# Airborne Toxics in Western National Parks: Western Airborne Contaminants Assessment Project (WACAP)

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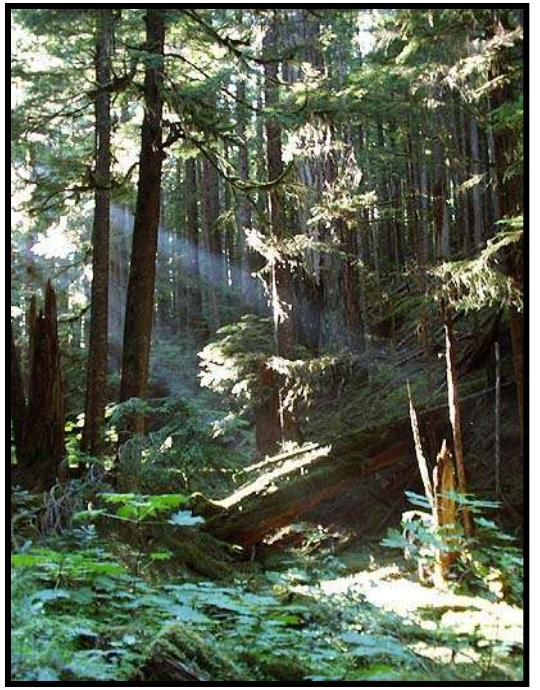
March 2, 2010



# TARGET ANALYTES

## Electron Impact Ionization

**PAHs:** Acenaphthylene, Acenaphthene, Fluorene, Phenant… Pyrene, Retene, …phenylene, Benzo[… …ne, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene

Combustion

**Pesticides and degradation products:**

o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-D… Etradiazole, Malath… …ion, Phorate, Metola… Alachlor, Prometon, Pebulate, EPTC, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine

Agriculture

**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 10… ),
PCB 11… ),
PCB 13… …yl),
PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl),
PCB 183 (2,2',3,4,4',5',6-Heptachlorobiphenyl),
PCB 187 (2,2',3,4',5,5',6-Heptachlorobiphenyl)

Industry

**Pesticides and degradation products:**

Hexachlorocyclohexanes (HCH) - α, β, γ-(lindane), and δ, Chlorda… …cis, trans, Heptach… …lfans - I, II, and sulfate, …ldehyde, Hexachlorobenzene, Dacthal, Chlorothalonil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Triallate, Mirex

Agriculture

**PBD**… …ta cl…

Flame Retardants

**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, $d_{14}$-Trifluralin

**Internal Standard:** $^{13}C$… PCB 138

Metals such as mercury

# Park Managers Wanted to Know…

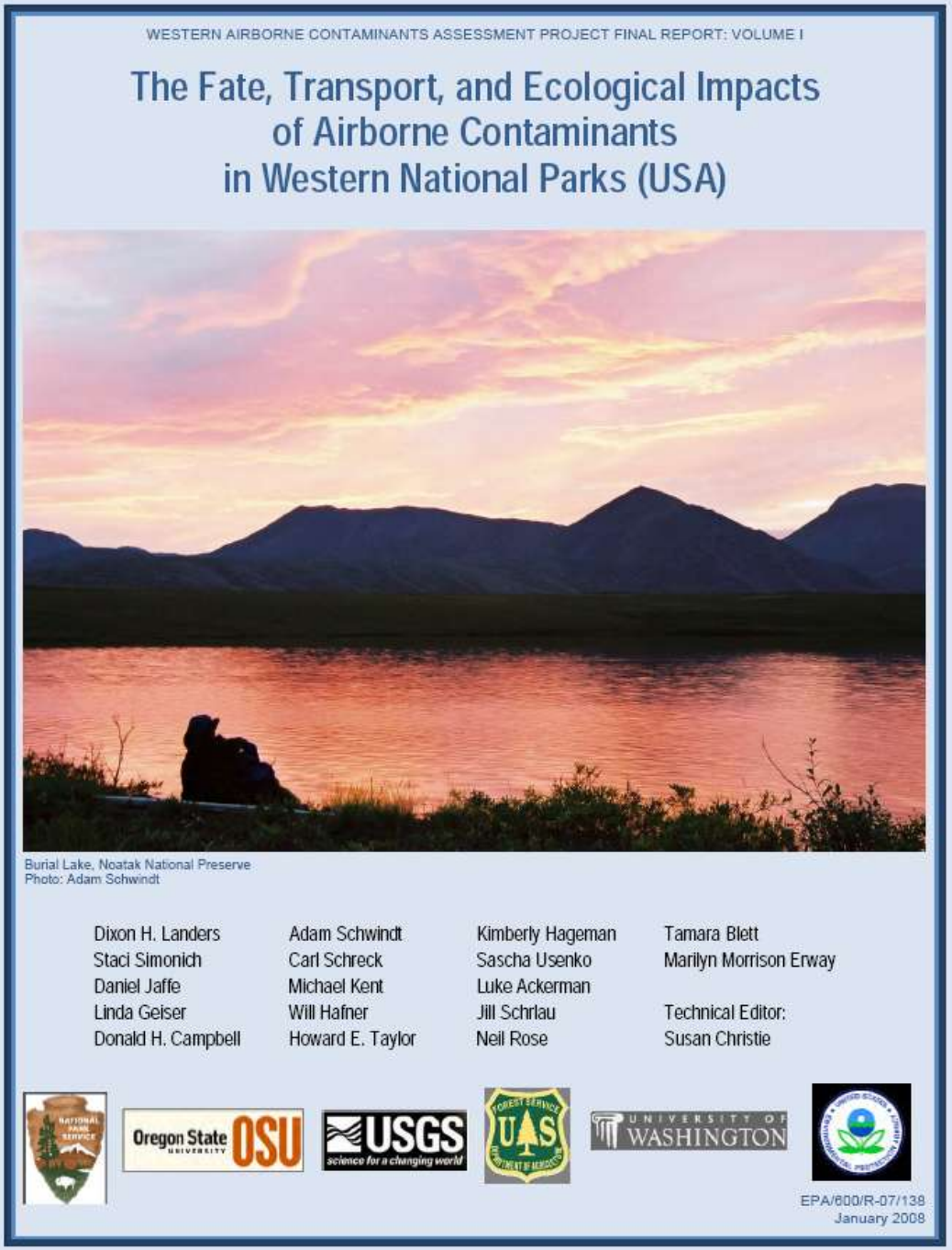
**Are toxic air pollutants causing harm to park resources, and if so, what should we do about it?**

- Are they present?
  - Which ones? In what? Where? How much?
- What are effects?
  - Are they "adverse"?
- Where are they coming from?
- What can be done?

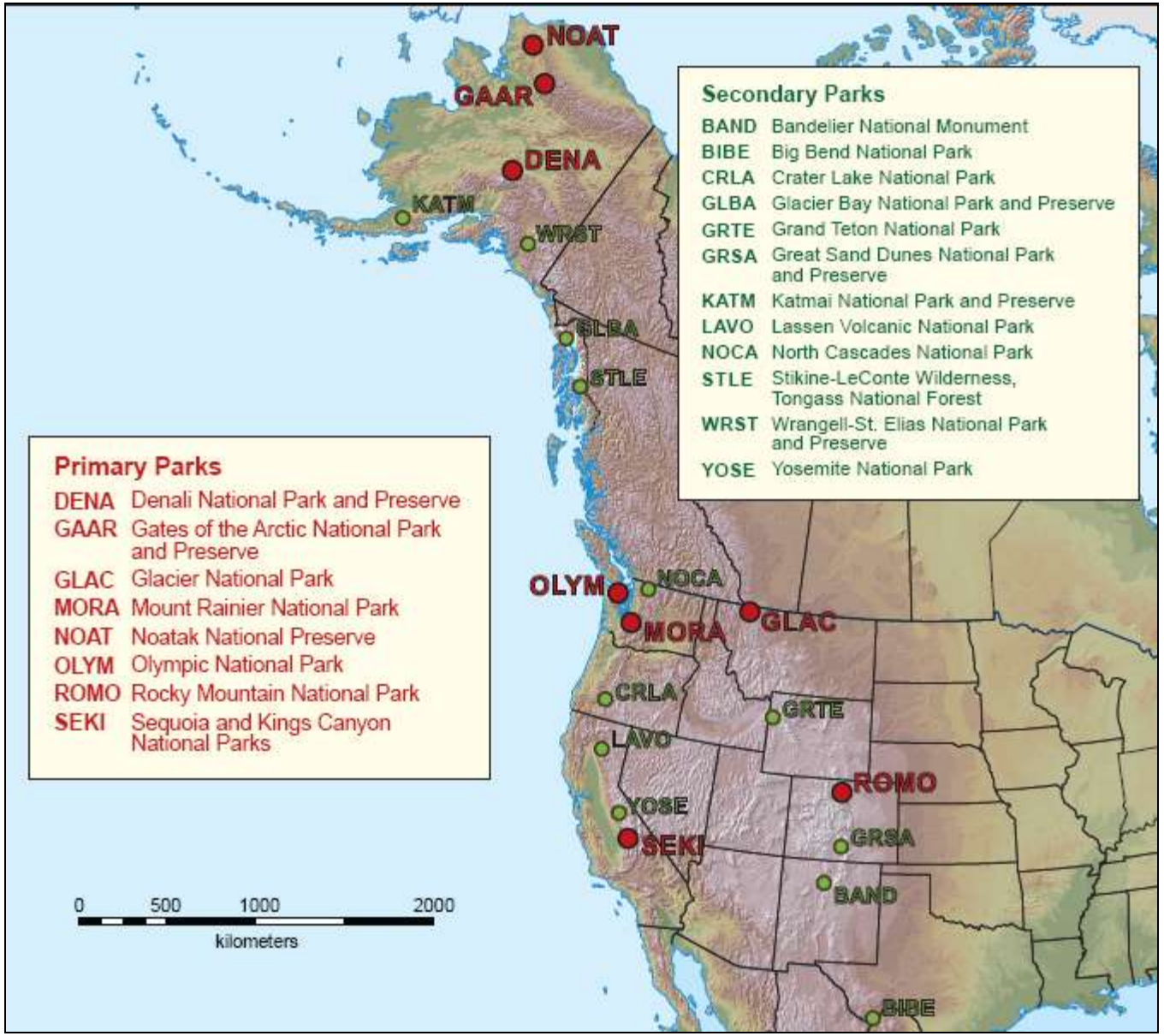
# WACAP Goal:

