Sustainability and Environmental Chemistry in Semi-Arid/Arid Regions: A Unique Research Opportunity with Global Implications

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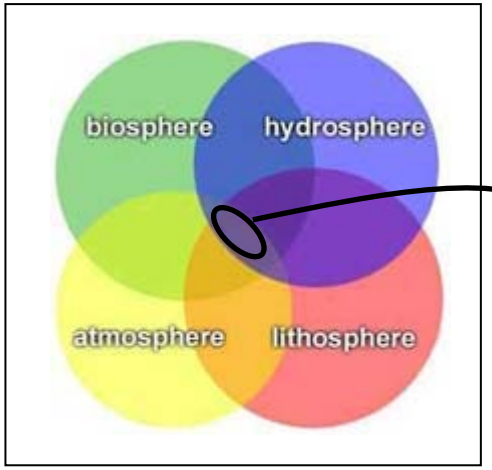
What is Environmental Chemistry?

- Definition depends on where you look:
  - "Study of chemical phenomena in natural places"
  - Not be confused with green chemistry
    - Seeks to reduce potential pollution at source

unsatisfactory

- Study of the sources, reactions, transport, effects, and fates of chemical species in the
  - air (atmosphere)
  - soil/rock (lithosphere)
  - biological (biosphere),
  - and water (hydrosphere) environments,
  - and the effect of human activity on these

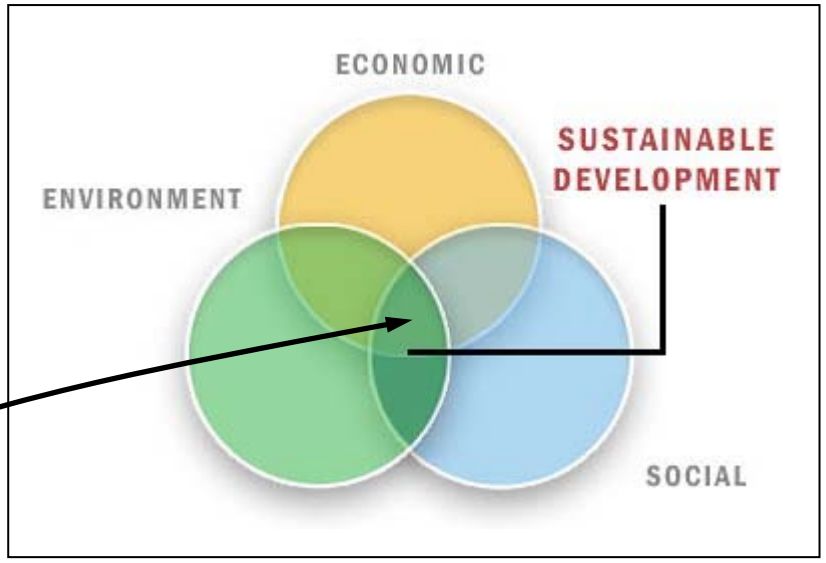


Want to work here

Definition "feeds back" on green chemistry, so necessarily includes components of this...

Sustainability: What is it? How is multidisciplinary environmental chemical research related?

1. Provide for the needs of the present
2. Not diminish the ability of future generations to provide for themselves
3. Repeatable process with no negative environmental consequences



- To work here, our group must (collectively) have broad academic backgrounds and collaborate with:
  - Biologists, biochemists, toxicologists, …
  - Geographers, geologists, physicists, math/statistics …
  - Economists, political scientists, …

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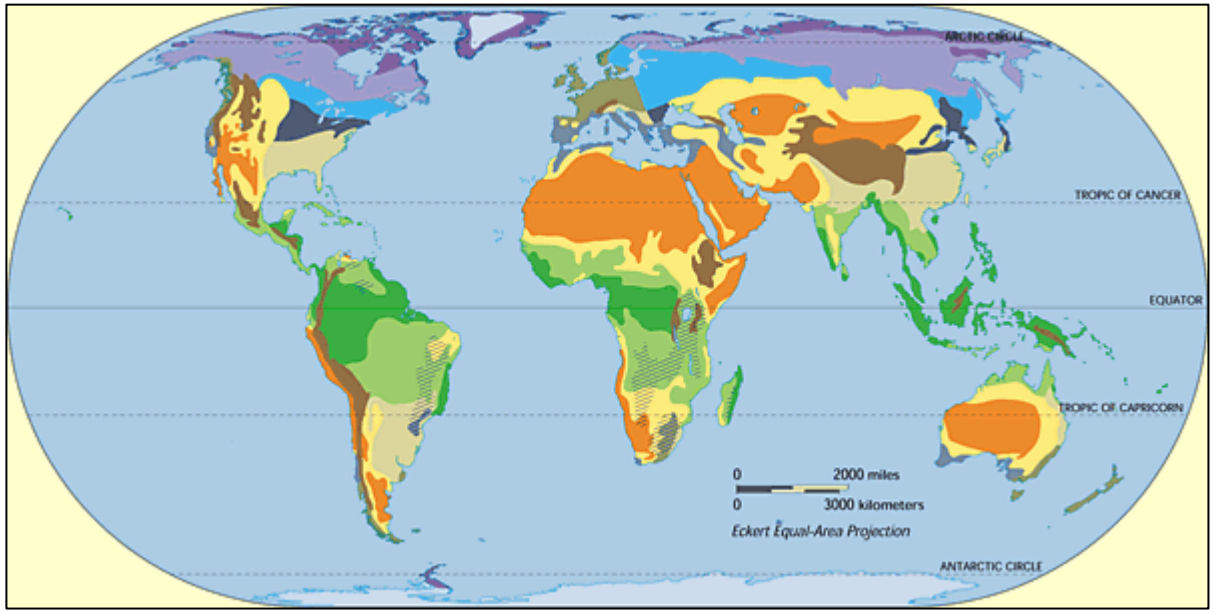
Semi-Arid/Arid Regions

- Characterized by low (generally <0.5 m) annual precipitation
- Also undergoing rapid population growth and development:
  - Sub-Saharan Africa
  - India
  - Southern California
  - South-Central British Columbia and Northern Alberta/NWT

