WACAP Air, Snow and Vegetation Results: A Focus on OLYM, MORA, and NOCA

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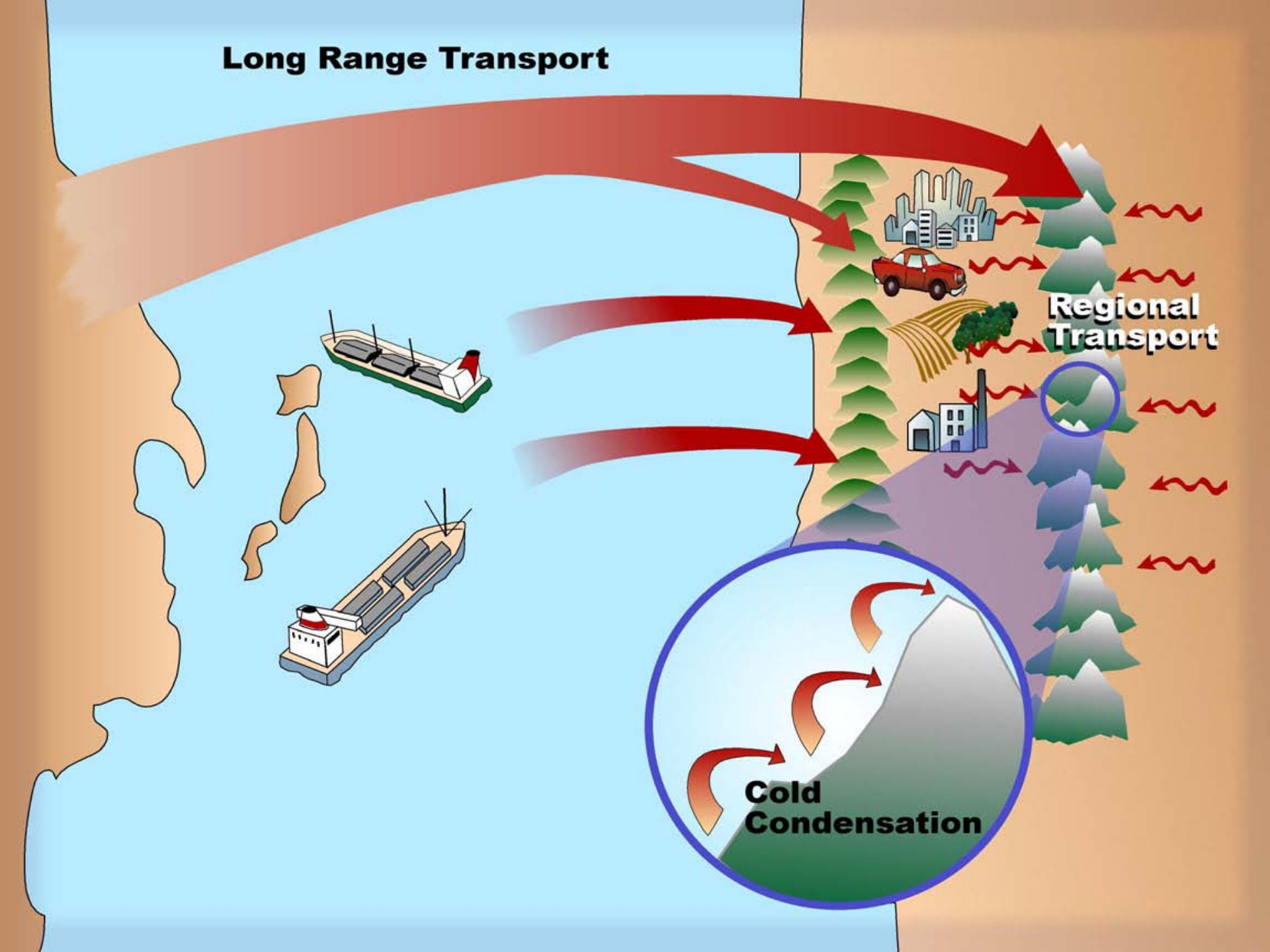

Long Range Transport
Regional Transport
Cold Condensation

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

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

Electron Capture Negative Ionization

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:

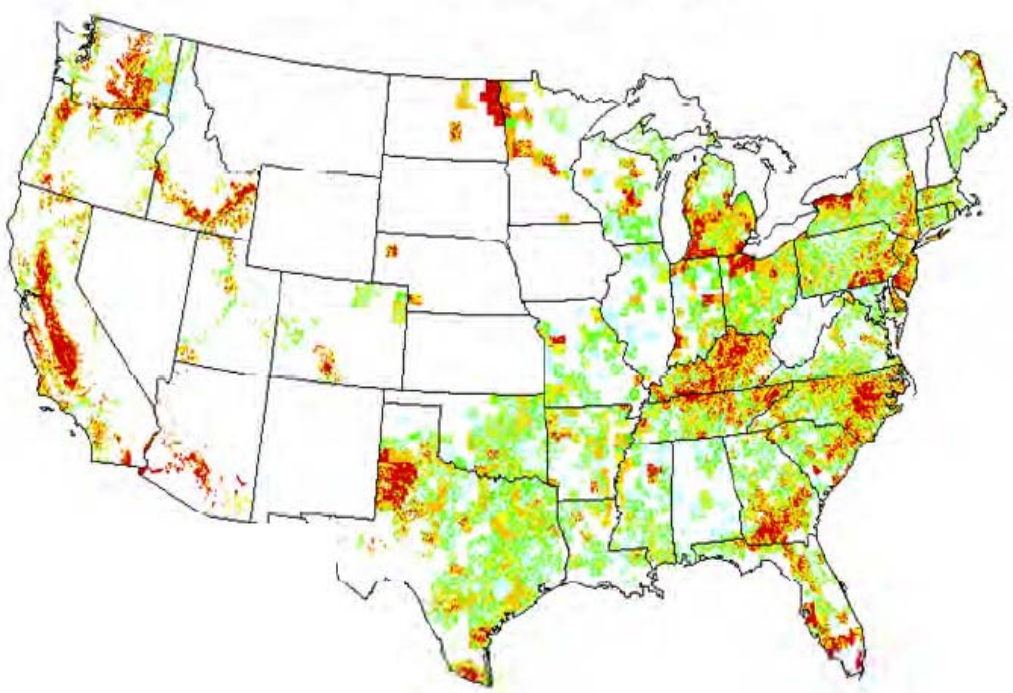
Hexachlorocyclohexanes (HCH) - α*, β, γ-(lindane), and δ, Chlordanes – cis*, trans*, oxy*, Nonachlor – cis, trans, Heptachlor*, Heptachlor Epoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorothalonil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Triallate, Mirex

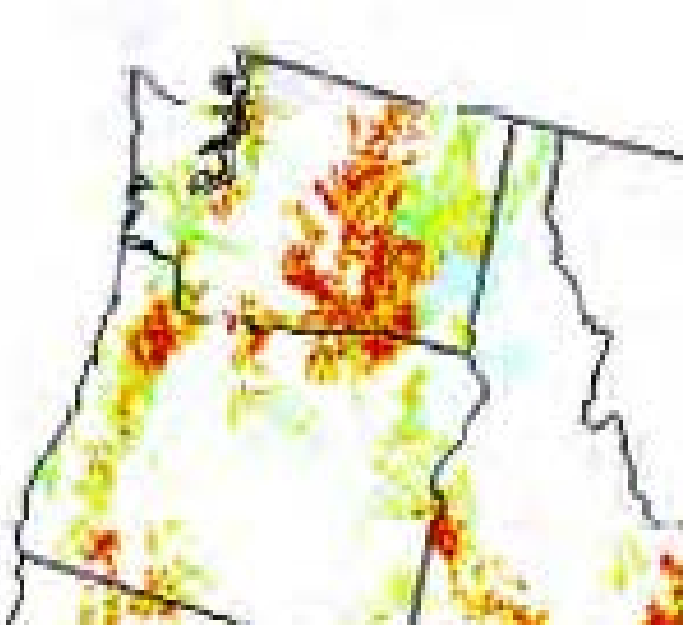
Polybrominated Diphenyl Ethers

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

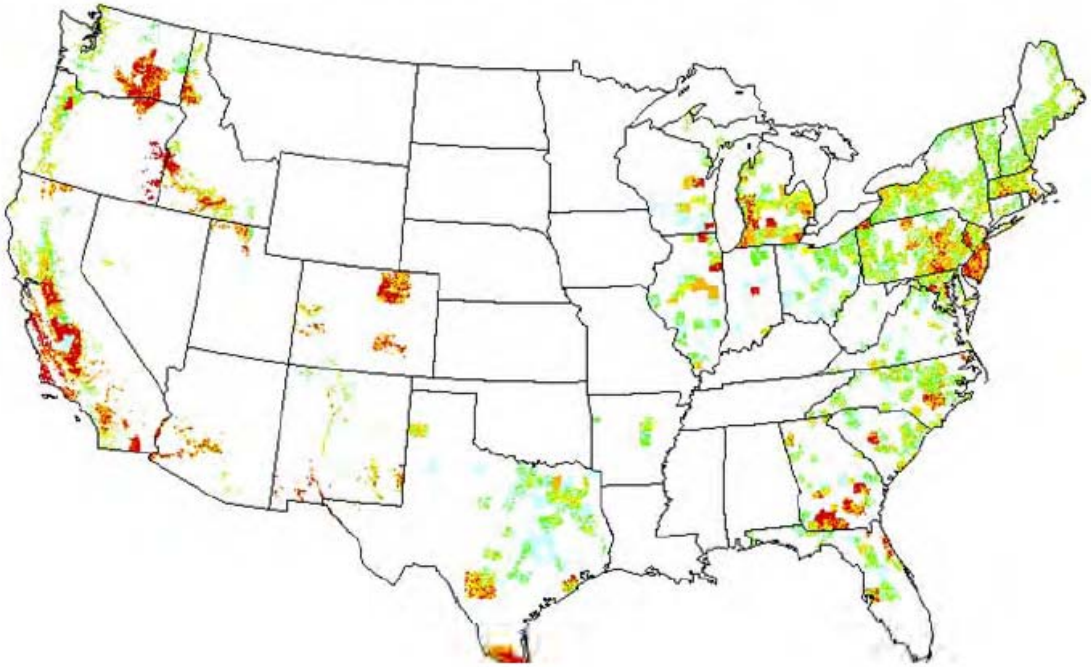


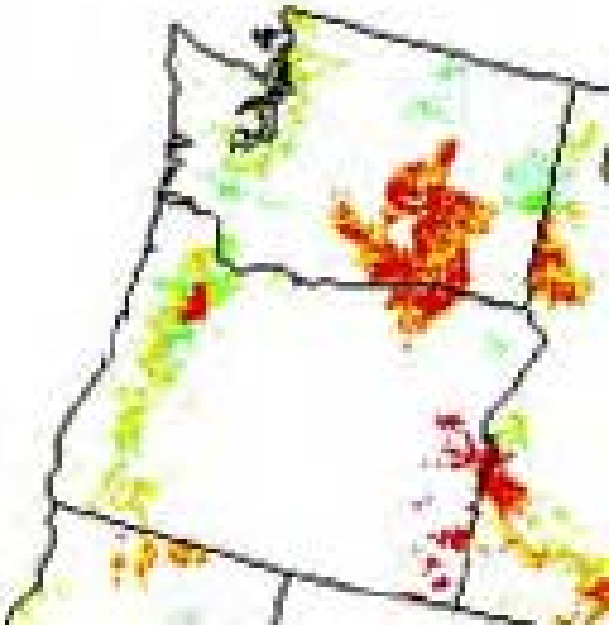


• Chlorinated Insecticide first used in 1954

• Nationwide Use: cotton, tomatoes, potatoes, apples, tobacco, pears, cucumbers, lettuce, green beans, squash

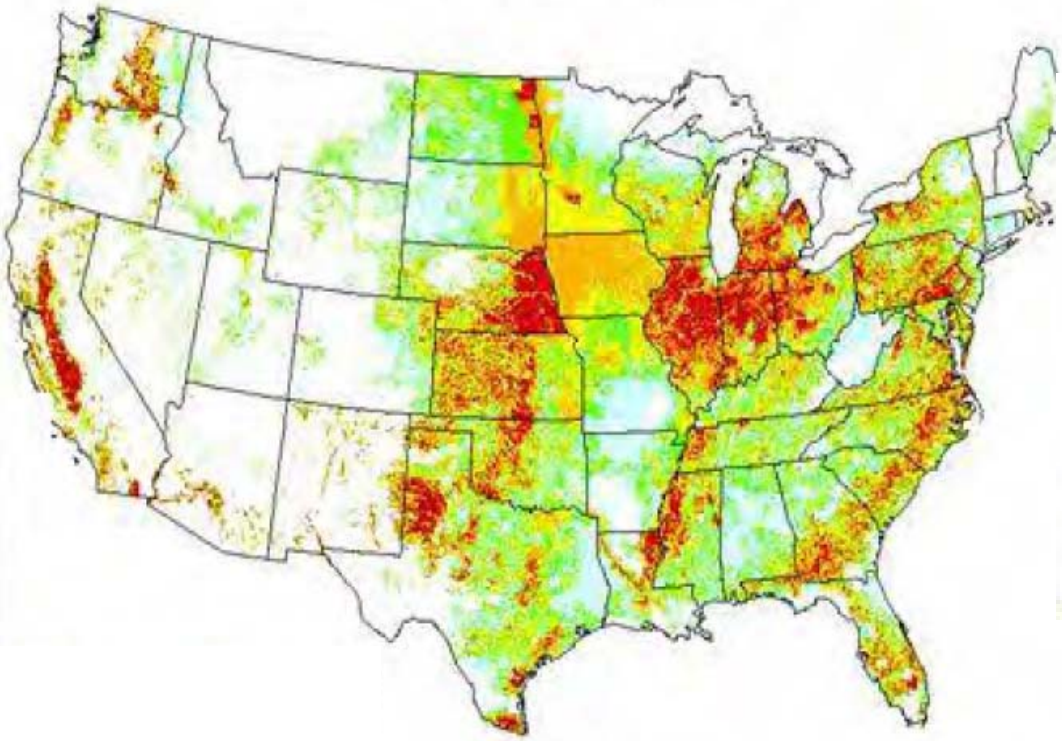
DACTHAL (DCPA)

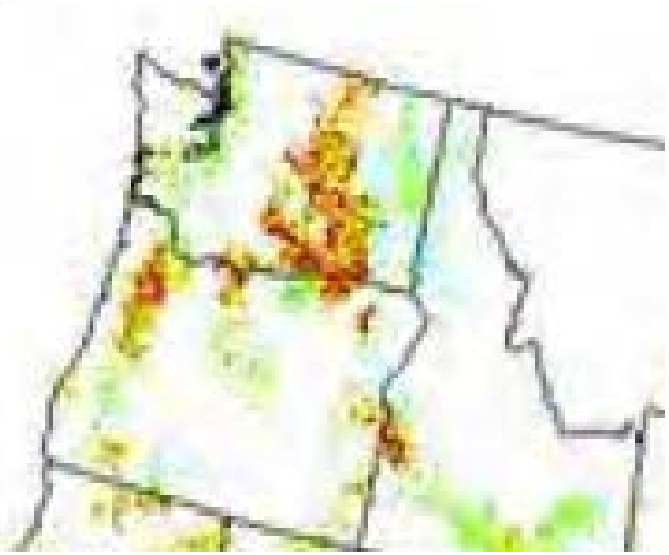




- Herbicide first used in 1955
- Nationwide Use: onions, broccoli, sod, cabbage, cauliflower, squash, collards, dry beans, strawberries

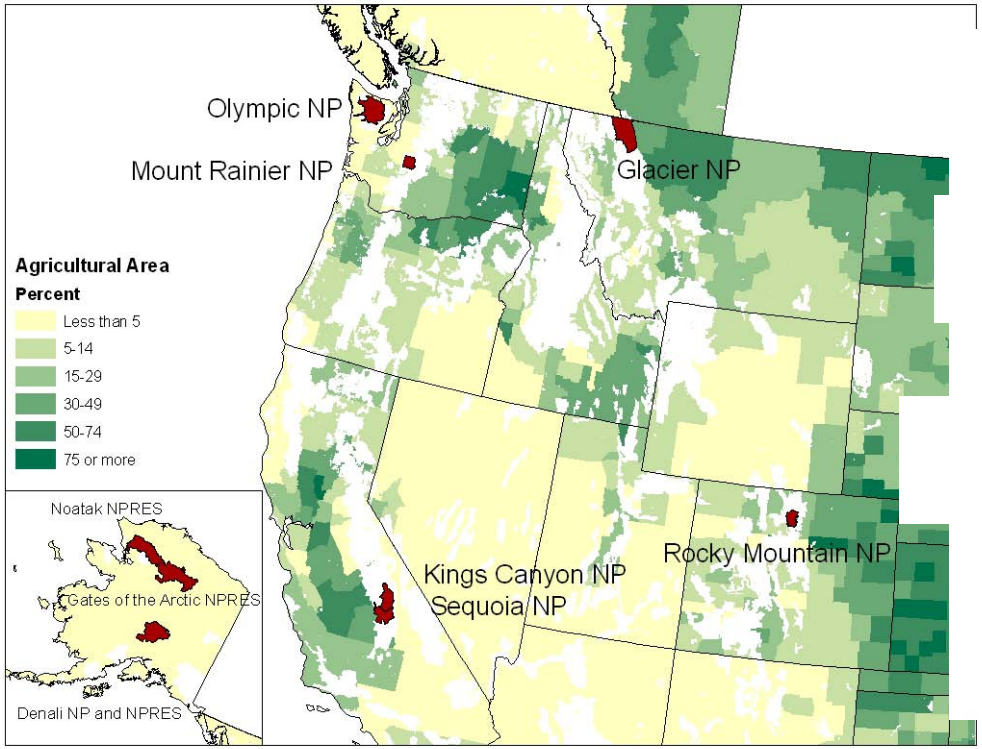
CHLORPYRIFOS

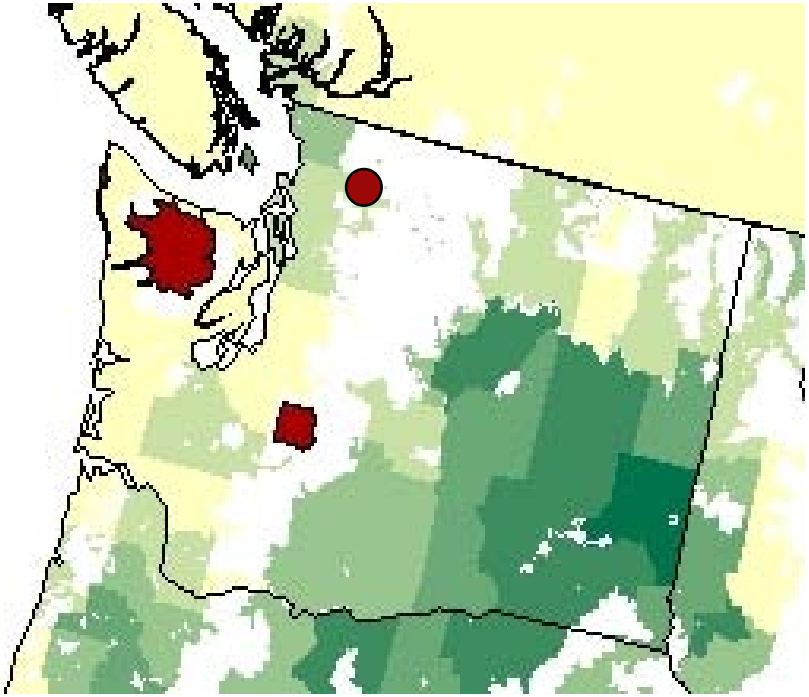




- Insecticide first used in 1965
- Nationwide Use: corn, cotton, hay, wheat, citrus, apples, peanuts, soybeans, pecans, tobacco

CROPLAND INTENSITY





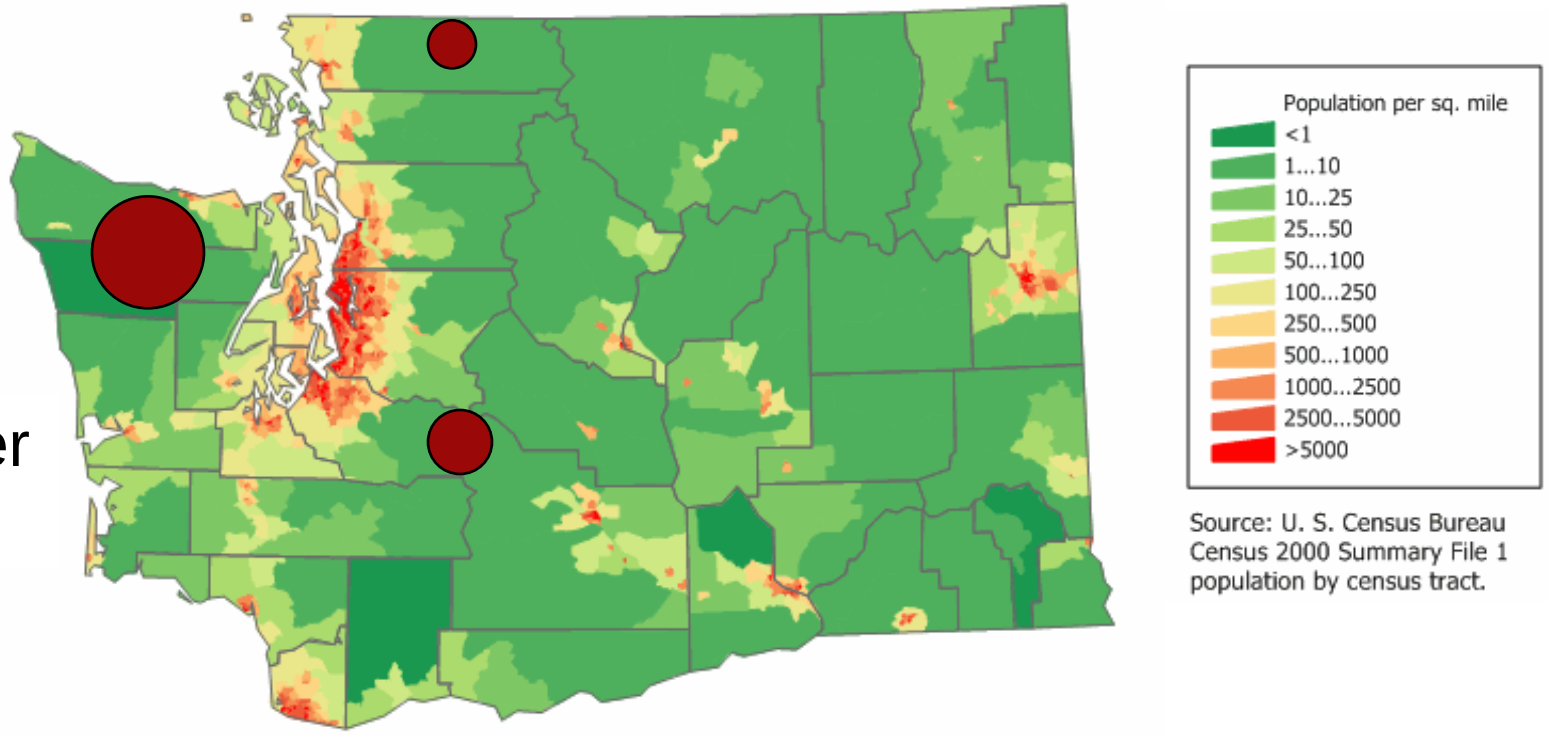
An indication of where historic use pesticides were used