**To assess the deposition of airborne contaminants in western National Parks, providing regional and local information on exposure, accumulation, impacts and probable sources**

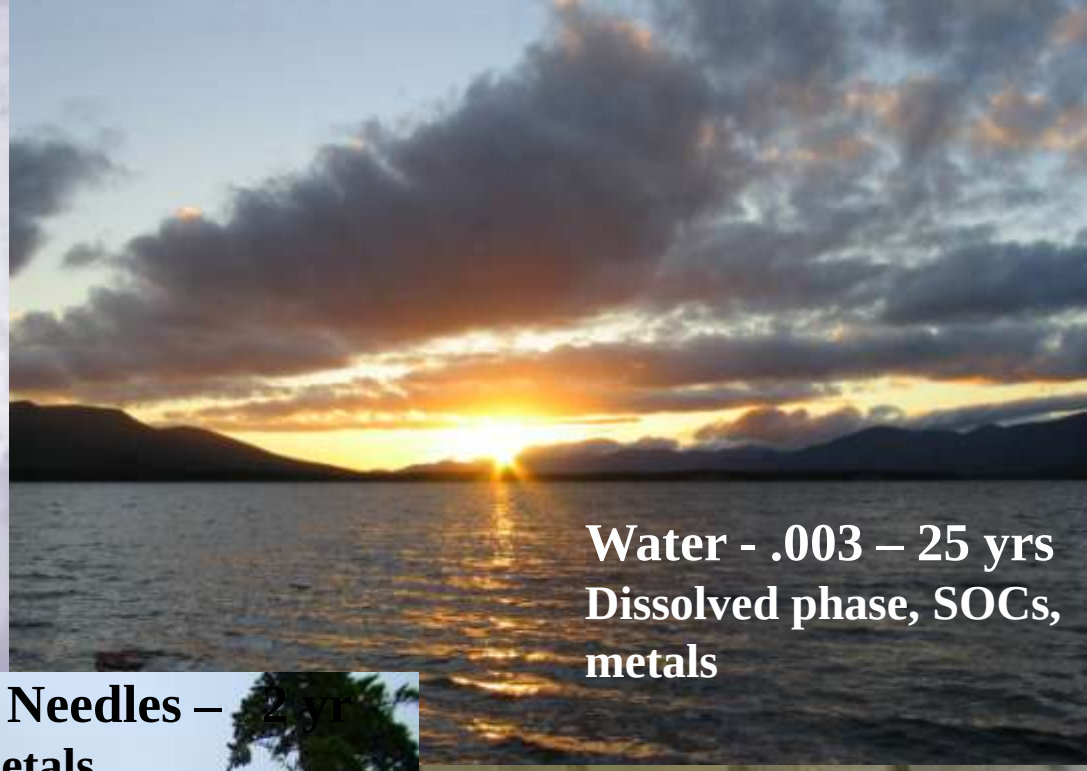
Final Report – Feb 2008



# WACAP sampling locations




Snow – annual flux
SOCs
and metals


Water - .003 – 25 yrs
Dissolved phase, SOCs, metals


Lake
Sediment ~ 135 y
Chronology
SOCs, metals, SCPs


Conifer Needles – 2 yr
SOCs, metals
Lichen – unknown age
N, S, metals


Fish: 2 – 34 yr (selectable)
SOCs, metals, condition, enzymes, pathology

# WACAP Results – Key Findings

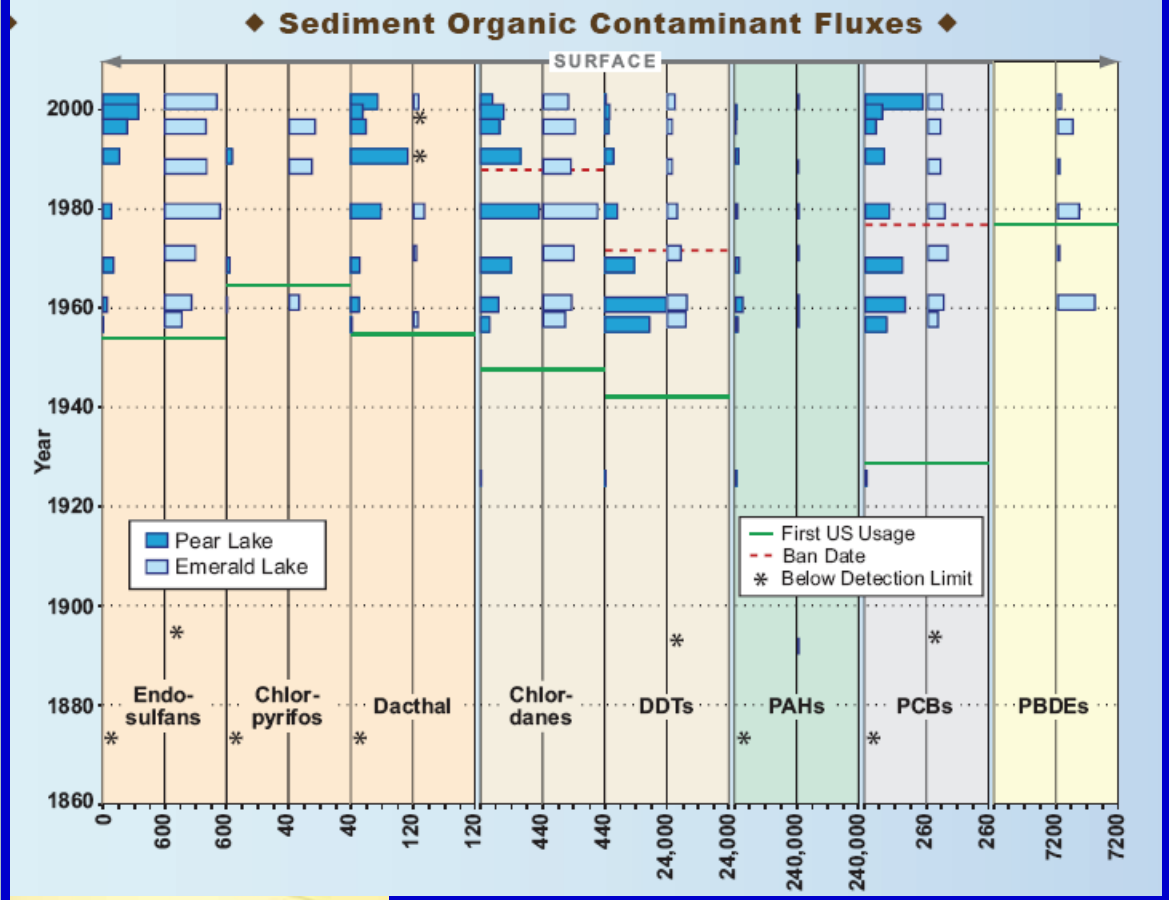

**1. Are contaminants present in western National Parks?**

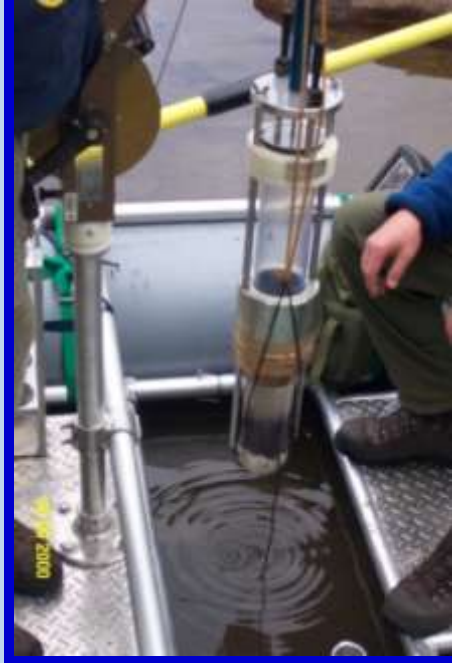
- **Over 70 current use and historic (banned) contaminants were found in snow, water, vegetation, fish and lake sediment at the 8 core parks**
- **Many current-use (new) chemicals were found in air and vegetation in the 20 parks/wilderness areas studied**
- **Historic pesticides generally decreasing, while current use compounds (PBDE, endosulfans, PAH) often increasing**