>250 million over next 5 years

Stress on resources

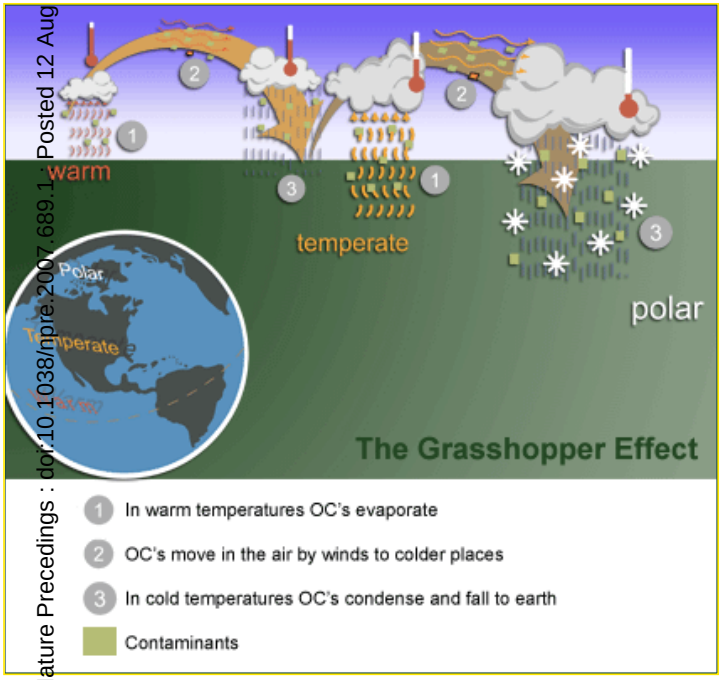


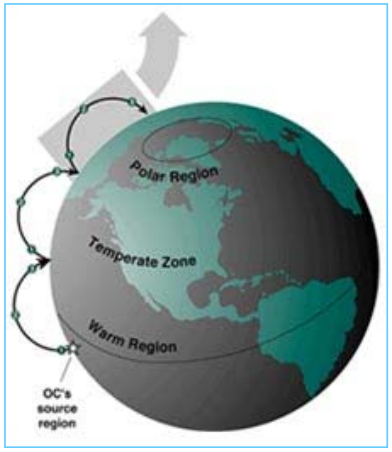
Semi-Arid/Arid Regions and History

First great civilizations arose on banks of rivers in semi-arid/arid regions:

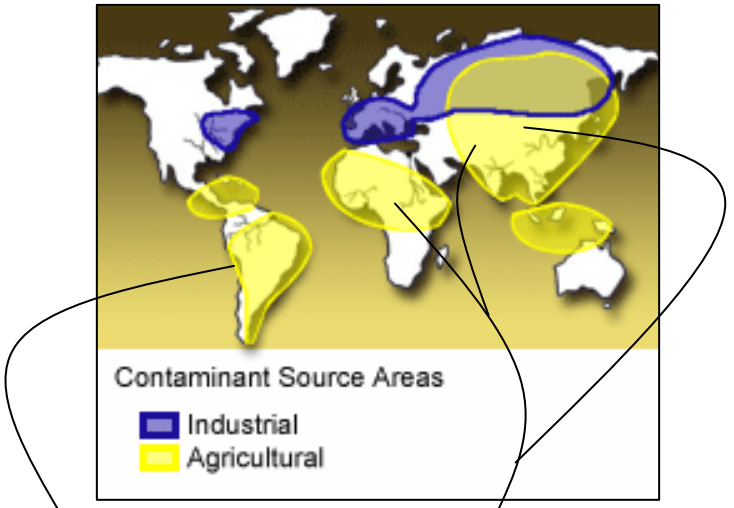
1. the Nile in Egypt
2. the Tigris-Euphrates of Mesopotamia
3. the Indus in Pakistan
4. the Hwang Ho "Yellow" of China
5. Kamloops on the Thompson??

Semi-Arid/Arid Regions in Global Contaminant Cycling





Are not major sources of global industrial contaminant inputs



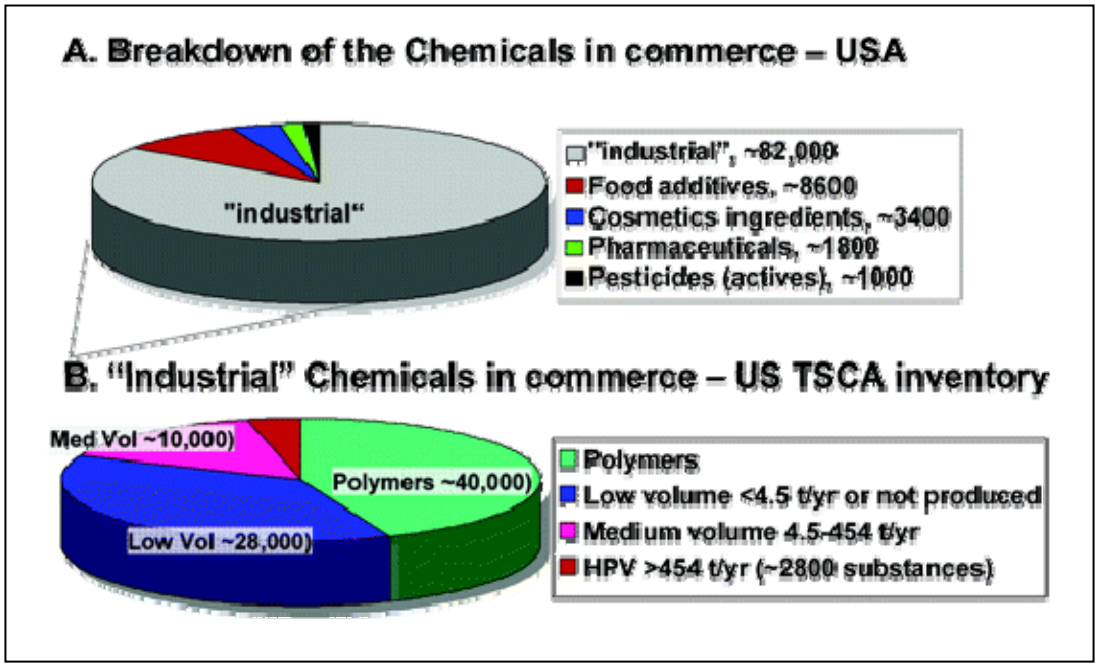
But can be significant agricultural chemical sources

- Also operate as 'stop-over' points in the poleward movement of pollutants
  - Little known about how this 'semi-arid layover' affects the amount and 'signatures' of global contaminant fluxes

→ "path dependence?" or, not a state function?

Which Chemicals Do We Study?

- Having decided to embark on our research program, which compounds do we invest in?



- Short answer: it's a bit of a guess …
  - 'the most toxic we know', societal factors, industry trends, …

What is our focus?

Chemical dynamics in environmental systems

- We have two main goals:
  1. Understand the pathways by which "already known" overall chemical reactions occur in aquatic systems

known

$A \rightarrow B$

"passive observers"

we work on how 'A' goes to 'B'

$A \rightarrow [C] \rightarrow [D] \rightarrow B$

"active participants"

by knowing the path(s) of a
chemical reaction in the environment,
we can control it
="harnessing science & technology"

What is our focus?

Chemical dynamics in environmental systems

2. Uncover new pathways for chemical transformations in aquatic systems

unknown

$A \rightarrow ?$

"ignorant observers"

we find out what happens to A

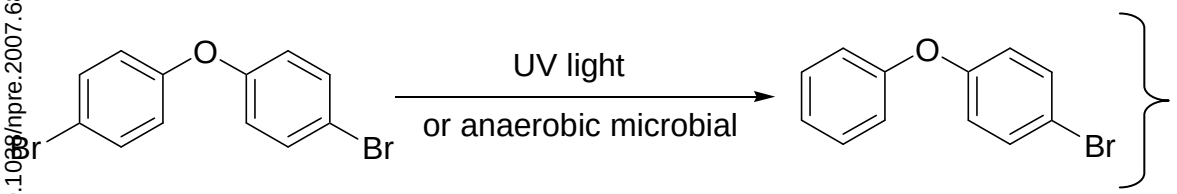
$A \rightarrow [C] \rightarrow [D] \rightarrow B$

"active participants"

now we can make informed decisions as to whether to allow 'A' to exist, or under what conditions it should exist

Nice Theory …
Give Practical Examples!

