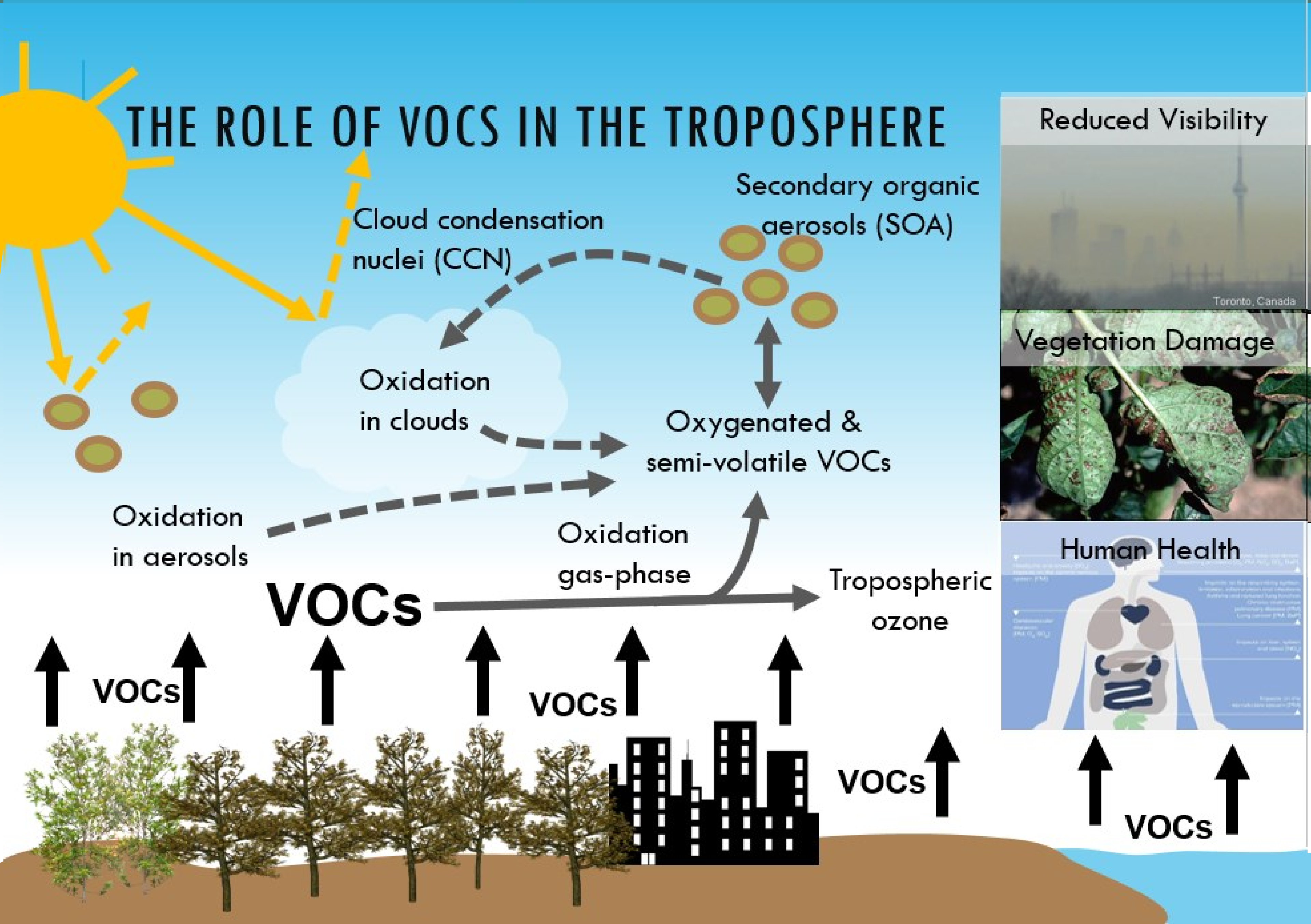
DETERMINATION OF THE ATMOSPHERIC IMPORTANCE OF MICROBIALLY PRODUCED TERRESTRIAL VOLATILE ORGANIC COMPOUNDS

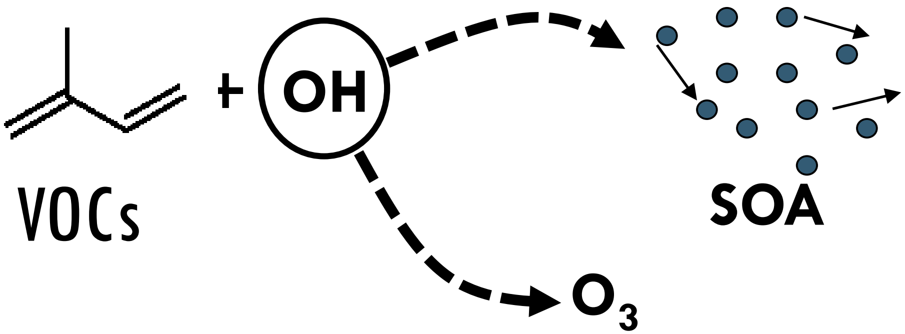
Sarah Kavassalis

Environmental Chemistry Research Proposal

November 12th, 2015


THE ROLE OF VOCS IN THE TROPOSPHERE
Cloud condensation nuclei (CCN)
Secondary organic aerosols (SOA)
Oxidation in clouds
Oxygenated & semi-volatile VOCs
Oxidation in aerosols
Oxidation gas-phase
VOCs
Tropospheric ozone
VOCs
VOCs
VOCs
VOCs
Reduced Visibility
Toronto, Canada
Vegetation Damage
Human Health

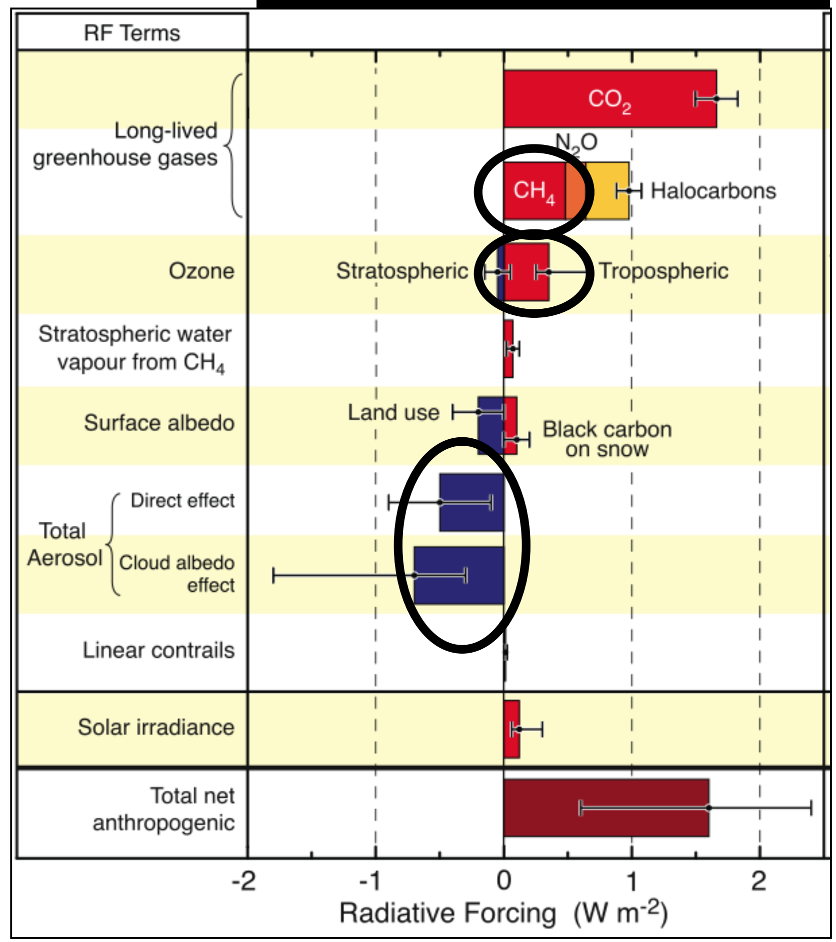
THE ROLE OF VOCS IN THE TROPOSPHERE



VOCs deplete OH, which increases CH_4 lifetime

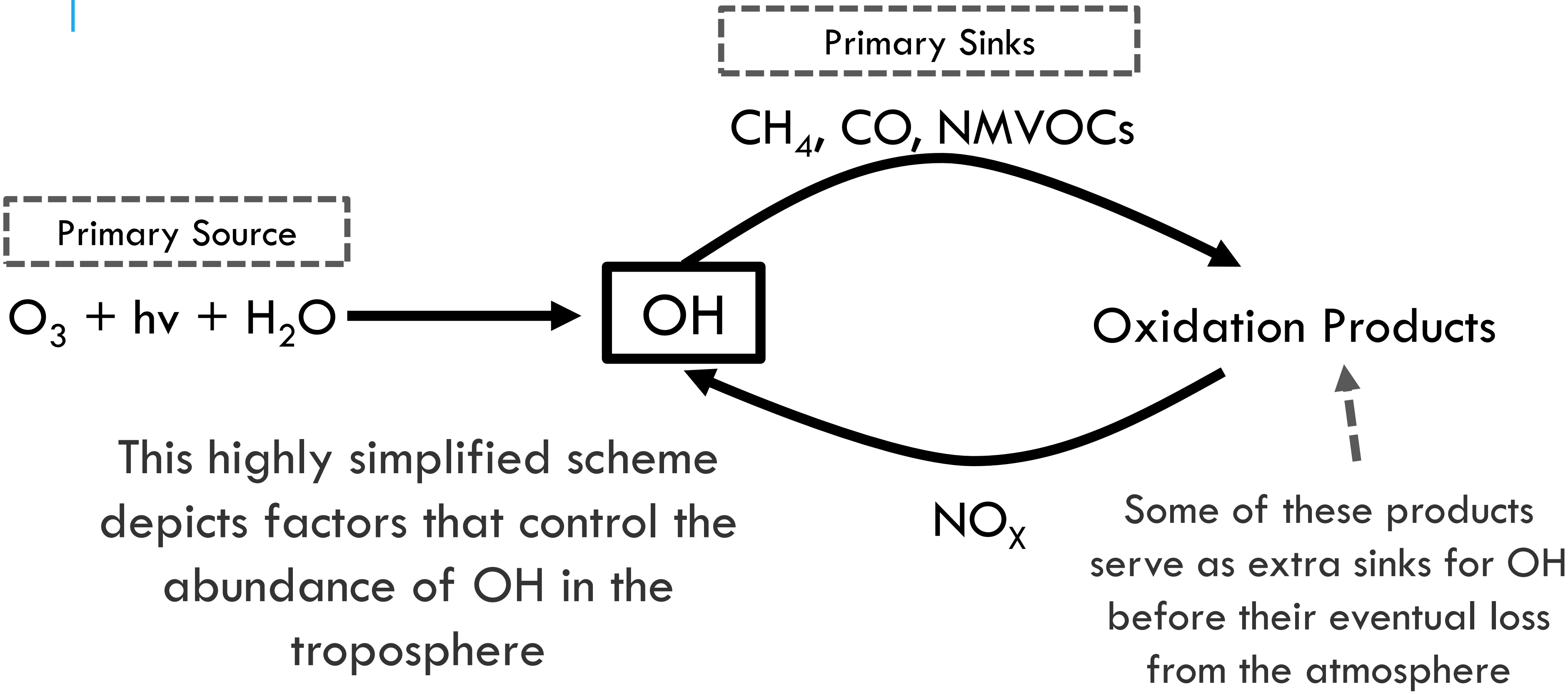
$$CH_4 + OH \longrightarrow CO_2 + H_2O$$

CONSEQUENCES FOR CLIMATE



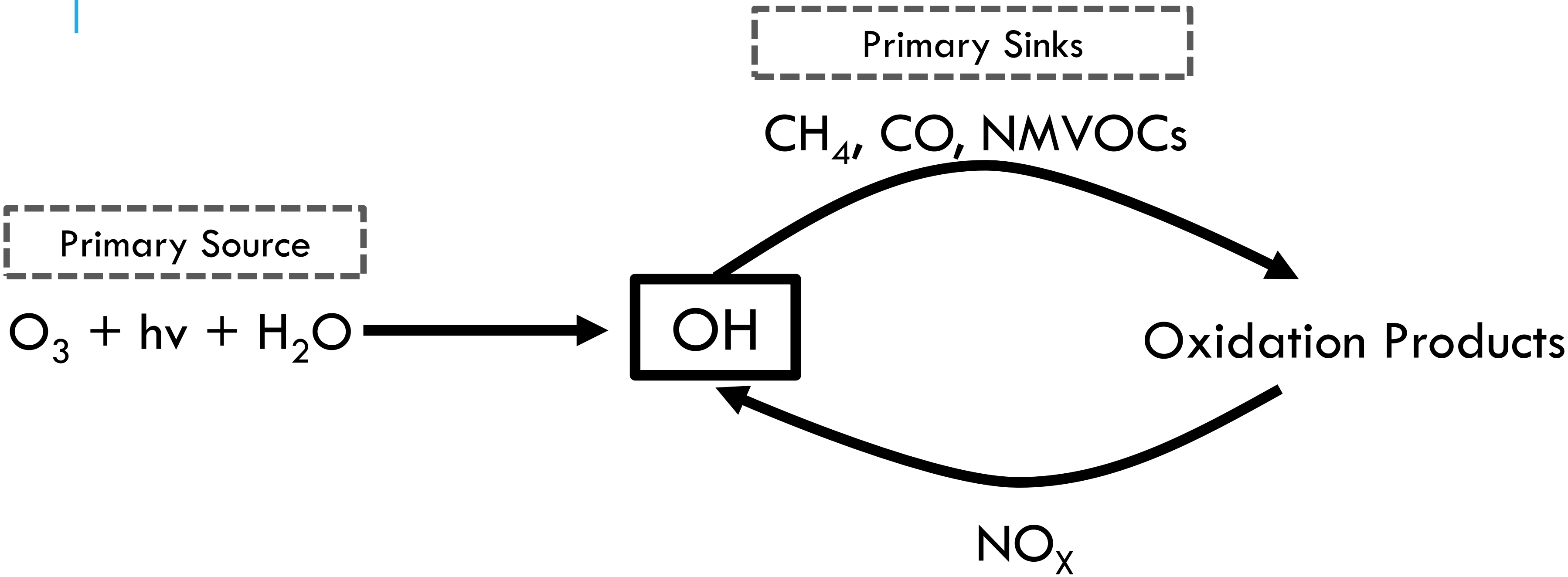
IPCC, 2007

THE TROPOSPHERIC OH BUDGET



NO_x: reactive nitrogen oxides NO, NO_2, NO_3, etc.
NMVOCs: Non-Methane Volatile Organic Compounds (VOCs)