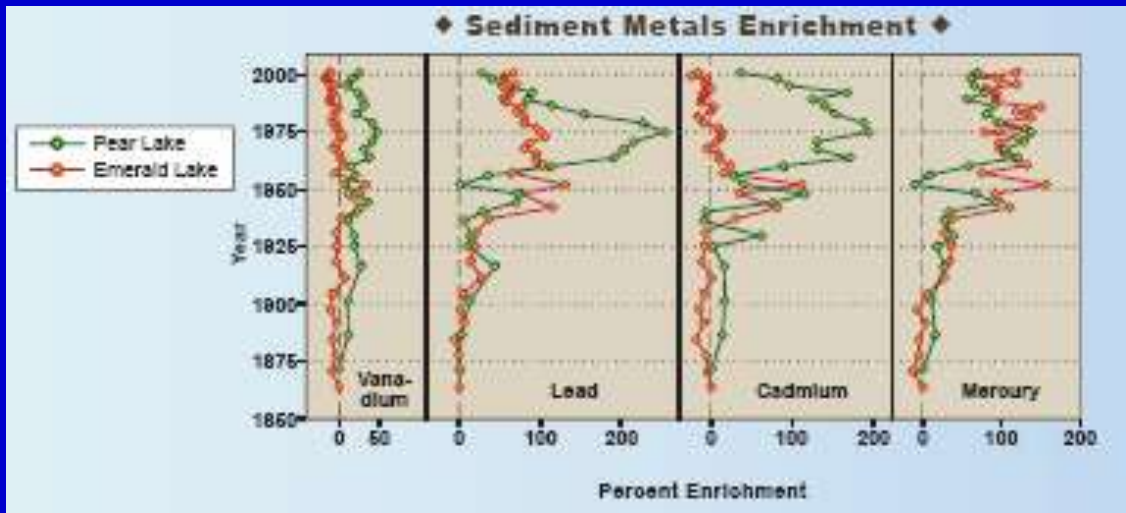
RESEARCH & DEVELOPMENT

*Building a scientific foundation for sound environmental decisions*

**WACAP**





## 2. Where do contaminants accumulate (ecologically and geographically)? (where the FS might focus first)

- The parks closer to sources of contaminants (agricultural or industrial) had higher concentrations in the ecosystem
- Higher elevations have higher concentrations of PCBs and some pesticides
- Toxic compounds were shown to bio-accumulate in fish and vegetation (but deposition doesn't predict bioaccumulation for Hg)

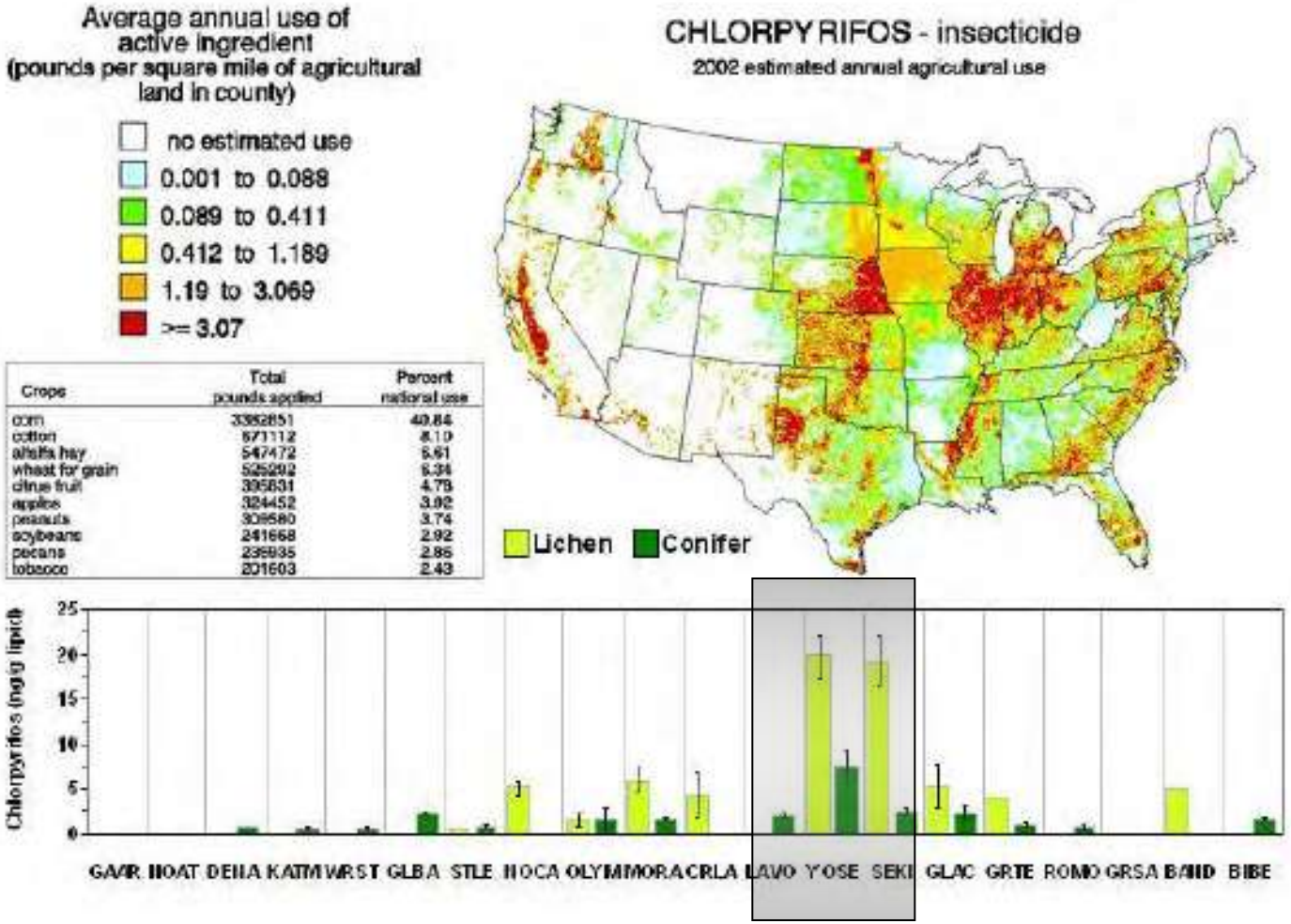



**Figure 4-14. Uses and Estimated Application Intensity in 2002 of the Current-Use Insecticide Chlorpyrifos in the Conterminous 48 States vs. Mean Concentration in Vegetation (ng chlorpyrifos/g lipid conifer needles or lichens) from WACAP Parks.** Chlorpyrifos were detected in vegetation in all parks except NOAT and GAAR, but highest concentrations were observed in SEKI and YOSE, close to the San Joaquin Valley in California, a particularly high use area. Error bars indicate one standard error.

Source of chlorpyrifos data:
http://ca.water.usgs.gov/pnsp/pesticide_use_maps/show_map.php?year=02&map=m6009.