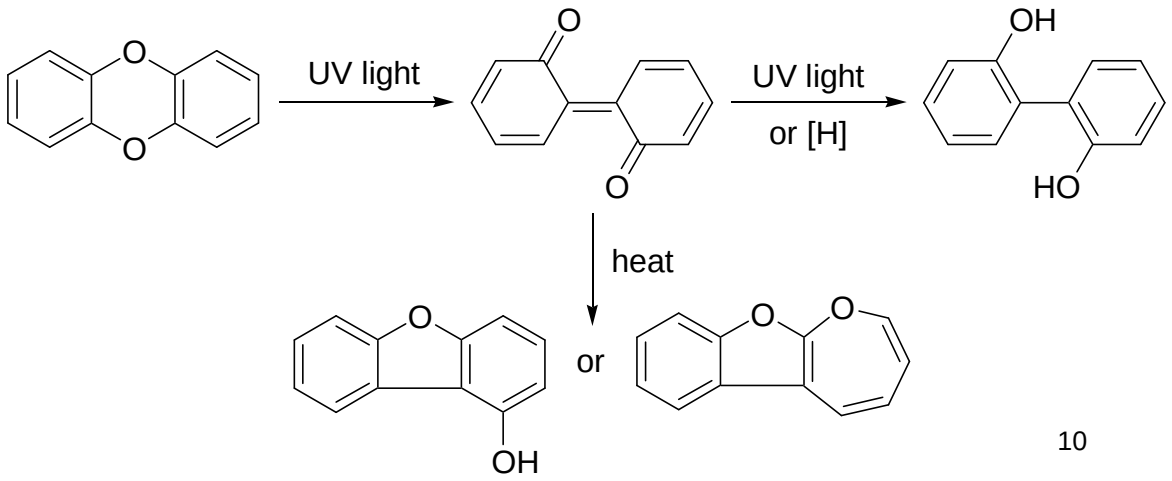
1. Understand the pathways by which "already known" overall chemical reactions occur in aquatic systems
   - PBDE (polybrominated diphenyl ether) debromination



lower brominated compounds found in environment, previously only speculation on how they came to be

2. Uncover new pathways for chemical transformations in aquatic systems
   - dioxin photochemistry

>3 decades of research before our findings



Photochemistry: Our Primary Perspective

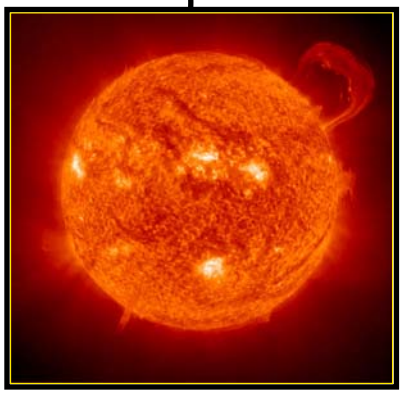
biotic (e.g., microbes, plants, animals)

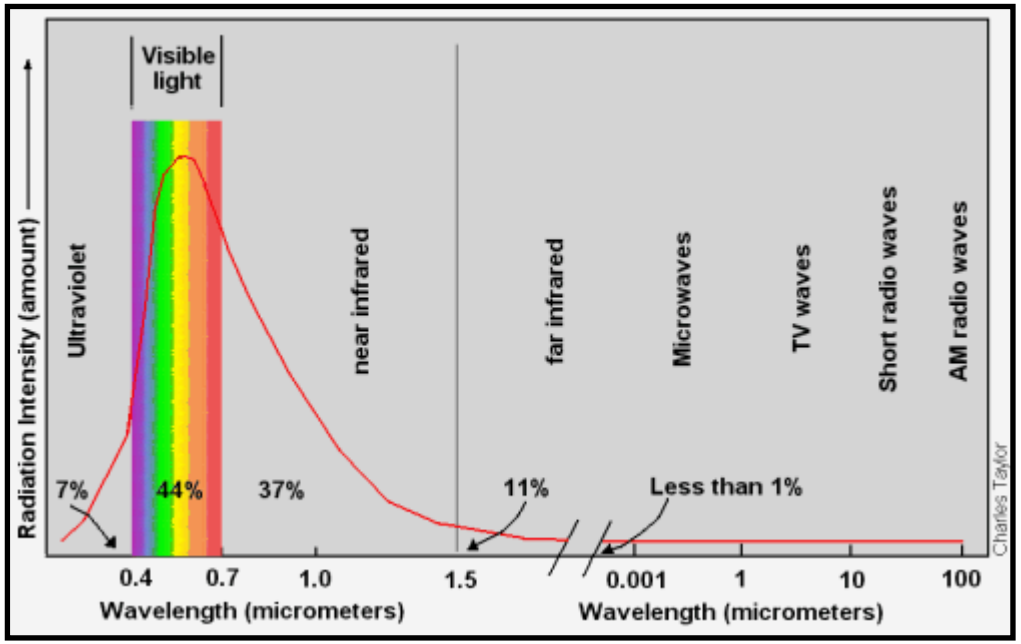
A

thermal abiotic (e.g., heat, oxid^{n}, red^{n})