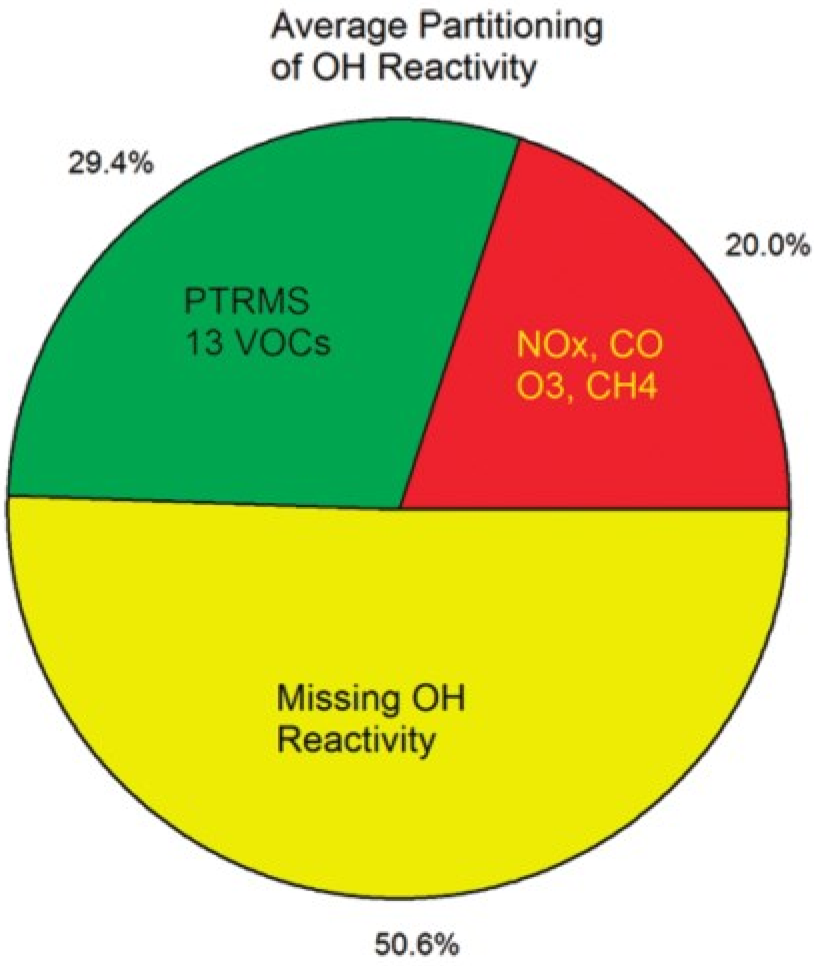
THE TROPOSPHERIC OH BUDGET



$$\text{Total OH reactivity } (s^{-1}) = \sum_n k_{X_n+OH}[X_n]$$

where k_{X_n+OH} is the rate coefficient for the reaction of species X_n with OH.

MISSING OH REACTIVITY

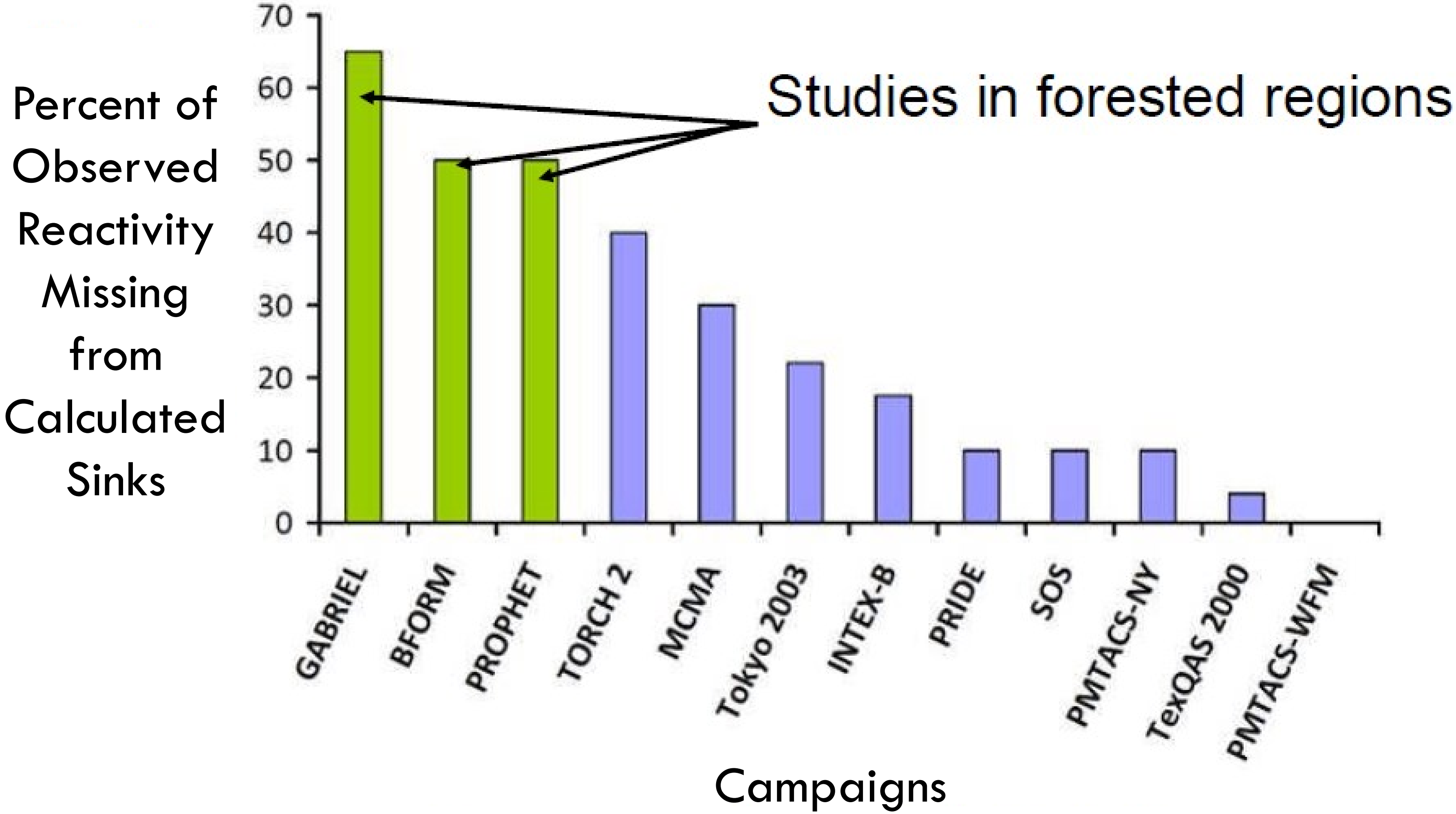


Total OH reactivity $(s^{-1}) = \sum_n k_{X_n+OH}[X_n]$

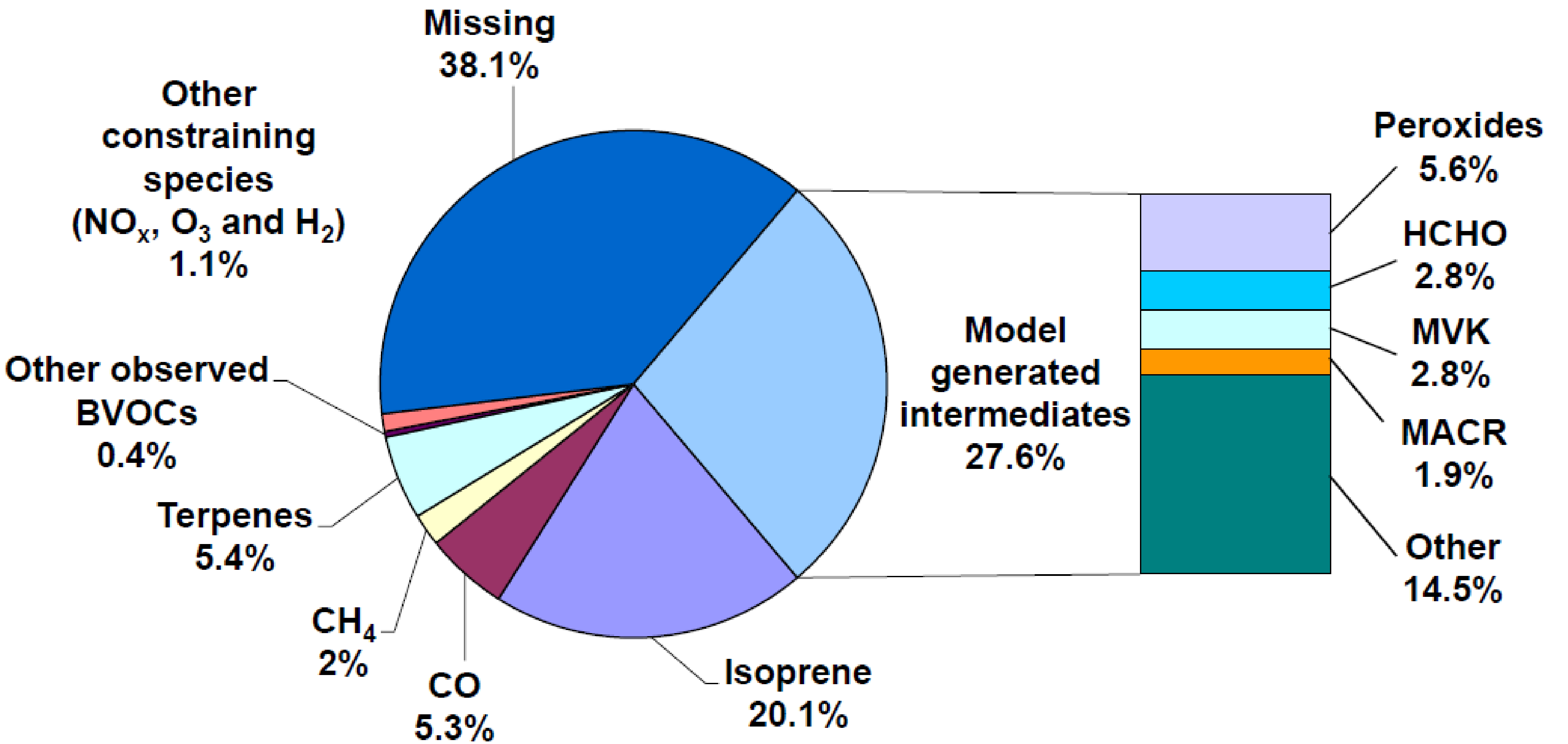
$$OH + CO \xrightarrow{O_2} HO_2 + CO_2$$
$$OH + CH_4 \xrightarrow{O_2} CH_3O_2 + H_2O$$
$$OH + NO_2 \xrightarrow{M} HNO_3$$
$$OH + VOCs \xrightarrow{O_2} RO_2 + products$$

Sinha et al., ES&T, 2010

Missing OH Reactivity



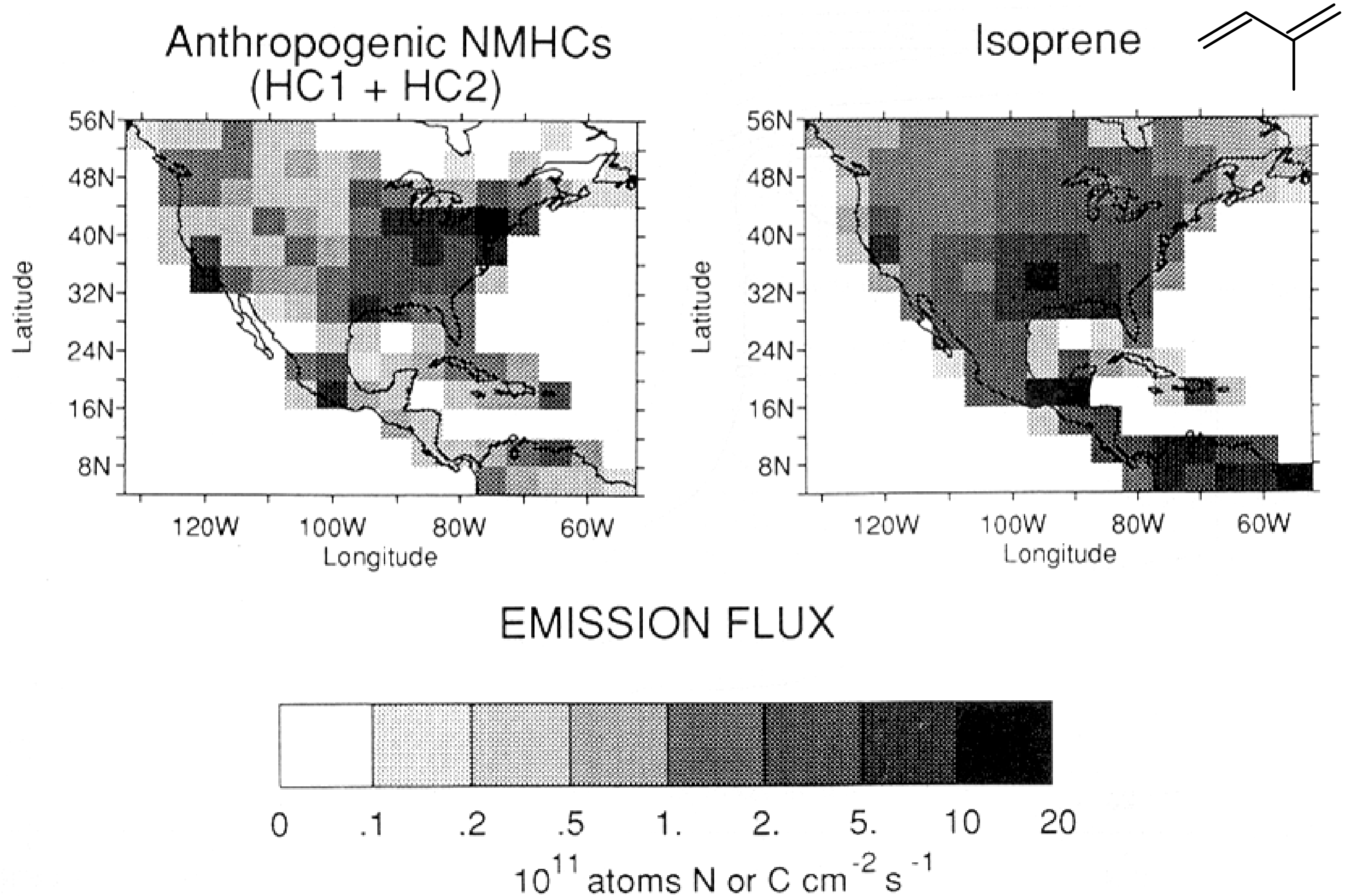
Missing OH Reactivity



Measurements of other reactive species needed!