RESEARCH & DEVELOPMENT

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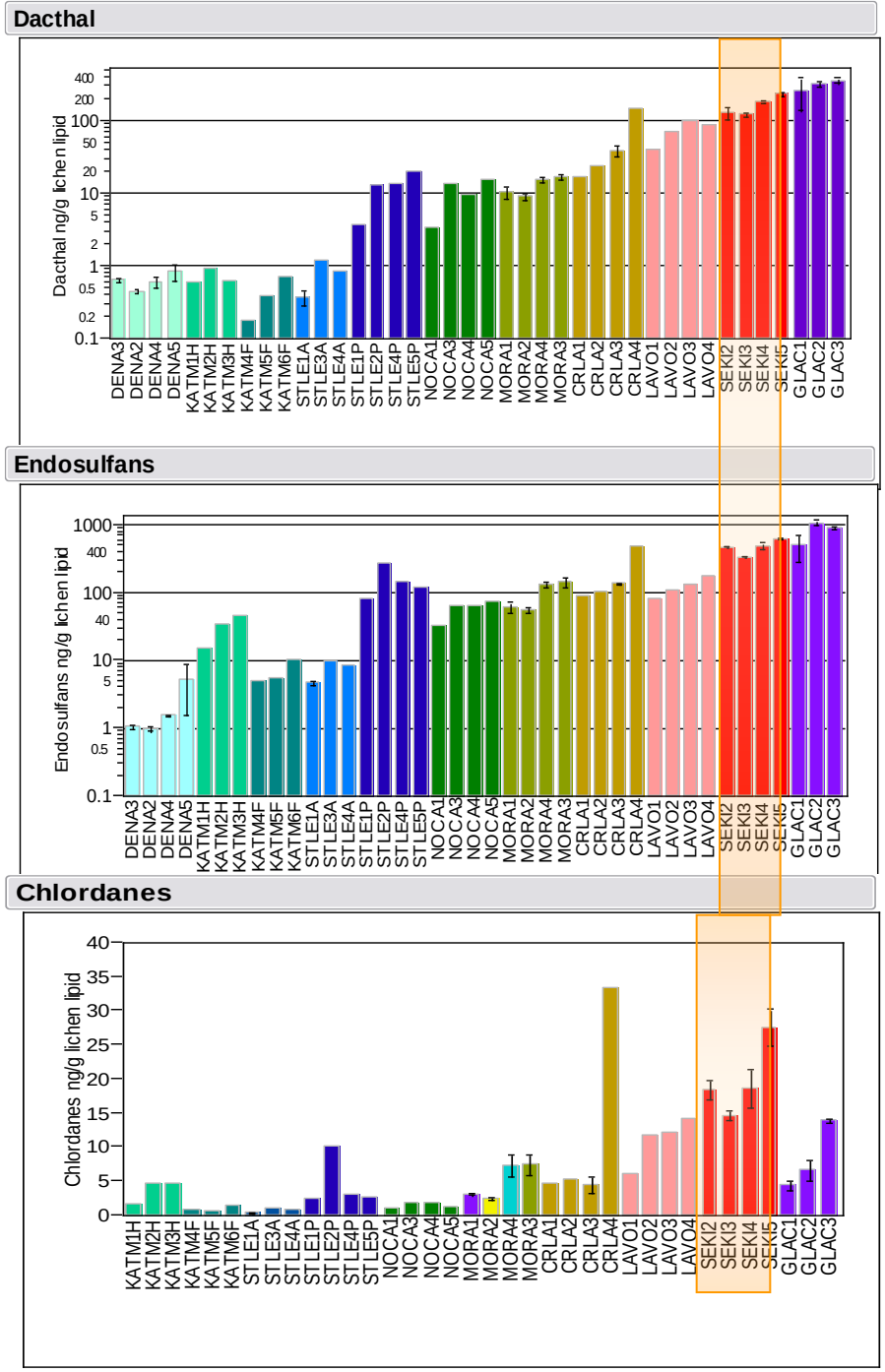
**WACAP**




# Lichens plotted by elevation within Parks

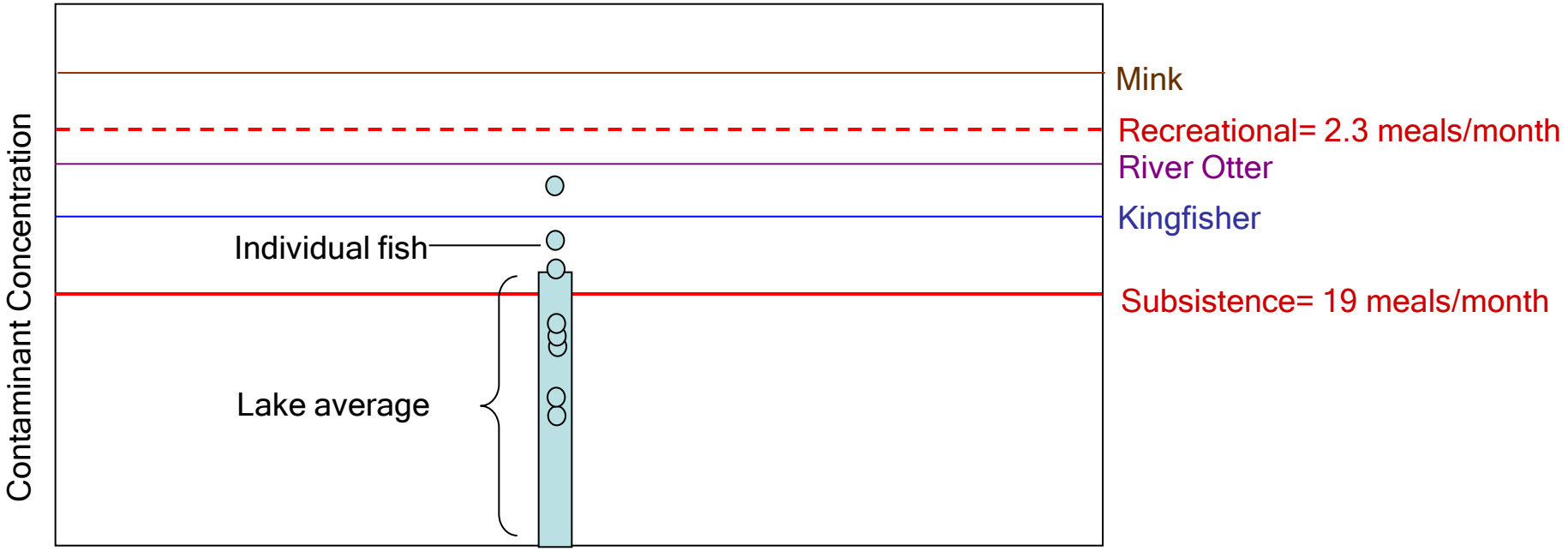
Figure 4-22. Elevational Gradients for Sum Dacthal, Sum Endosulfan, and Sum Chlordane Concentrations in Lichens. Within each park, sites are listed in order of increasing elevation. Codes H, F, A, and P refer to lichen species sampled (see Table 4-4). Bars show the standard error. Statistical analyses of elevational gradients are reported in Tables 4-3 and 4-4. Additional graphic displays for other SOCs are given in Appendix 4A.10. See Chapter 3 for data selection criteria for elevational trends analyses.

# 3. Which contaminants pose the greatest ecological threat?

- **Dieldrin, DDT, chlordane PCBs, PAH and mercury are compounds/elements of highest concern - higher concentrations and/or greatest toxicity**
- **Emerging (current) contaminants PBDEs, endosulfans chlorpyrifos, HCH are increasing in park ecosystems**
- **Mercury thresholds for fish consumption exceeded for birds/wildlife in most parks, and humans in 2 AK parks.**
- **DDT and Dieldrin thresholds exceeded for human fish consumption at several parks**