photochemical

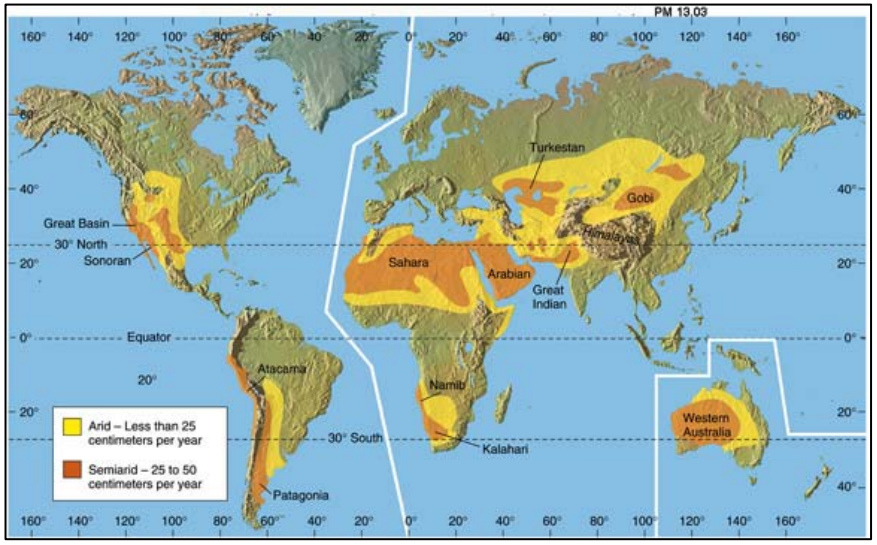
but we consider all pathways

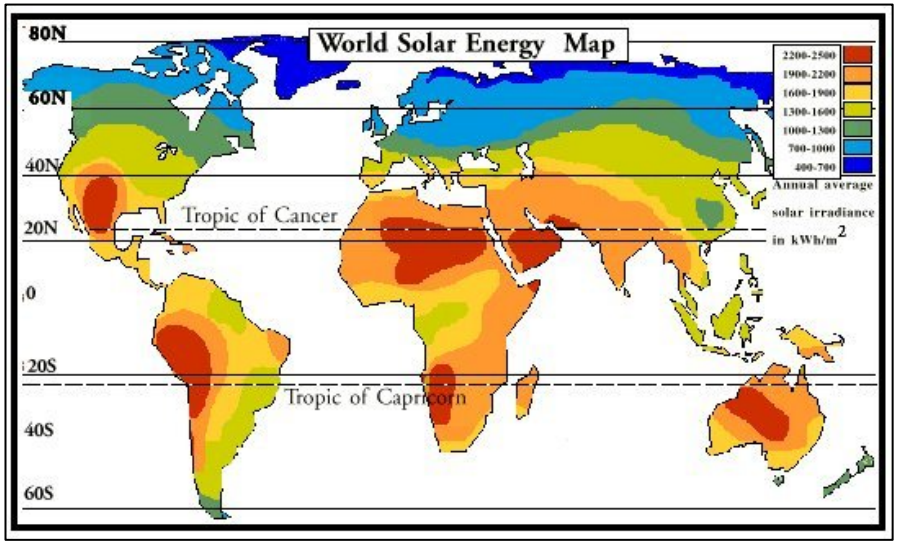




Semi-Arid/Arid Regions and Photochemical Research: A Good Fit?

Correlation between semi-arid landscapes and regions of high solar intensity



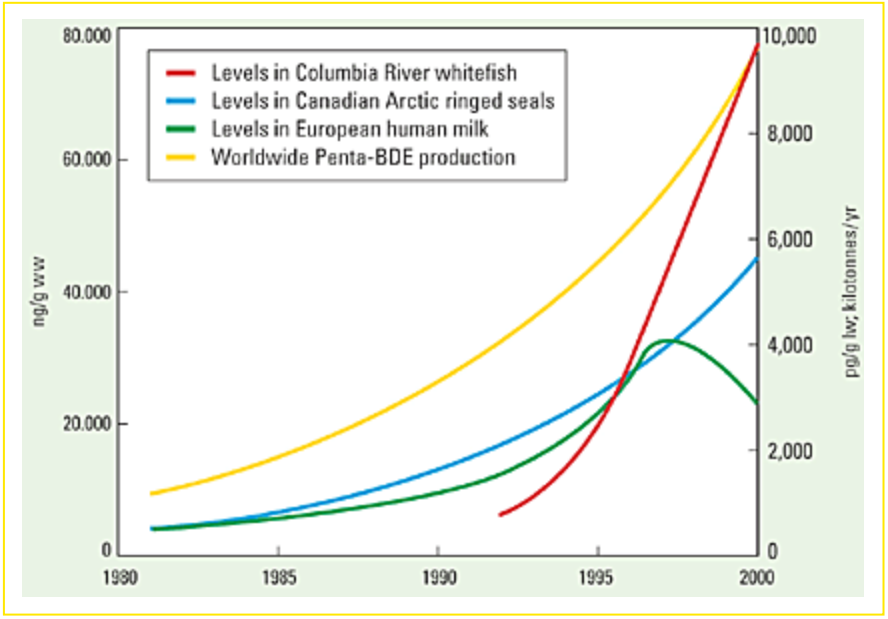


What Else is Interesting About Semi-Arid/Arid Regions to Environmental Chemists?

- Unique hydrology/ecology can often "focus" contaminants into biota:
  - major lakes/streams can often have low allochthonous organic matter content
  - hydrophobic compounds head for the only carbon around ⇒ biota

We found levels of brominated flame retardants in the Columbia River at near 'world-high' concentrations

… linked only to septic field sources!!!



SUMMARY…

Semi-arid/arid aquatic systems may allow us to study contaminant processes that are masked elsewhere

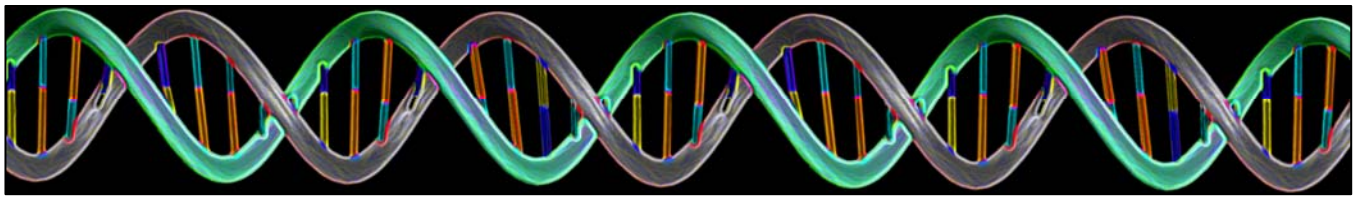
Reactive Intermediates in Environmental Systems: Why Care?

- What is a reactive intermediate?

recall $\boxed{A \rightarrow [C] \rightarrow [D] \rightarrow B}$

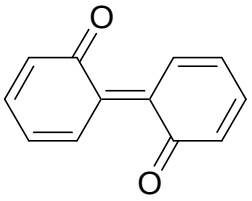
[C] and [D] are reactive intermediates

- How long do they 'live'?
  - Practical boundaries: nanoseconds → hours
  - Determined by their environment
- What do they react with?
  - Depends …
  - We're interested in RI's that react with DNA and other biological materials

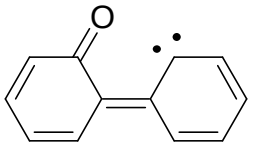


What Types of Reactive Intermediates?

- We're currently focused on two major groups:
  1. Biphenylquinones:



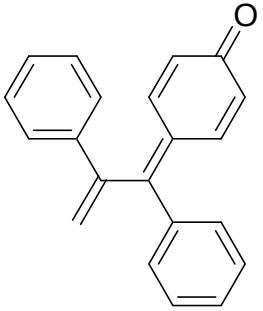
  2. Quinone methide carbenes:



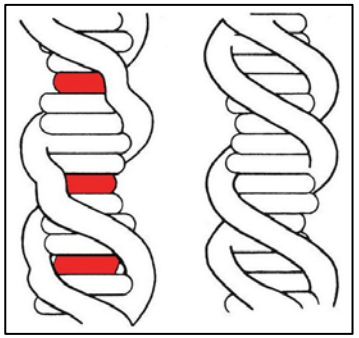
so we hypothesize that these RIs are DNA "intercalaters"

- Why these ones?
  - Structurally related to quinone methides ⇒ known to intercalate DNA

e.g.