POPULATION DENSITY

North Cascades NP

Olympic NP

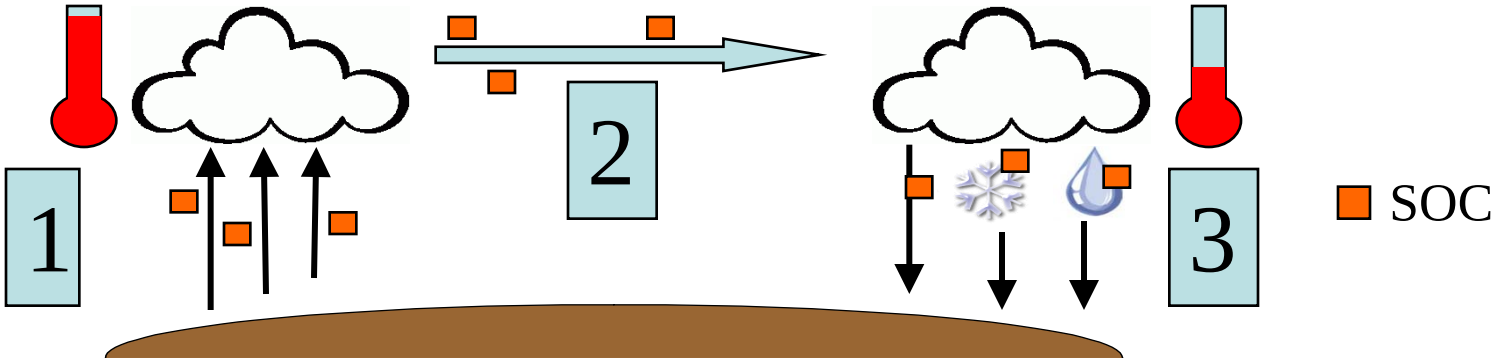
Mt. Rainier NP



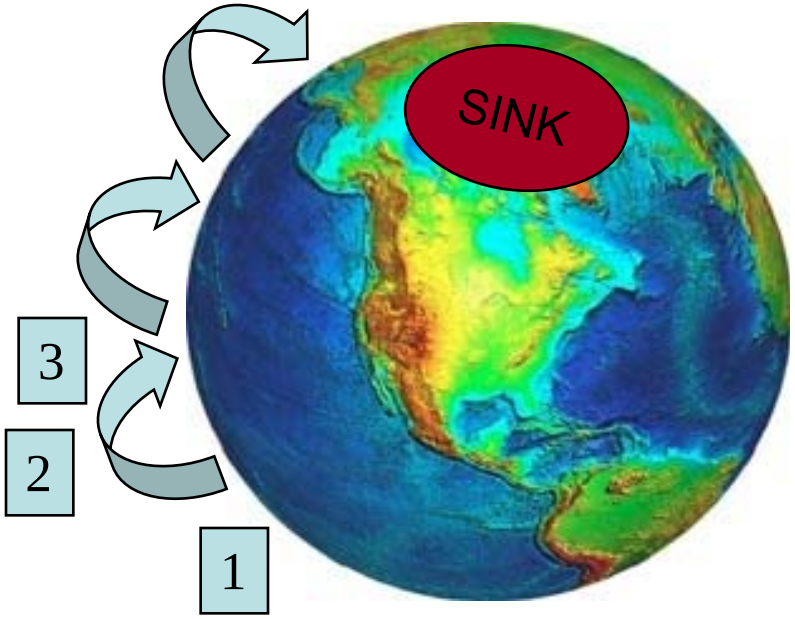
Map from www.commons.wikimedia.org

An indication of where PAHs and PBDEs are emitted

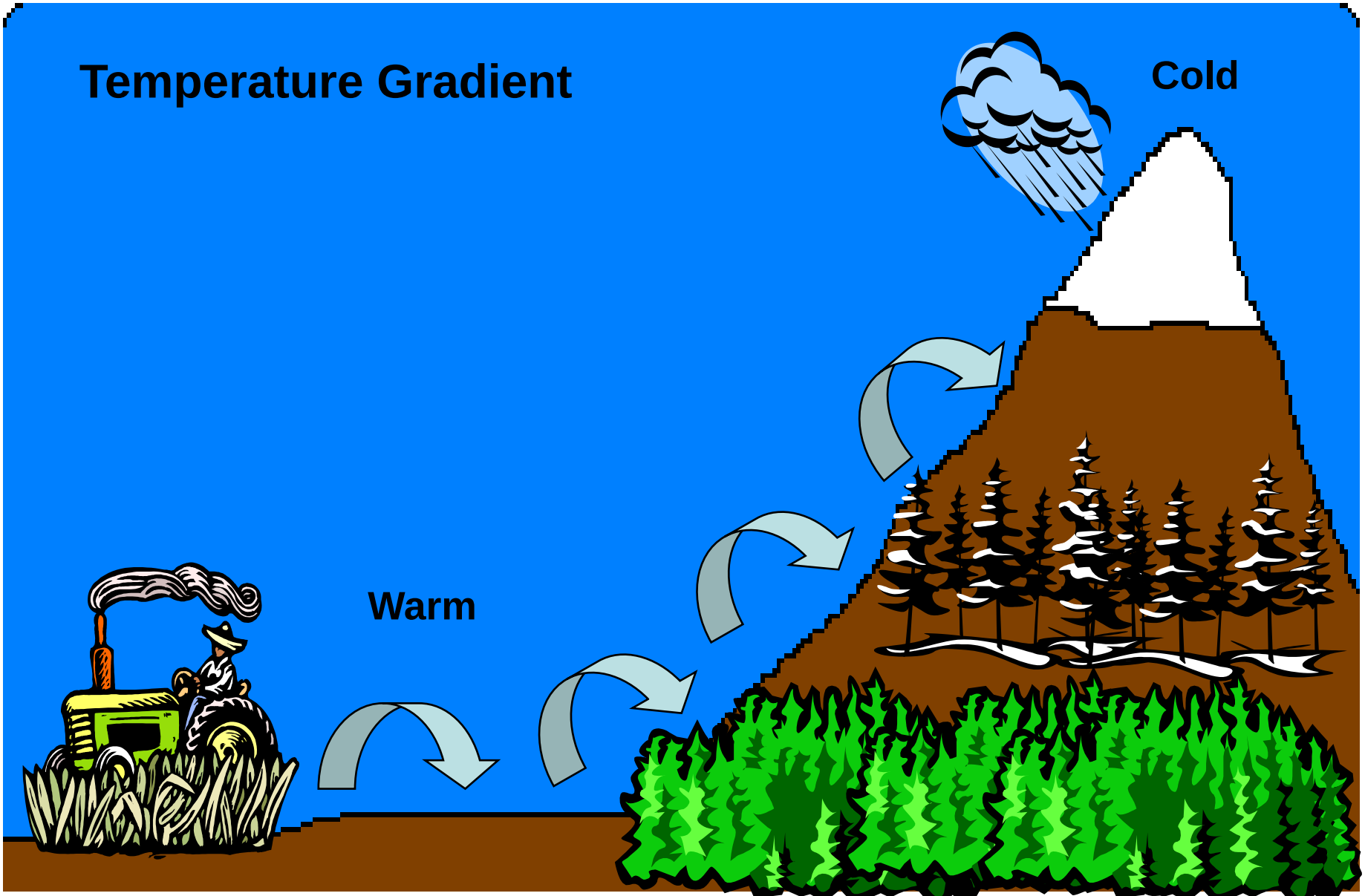
GLOBAL DISTILLATION or COLD CONDENSATION



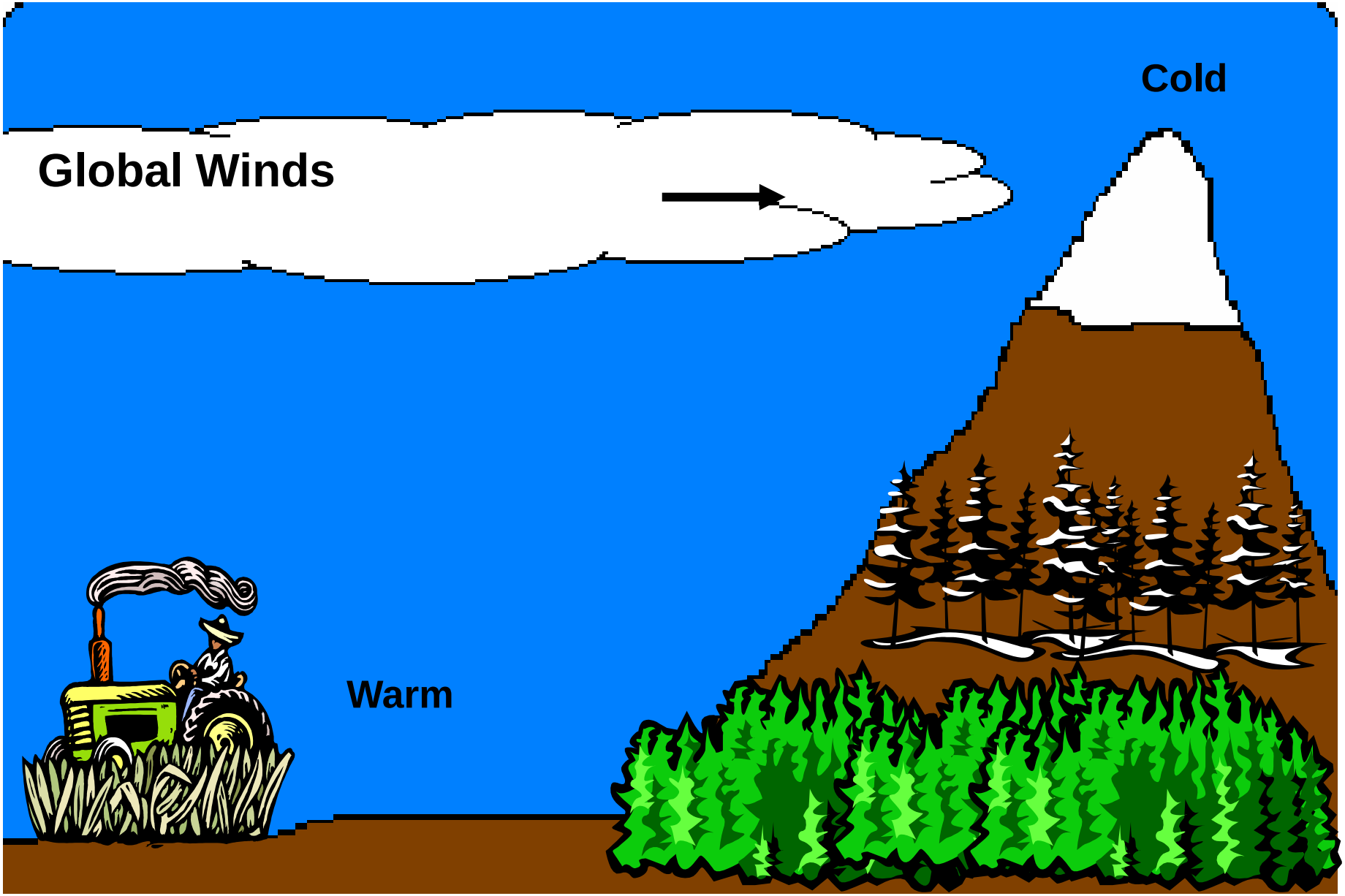
1. At warm temps, semi-volatile organic compounds (SOCs) volatilize into the atmosphere.
2. SOCs are transported in the atmosphere.
3. At cold temps, SOCs condense and undergo deposition.