# Chemical Concentrations and Risk Assessment

Fish eating Human Health and Wildlife Health Consumption Thresholds




Noatak= NOAT

Gates of the Arctic= GAAR

Denali= DENA

Glacier= GLAC

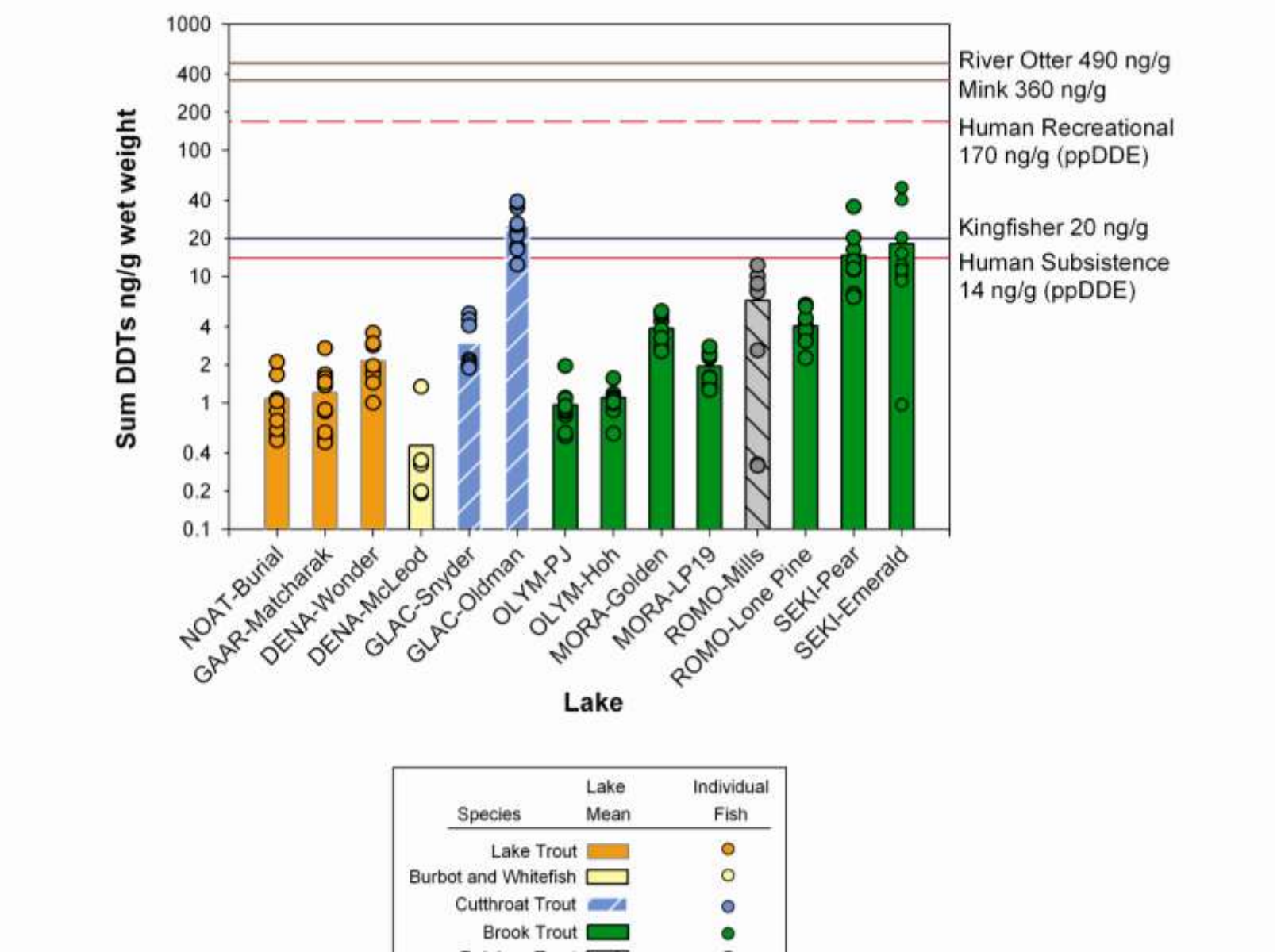
Olympic= OLYM

Mt Rainier= MORA

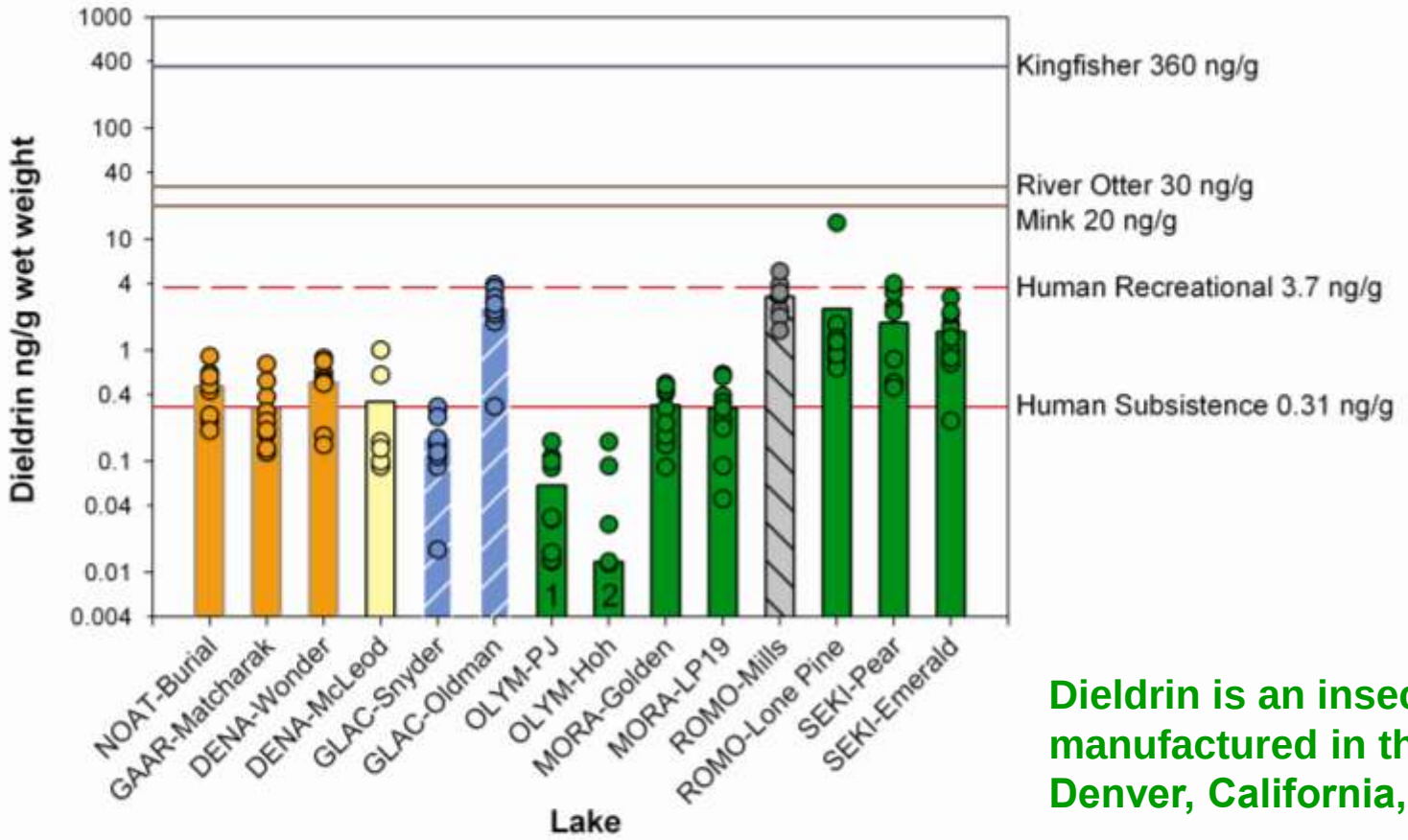
Sequoia= SEKI

Rocky Mountain= ROMO

# Mean Whole Body Fish Sum DDTs



# Mean Whole body fish Dieldrin

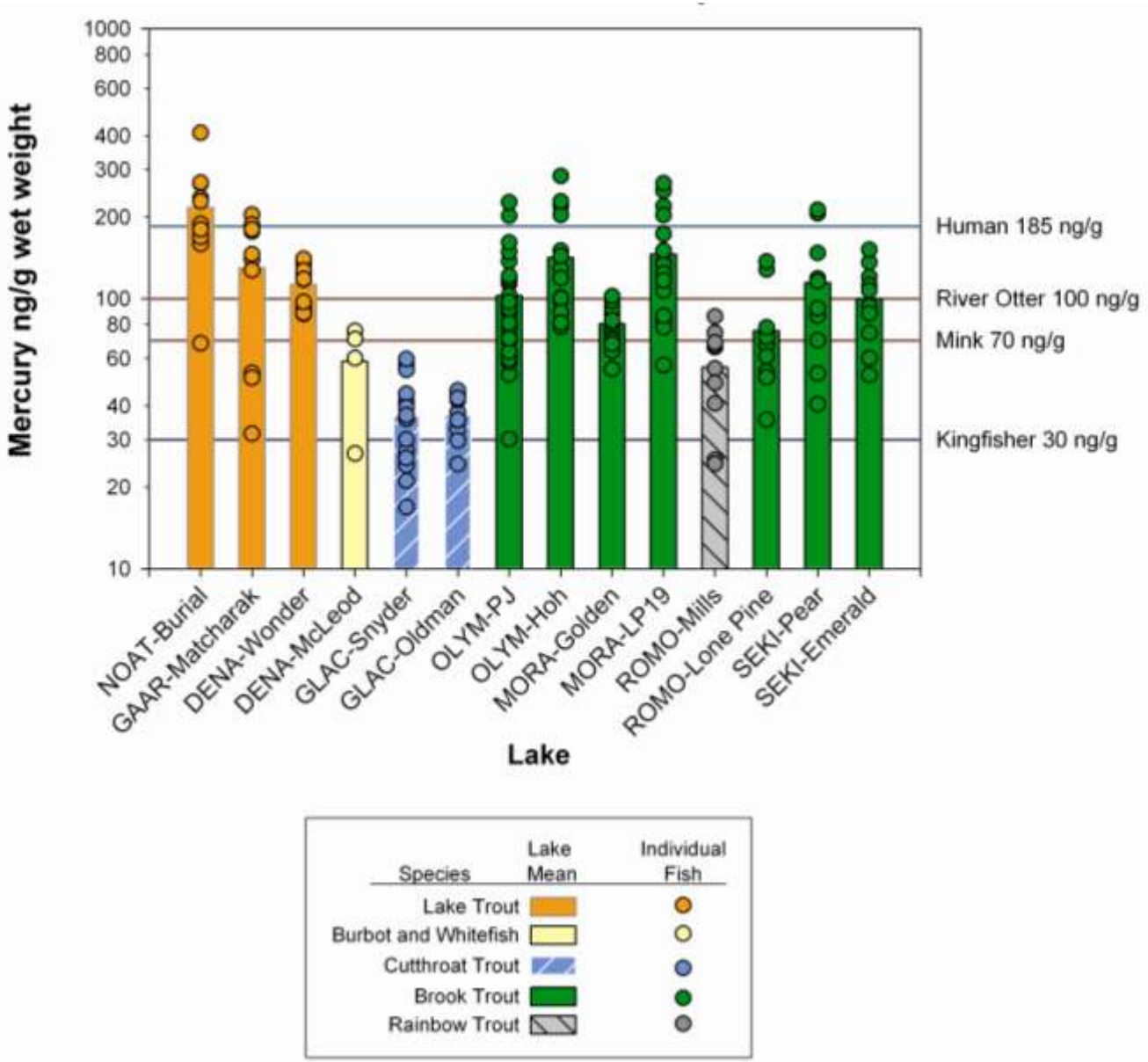



**Dieldrin is an insecticide manufactured in the 1950s-1980s in Denver, California, Seattle….**

| Species | Lake Mean | Individual Fish |
|---|---|---|
| Lake Trout | | |
| Burbot and Whitefish | | |
| Cutthroat Trout | | |
| Brook Trout | | |
| Rainbow Trout | | |

If no label is present in the bar, the component was detected in at least 70% of the samples.
"1" indicates the analyte was detected in 50 - 70% of the samples,
"2" indicates the analyte was detected in less than 50% of the samples.