Whalley, ACPD, 2015

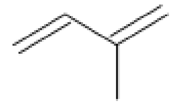
VOCS IN THE TROPOSPHERE



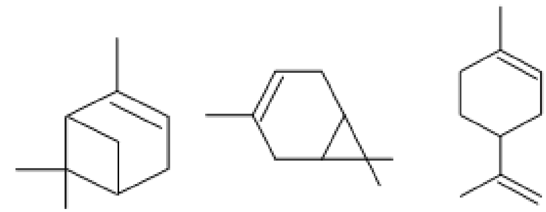
Jacob et al., 1993

VOCS IN THE TROPOSPHERE

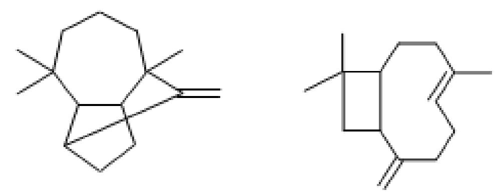
Isoprene (C_5H_8)

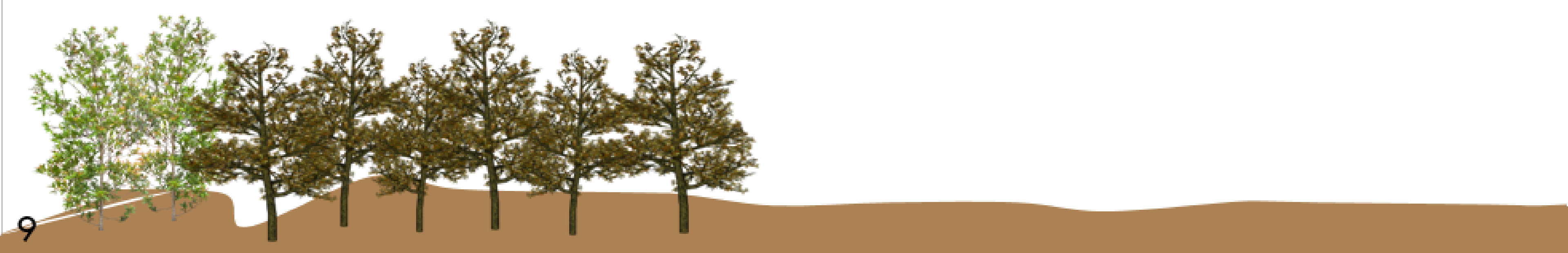


Monoterpenes($C_{10}H_{16}$)

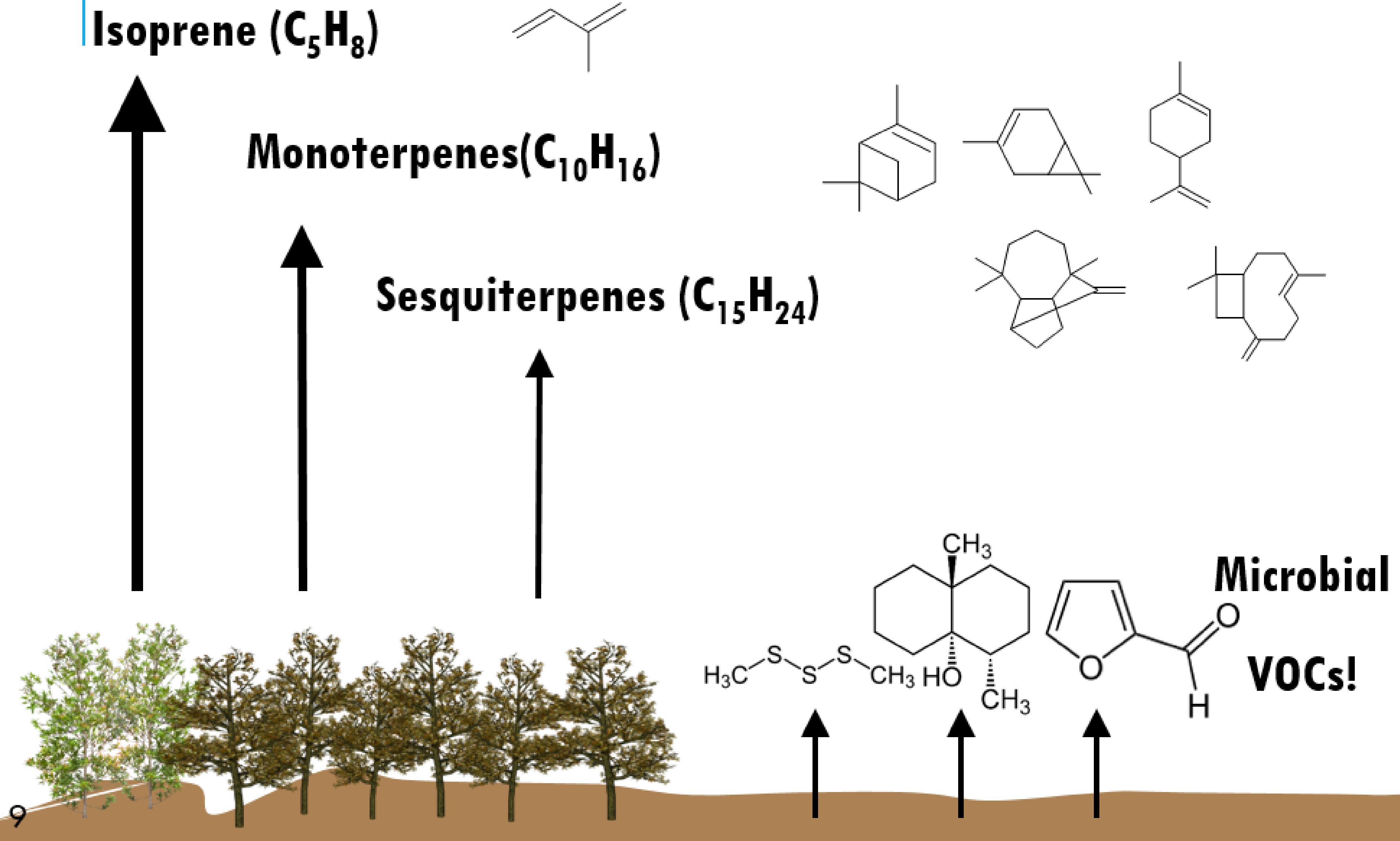


Sesquiterpenes ($C_{15}H_{24}$)



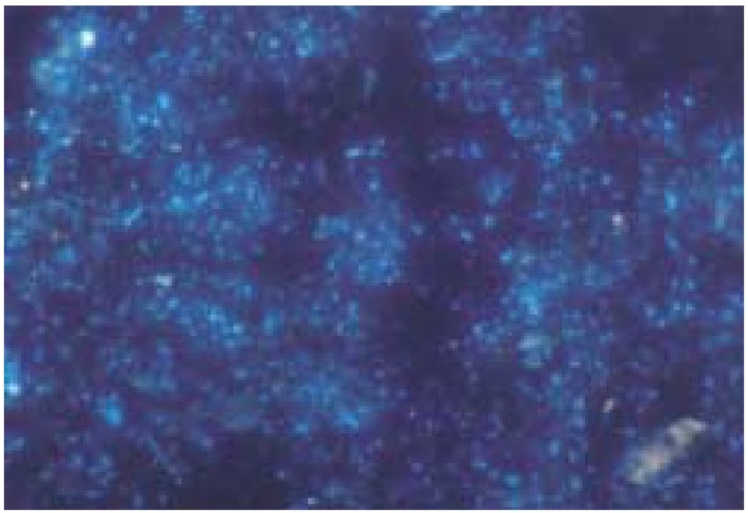


BVOCS IN THE TROPOSPHERE



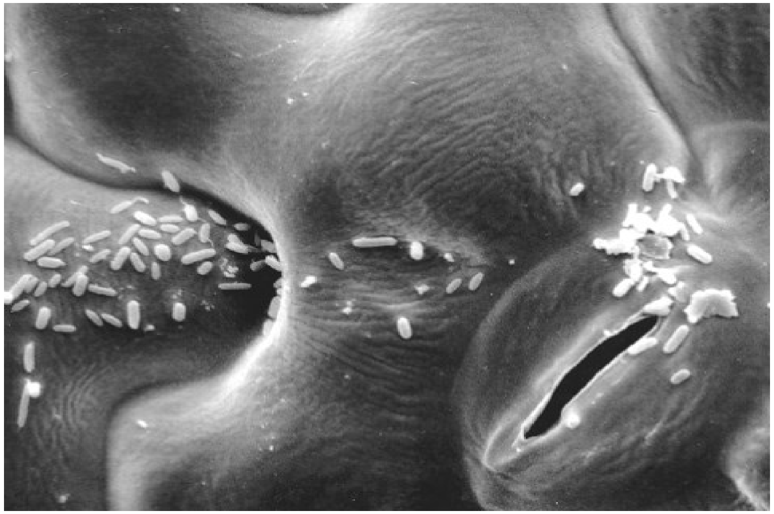
MICROBIAL VOLATILE ORGANIC COMPOUNDS

Microbes are everywhere!



Current Opinion in Microbiology

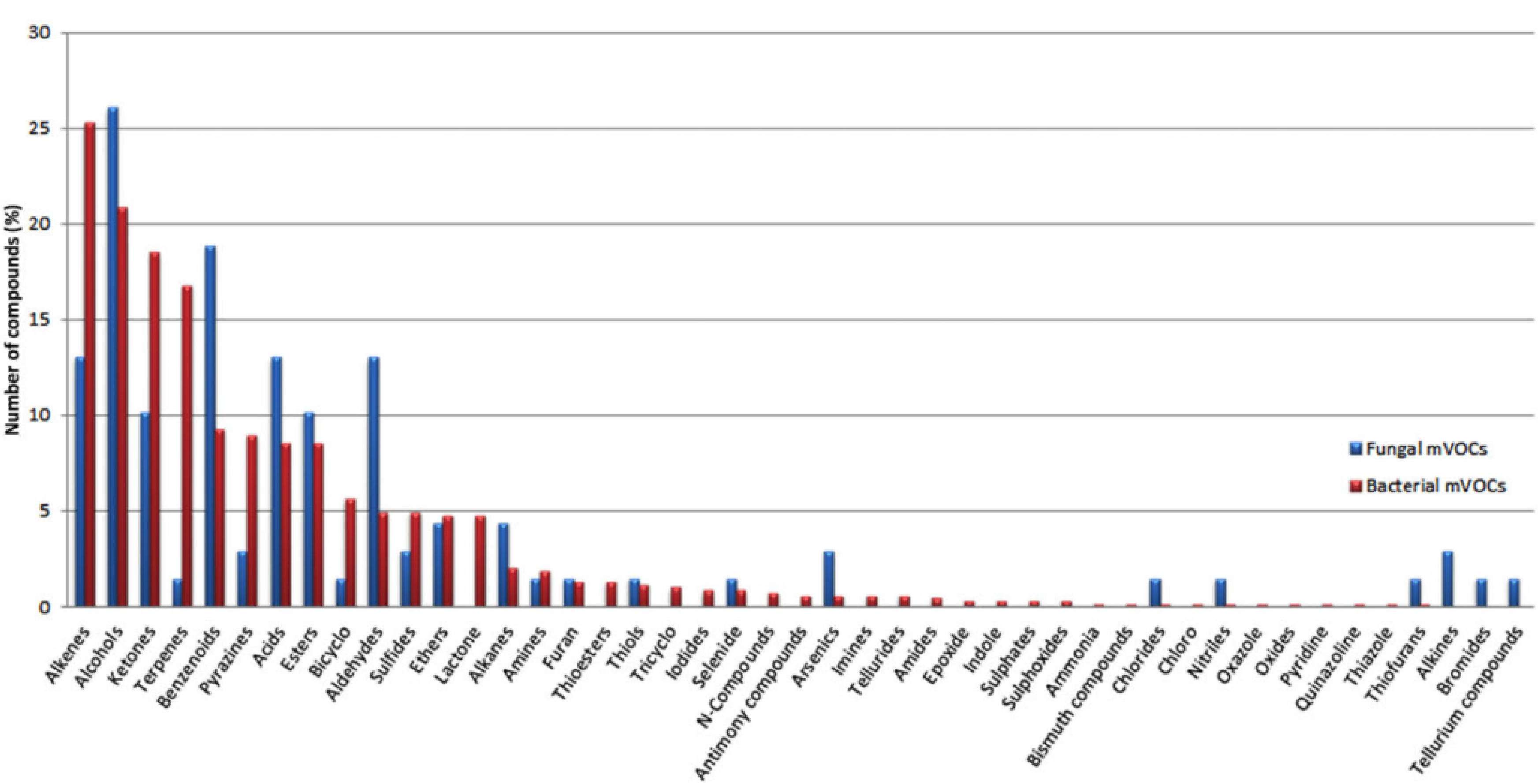
Bacteria are abundant in soils. Fluroescence micrography of soil microorganisms The total bacterial count was 4.2×10^{10} cells $gram^{-1}$ soil (dry weight).



Bacteria are the dominant inhabitants of leaf surfaces (10^7 $cells/cm^2$). Image shows scanning electron micrographs of bacteria on bean leaves.