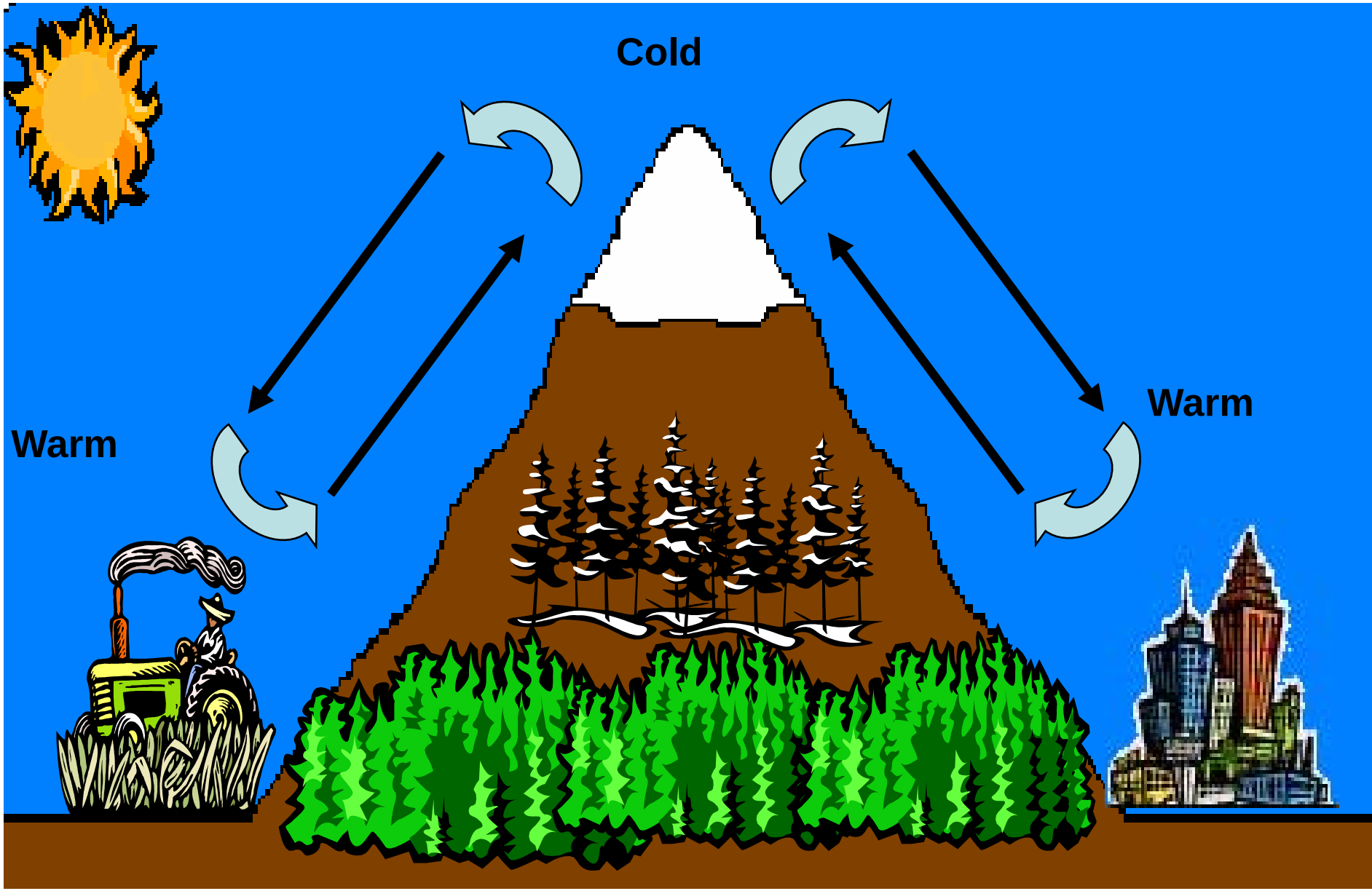
OROGRAPHIC COLD TRAPING



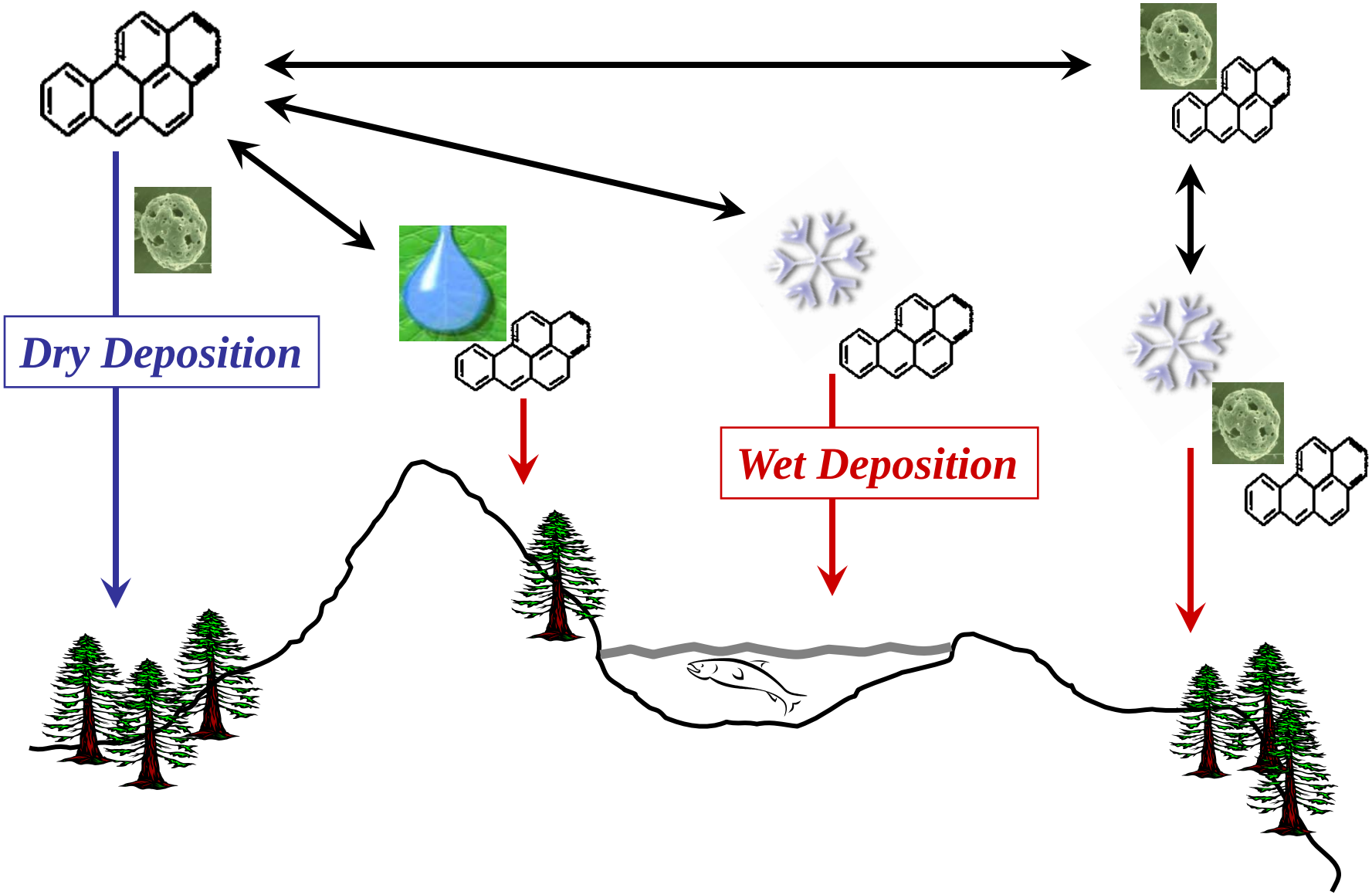
LONG-RANGE TRANSPORT AND DEPOSITION



REGIONAL/LOCAL TRANSPORT AND DEPOSITION



IMPORTANCE of SNOW in SCAVENGING POPs



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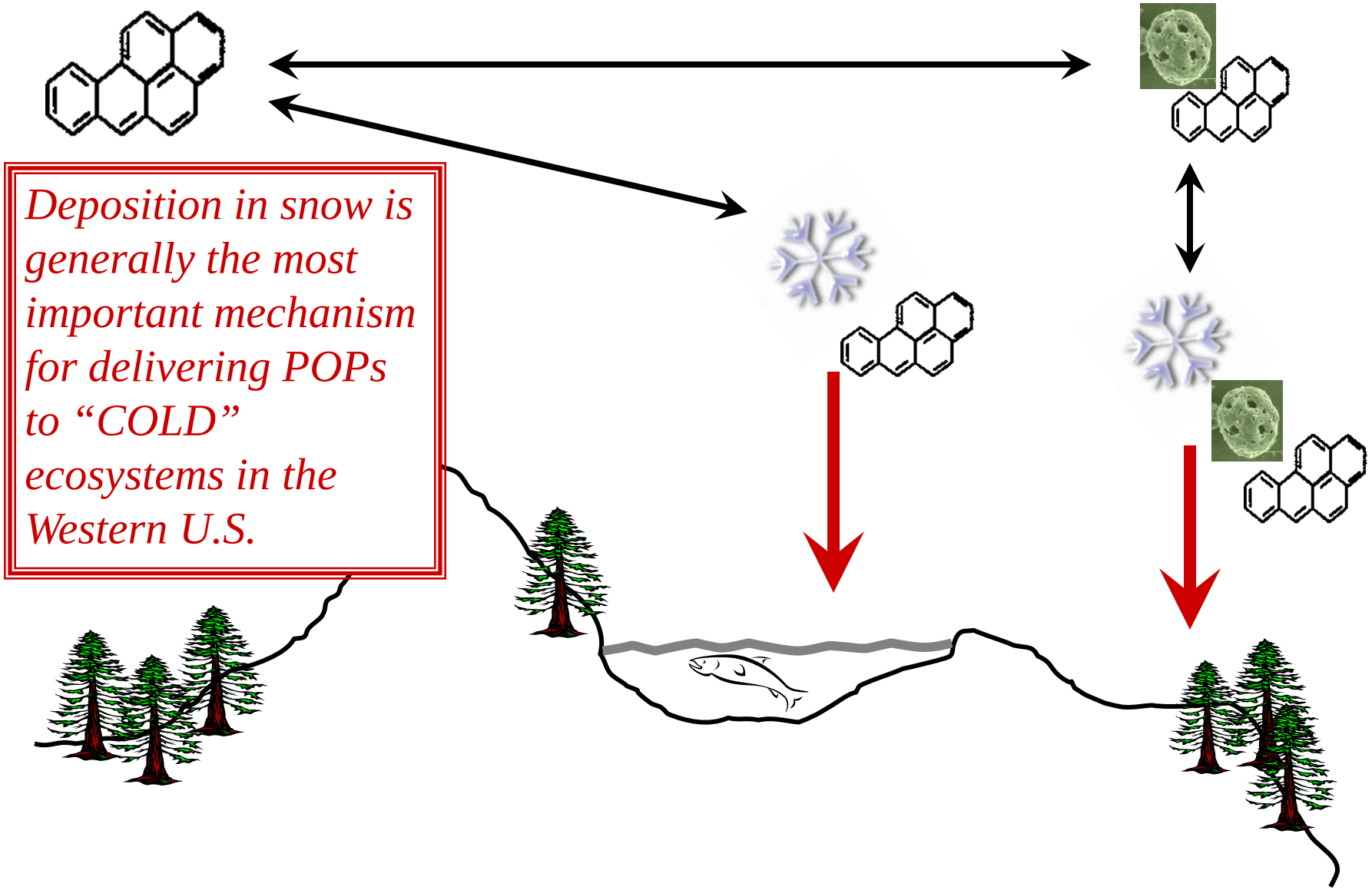
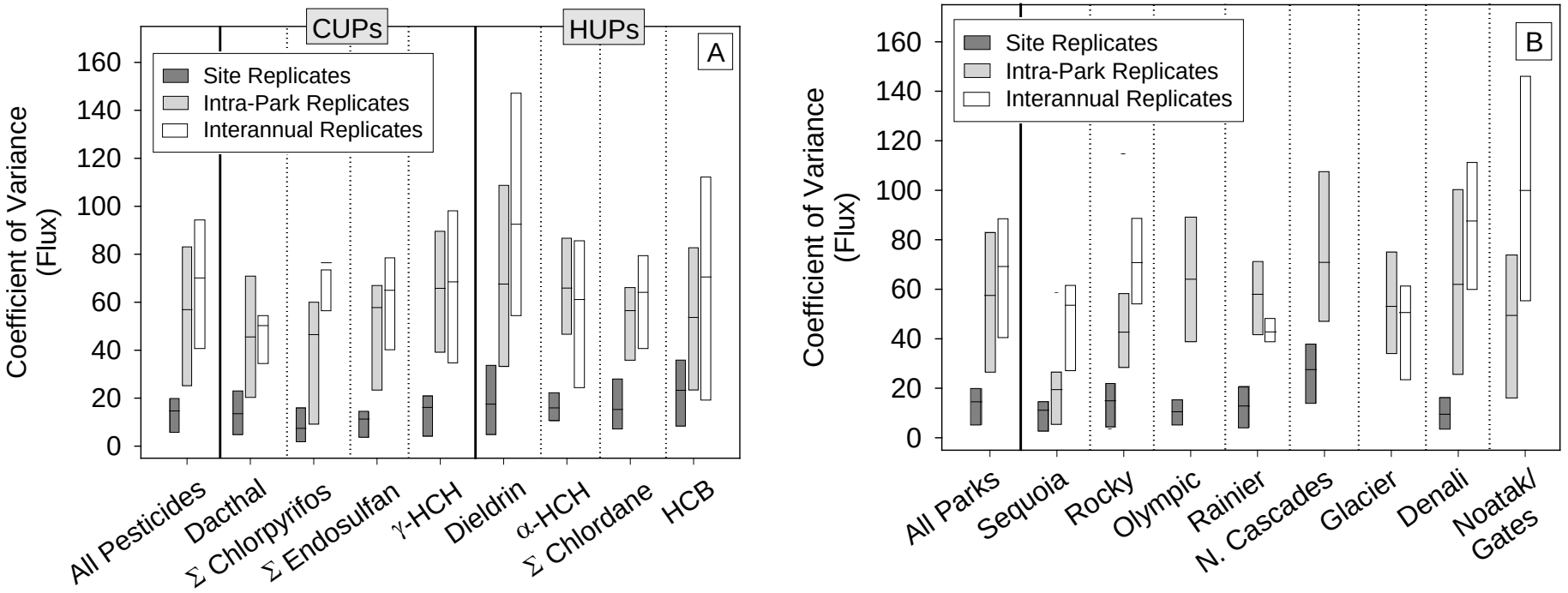


Deposition in snow is generally the most important mechanism for delivering POPs to "COLD" ecosystems in the Western U.S.

VARIATION IN PESTICIDE FLUX IN SNOWPACK

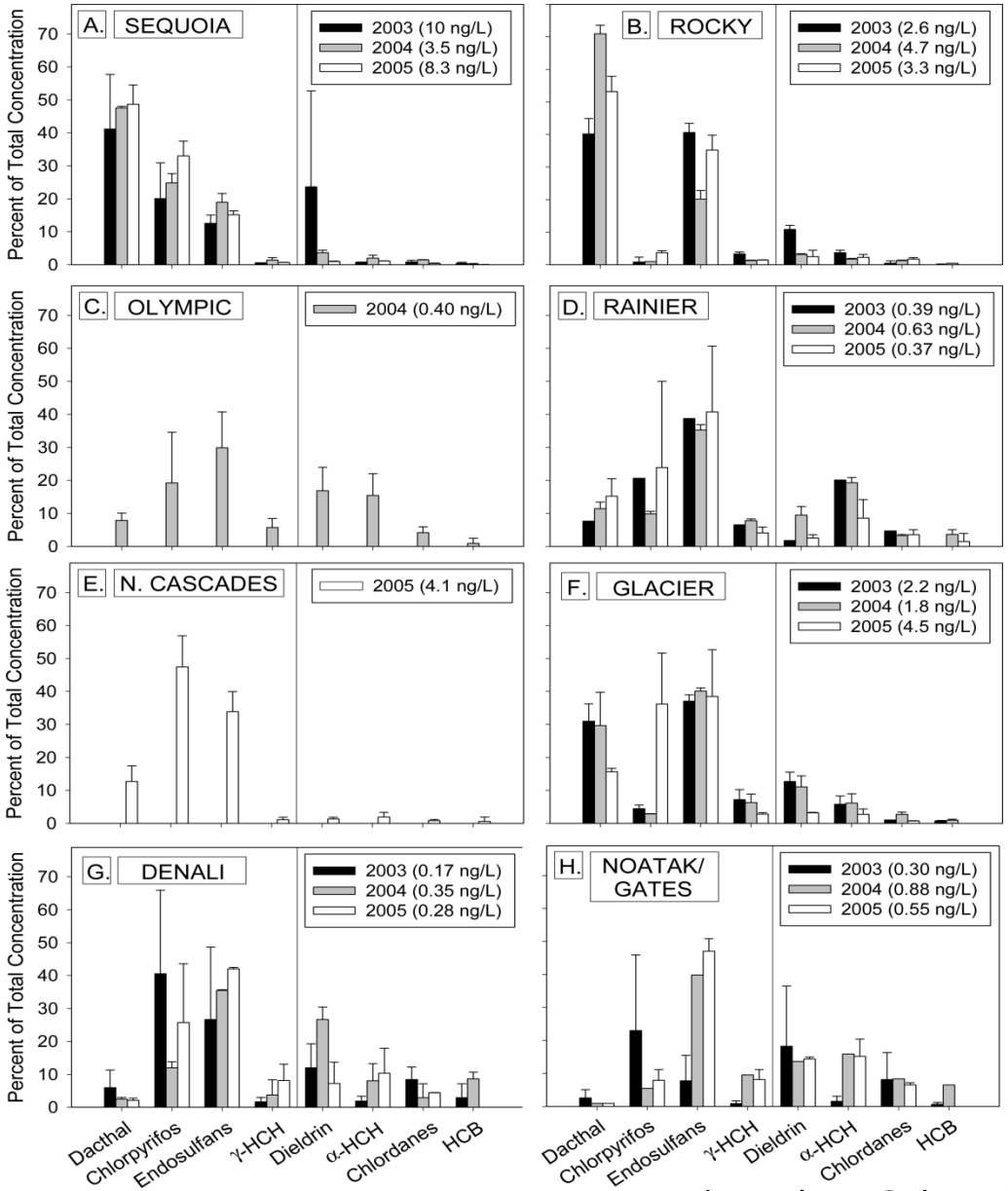
2003, 2004, and 2005



Hageman et al, *Environ. Sci, Technol*., **2010**

Sample sites during same year to reduce variability and compare sites.

ANNUAL PESTICIDE PROFILE IN SNOWPACK



- Pesticide profile is unique to each Park (different sources)
- Park pesticide profile is consistent year to year (same sources each year)
- HUPs due to revolatilization from historically contaminated soils
- CUPs from current regional pesticide use
- OLY, MORA and NOCA: CUPs + some HUPs

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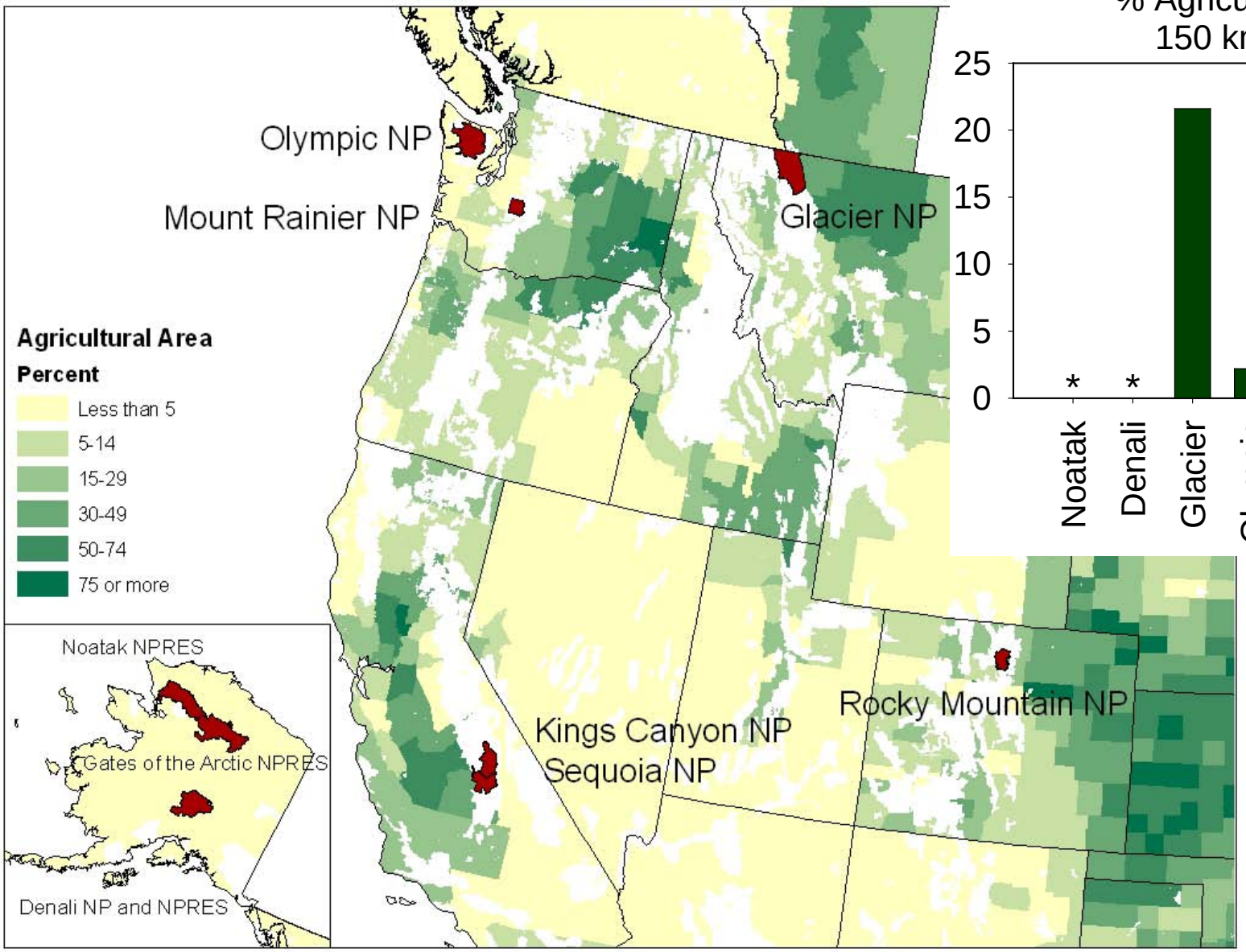
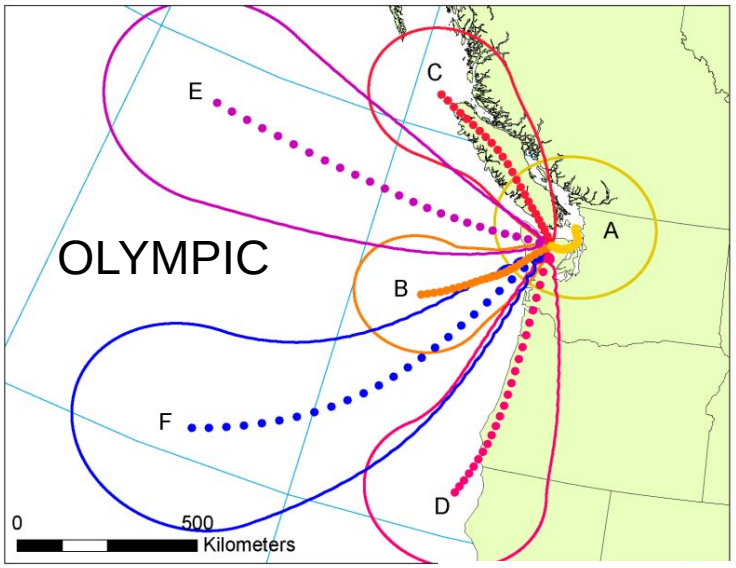
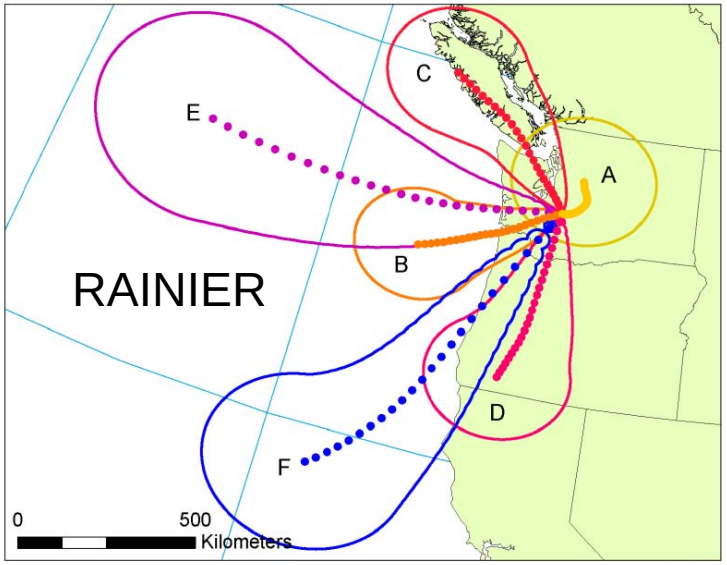
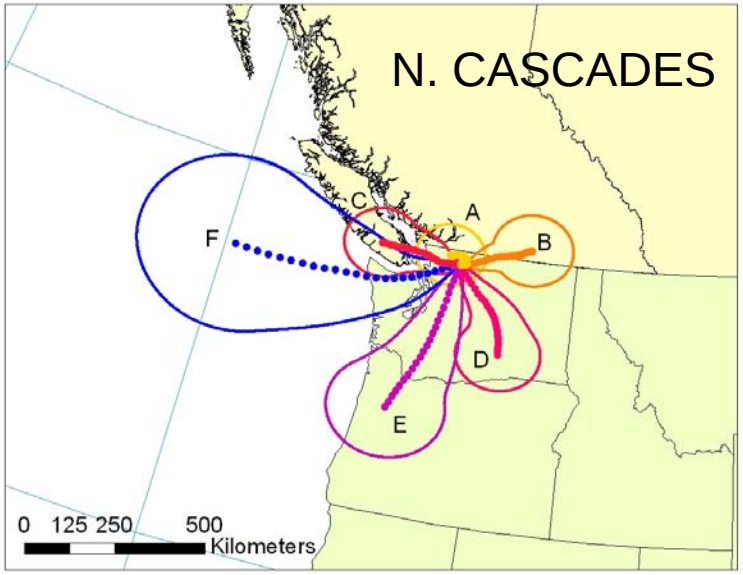
Agricultural Lands in the Western US and Canada



ONE DAY “AIRSHEDS”







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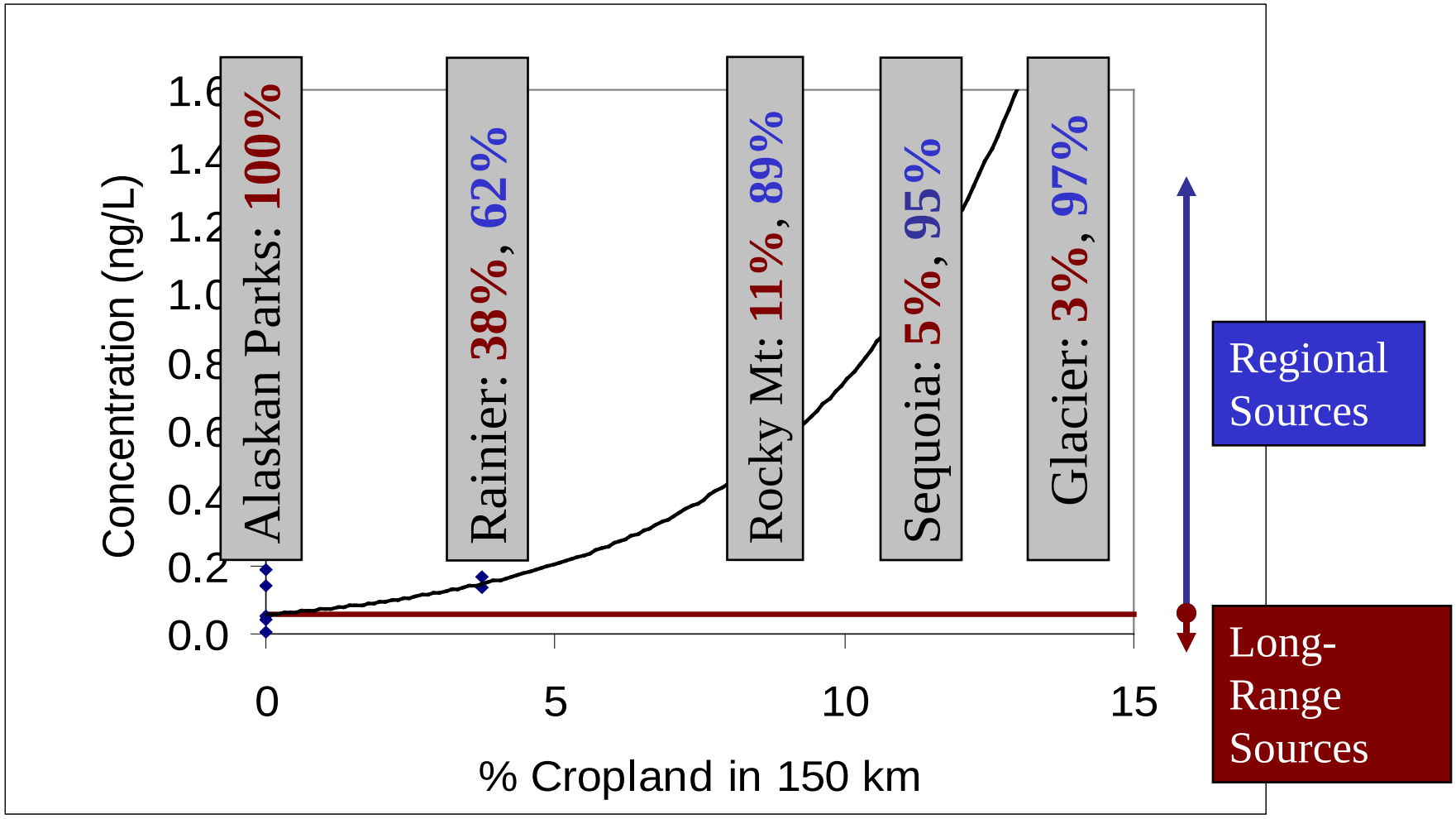
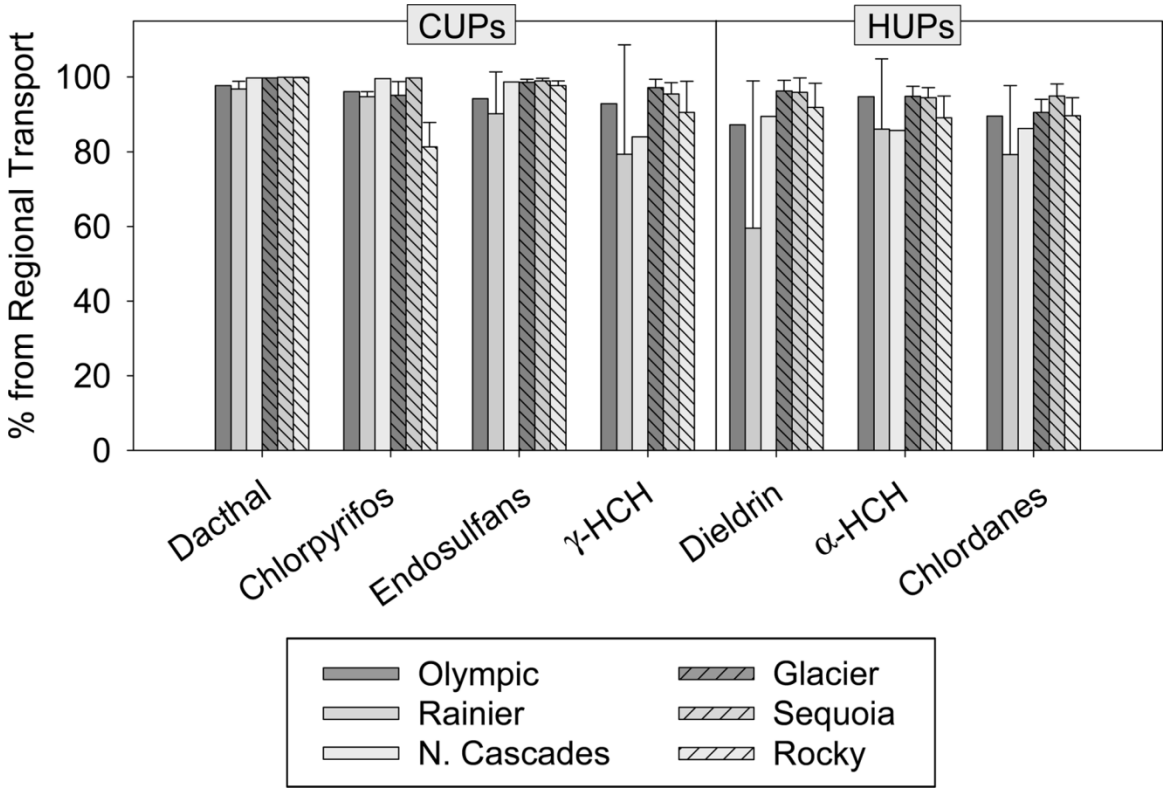
ENDOSULFANS – % Long Range vs. % Regional