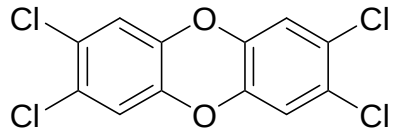


metabolite of Tamoxifen



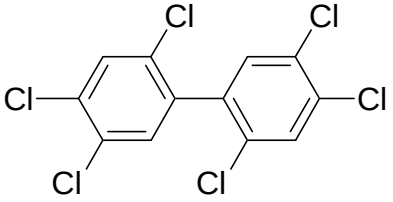
Where Do These RIs Come From?

- "Dioxins" and PCBs are two primary sources:
  1. Dioxins:
     - Not produced intentionally
     - Byproducts of combustion sources and chlorination of organics
     - Very acutely toxic (LD_{50} as low as 1 µg/kg body wgt.)
     - Much unknown about cause of long-term cancer risks
       - much $$ spent over past several decades…

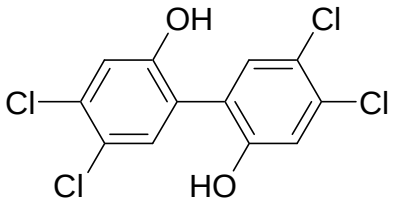


"dioxin"
(2,3,7,8-tetrachlorodibenzo[1,4]dioxin)

  2. PCBs:
     - Were produced intentionally
       - Flame retardants, insulators, …
     - Not acutely toxic
     - Long-term health effects at issue
       - cancer?



a PCB



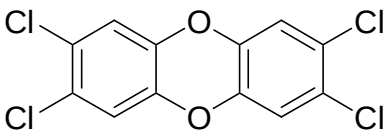
a hydroxy-PCB

     - Hydroxylated derivatives are known problems
       - endocrine disruptors, cancer?

The Dioxin-PCB-RI Connection

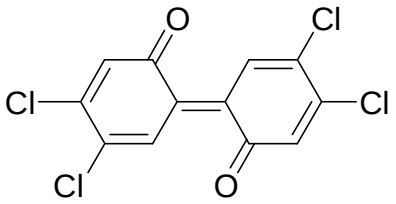
reduction

[excited or ground state]



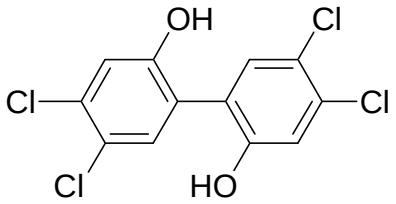
"dioxin"
(2,3,7,8-tetrachlorodibenzo[1,4]dioxin)

UV light



a biphenylquinone
reactive intermediate
(lifetime <1 s)

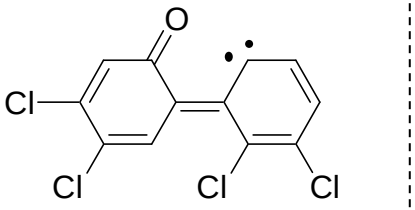
oxidation



a hydroxy-PCB

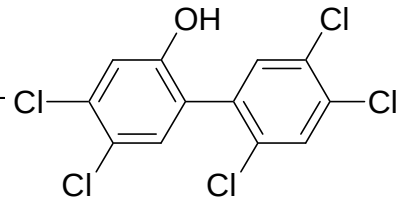
reactions with DNA?

1. biochemical or
2. UV light in water



a quinone methide carbene
reactive intermediate
(lifetime ???)

UV light



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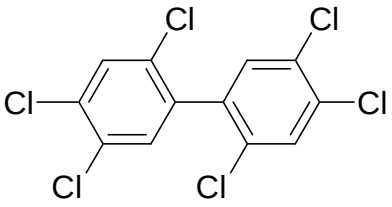
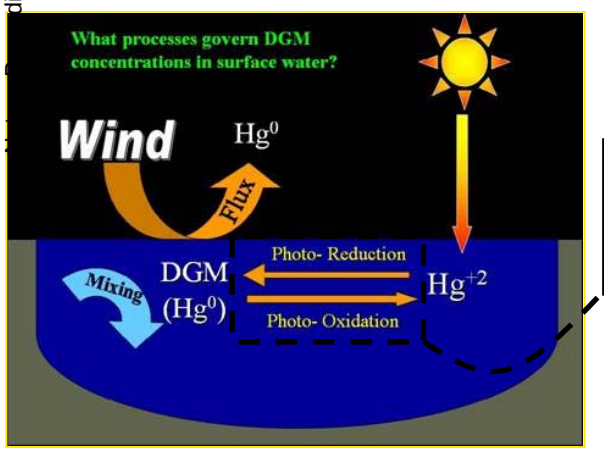


PCB #153

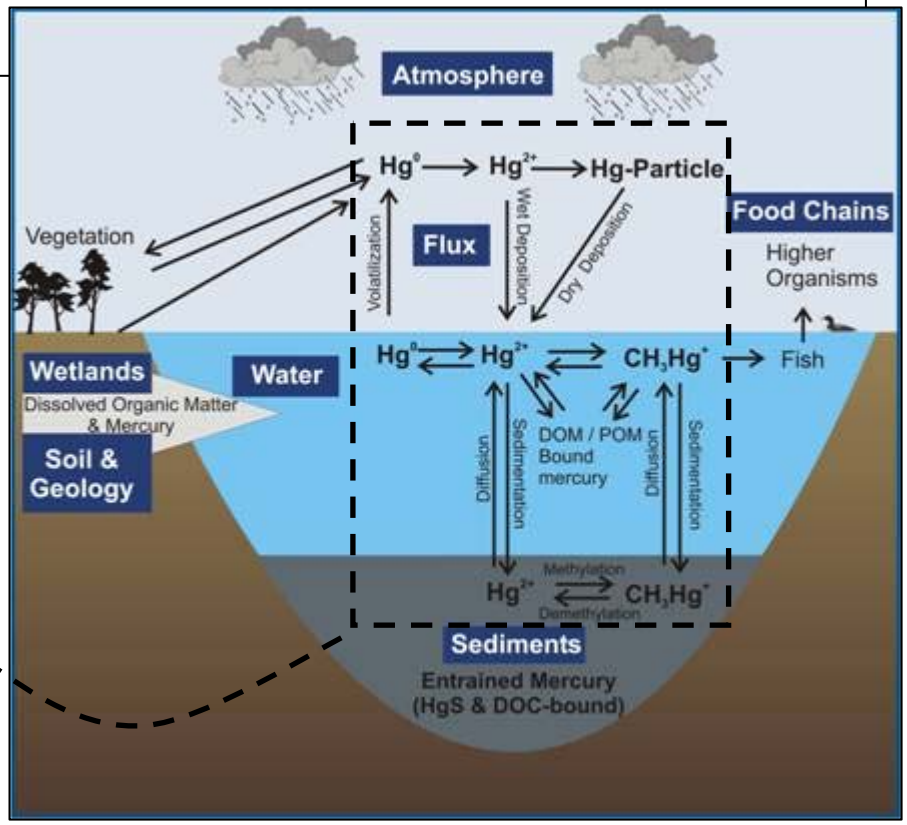
Biogeochemical Cycling of Toxic Metals: Role of Photochemistry?