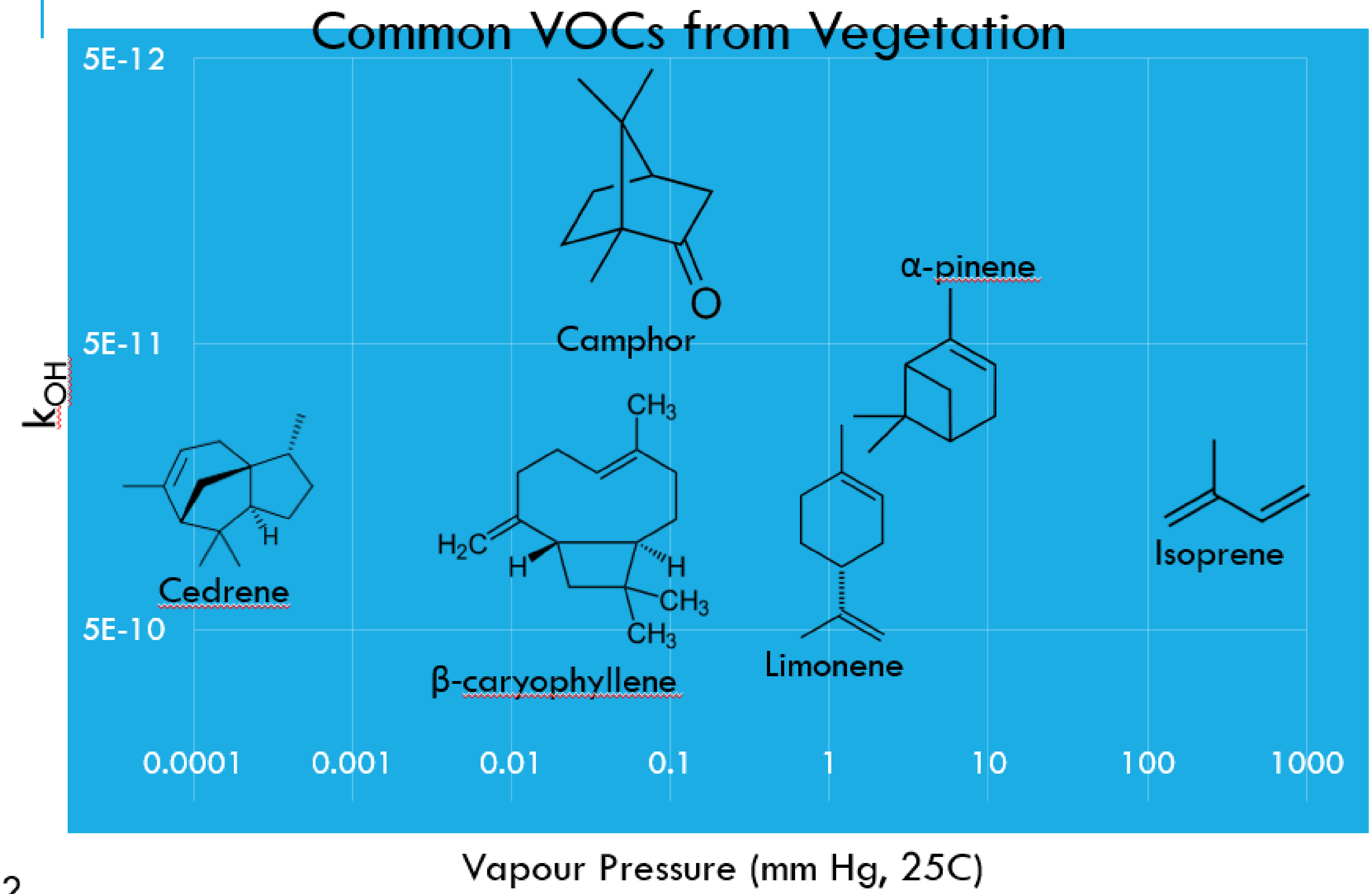
Torsvik, Curr. Op. Microbio., 2002

MICROBIAL VOLATILE ORGANIC COMPOUNDS (MVOCS)

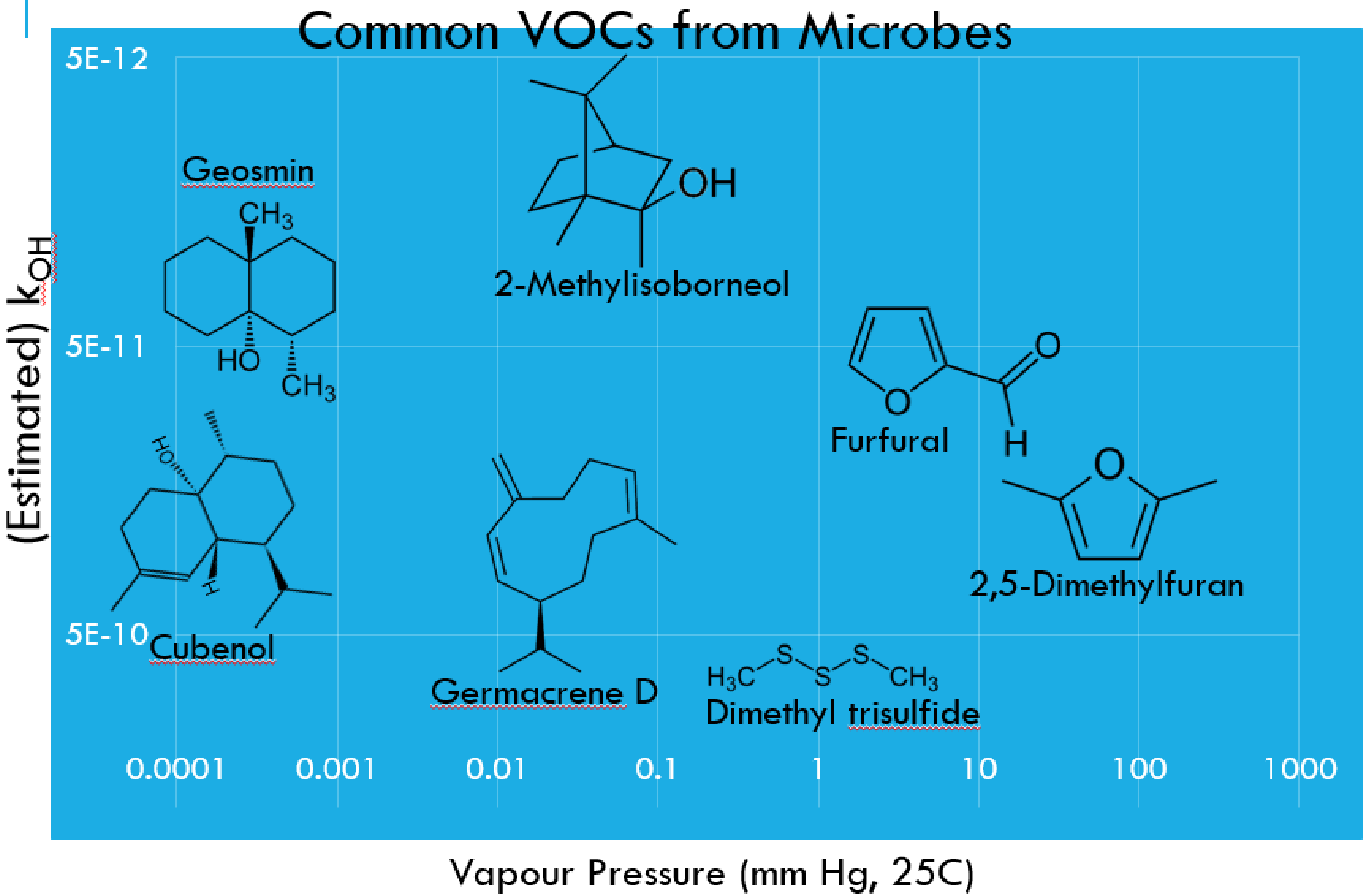


Lemfack, Nucleic acids research, 2014

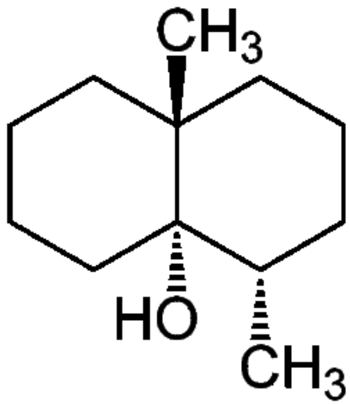
MICROBIAL VOLATILE ORGANIC COMPOUNDS



MICROBIAL VOLATILE ORGANIC COMPOUNDS



MICROBIAL VOLATILE ORGANIC COMPOUNDS



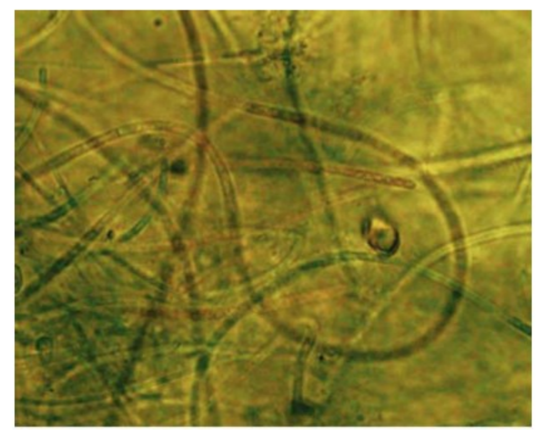
Geosmin

"Earth-smell"

Some mVOCs are unique and well known (even if people don't know that they're well known)

Geosmin producing *Chaetomium* fungi

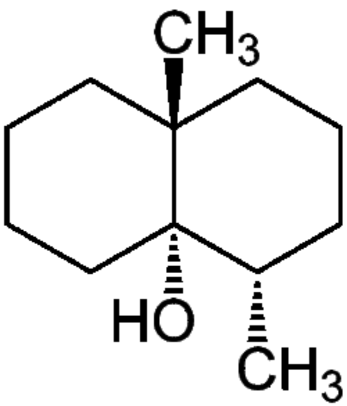
Geosmin producing *Streptomyces* bacteria



Geosmin producing Cyanobacteria

MICROBIAL VOLATILE ORGANIC COMPOUNDS

Simons, 2003

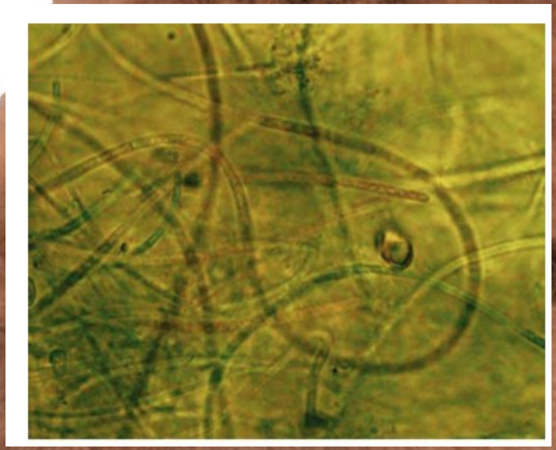


Geosmin

"Earth-smell"

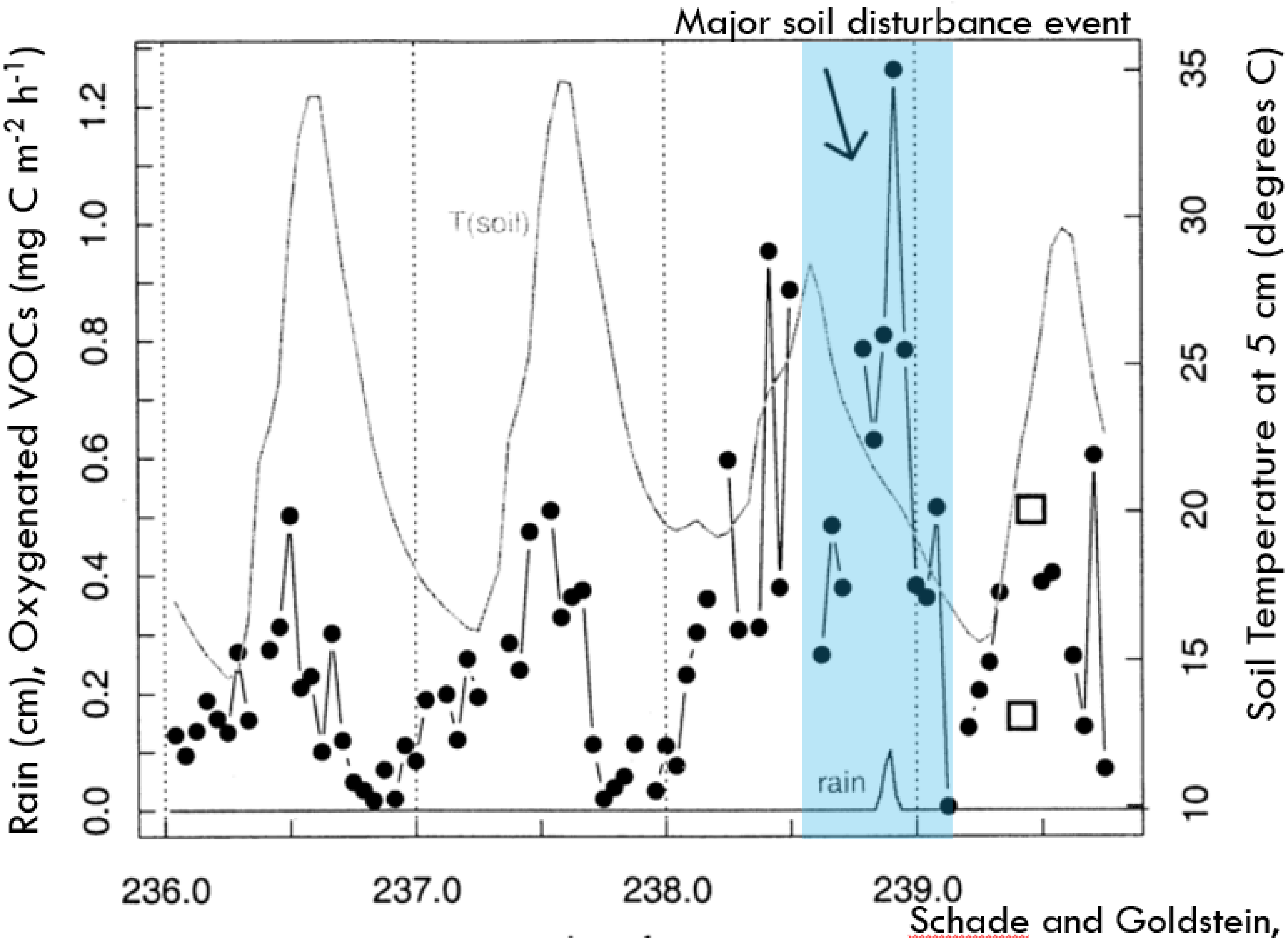
Geosmin producing *Chaetomium* fungi

Geosmin producing *Streptomyces* bacteria



Geosmin producing Cyanobacteria

ATMOSPHERIC IMPORTANCE OF MVOCS



Schade and Goldstein, JGR, 2001

ATMOSPHERIC IMPORTANCE OF MVOCS

We know:

- We are missing VOCs
- We are not measuring mVOCs

So…

REQUEST FOR FINANCIAL SUPPORT FOR CAMEL: CONTRIBUTIONS OF ATMOSPHERIC MICROBIAL EMISSIONS TO OH LIFETIME

PI: Sarah Kavassalis (UofT)
Collaborators: XXXXXXXXXXXXXXXXXXXXXXXXXX

Science Objective: To understand the role that terrestrial non-methane microbial emissions have on OH chemistry.