CONTRIBUTION OF REGIONAL SOURCES TO PESTICIDES IN SNOWPACK



- DENA, GATES, and NOAT have greatest long-range transport contribution (100%)
- OLYM, MORA and NOCA have some long-range transport contribution (2-15%)
- CUPS more likely from regional sources
- HUPS from long-range sources as well as revolatilization from historically contaminated soils

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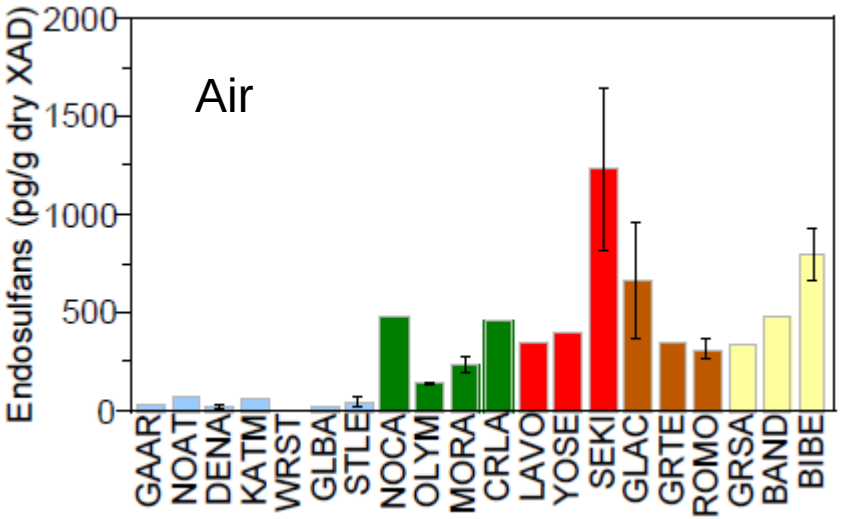
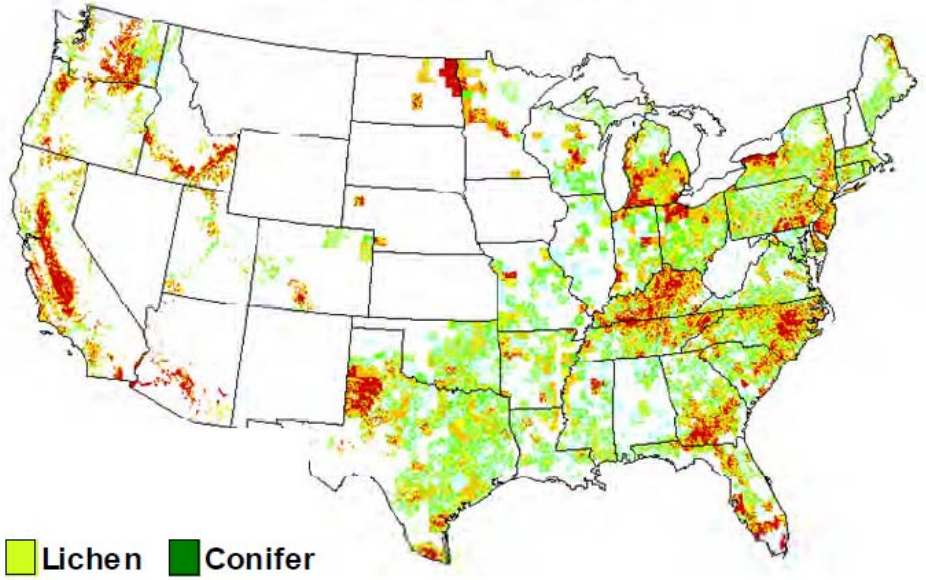
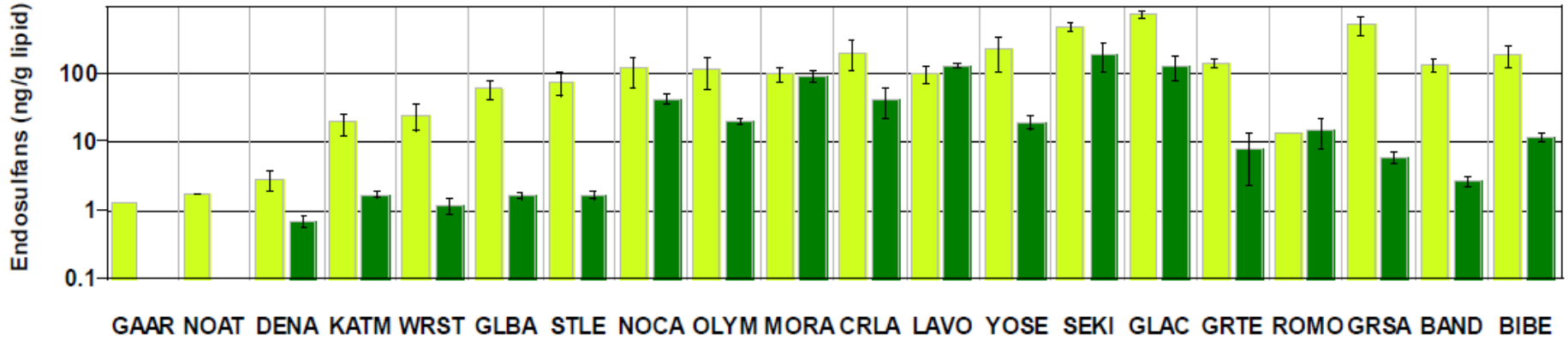
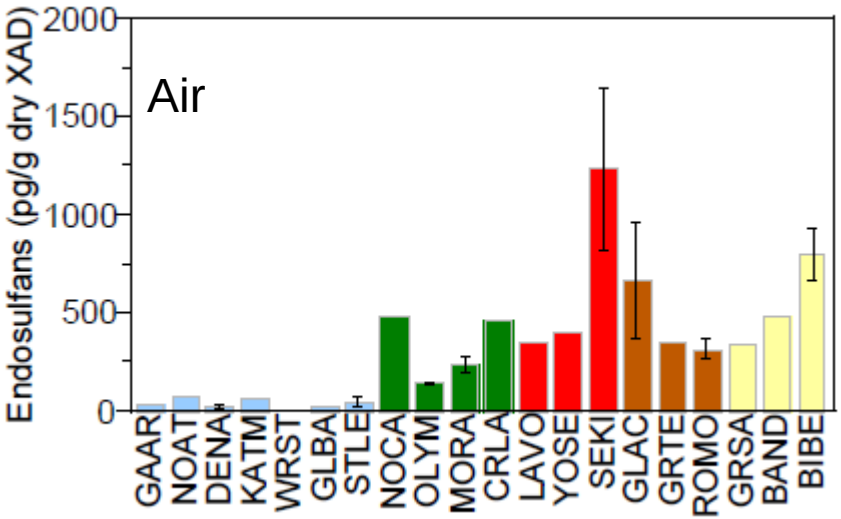
ENDOSULFAN


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
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CRLA
LAVO
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ROMO
GRSA
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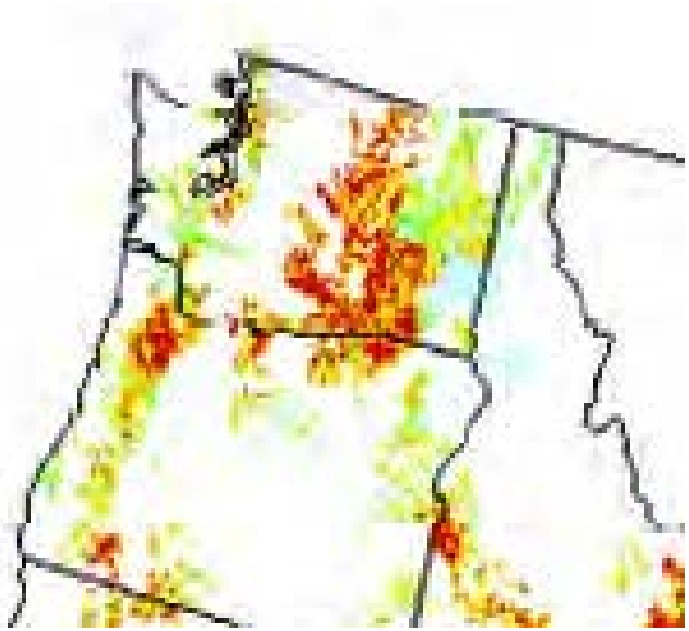
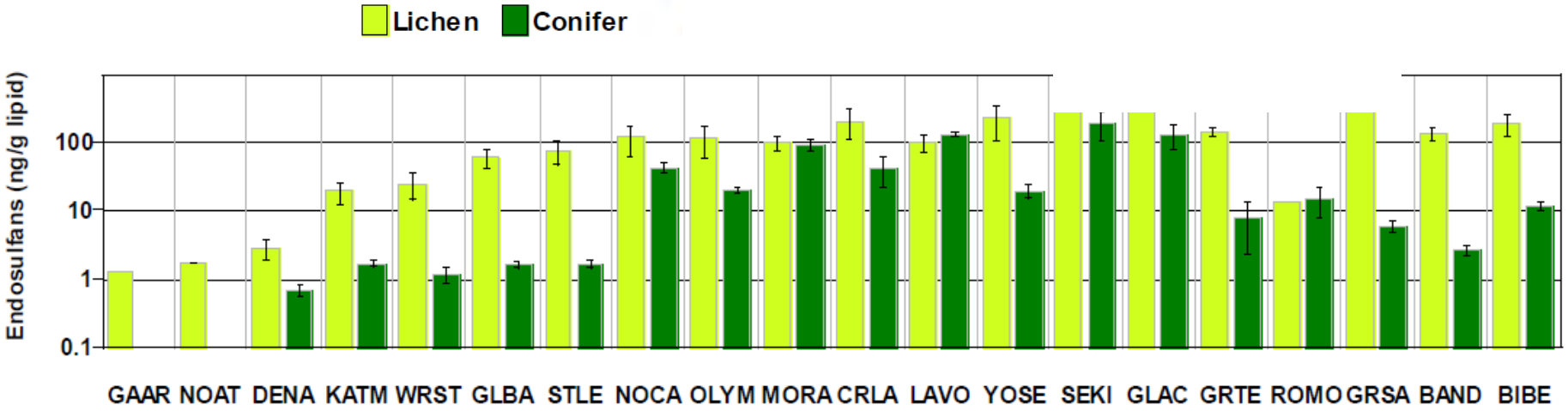
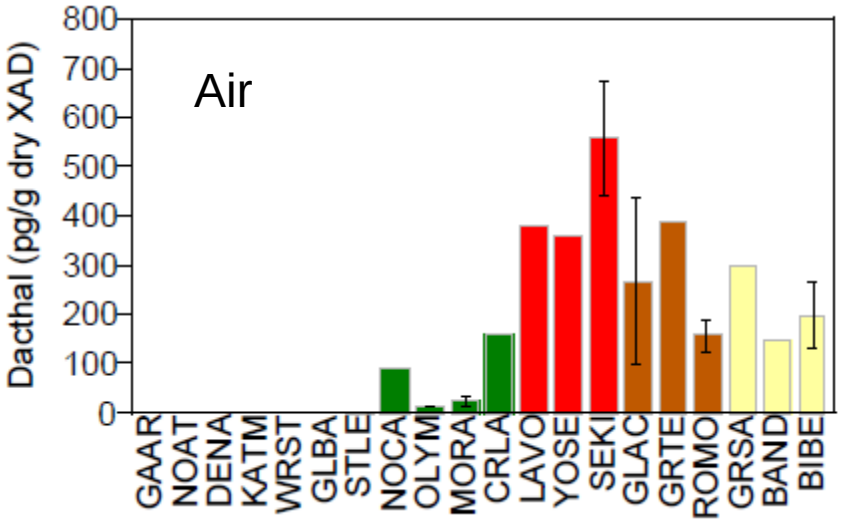
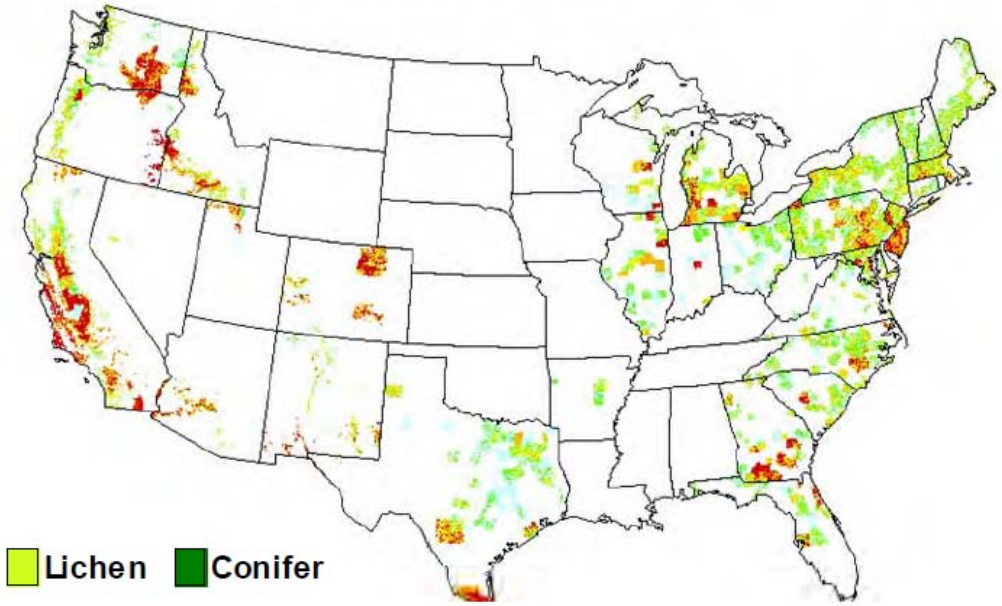
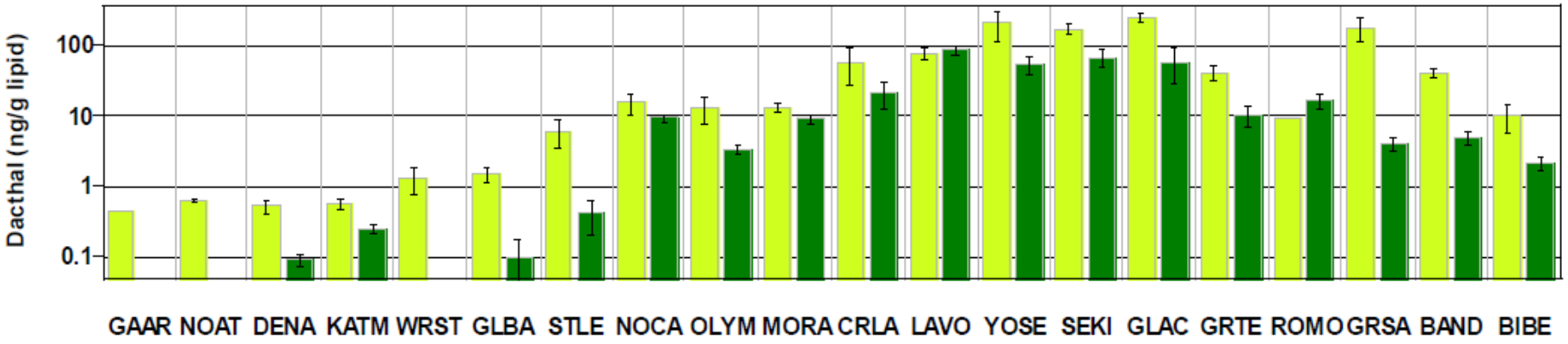



Lichen
Conifer
Endosulfans (ng/g lipid)
100
10
1
0.1
GAAR NOAT DENA KATM WRST GLBA STLE NOCA OLYM MORA CRLA LAVO YOSE SEKI GLAC GRTE ROMO GRSA BAND BIBE

DACTHAL (DCPA)