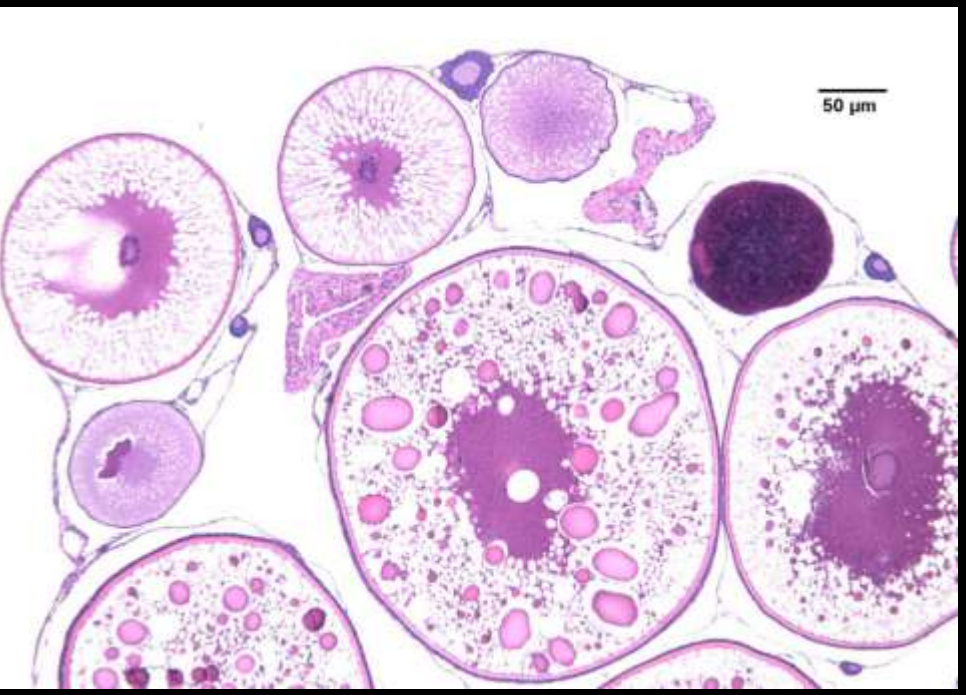
# Mean Whole Body Fish Total Hg



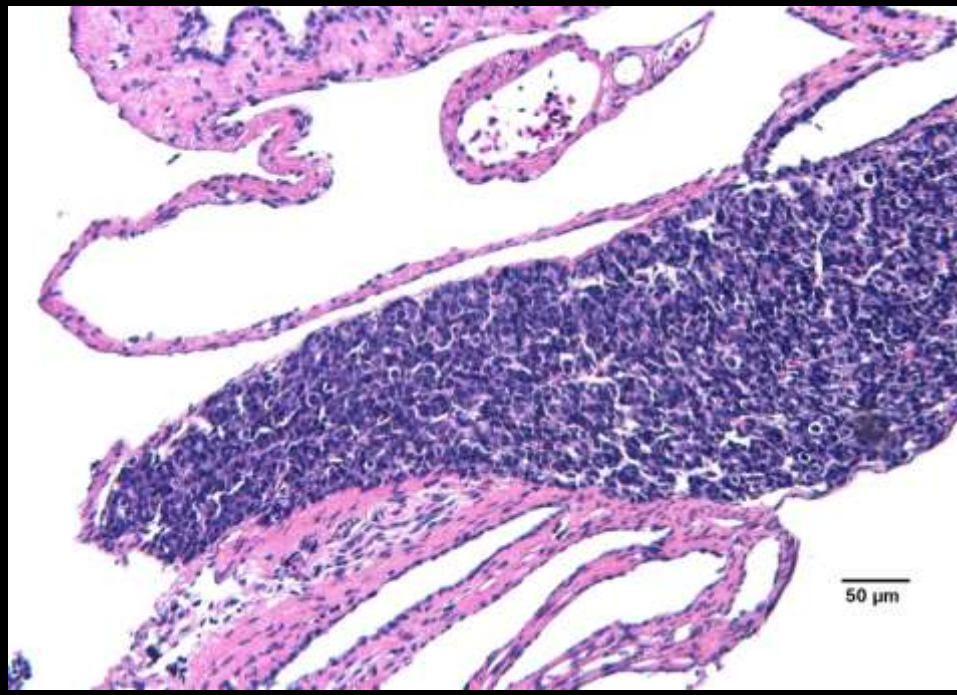
# 4. Which ecological *indicators* are the most useful in interpreting contamination?

- Fish are key indicators because bioaccumulation puts them at risk for adverse effects (some wildlife and human health thresholds exceeded)
- "Intersex" fish found in Rocky Mtn and Glacier (not in other 6 parks) show health impacts occurring (unknown link to contaminants)
- Sediment cores showed change in contaminants over time
- Conifer needles (second year) allowed comparisons over large geographic areas.