Projects:

1. To characterize the volatile metabolome for a few common soil bacteria.
2. To preform ambient measurements of mVOCs in Southern Ontario and provide the first in situ measurements of uniquely microbial VOCs.
3. To determine how microbial VOCs impact OH reactivity in a simplified chamber environment.

PROJECT 1: MVOC EMISSIONS FROM COMMON SOIL BACTERIA IN LABORATORY SETTING

Hypothesis: Soil bacteria cultured in the laboratory can represent certain characteristics of in situ soil bacteria and be used as a surrogate to study ambient mVOC emissions.

Objective: To characterize and quantify the volatile metabolome for a few common soil bacteria.

Collaborators: XXXXXXXXXXXXXXX

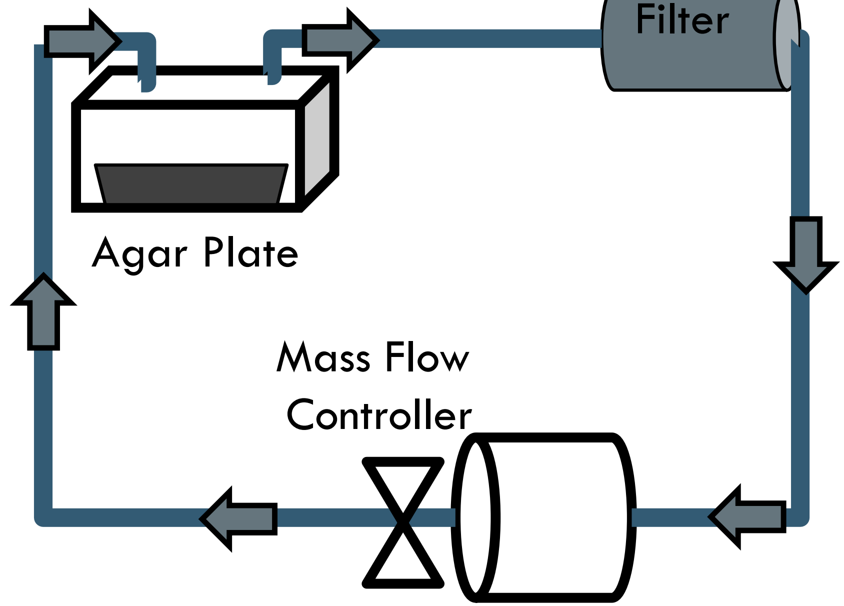
PROJECT 1: MVOC EMISSIONS FROM COMMON SOIL BACTERIA IN LABORATORY SETTING

Experimental Design:

- Culture soil bacteria on agar plates
- Closed loop-stripping apparatus (CLSA) and GCxGC-MS headspace analysis

Precedent:

CLSA+GC-MS has been used successfully to characterize VOC profiles of plants[1], arctic and marine microbes [2], and terrestrial bacteria [3].



[1] Donath & Boland, Phytoch., 1995. [2] Dickschat et al., ChemBiodiv., 2005.
[3] Dickschat et al., Chembiochem, 2004.

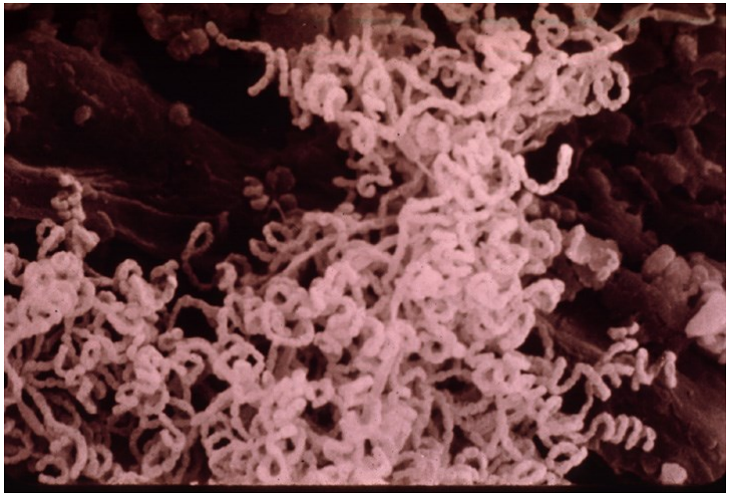
PROJECT 1: MVOC EMISSIONS FROM COMMON SOIL BACTERIA IN LABORATORY SETTING

Genera Selection: [1]

- *Streptomyces*
- *Pseudomonas*
- *Arthrobacter*
- *Mycobacterium*
- *Bacillus*

Culture Media Selection: [2]

- Soil Extract Agar
- Tryptone Soya Agar
- Casein Starch Agar



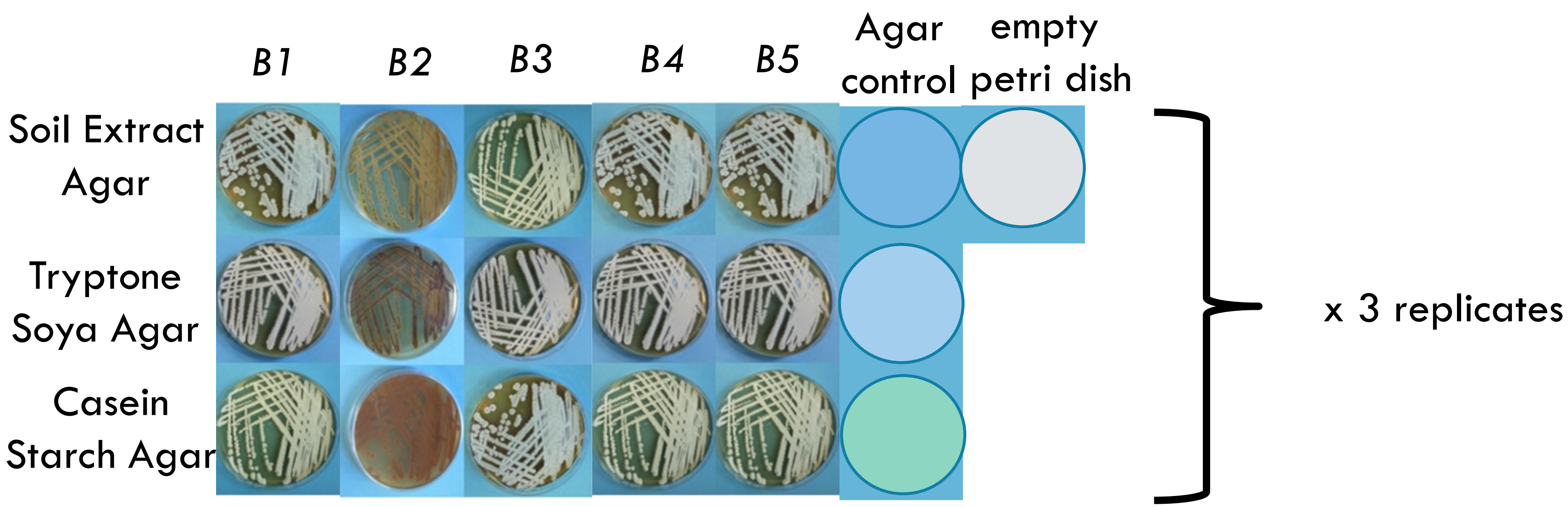
Streptomyces. Soil Microbiology and Biochemistry Slide Set. *1976. J.P. Martin, et al., eds. SSSA, Madison, WI.*

[1] Janssen, Appl. Environ. Microbiol., 2006. [2] Vieira and Nahas, Microbiol. Res., 2005.

PROJECT 1: MVOC EMISSIONS FROM COMMON SOIL BACTERIA IN LABORATORY SETTING

Experimental Design:

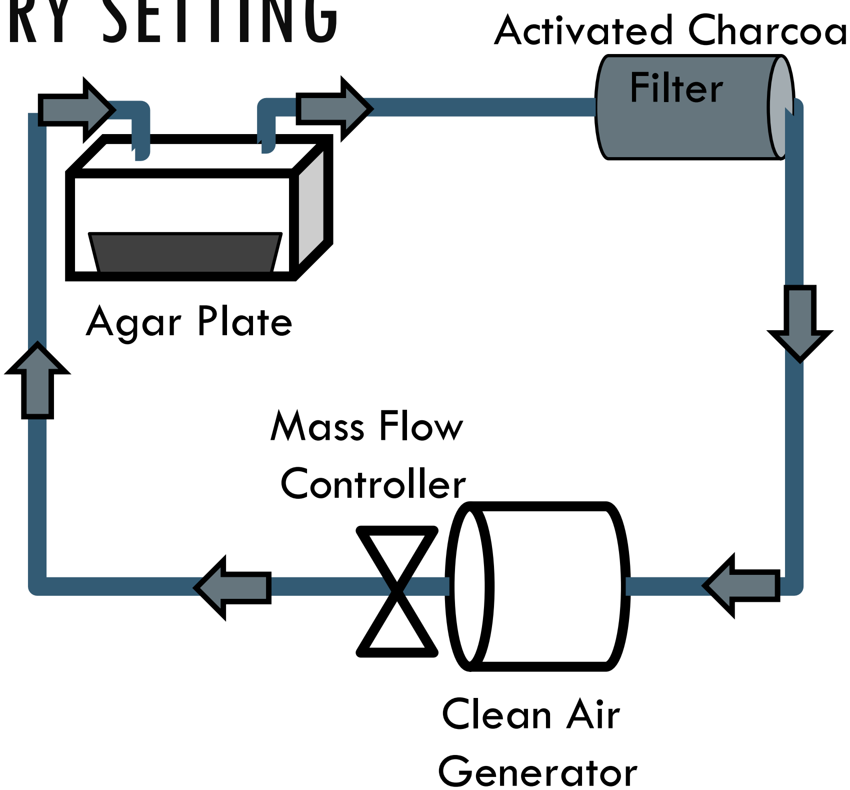
- Cultures will be 10-30 old, depending on species
- 3 x culture for each media for each bacteria (3 x 3 x 5 experiments)
- 3 x empty growth media controls (3 + 3 x 3 controls) + 3 x empty petri dish control



PROJECT 1: MVOC EMISSIONS FROM COMMON SOIL BACTERIA IN LABORATORY SETTING

Analytical Technique:

- Air will be circulated for 6 to 24 hours within the CLSA before extraction
- The filter will be extracted with 20 mL of CH_2Cl_2
- Offline injection on comprehensive GCxGC - MS

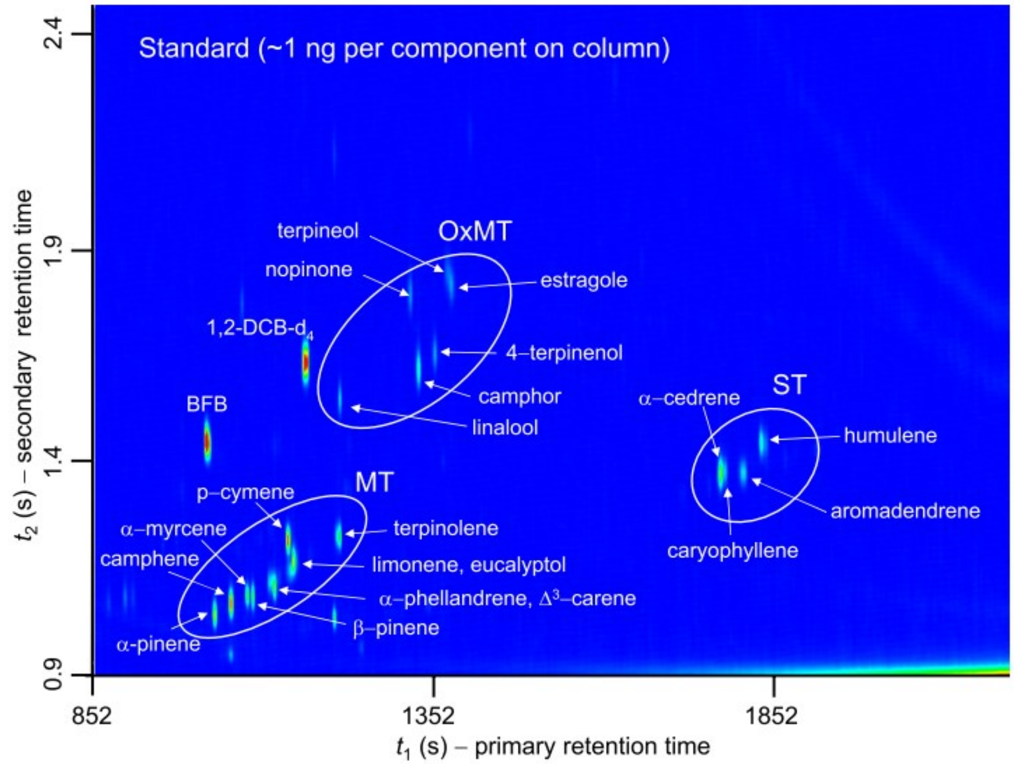


Closed loop-stripping apparatus (CLSA)

PROJECT 1: MVOC EMISSIONS FROM COMMON SOIL BACTERIA IN LABORATORY SETTING

Expected Outcomes: We will identify the VOC emission profiles of five common soil bacteria strains

Now we know what VOCs we should look for…



Example GCxGC spectra

PROJECT 2: FIELD OBSERVATIONS OF MVOCS IN TERRESTRIAL ENVIRONMENTS

Hypothesis: Terrestrial microbes provide an important source of VOCs to the atmosphere. mVOCs that are unique to the soil microbial community will be most apparent after soil disruptions.