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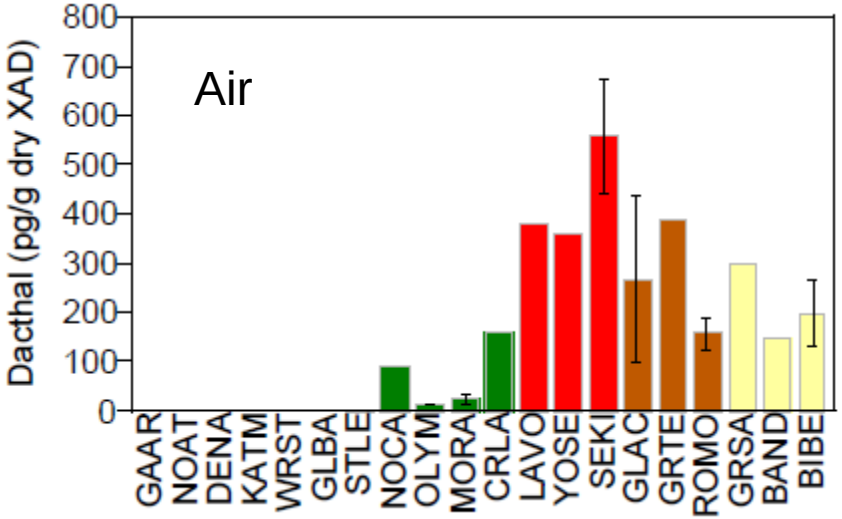
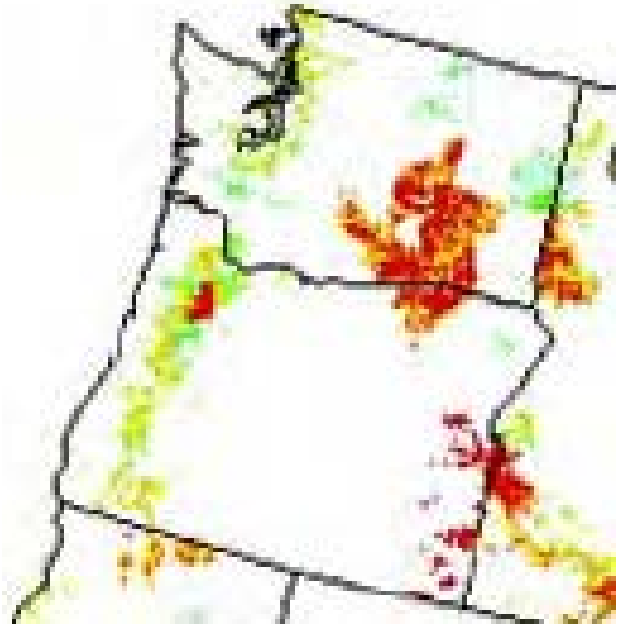
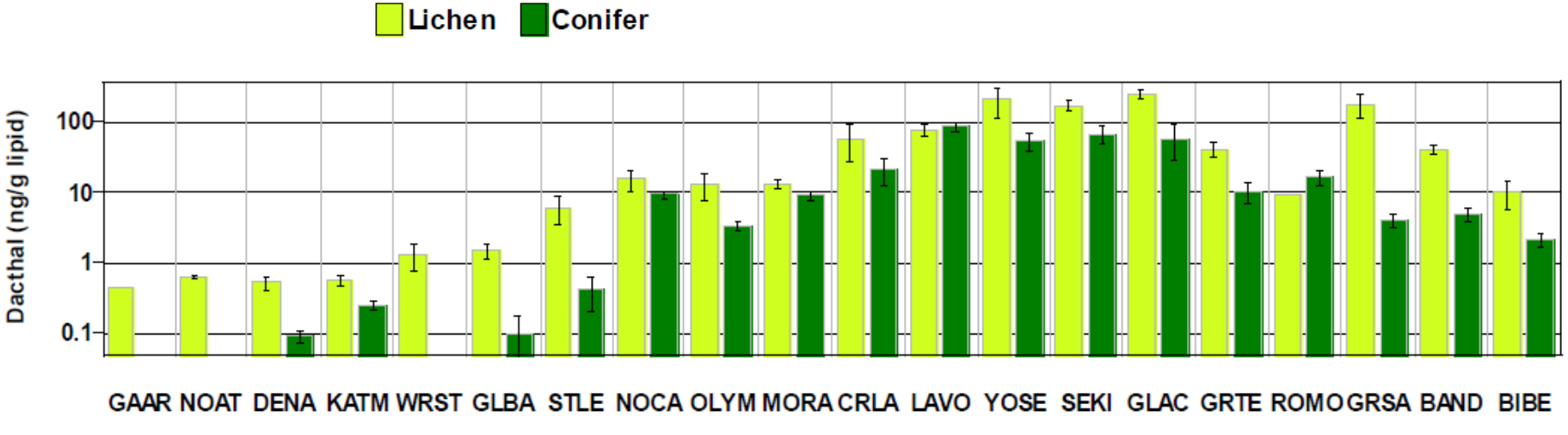
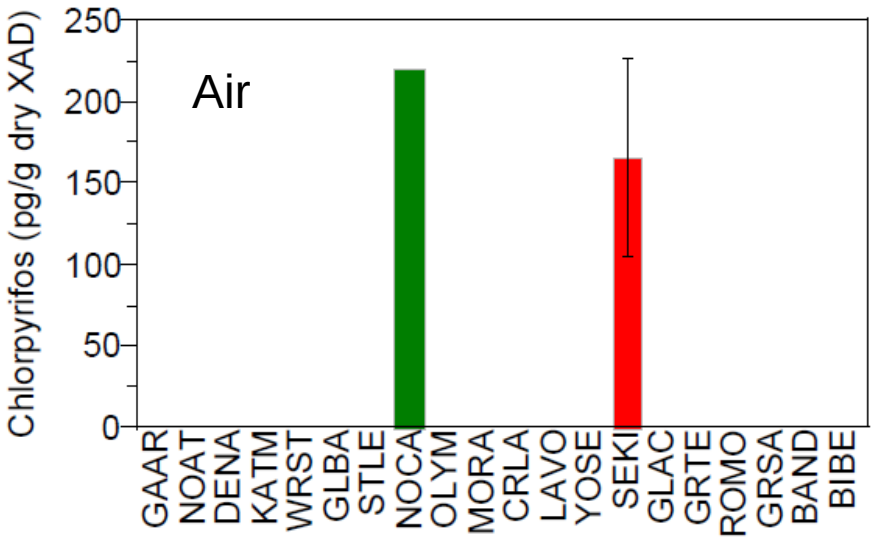
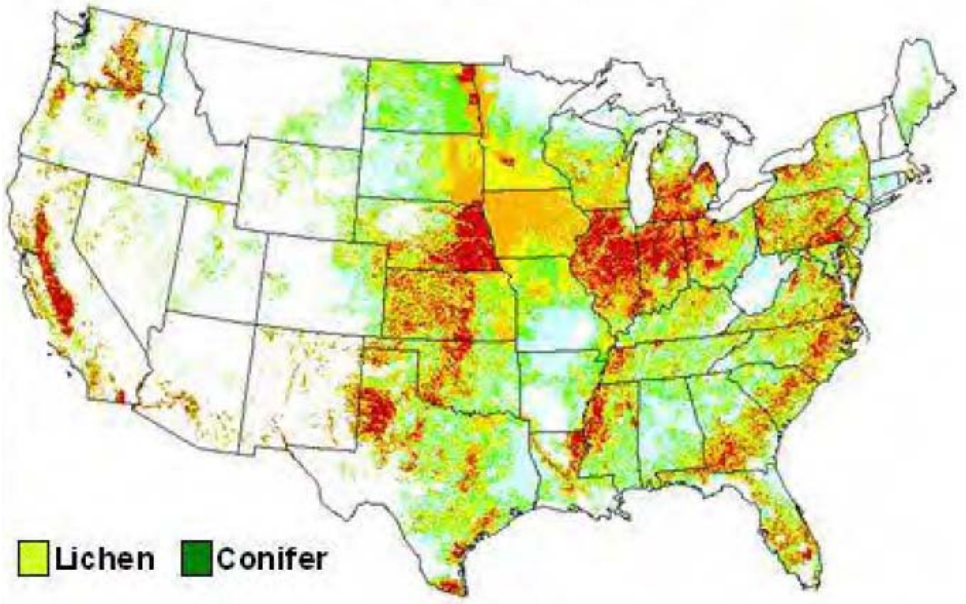


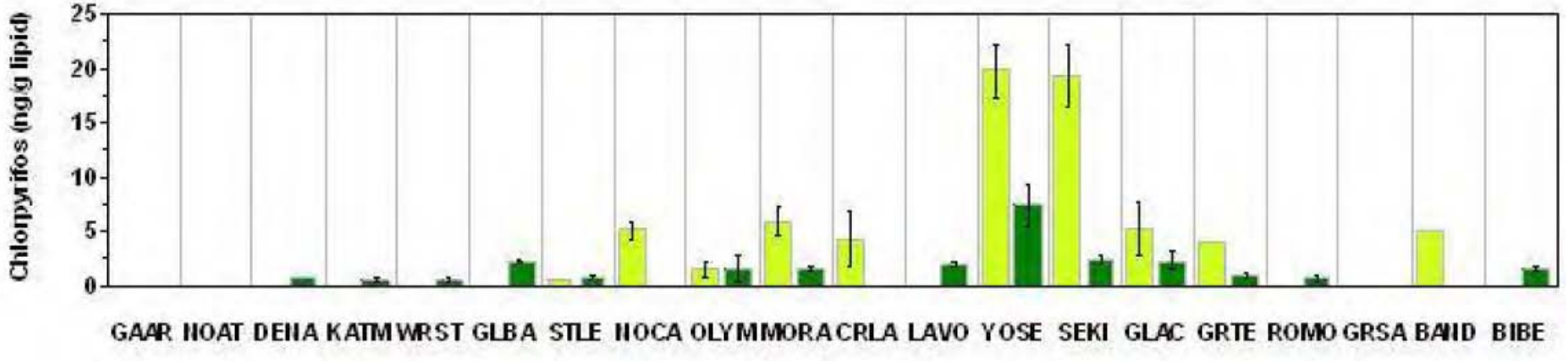




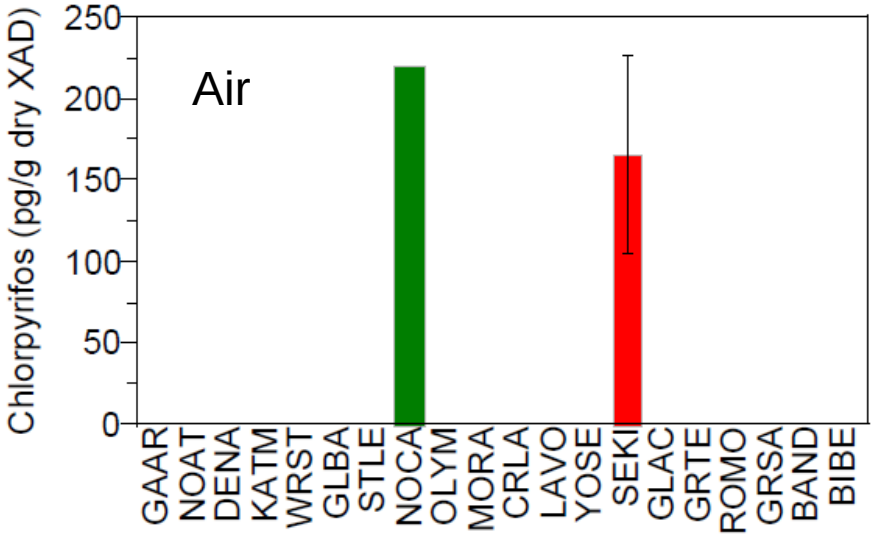
CHLORPYRIFOS

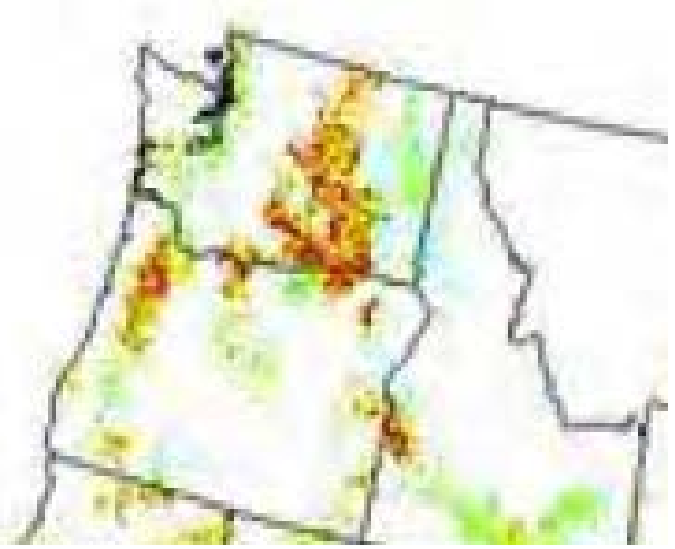


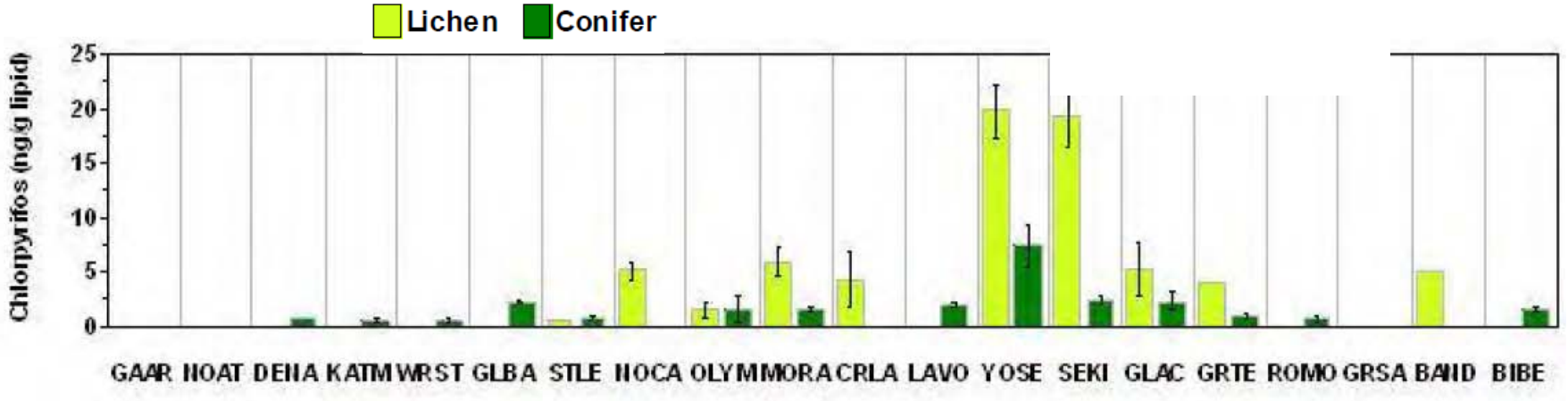




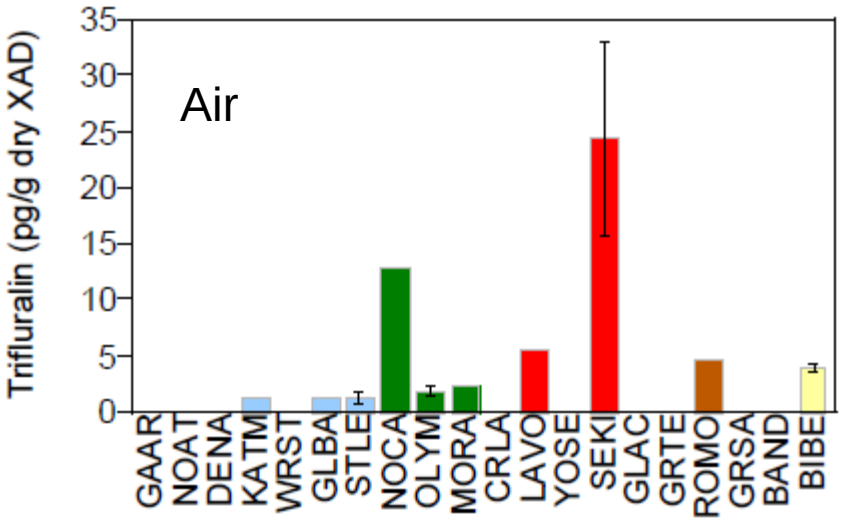
CHLORPYRIFOS

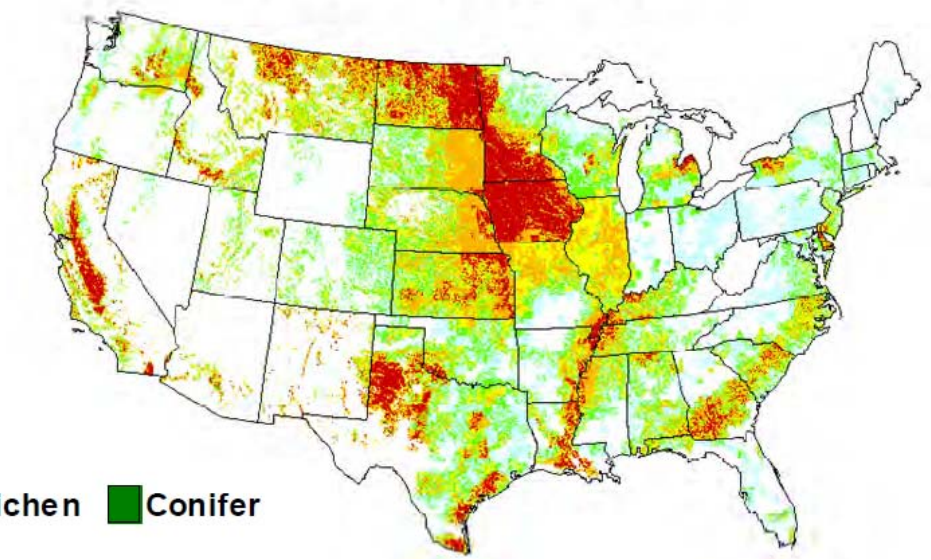


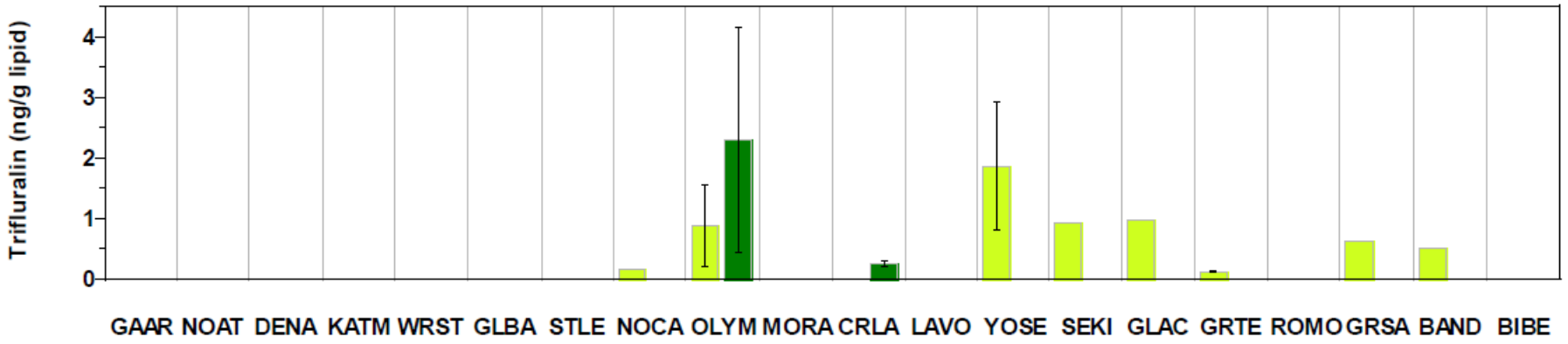




TRIFLURALIN







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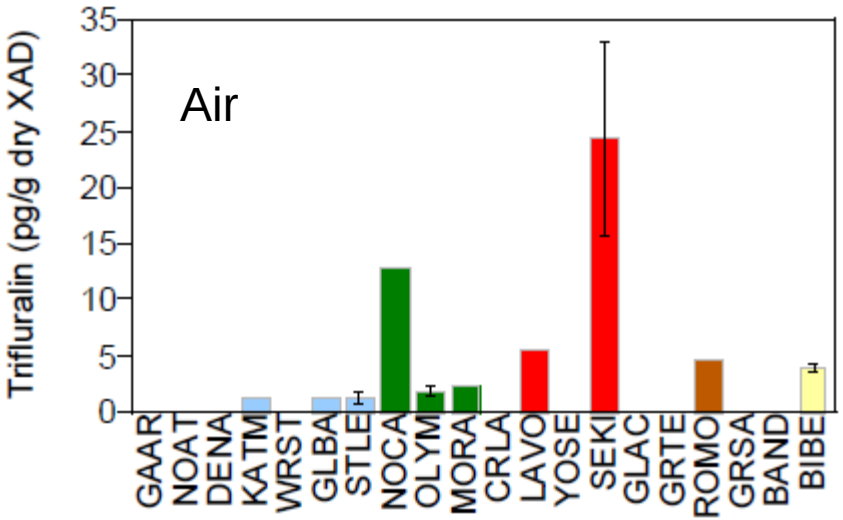
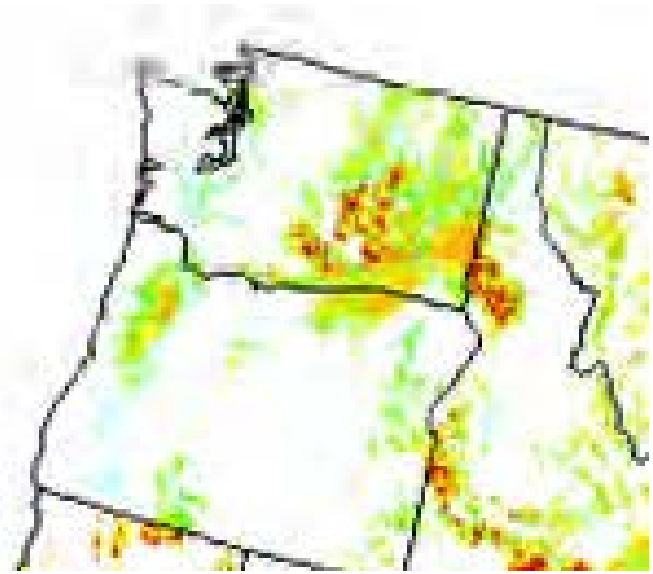
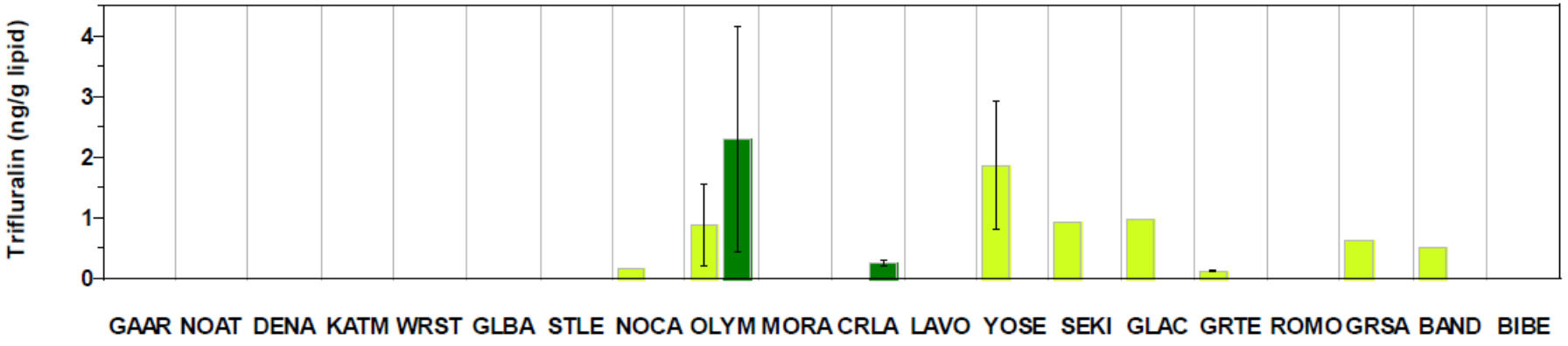
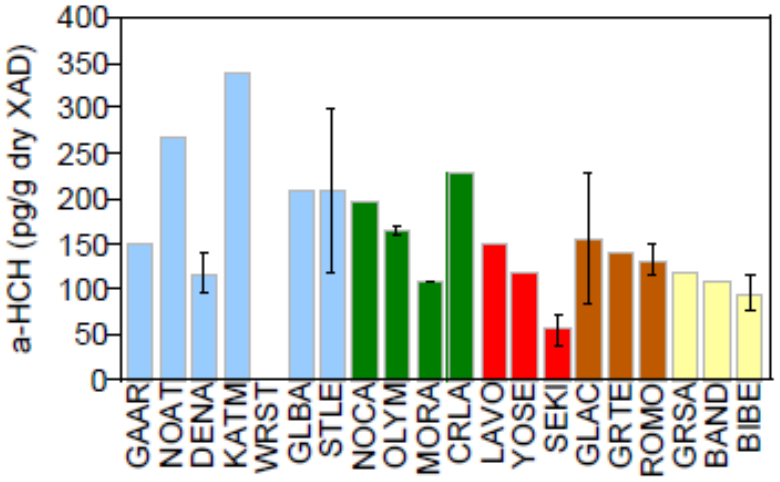






