G.R. Wilson, S.L. Simonich. **2005**. "Trace Analysis of Semi-Volatile Organic Compounds in Large Volume Samples of Snow, Lake Water, and Groundwater", *Environmental Science and Technology*, 39, 6006-6015.

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