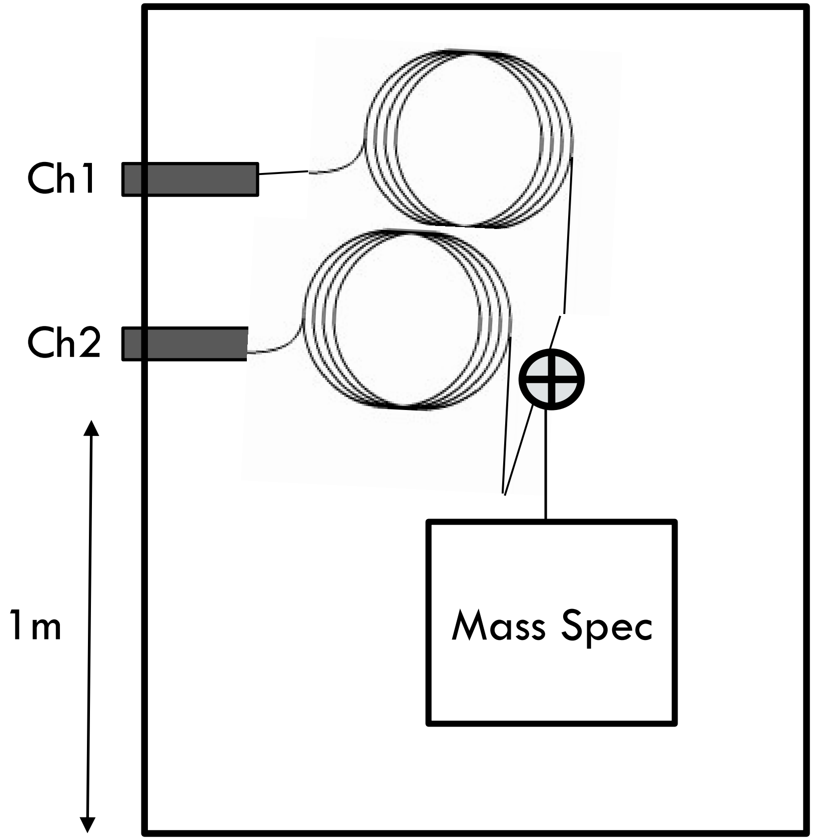
Objective: To detect and quantify mVOCs in Southern Ontario and to estimate the contribution of microbes to the total VOC pool.

Collaborators: XXXXXXXXXXXXX

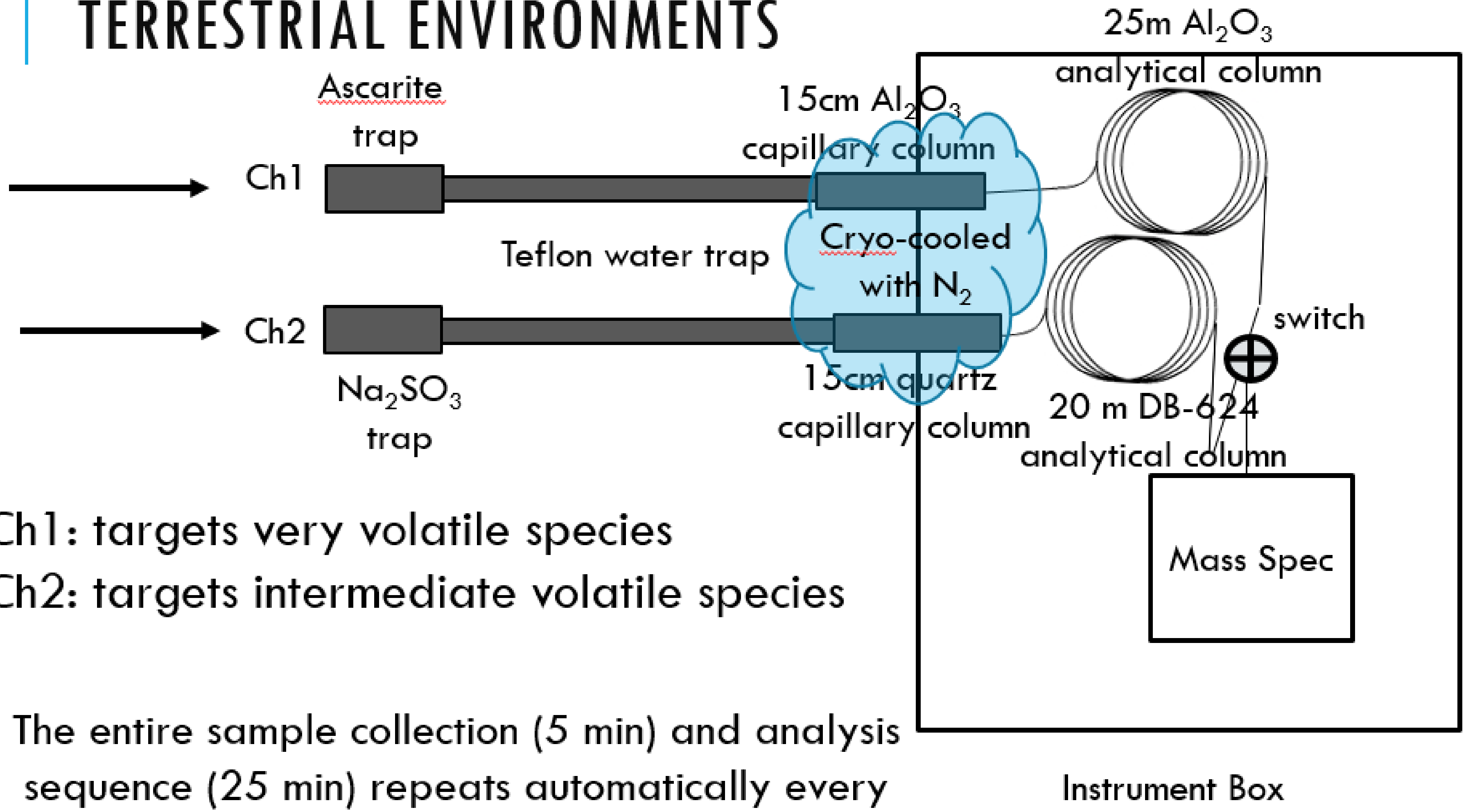
PROJECT 2: FIELD OBSERVATIONS OF MVOCS IN TERRESTRIAL ENVIRONMENTS

Experimental Design:

- *In situ* dual-channel GC-MS measurements will provide speciated VOC time series at multiple field sites
- Air inlet will sample at 1m, to constrain our foot print
- Soil samples will be sent to the Fulthorpe group for bacterial community analysis
- VOCs for quantification will be chosen based on the results of project 1 and expected reactivities



PROJECT 2: FIELD OBSERVATIONS OF MVOCS IN TERRESTRIAL ENVIRONMENTS



Ch1: targets very volatile species

Ch2: targets intermediate volatile species

The entire sample collection (5 min) and analysis sequence (25 min) repeats automatically every 30 min beginning on the hour and half-hour.

Gilman et al., ACP, 2010.

PROJECT 2: FIELD OBSERVATIONS OF MVOCS IN TERRESTRIAL ENVIRONMENTS

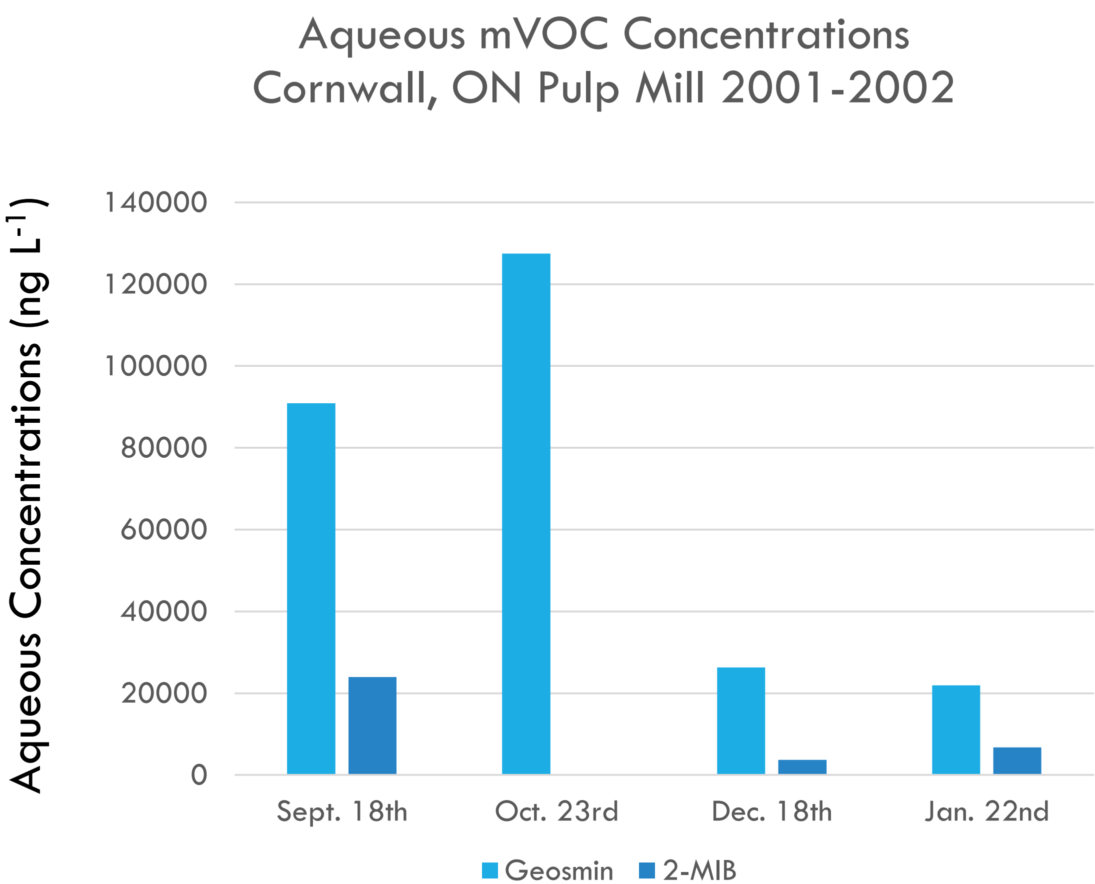
Site Selection:

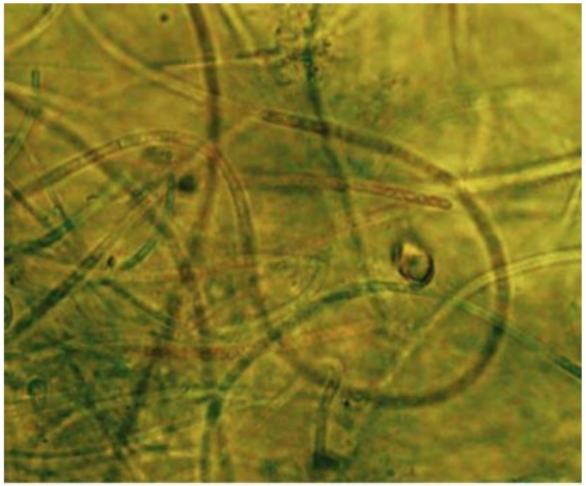
1. **One forested site:** Environment Canada's Borden Forest Research Station (where meteorological measurements, including precipitation, soil moisture and soil temperature, along with soil CO_2 flux are ongoing)
2. **One cleared site:** Environment Canada's Egbert site (collocated with the Egbert CAPMoN station, providing precipitation data, as well as surface ozone and reactive nitrogen concentrations)
3. **One active agricultural site** (to be chosen based on ease of access and frequency of tilling)
4. **One industrial pulp & paper mill site**

Campaign Length: four to six weeks each over the summer-fall season transition. Rain events or other sources of soil disruption, like agricultural tilling, will be noted.

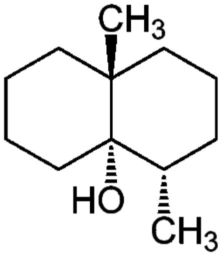
PROJECT 2: FIELD OBSERVATIONS OF MVOCS IN TERRESTRIAL ENVIRONMENTS

Site: Industrial pulp & paper mill site

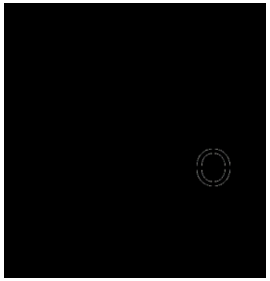




Fluorescence microscopy showing filamentous cyanobacteria (including cf. Leptolyngbya) and bacteria associated with activated sludge



Geosmin



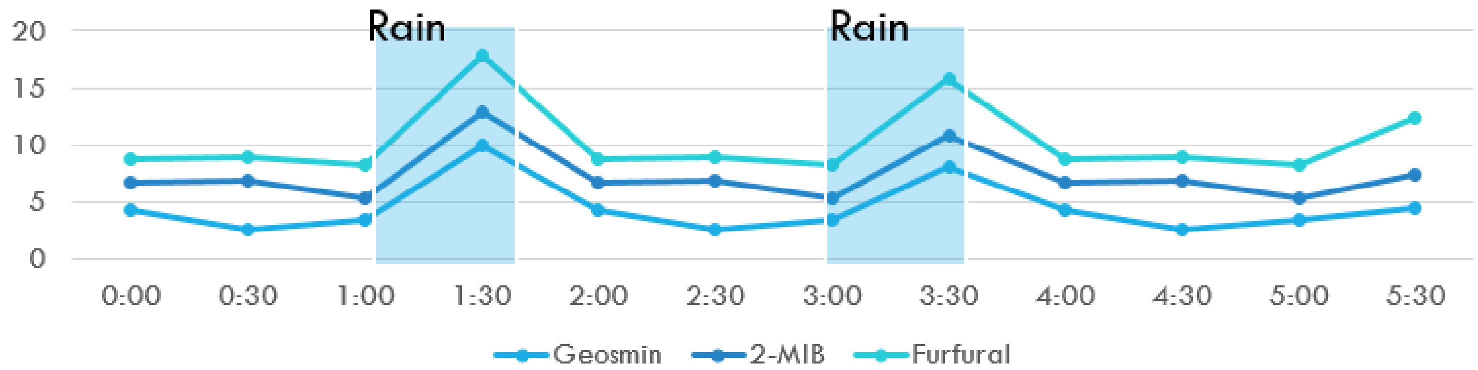
2-Methylisoborneol

Watson et al., Chemosphere, 2003.

PROJECT 2: FIELD OBSERVATIONS OF MVOCS IN TERRESTRIAL ENVIRONMENTS

Expected Outcomes:

- We will create detailed speciated VOC time series
- We will provide the first ambient time series for geosmin and other uniquely microbial VOCs.
- We will be able to estimate the mVOC contribution to the local VOC budget.
- We will have microbial community descriptions to associate with the observed VOCs



PROJECT 3: THE IMPACT OF MVOCS ON NEAR-SURFACE HOX CHEMISTRY

Hypothesis: We can account for the total OH reactivity in a soil bacteria chamber by performing speciated GC-MS measurements of mVOCs in addition to measurements of conventional sinks.