HUPs in AIR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350
300
250
200
150
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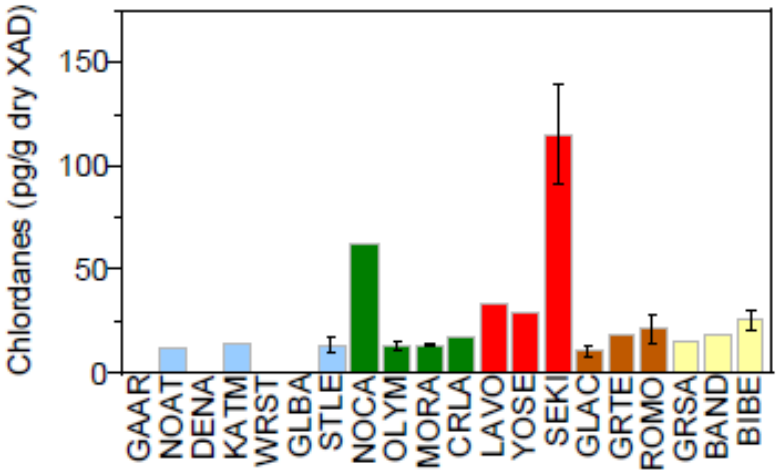
50
0
GAAR
NOAT
DENA
KATM
WRST
GLBA
STLE
NOCA
OLYM
MORA
CRLA
LAVO
YOSE
SEKI
GLAC
GRTE
ROMO
GRSA
BAND
BIBE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GAAR
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YOSE
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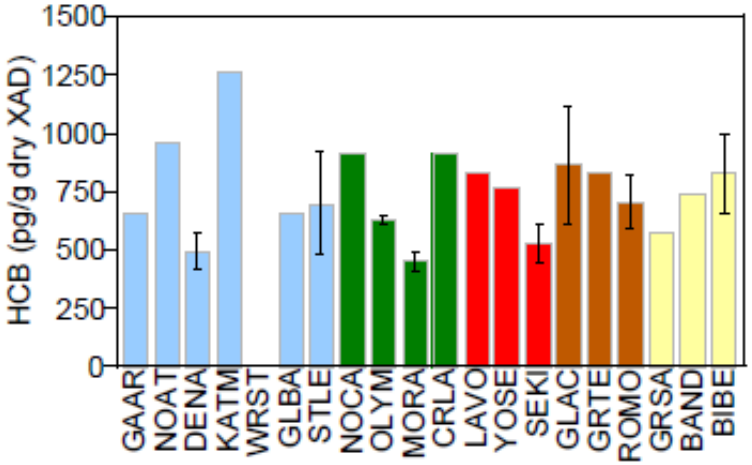
GRTE
ROMO
GRSA
BAND
BIBE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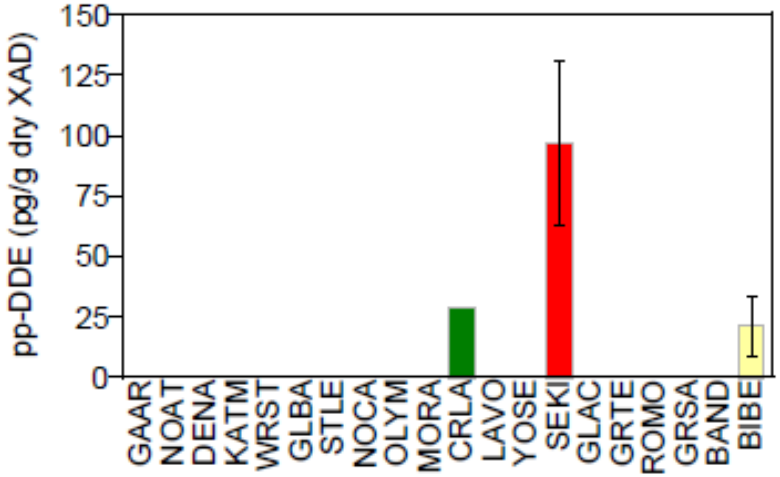
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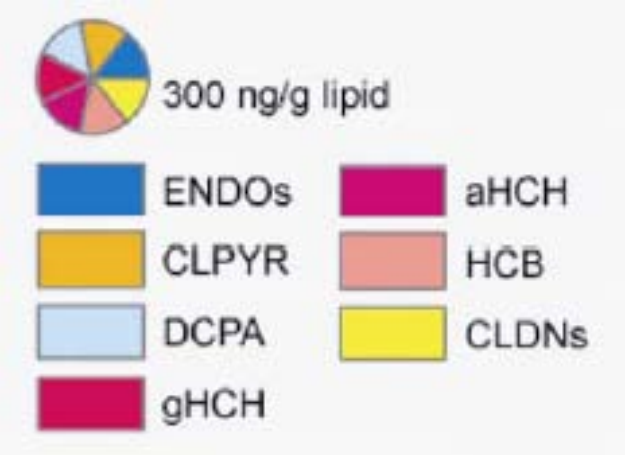
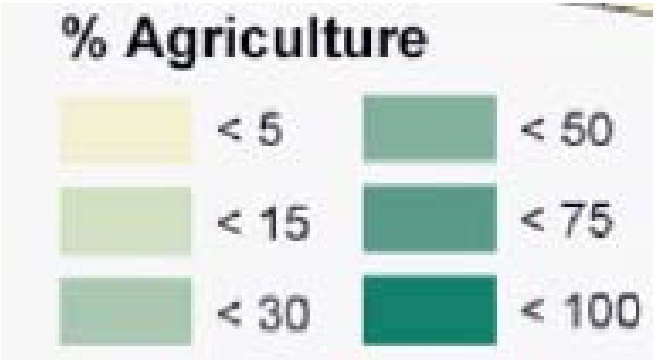
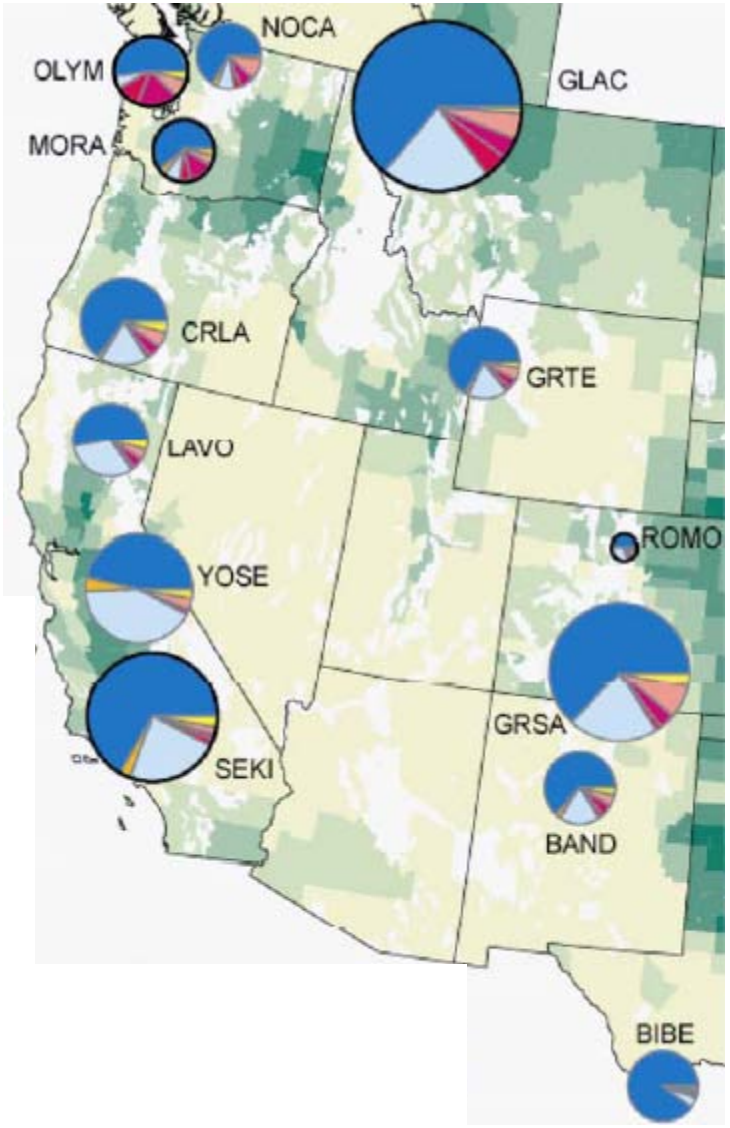
GRSA
BAND
BIBE

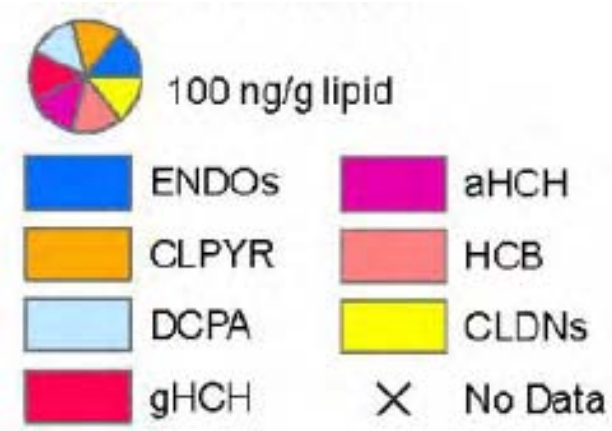
PESTICIDES in LICHEN

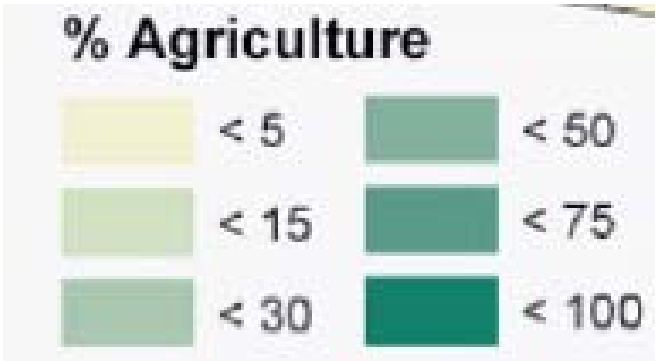


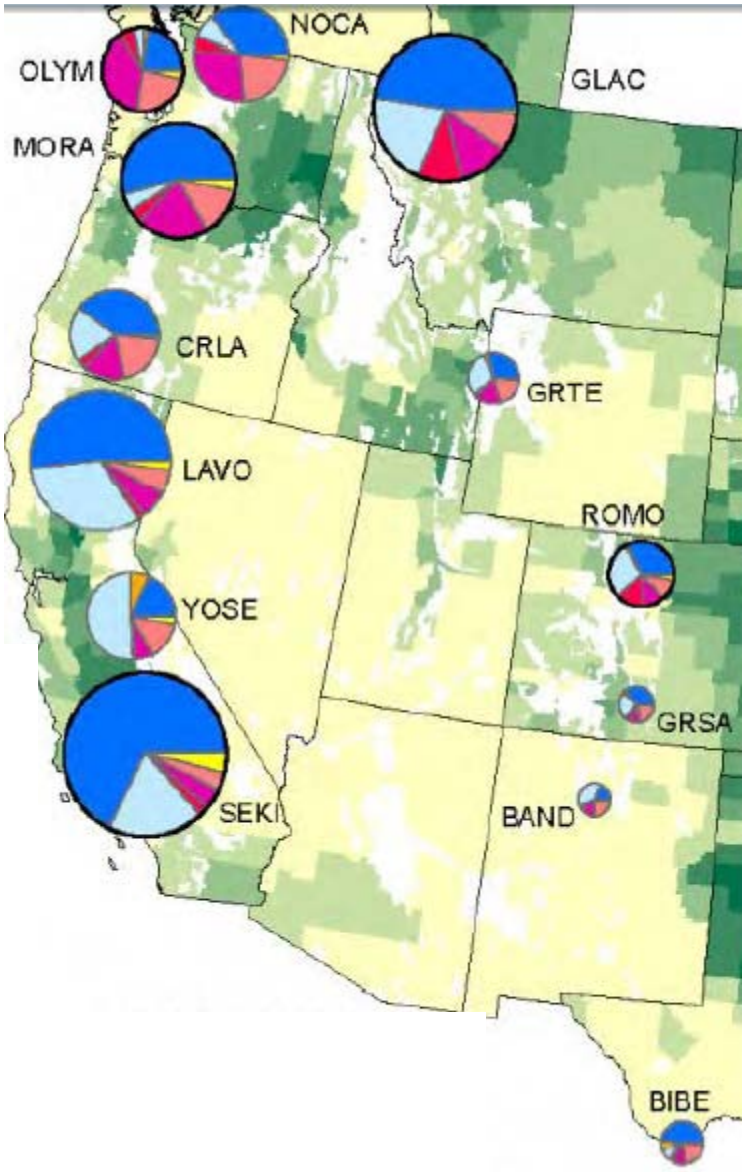




PESTICIDES in CONIFER





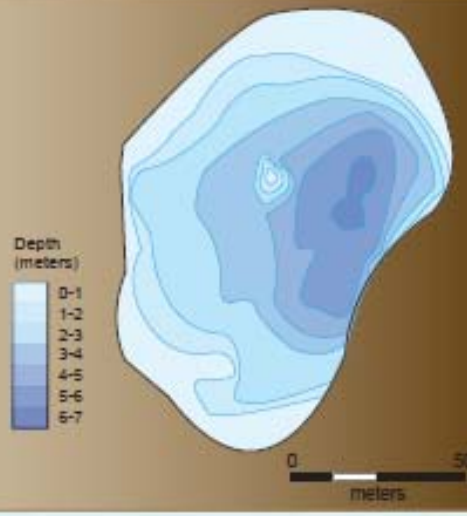


Olympic National Park: *Site Characteristics*

OLYM

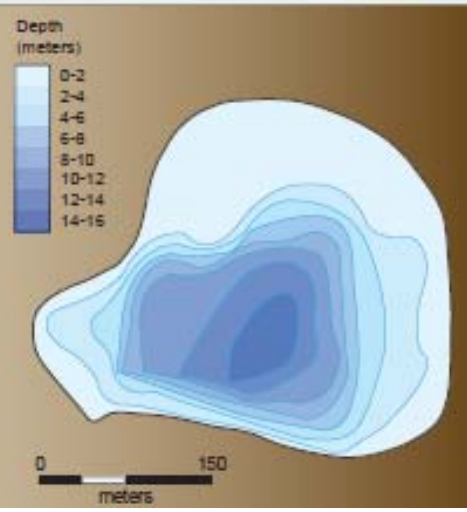
PJ Lake

Location: 47.95N 123.42W
Elevation: 1383.8 m
Maximum Depth: 6.4 m
Surface Area: 0.8 ha
Watershed Area: 56.2 ha

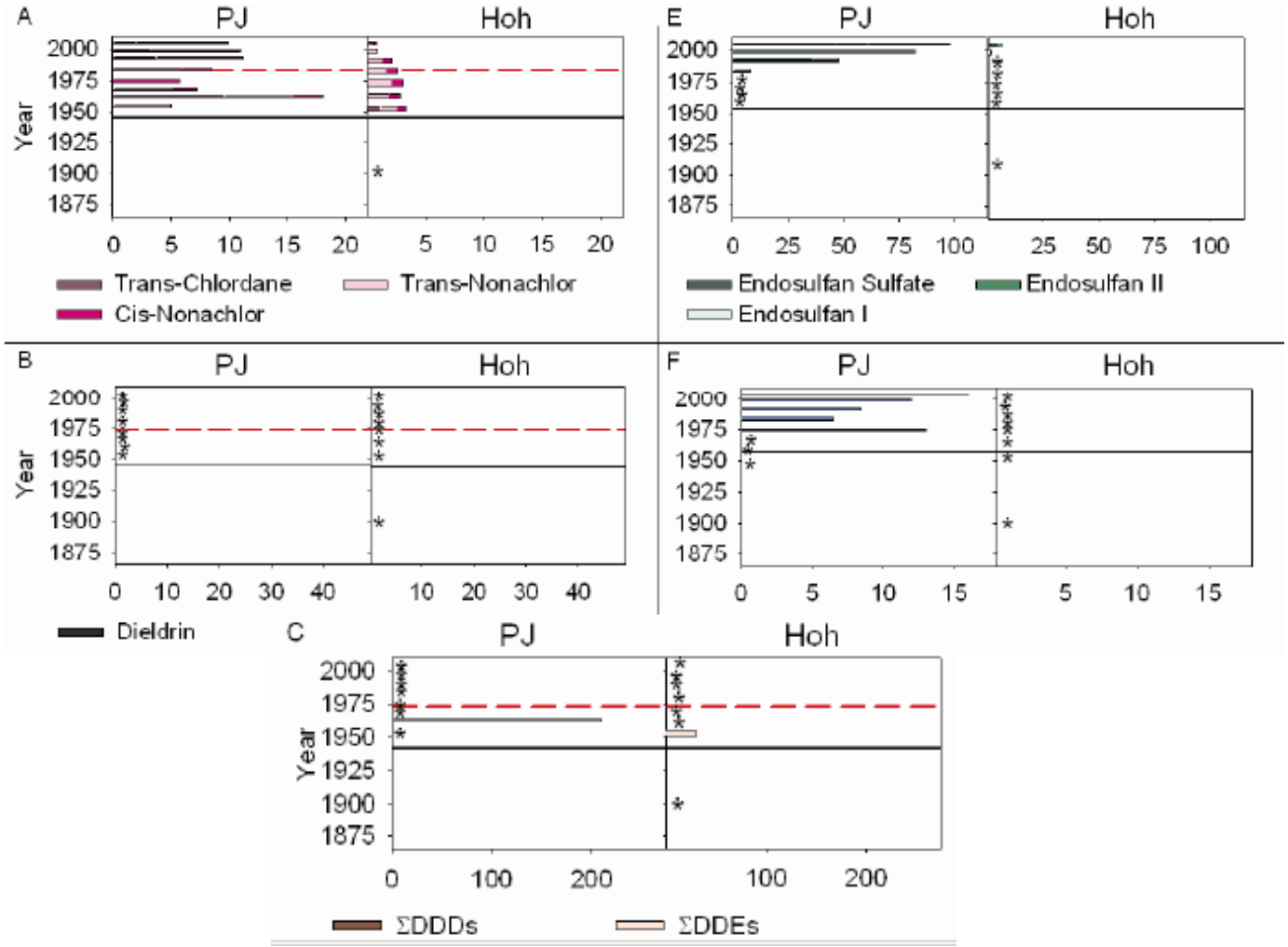


Hoh Lake

Location: 47.90N 123.79W
Elevation: 1379.2 m
Maximum Depth: 14.9 m
Surface Area: 7.7 ha
Watershed Area: 43.9 ha



PESTICIDES IN OLYM SEDIMENT



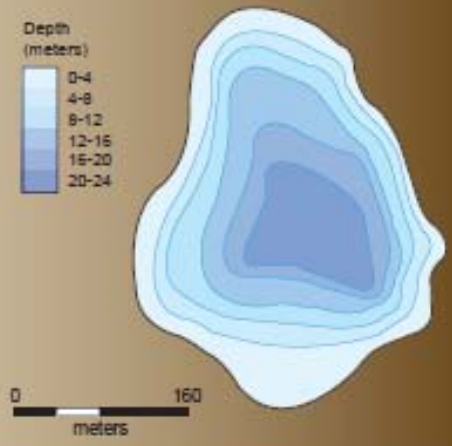
- PJ more influenced by agriculture than Hoh
- CUPs going up and HUPs going down

Mount Rainier National Park: *Site Characteristics*

MORA

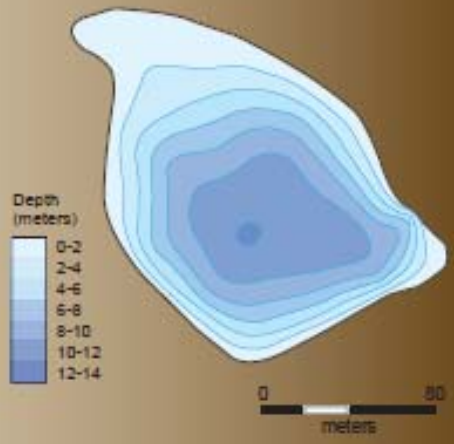
Golden Lake

Location: 46.89N 121.90W
Elevation: 1368.6 m
Maximum Depth: 23.9 m
Surface Area: 6.6 ha
Watershed Area: 106.1 ha