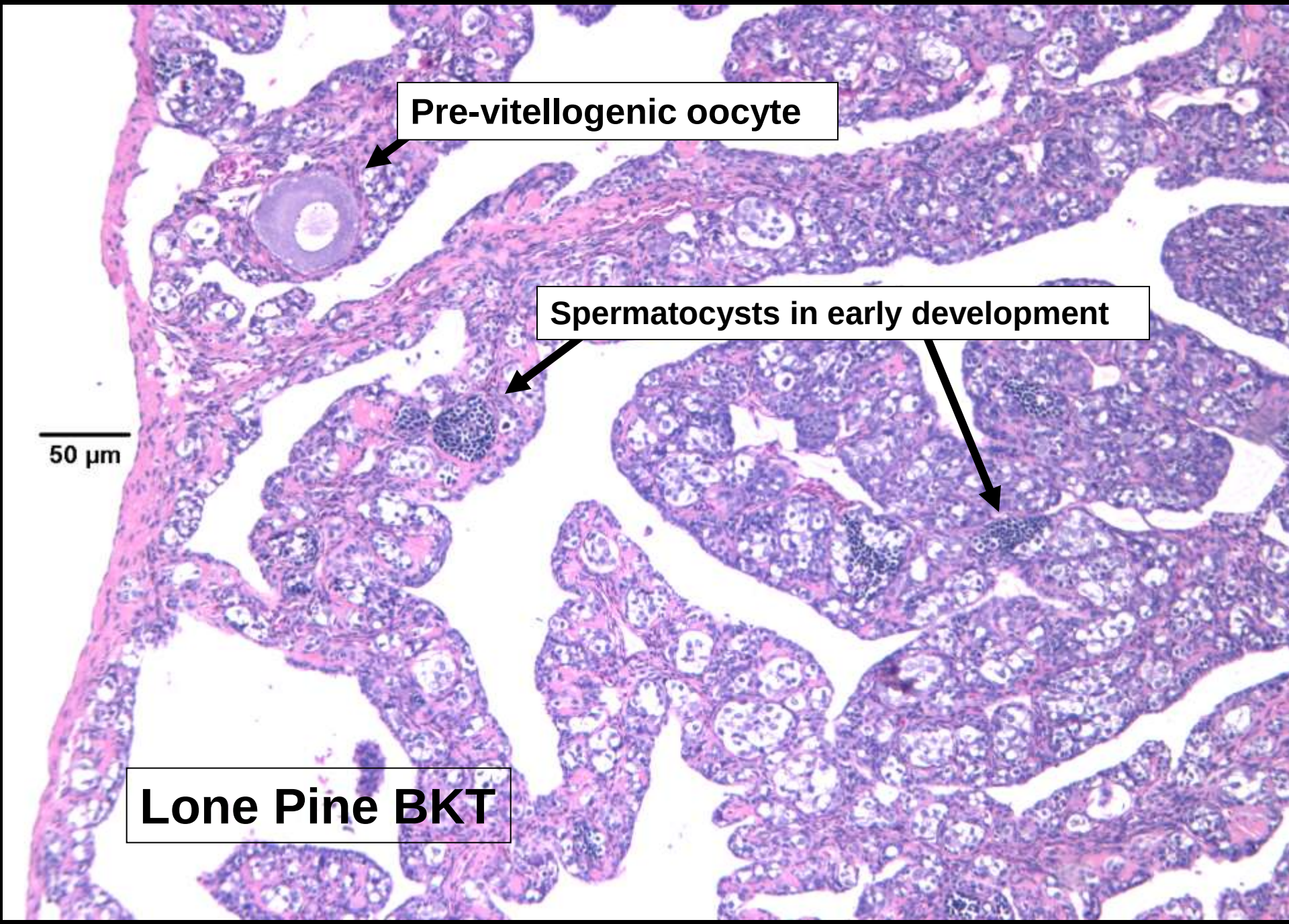
# Normal Brook Trout Gonads




Female

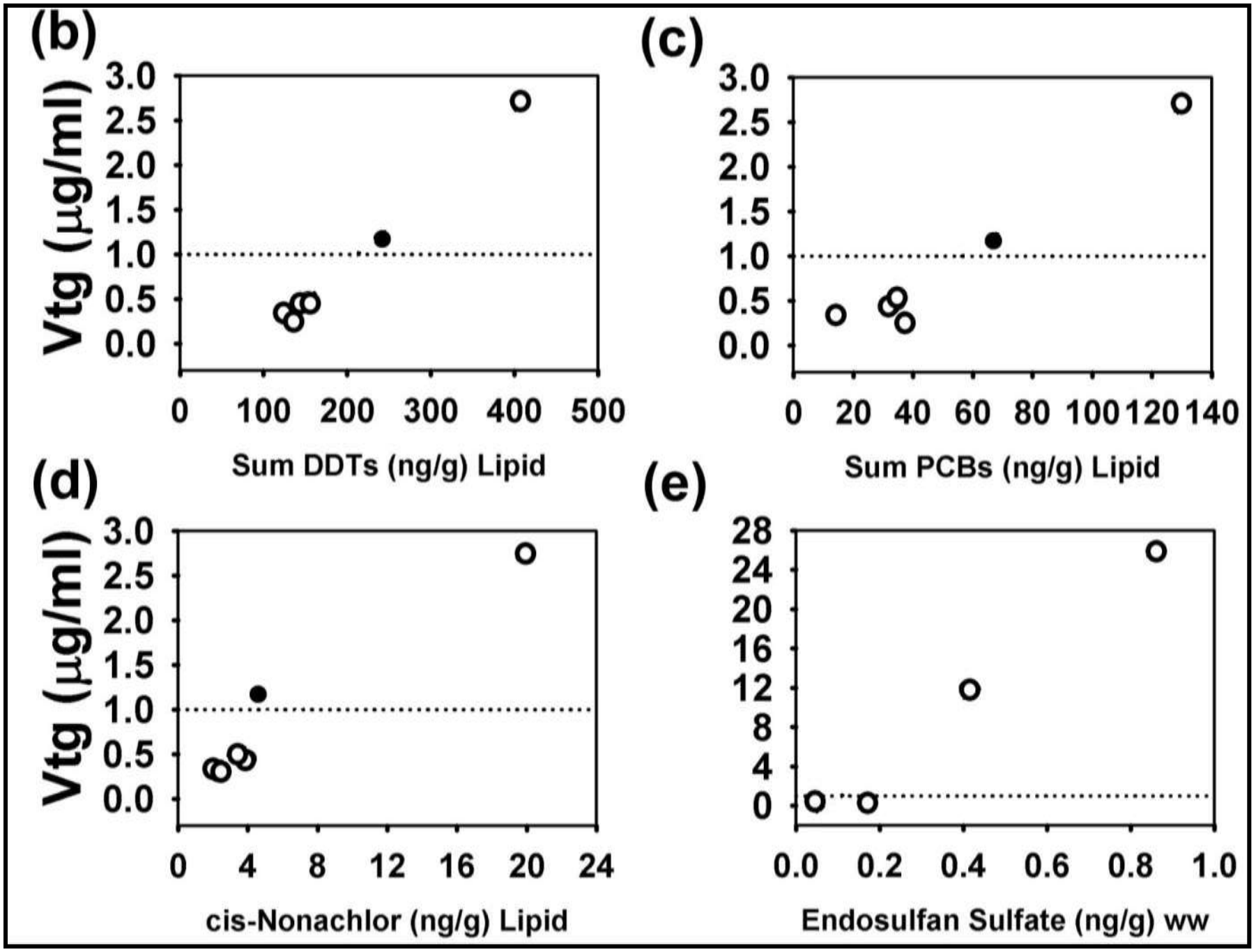



Male


Pre-vitellogenic oocyte
Spermatocysts in early development
50 µm
Lone Pine BKT

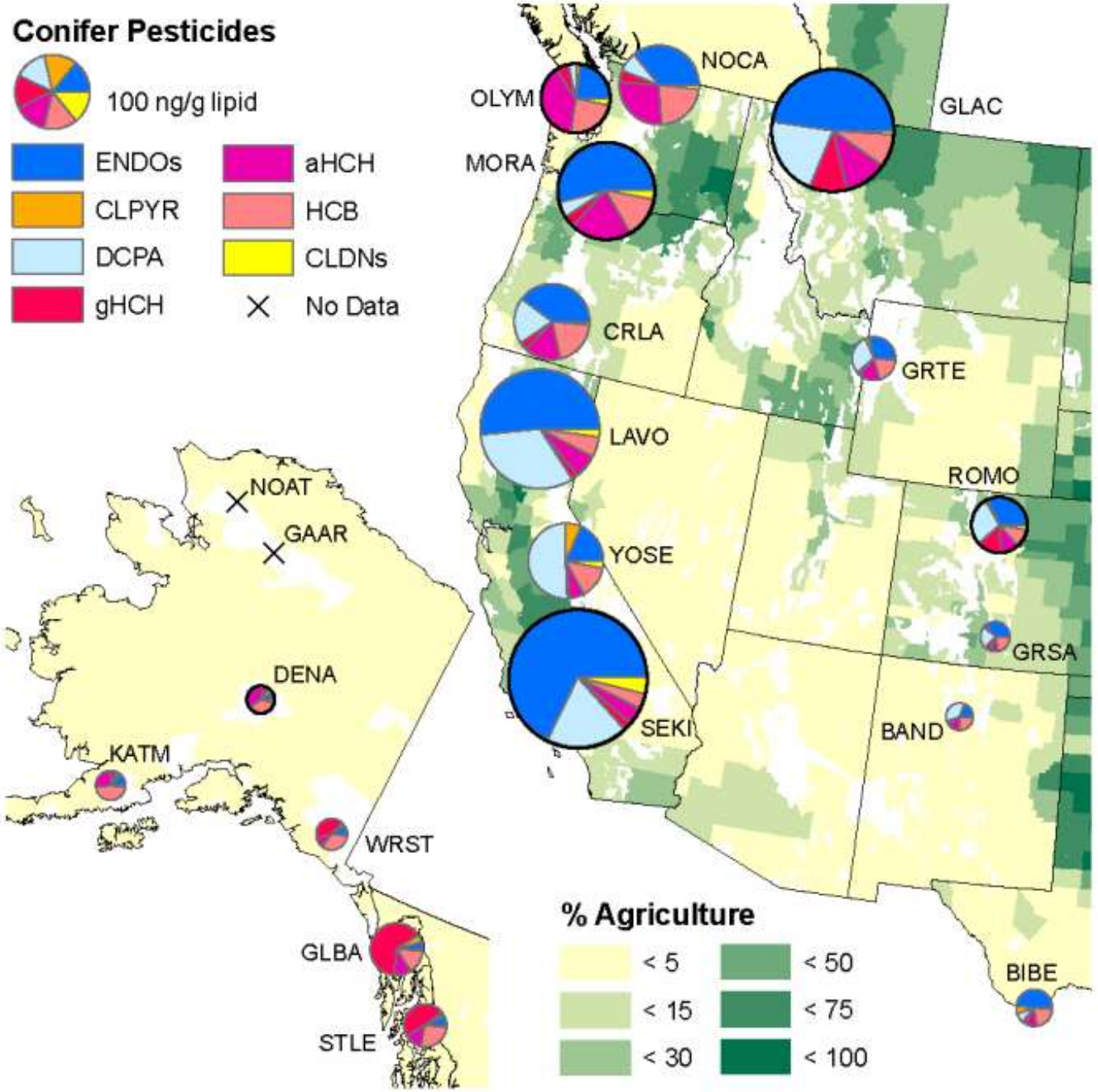
# Categorization of Trout Testes by Abnormality, Geographic Region, and Current or Historic Sampling.