Objective: To determine how mVOCs impact OH reactivity in a simplified chamber environment and ensure OH closure is achievable.

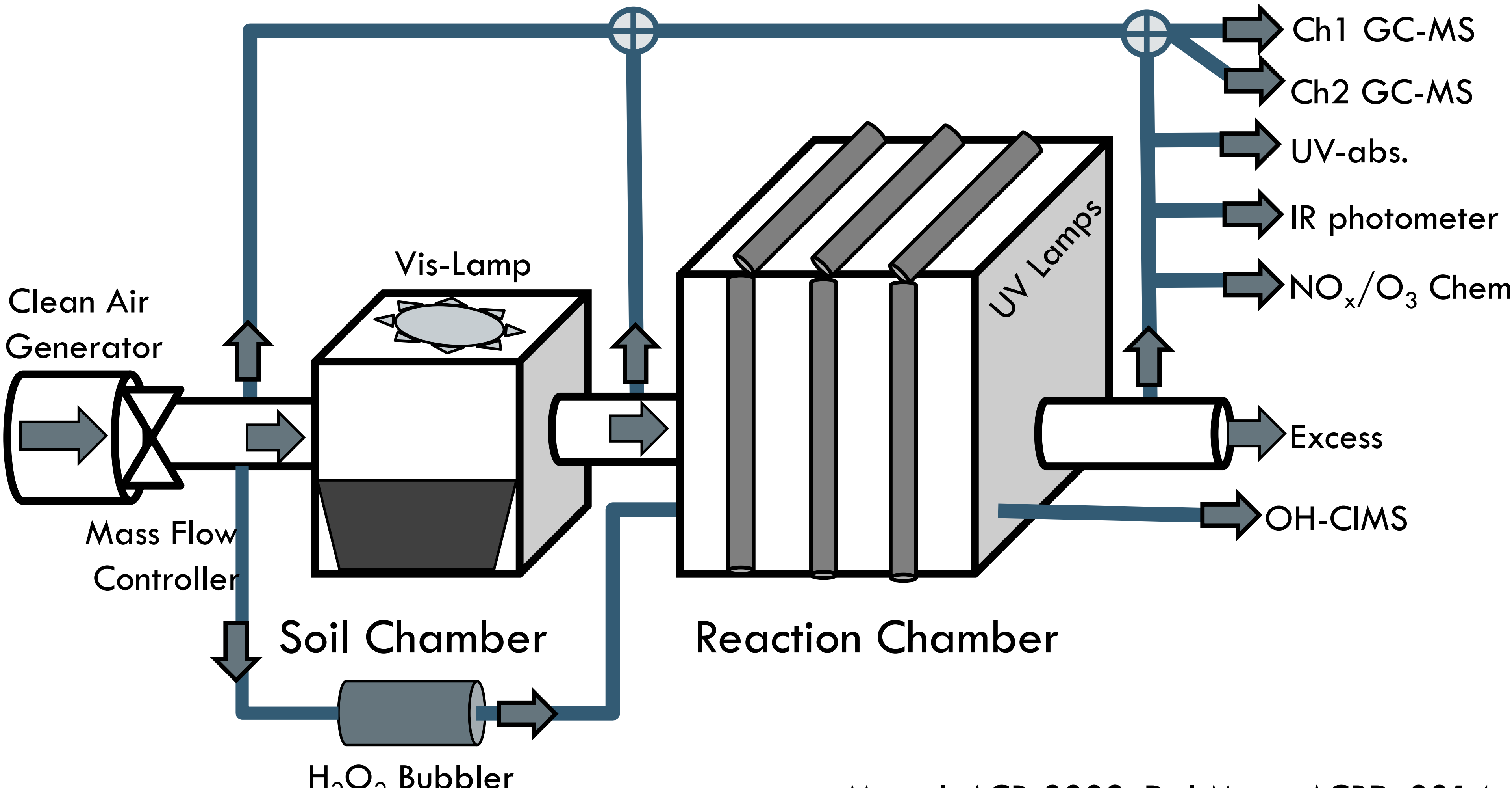
Collaborators: XXXXXXXXXXXXXXXXXX

PROJECT 3: THE IMPACT OF MVOCS ON NEAR-SURFACE HOX CHEMISTRY

Experimental Design:

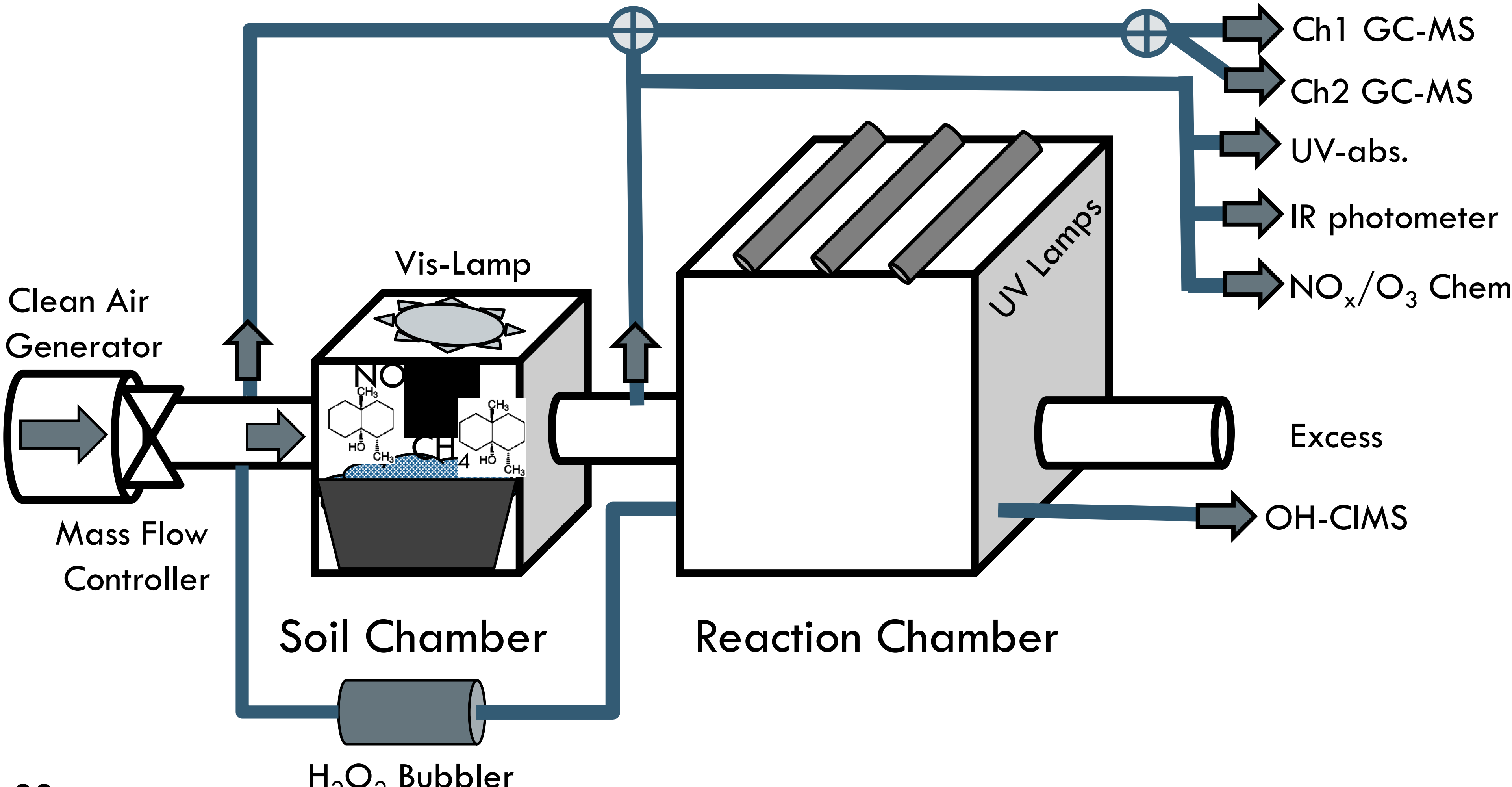
- Construction of coupled soil-reaction chamber to study controlled mVOC emissions and OH reactivity
- Dual Channel GC-MS will provide online VOC speciation
- OH-CIMS (XXXXXXX) will provide a OH reactivity measurement
- Soil samples will be collected from field sites and microbial community culture preformed (XXXXXXXXXX)

PROJECT 3: THE IMPACT OF MVOCS ON NEAR-SURFACE HOX CHEMISTRY



Mentel, ACP, 2009. Dal Maso, ACPD, 2014.

PROJECT 3: THE IMPACT OF MVOCS ON NEAR-SURFACE HOX CHEMISTRY



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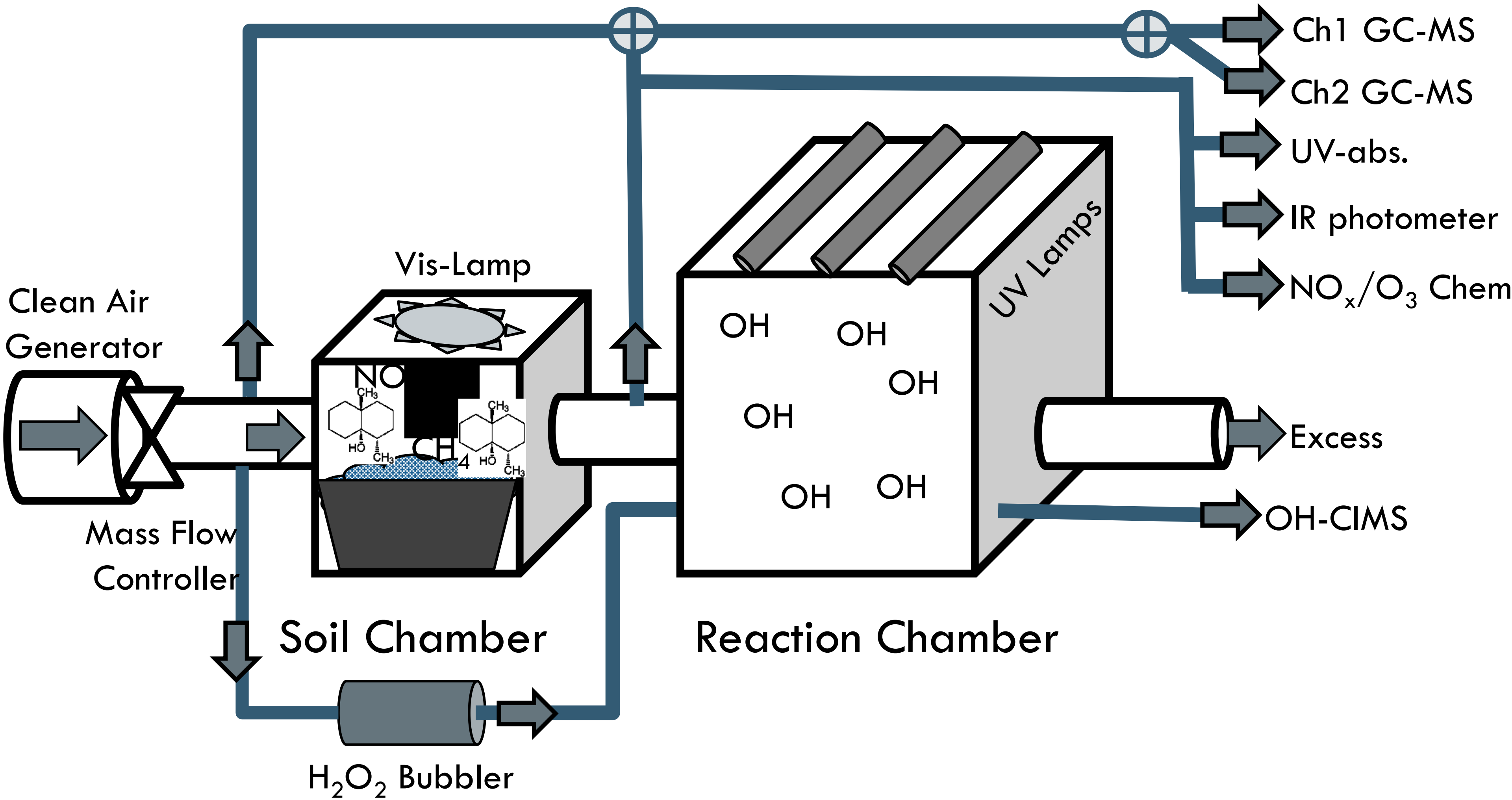