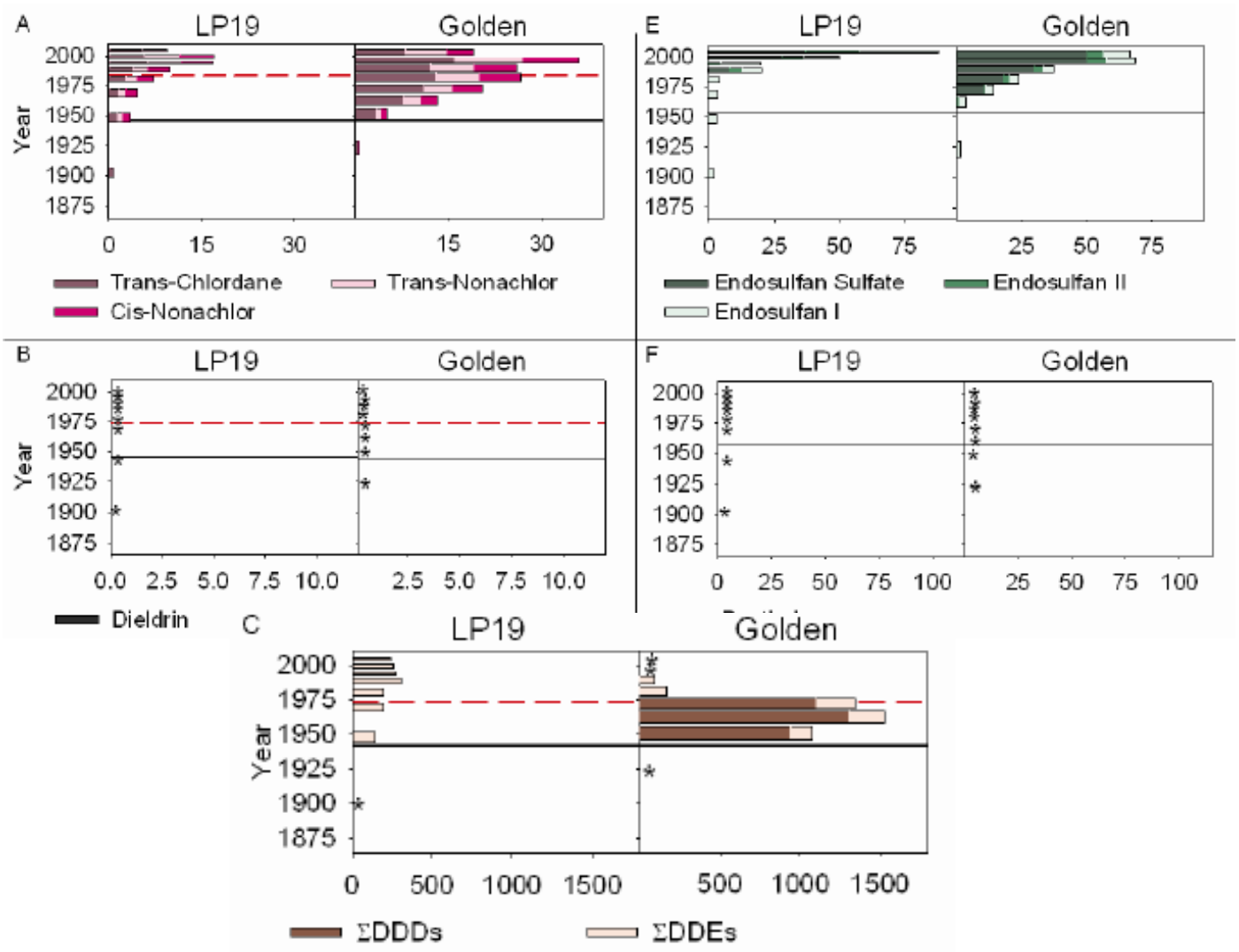


LP19

Location: 46.82N 121.89W
Elevation: 1371.6 m
Maximum Depth: 12.1 m
Surface Area: 1.8 ha
Watershed Area: 44.9 ha

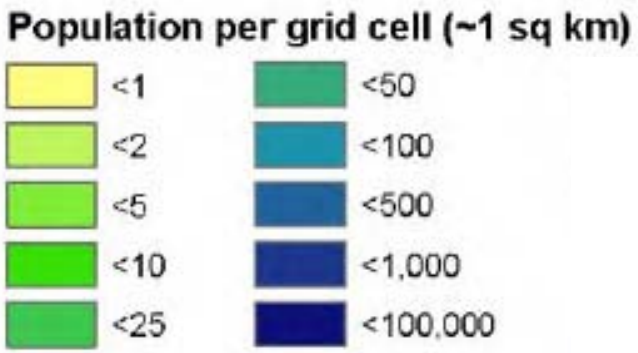


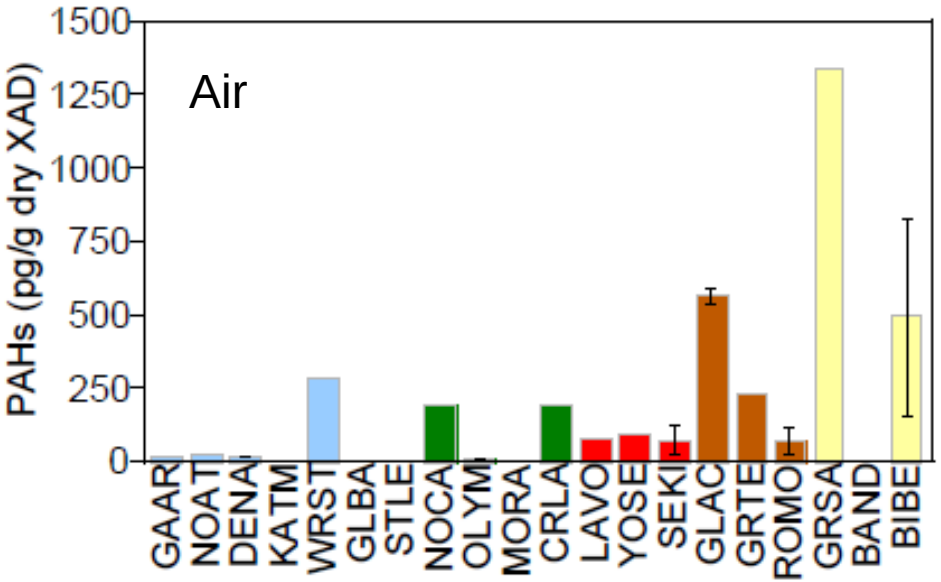
PESTICIDES IN MORA SEDIMENT

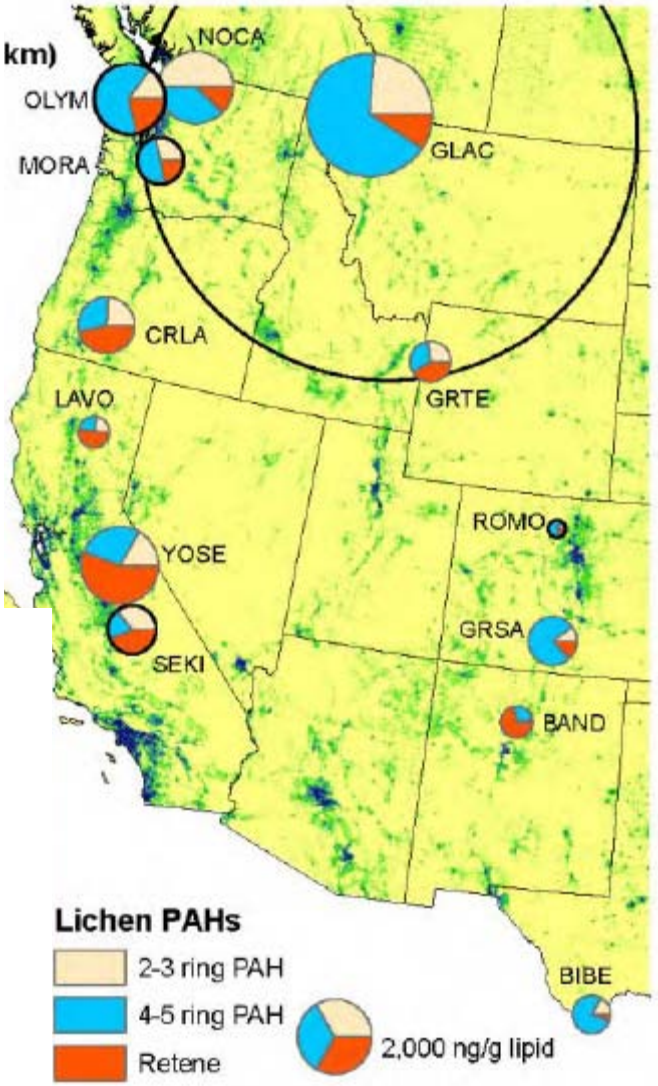


- Golden more influenced by agriculture than LP19 (?)
- CUPs going up and HUPs going down

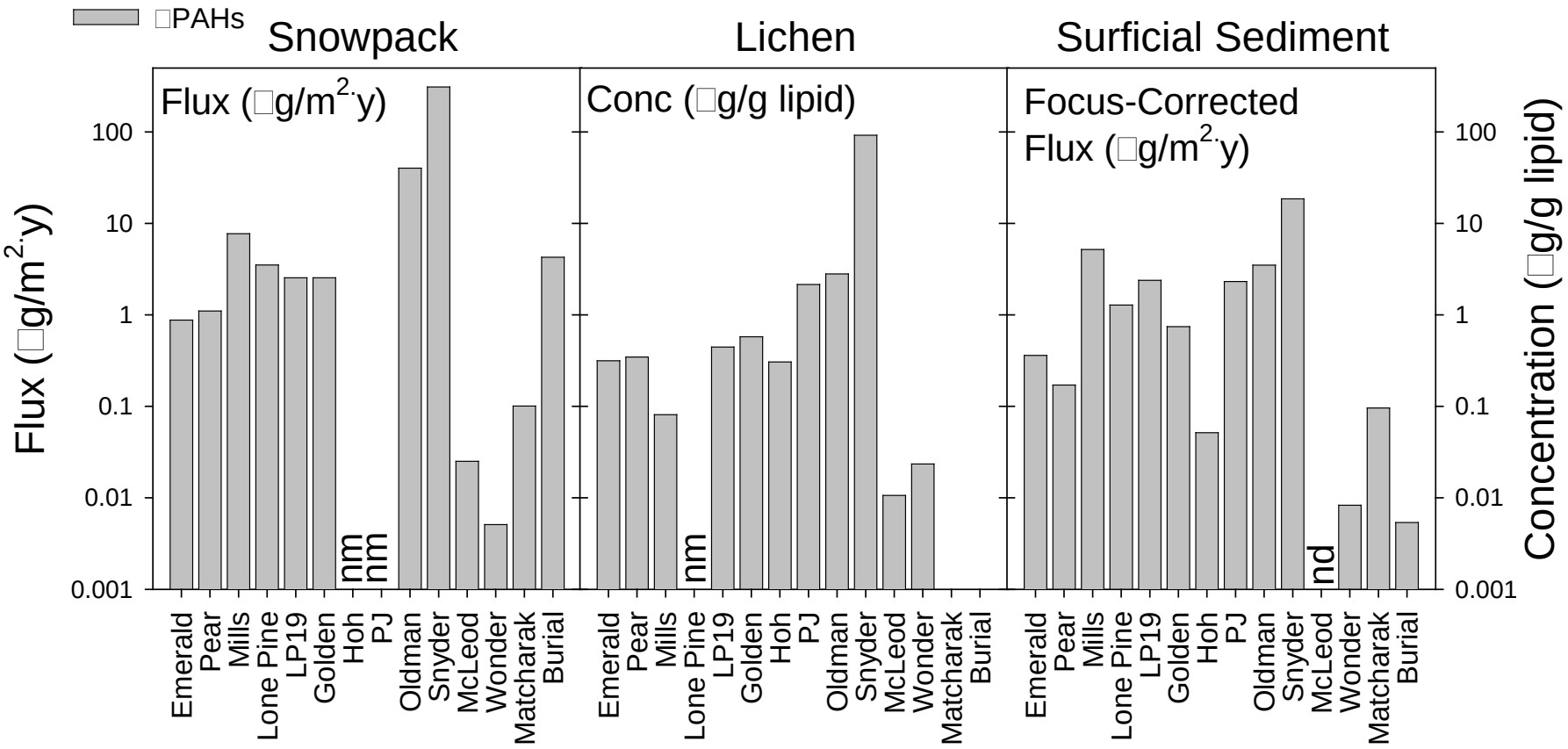
POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)







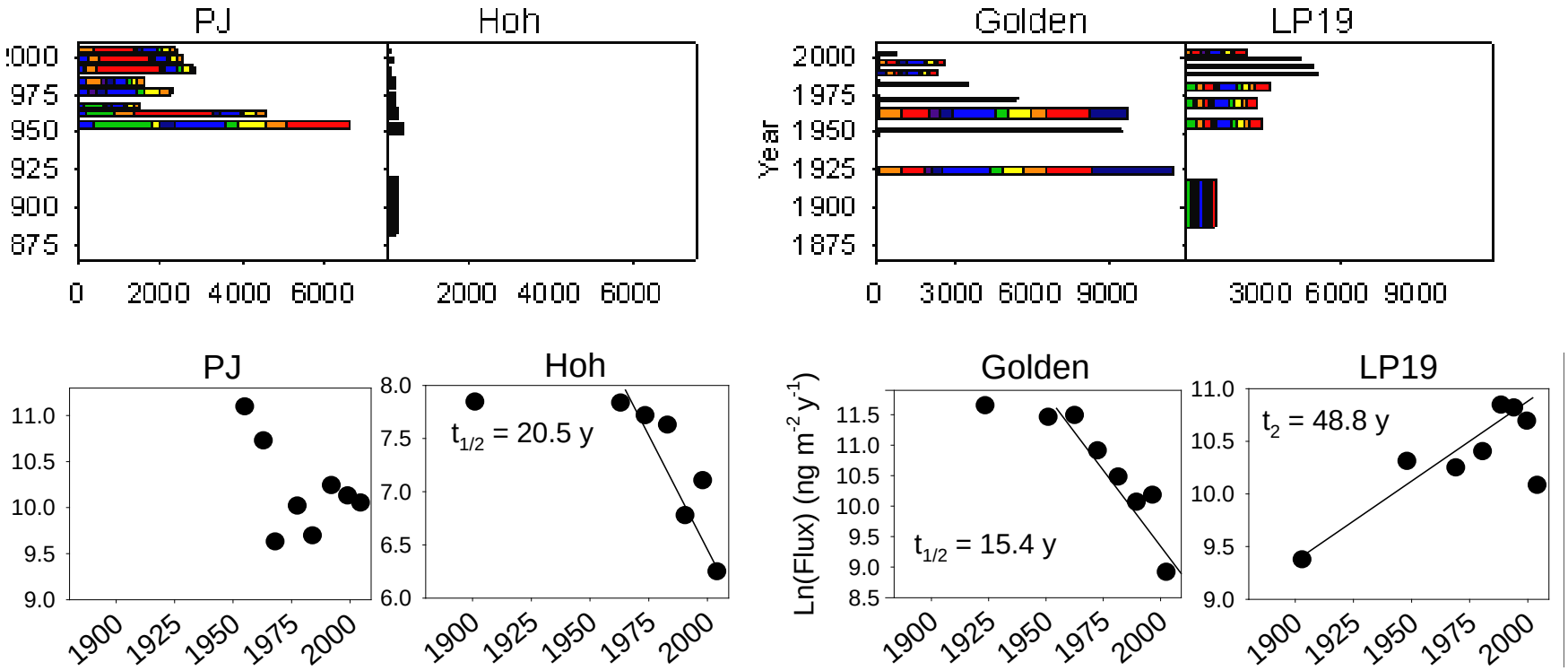
PAHs IN SNOW, LICHEN AND SURFICIAL SEDIMENT



Usenko et al, *Environ. Sci, Technol*., **2010**

- GLAC > OLYM and MORA and ROMO and SEKI > NOAT and DENA
- OLYM and MORA ~ SEKI and ROMO

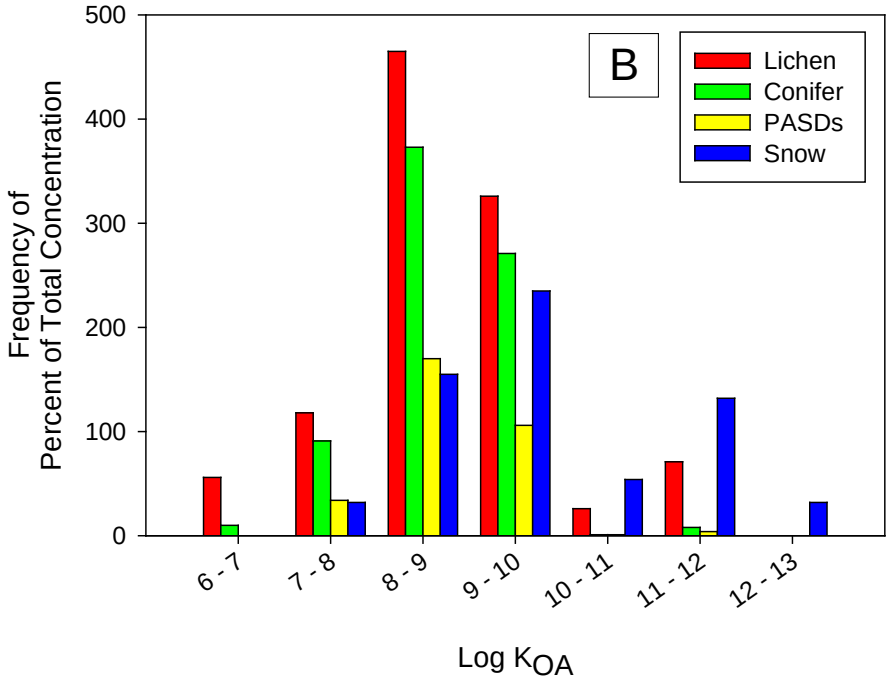
PAHs IN THE SEDIMENT COREs

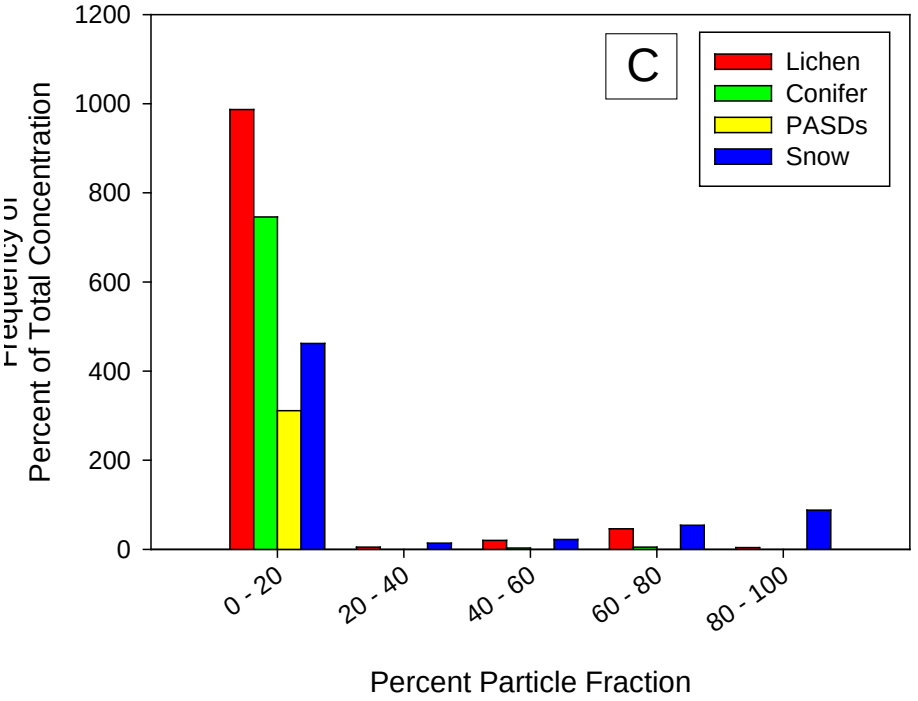


Usenko et al, *Environ. Sci, Technol.*, **2010**

- PJ and Golden more influenced by ships/urban areas
- PAH flux is decreasing in Golden and Hoh and increasing in LP19

Which Passive Air Sampler Should You Use?

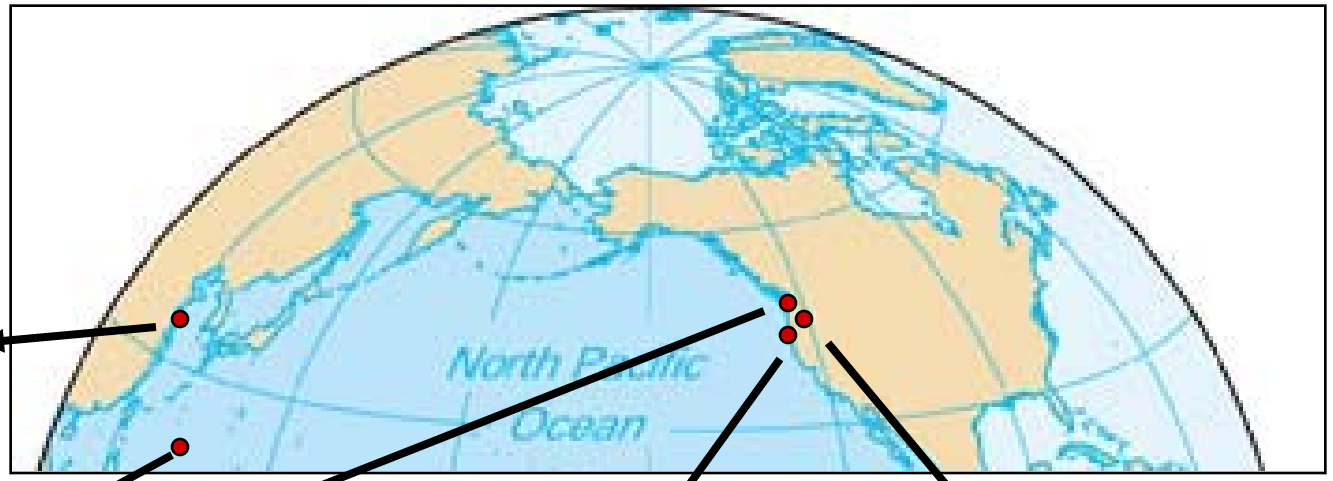




- Lichen – part of ecosystem, G+P, ease of collection, unknown exposure period
- Conifer Needles – part of ecosystem, G, ease of collection, known exposure period, more difficult chemistry
- PASDs – man made (uniform), G, 2 trips, known exposure period, low accumulation
- Snow – part of ecosystem, G+P, difficult to collect, known exposure period

Atmospheric Transport from Asia to the U.S.