- Photochemistry known to play a major role in the environmental cycling of 'cationic' heavy metals:
  - e.g., mercury, lead, etc.

Speciation and mobility of Hg greatly influenced by solar irradiation and dissolved organic matter (DOM)



UV-mediated Hg-DOM "redox shuttling"



The Information Gap: Photochemistry and the Metal Oxyanions

- Nothing known about photochemistry of 'oxyanion-formers' ("Oxy"):
  - e.g., arsenic, molybdenum, selenium, uranium, …
- Have similar structures to the orthophosphate ion (PO_4^{3-}):
  - AsO_4^{3-}
  - MoO_4^{2-}
  - SeO_4^{2-}
  - UO_4^{2-}

analogous complexes known for the "Oxy" team

DOM-Cat-Oxy

Forms ternary complexes with DOM and Fe^{3+} and other metal cations ("Cat") (e.g., Al^{3+}, etc.)

DOM-Cat-P

- Bioavailability of P strongly influenced by photochemical release of PO_4^{3-} from DOM-Cat-P complexes (reduction of Fe^{3+} to Fe^{2+} via DOM-redox shuttle)

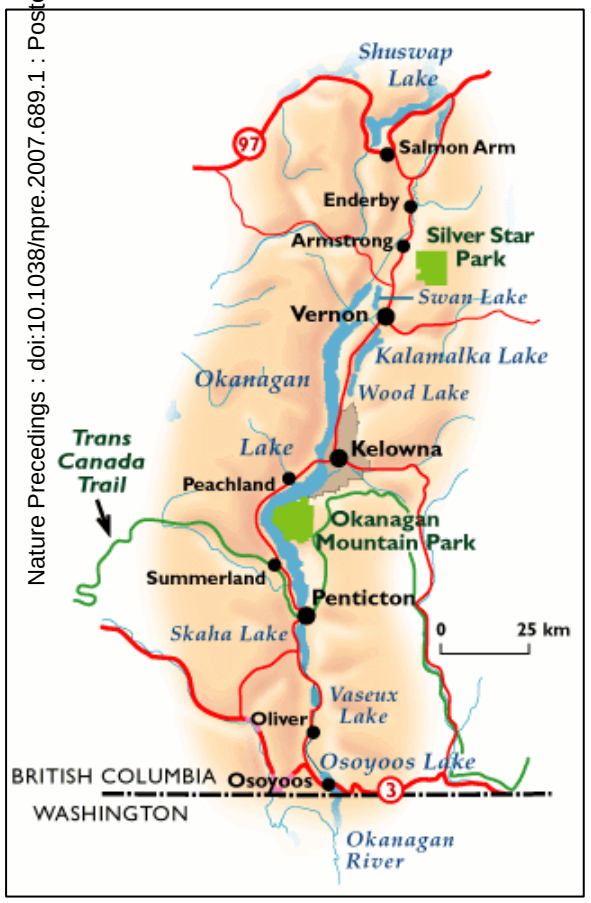
does photochemical release of As, … also govern bioavailability?

Thompson-Okanagan: The "Perfect Fit"

why?

There is no other region worldwide better suited to this research!

want to probe the DOM-Cat-Oxy photochemistry across all trophic gradients, geochemical signatures, etc.



Oligotrophic
(low C, N, P)
Ca-P ppt^{n}

Ultra-Oligotrophic
(very low C, N, P)
Autochthonous C

Humic
(high C, low N+P)
Allochthonous C

Mesotrophic
(low/mid-C, mid-N+P)
Autochthonous C

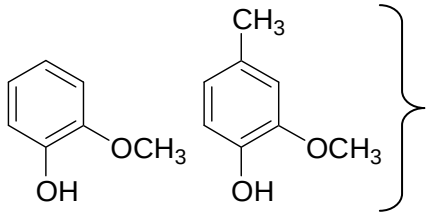
Eutrophic
(mid-C, high-N+P)
Autochthonous C

Saline

Wine Chemistry/Biochemistry of Phenolics

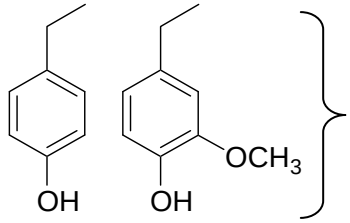
Three major projects:

1. Phenols from grapes exposed to forest fire smoke

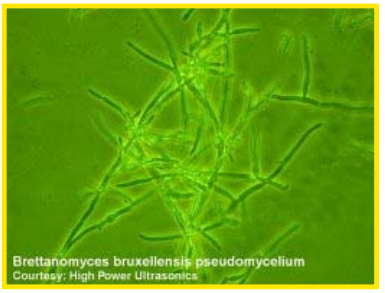


- concentrations
- distribution in grapes/vines
- atmospheric modeling

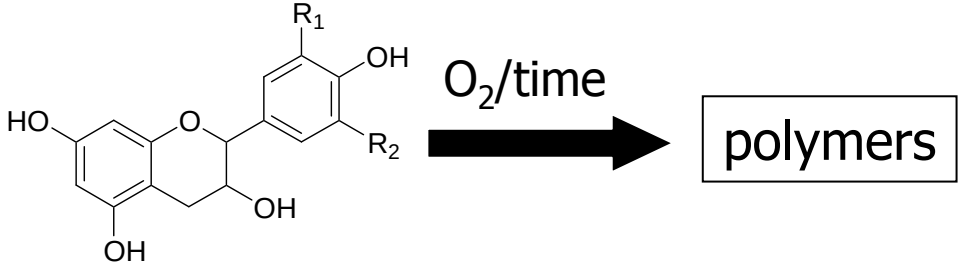
2. Volatile phenols derived from *Brettanomyces* yeasts



- concentrations/speciation
- abiotic/biotic controls on formation/degradation



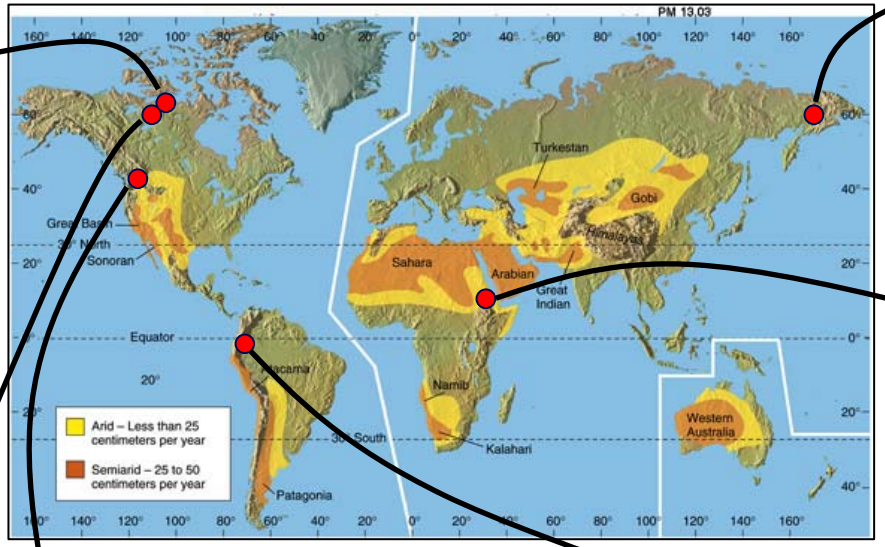
3. Effects of micro-oxygenation on polyphenols



bitter, unstable color less bitter, stable color

Mining Geochemistry: Projects Worldwide

Doris North (Nunavut, Canada)