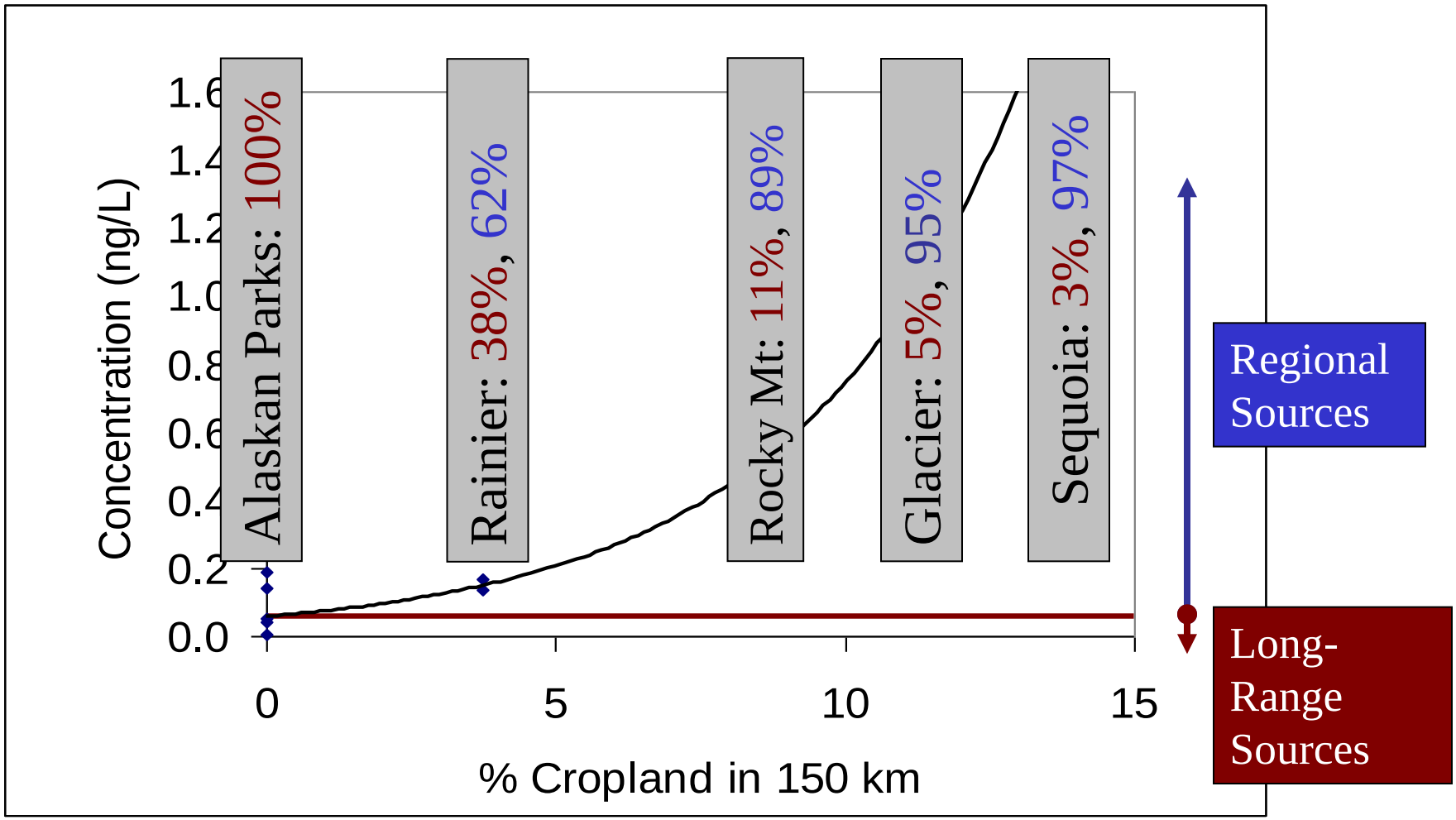
| Region | Sample | Total Males | Testis Category | | | |
|---|---|---|---|---|---|---|
| | | | ~~normal~~ a | b | c | d |
| Rockies | Current | 117 | 107 | 2 | 5 | 3 |
| | Historic | 30 | 28 | 0 | 2 | 0 |
| Sierras | Current | 25 | 25 | 0 | 0 | 0 |
| | Historic | 12 | 11 | 0 | 0 | 0 |
| Olympics / Cascades | Current | 40 | 40 | 0 | 0 | 0 |
| | Historic | 1 | 1 | 0 | 0 | 0 |
| Denali | Current | 10 | 10 | 0 | 0 | 0 |
| | Historic | 0 | | | | |
| Arctic | Current | 15 | 15 | 0 | 0 | 0 |
| | Historic | 0 | | | | |


(b)
Vtg (µg/ml)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
Sum DDTs (ng/g) Lipid
(c)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
140
Sum PCBs (ng/g) Lipid
(d)
Vtg (µg/ml)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
4
8
12
16
20
24
cis-Nonachlor (ng/g) Lipid
(e)
28
24
20
16
12
8
4
0
0.0
0.2
0.4
0.6
0.8
1.0
Endosulfan Sulfate (ng/g) ww

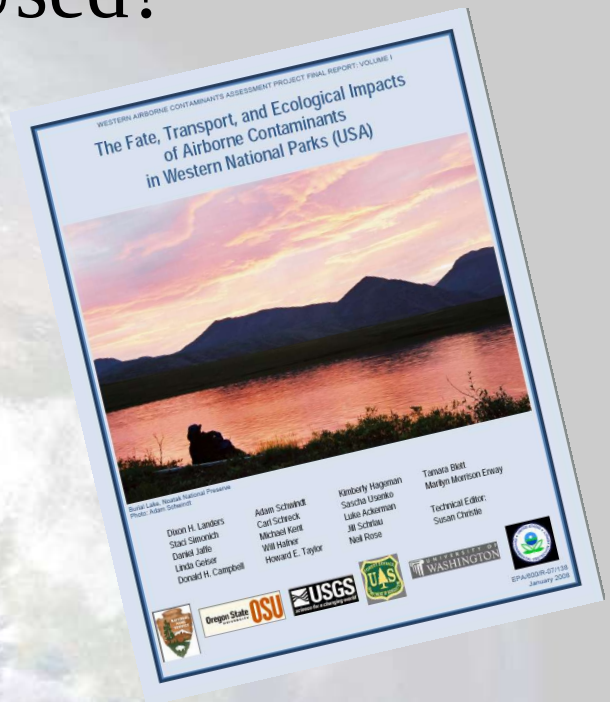
# 5. What are the likely sources of contaminants to the National Park sites?

- **Pesticides in snow and veg. were highest in parks near agricultural areas (Sequoia, Glacier, Rocky Mtn)**
- **Global background impacts at all sites, main influence in AK parks**
- **Some "hot spots" near industry– PAH (Columbia Falls Smelter) in Glacier, SCP (coal combustion sources) in Sequoia, and Dieldrin (Rocky Mtn Arsenal) in Rocky Mtn NP**


Conifer Pesticides
100 ng/g lipid
ENDOs
aHCH
CLPYR
HCB
DCPA
CLDNs
gHCH
No Data
NOCA
OLYM
GLAC
MORA
CRLA
GRTE
LAVO
ROMO
NOAT
GAAR
YOSE
GRSA
DENA
SEKI
BAND
KATM
WRST
GLBA
BIBE
STLE
% Agriculture
< 5
< 50
< 15
< 75
< 30
< 100


Concentration (ng/L)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
% Cropland in 150 km
Alaskan Parks: 100%
Rainier: 38%, 62%
Rocky Mt: 11%, 89%
Glacier: 5%, 95%
Sequoia: 3%, 97%
Regional Sources
Long-Range Sources

# How Have WACAP Results Been Used?




**Products/Science**

- WACAP Final Report out – Feb 2008
- WACAP "Results" Fact Sheet
- 11 Journal Articles from WACAP
- WACAP Articles in "Park Science" "Alaska Park Science" "NPS Natural Resources- Year in Review" "PNW Cooperative Ventures" "Alaska Caribou Trails"
- WACAP Web site …

**http://www.nature.nps.gov/air/studies/air_toxics/wacap.cfm**

## Follow-up Contaminants Workshops

•Montana Contaminants Workshop, Missoula, MT, April 2008

•Sierra Nevada Southern Cascades Contaminants Workshop (Sequoia, Yosemite, Lassen NPs and local partners) , April 2009

•**Pacific Northwest Contaminants Workshop- planned for November 4-5, 2010 (Seattle area**)

## Developing Partnerships/Policy : Follow- up

- Sierra Nevada Southern Cascades MultiAgency Contaminants Working Group formed
- Oregon State University –NPS Fish follow up contaminants study (FY08-FY10)
- Fed Register Notice-NPS Comment Letters Supporting Endosulfan Ban
- International POPs Treaties – Working with US State Dept and EPA International Office

# Relevance of WACAP to the FS

- High elevation western ecosystems are at risk from contaminant impacts (FLMs have legitimate basis for concern)
- Bioaccumulation in fish, wildlife, (humans) is the endpoint… monitor these when possible
- Screening inventories (e.g. water or vegetation may be OK to identify specific problems initially)
- FS Areas near agriculture may be accumulating toxics at highest levels
- Think about if you had the data what would you do with it? Hg? Pesticides?