Beijing, China
45 m



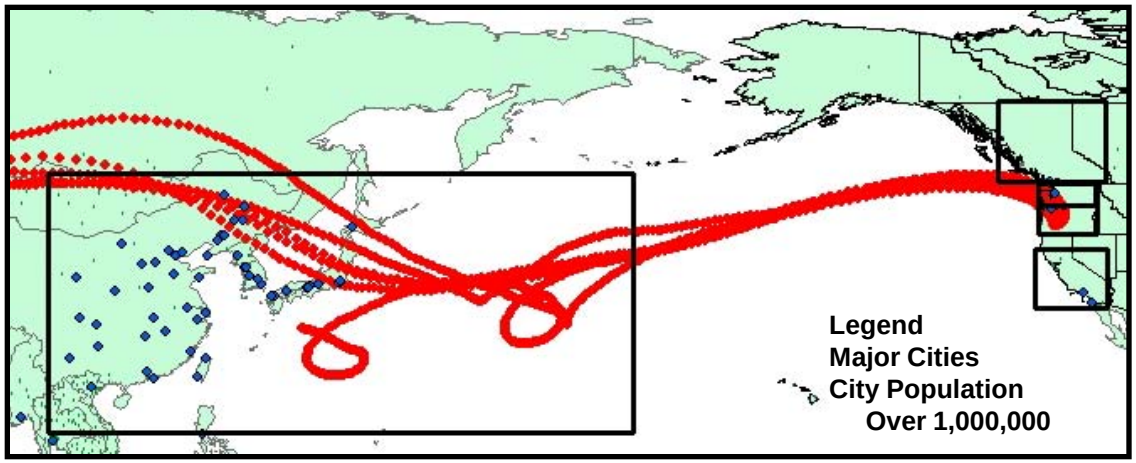
Cheeka Peak Observatory
Tip of Olympic Peninsula
500 m

Okinawa, Japan
60 m

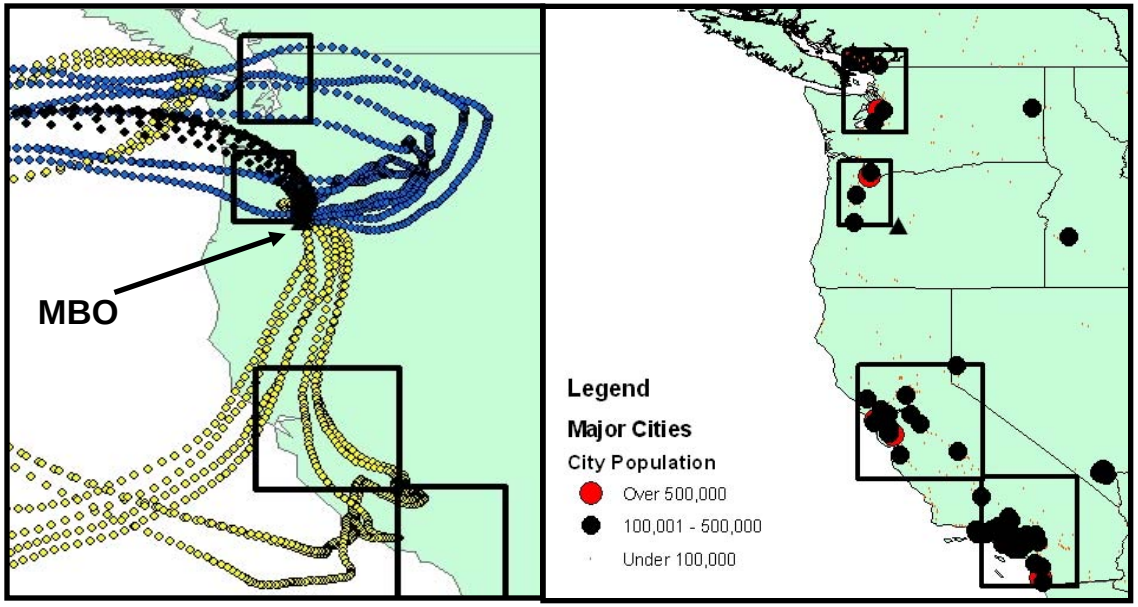
Marys Peak
Oregon Coast Range
1250 m

Mt. Bachelor
Oregon Cascade Range
2700 m

Mt. Bachelor Source Regions



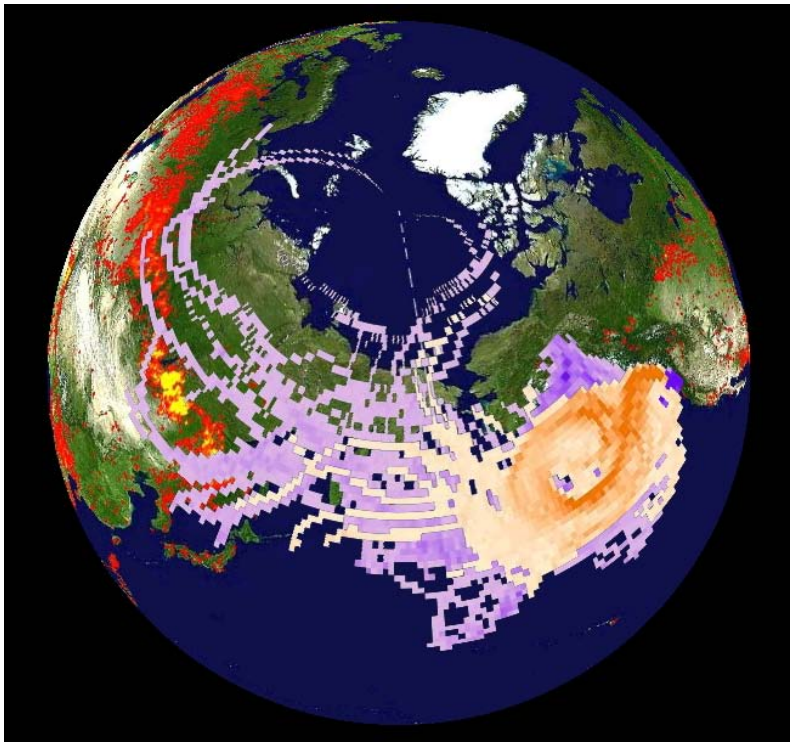
Asian and North American Source Regions



Western U.S. Urban Source Regions

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

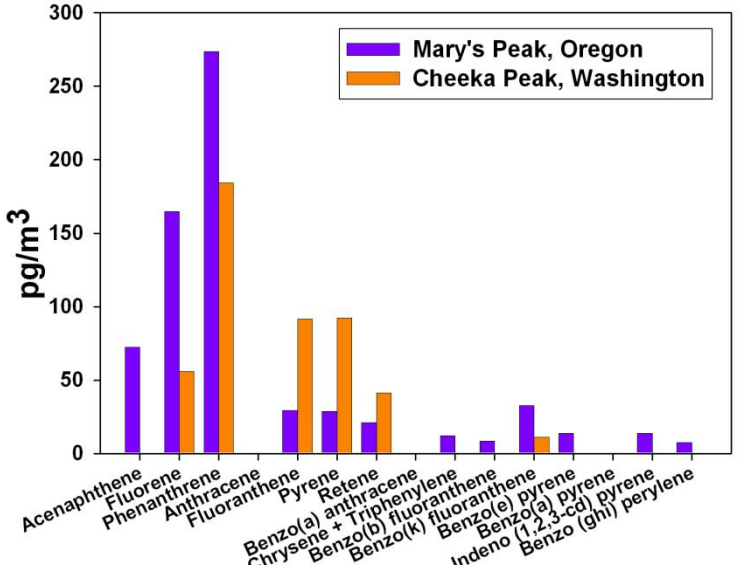
SOC Re-emission from Siberian Fires

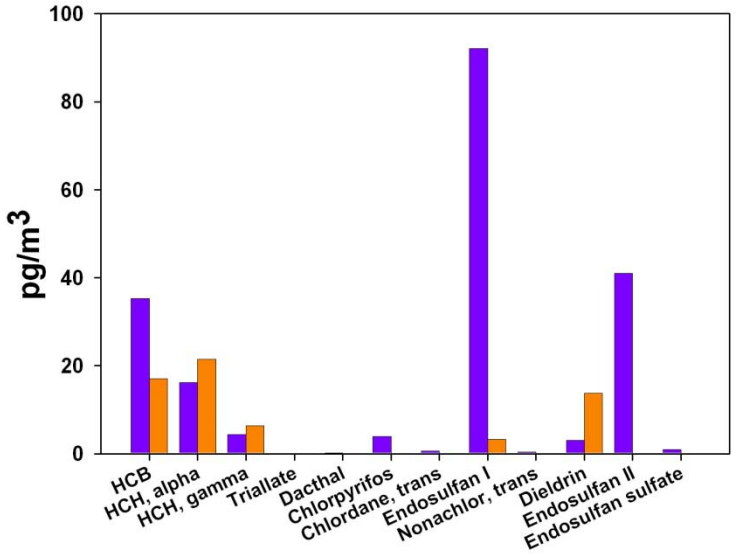


June 2, 2003

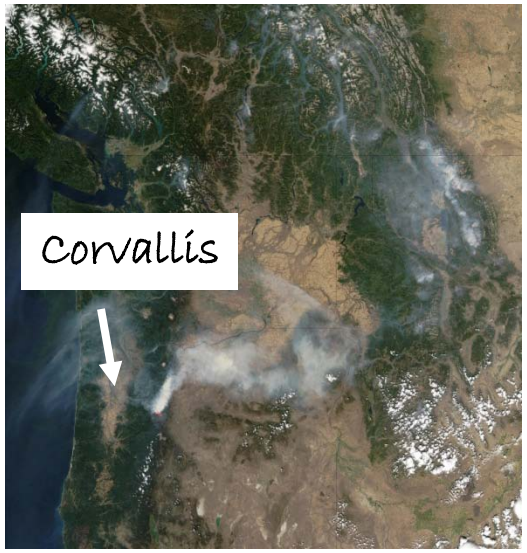
10-day Air Mass Back Trajectories

Marys Peak and Cheeka Peak





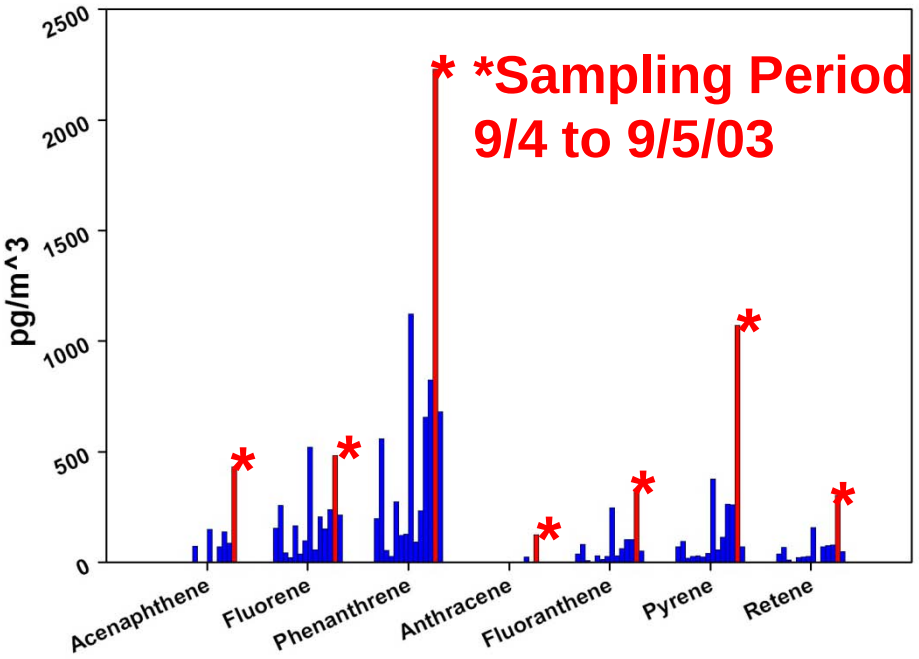
Genualdi and Simonich et al, *Environ. Sci. Technol.* **2009**



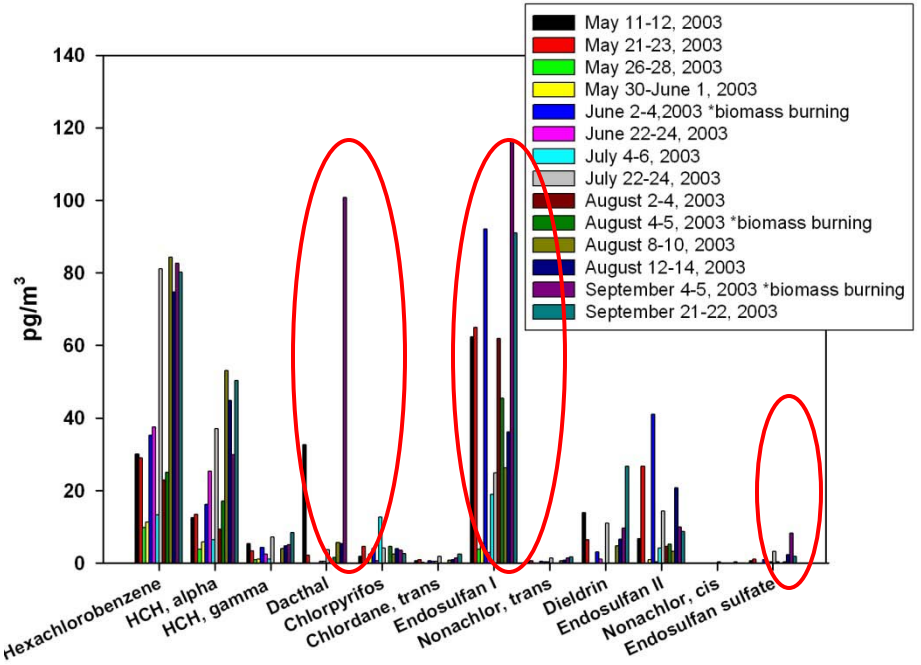
B & B Complex Fire
September 4-5, 2003

Marys Peak

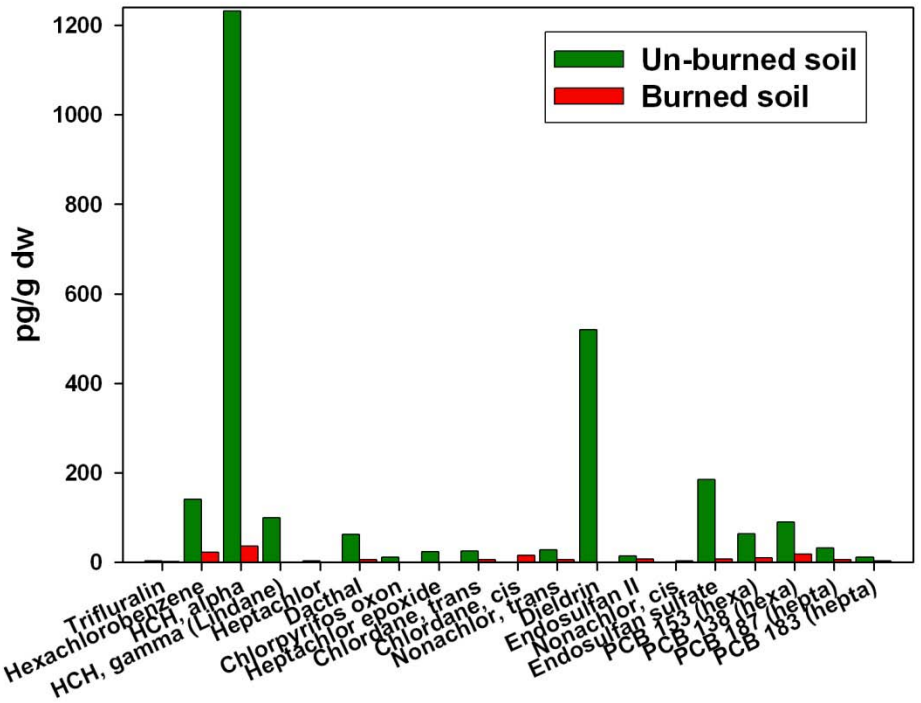
PAHs

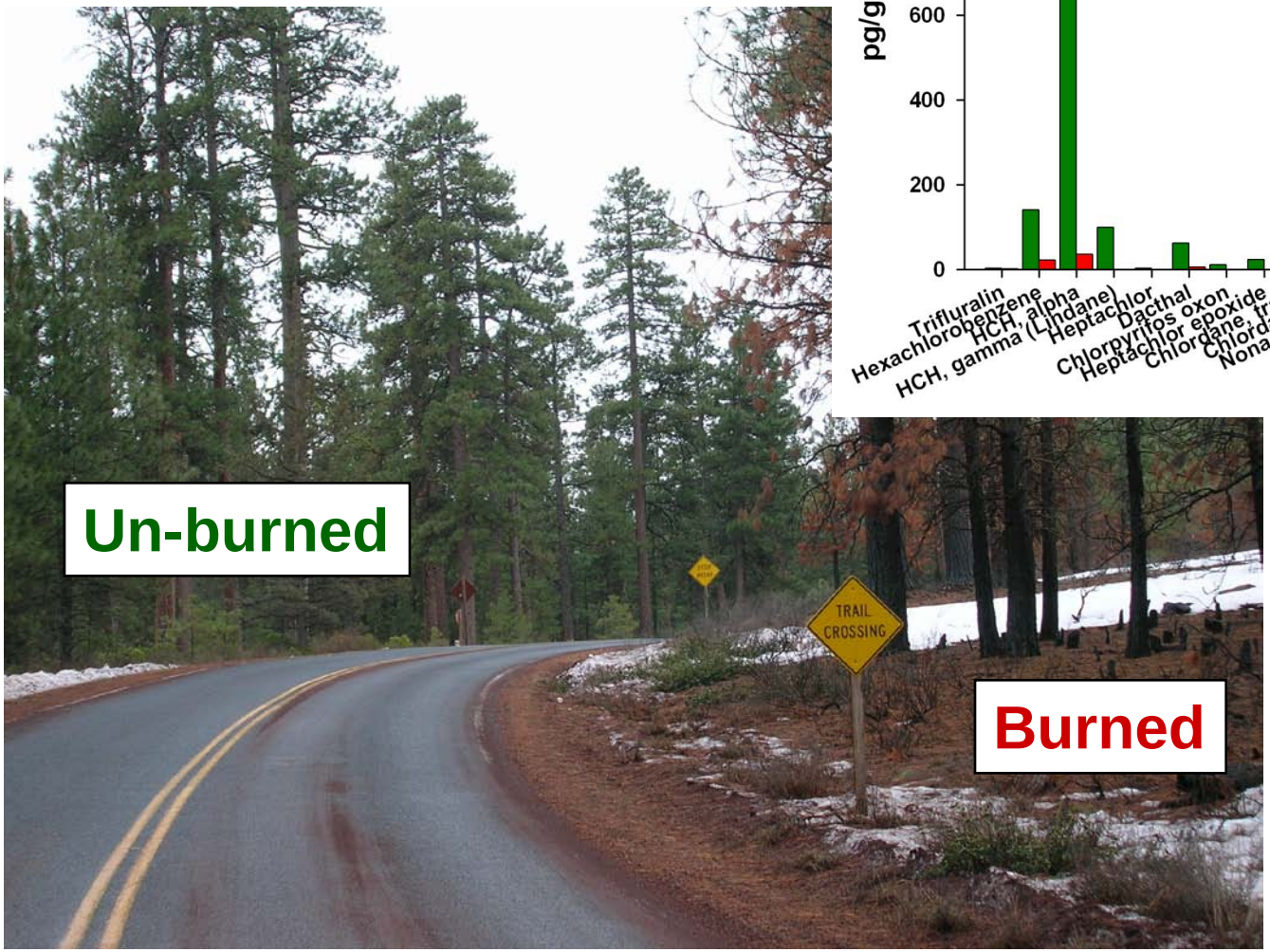


Pesticides



Soil from B & B complex fire





Genualdi and Simonich et al, *Environ. Sci. Technol.* **2009**

CONCLUSIONS

- Pesticides Concentrations: Less than SEKI and GLAC, approximate to ROMO

- CUPs going up, HUPs going down

- PAH Concentrations: Less than GLAC, approximate to SEKI and ROMO

- PJ and Golden Lakes are more influenced by agriculture and ships/population than Hoh and LP19 Lakes

- Long-range transport contribution to OLY, MORA and NOCA ~ 2-15%

SIMONICH LAB WACAP PUBLICATIONS TO DATE

1. J. Schrlau, L. Geiser, K.J. Hageman, D. Landers, S. Massey Simonich. **2010**. "Comparison of Lichen, Conifer Needles, Passive Air Sampling Devices, and Snowpack as Passive Sampling Media to Measure Semi-Volatile Organic Compounds in Remote Atmospheres". In preparation.
2. S. A. Genualdi, K.J. Hageman, L.K. Ackerman, S. Usenko, S. Massey Simonich. **2010**. "Sources and Fate of Chiral Organochlorine Pesticides in Western U.S. National Park Ecosystems". *Environmental Science and Technology*, submitted.
3. S. Usenko, S. Massey Simonich, K. Hageman, J. Schrlau, L. Geiser, D. Campbell, P. Appleby, D. Landers. **2010**. "Sources and Deposition of Polycyclic Aromatic Hydrocarbons to Western U.S. National Parks", *Environmental Science and Technology*, 44(12), 4512-4518.
4. K. Hageman, W. Hafner, D. Campbell, D. Jaffe, D. Landers, S.L. Massey Simonich. **2010**. "Variability in Pesticide Deposition and Source Contributions to Snowpack in Western U.S. National Parks", *Environmental Science and Technology*, 44(12), 4452-4458.
5. 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.
6. 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.
7. 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.
8. 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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Don Campbell – USGS
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Will Hafner – UW-Bothell