Kupol (Siberia, Russia)

Bisha (Eritrea)

Gahcho Kue (NWT, Canada)

Nickel Plate (BC, Canada)

Mirador(Ecuador)

Canadian Diamonds

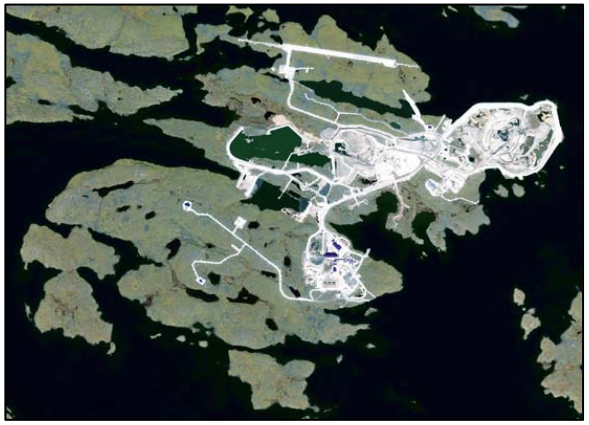
- Canadian diamond industry now a major world player:
  - >$2 billion in annual revenue
  - >15% of world production (behind only Russia and Botswana)
  - Several new mines operating proposed
    - in the NWT, Nunavut, AB, SK, and ON
    - Capital development costs often ~$1 billion

Diamond Mine Development: Geochemical/Water Quality Risks

- Diamond mine development primarily open-pit (cheaper)
  - Most mines have some underground component in late stages

Diavik

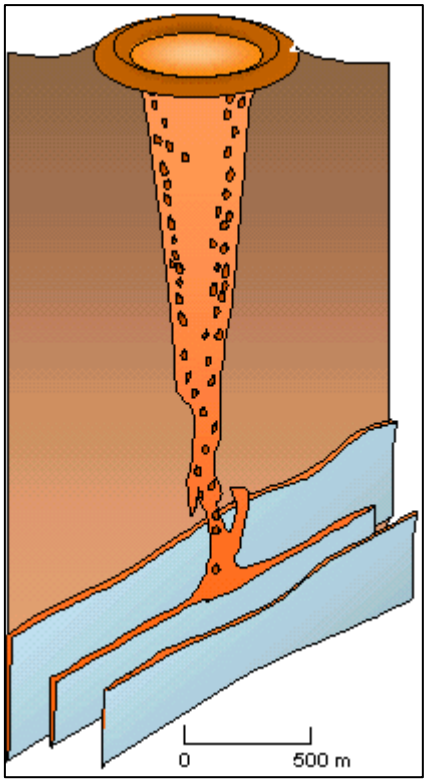
Ekati

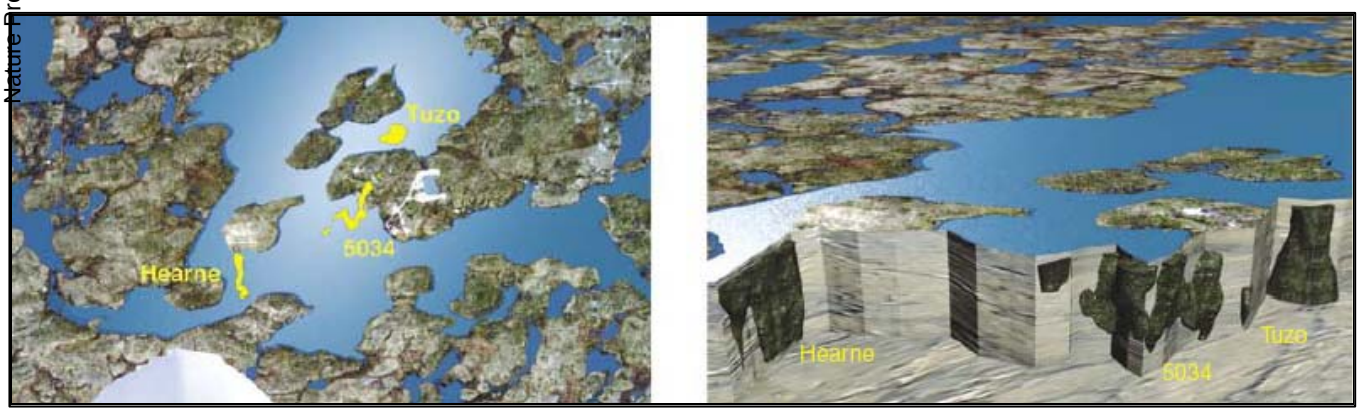


- Land use changes
- High sediment and metals loadings from waste rock and construction materials
- Saline inflows to open pits/underground
  - up to 1/20 as saline as seawater!

The Interesting Research Question: Risks from Kimberlite Waste?

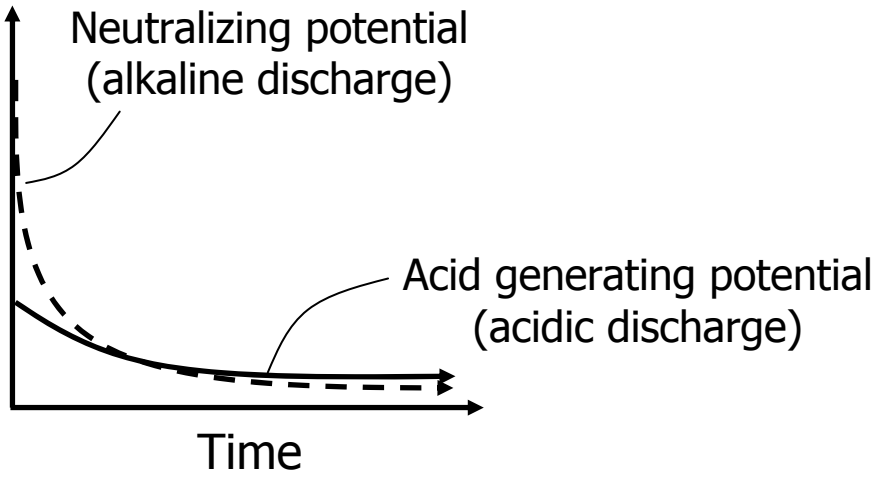
- Kimberlite hosts the diamonds:
  - hybrid, volatile-rich, potassic, ultrabasic igneous rock
  - formed at >150 km depth
  - transport diamonds to Earth's surface
- Diamond processing produces waste kimberlite:
  - referred to as PK (processed kimberlite)
    - crushed to mm and sub-mm silt/clay consistency
  - and lots of it ⇒ millions of tons…





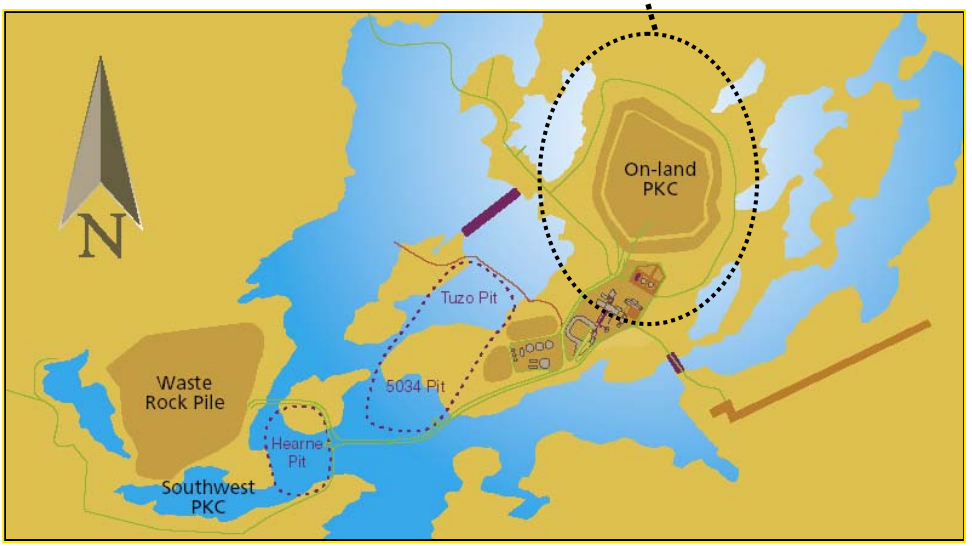
Geochemistry of Canadian Kimberlites – Unreactive as Previously Thought?

- Short answer is '<u>NO</u>'
- Previous ideology:
  - Waste PK drainage with elevated metal loadings from some elements (e.g., Al, Ni, Co, Sr, Zn) and little potential for net acid generation
- Our findings in 2004-2005:
  - Highly saline drainage (up to 10,000 mg/L, or 1/4 the strength of seawater)
  - Long-term risk of acid rock drainage (ARD)!!



Implications? Proposed Work…

~1 km^2, >30 m high



Canadian mines have PK waste strategies that rely on 'infinite' <u>freezing of facilities</u> after closure:

- Global warming?
- Ekati already seeing evidence of ARD from kimberlite waste…

What would we do?

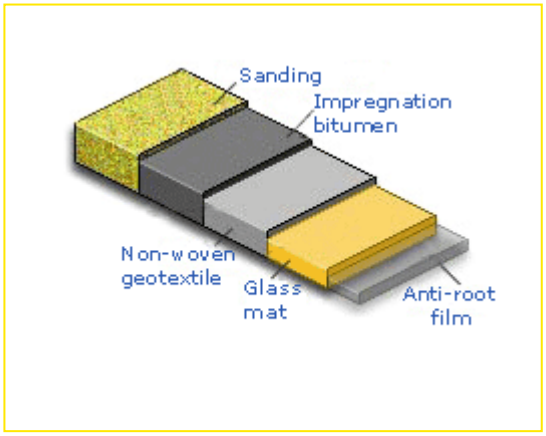
- Partner with industry on targeted research needs
- Use advanced laboratory- and field-based testing methods
  - Acid-base accounting (ABA), humidity cells, and leach columns
  - Optical microscopy, Rietveld XRD, and scanning electron microscopy
  - Field-scale leach pads and sample collection from operating mines
- Comparisons with South African and Russian raw/processed kimberlites?

Other Issues Warranting Research

Long-term stability of bituminous liner for kimberlite tailings facilities?

- Nitrogen from blasting residues in the tailings
- Kimberlite leaches phosphate
- Carbon from the bitumen

} microbial degradation?



Diavik (NWT, Canada)

Gahcho Kue (NWT, Canada)

Other Issues Warranting Research

Doris North (Nunavut, Canada)

- Long-term low levels of metals (e.g., Al) and arsenic leaching from waste rock
- Mitigation strategies to allow "walk-away" closure options?

Nickel Plate (Barrick Gold)

Kupol (Bema Gold)

- Both sites have high risk of ARD from exposed pit walls at closure
- Sealing of pit walls?
  - Urethane?
  - Plasticized concretes?

} materials science/ nanotech

How Does Proposed Mining Research Program Fit Into Overall Canadian Research Strategy?

- Currently have NSERC École Polytechnique-Université du Québec en Abitibi-Témiscamingue (UQAT) Industrial Research Chair in the "Environmental Management of Mining Wastes"

- The EP-UQAT chairs focused on geotechnical approaches:
  - e.g., covers for waste rock and tailings
- Additional work at UBC-Vancouver, Alberta, Saskatchewan, etc.
  - also focused on geotechnical and mining/civil engineering issues
- Room for a more multidisciplinary environmental focus from a chemical perspective…

Attracting Students to the Research Program: Part 1

- Build on their passions and career goals:
  - Not all students want to continue formal education past a B.Sc.
    - Short projects geared towards industrial applications
    - Enable life-long applied learning…
    - Emphasis on getting professional accreditation (P.Chem., P.Ag., P.Eng./P.Geo.)
  - Some want to be career researchers or take leadership roles in industry (M.Sc./Ph.D./post-docs)
    - "Pure science" – targeted projects to tackle fundamental environmental questions
      - Novel reactive intermediates (photochemically or thermally generated)
      - Biogeochemical cycling of metals/metalloids
      - New analytical methods
    - "Applied sciences" – aimed at specifically dealing with the problems
      - Pollution prevention strategies (UV, microbial, membrane?)
      - Materials science and mining geochemistry ("varnish the pit")
      - Agricultural chemistry (e.g., micro-oxygenation of wines…)

Attracting Students to the Research Program: Part 2

- Some prefer certain 'branches' of chemistry:
  - Organic:
    - Synthesis of starting materials and degradation products
    - 'Trapping studies' of reactive intermediates with biologically relevant materials
    - Mechanistic photochemistry
  - Inorganic:
    - Biogeochemical cycling of metals/metalloids
    - Mining geochemistry
  - Analytical:
    - New methods for environmental analysis (GC-MS, LC-MS, etc.)
    - Use of analytical tools to estimate physico-chemical properties
  - Physical:
    - Equilibrium/kinetic partitioning constants and modeling
    - Photophysical studies (e.g., "sunscreening" effects of dissolved carbon)

Attracting Students to the Research Program: Part 3

- Local or global?
  - Mines in semi-arid/arid regions worldwide for those who like to travel
  - Projects close to home in the 'best place on Earth'

Acknowledgements

- NSERC
- Fisheries and Oceans Canada (DFO)
- Environment Canada (EC)
- British Columbia Wine Institute (BCWI)
  - now the BC Wine Grape Council (BCWGC)
- Investment Agriculture Foundation of British Columbia (IAFBC)