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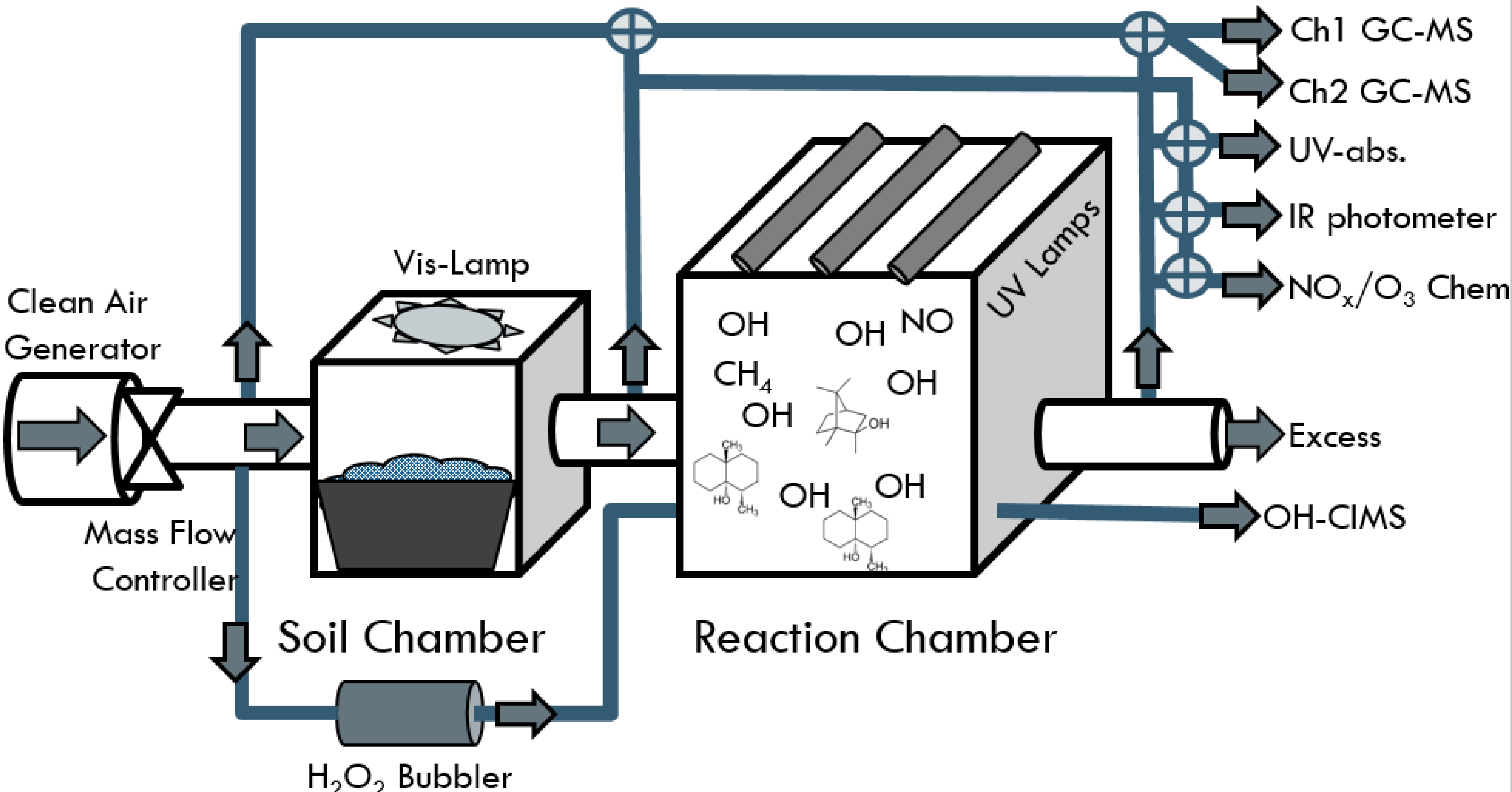

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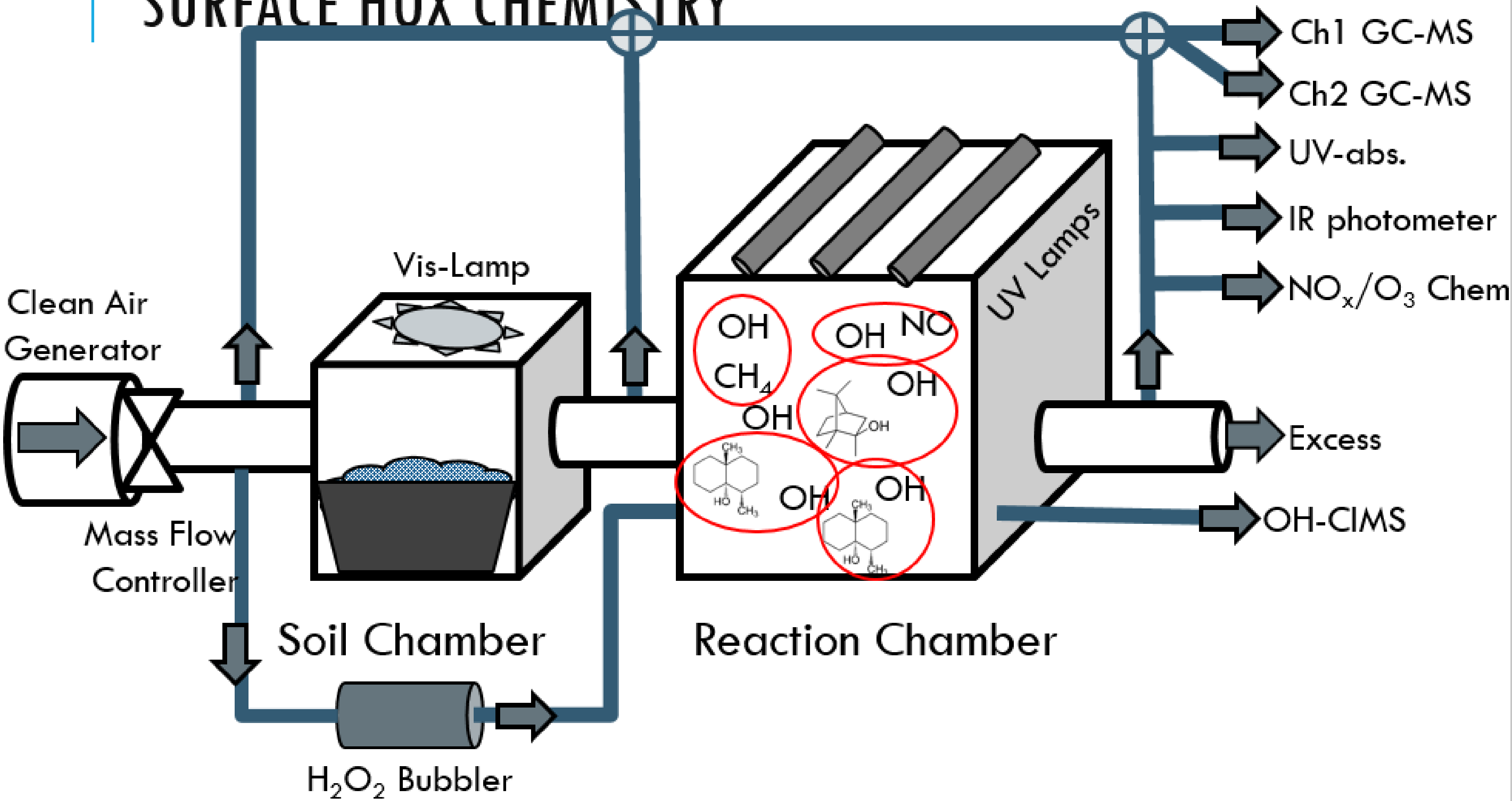

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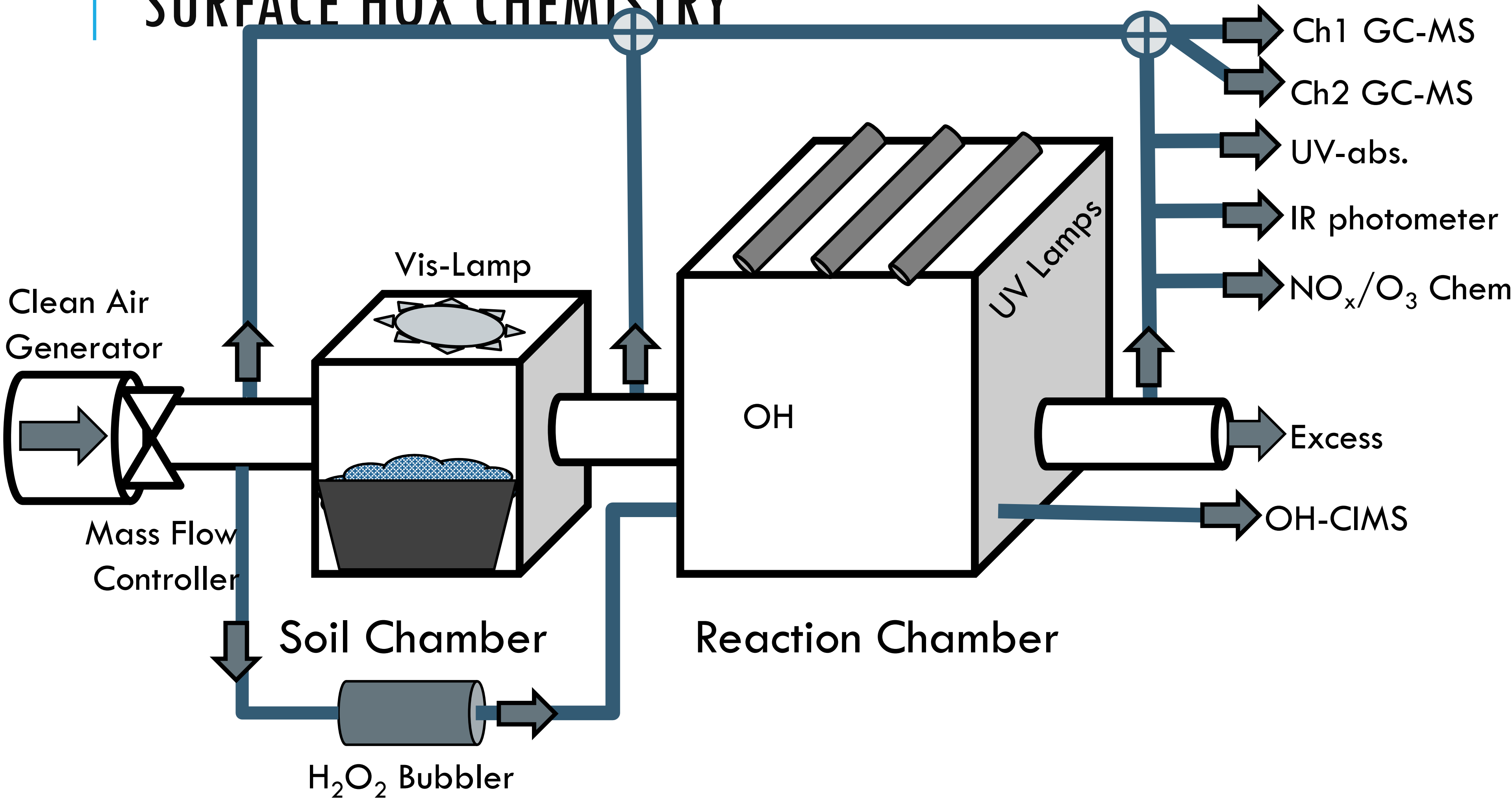
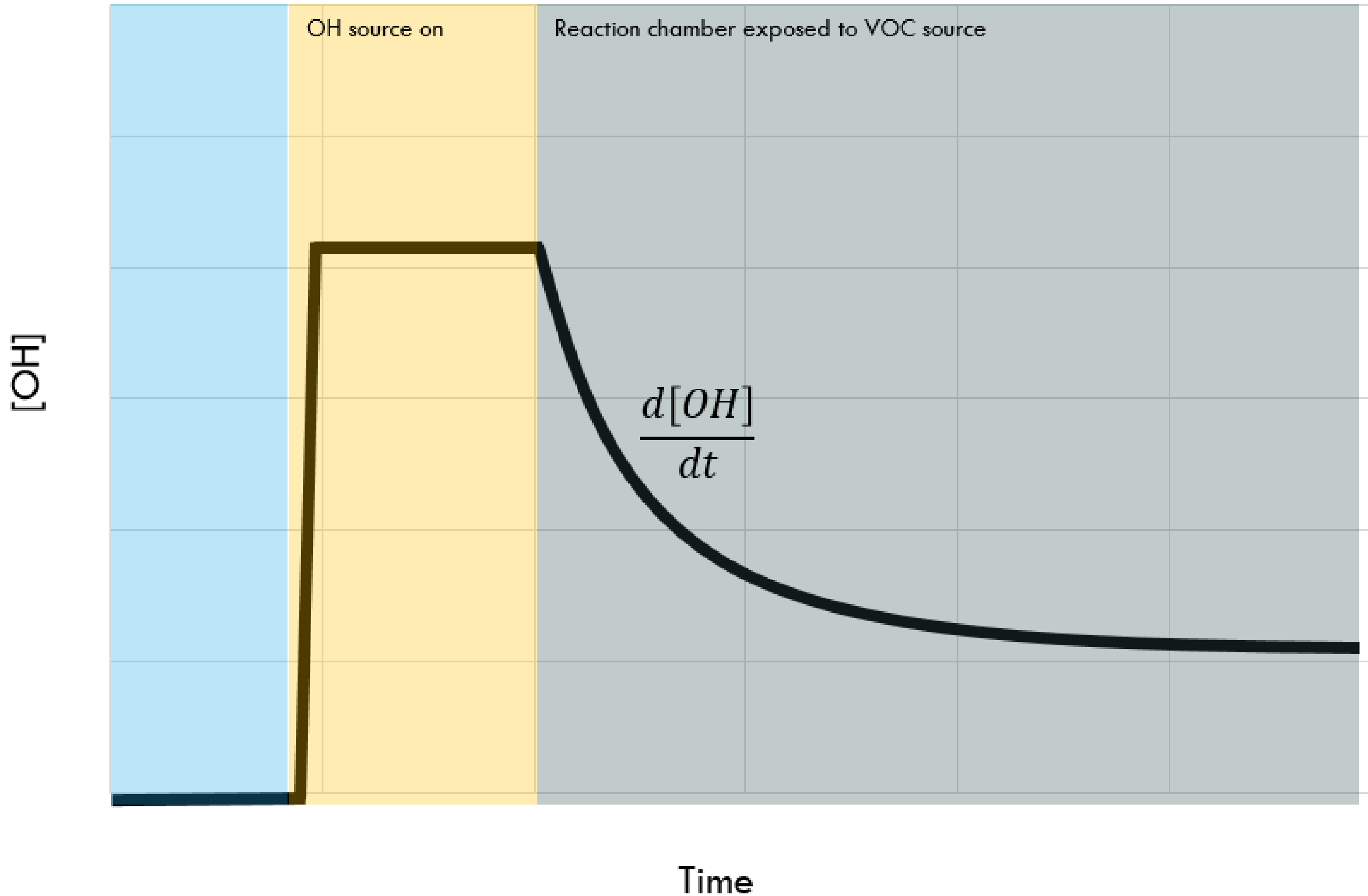


Project 3: The Impact of mVOCs on near-surface HOx Chemistry



PROJECT 3: THE IMPACT OF MVOCS ON NEAR-SURFACE HOX CHEMISTRY

Expected Outcomes:

- We will determine the OH reactivity of microbial emissions in an enclosure experiment
- We will confirm that OH budget closure is achievable in a simplified chamber environment through the use of speciated VOC measurements
- We will identify what mVOCs contribute most to OH reactivity

CAMEL EXPECTED OUTCOMES

Terrestrial microbes provide an important source of VOCs to the atmosphere that may help close the OH reactivity budget if they are targeted in ambient measurement campaigns. CAMEL will provide:

- A list of import mVOCs to include in future speciated VOC measurements
- Observational evidence for the times and places that reactive mVOCs will be most important
- Confirmation that OH closure is achievable if all reactive species are accounted for

THANK YOU

Terrestrial microbes provide an important source of VOCs to the atmosphere that may help close the OH reactivity budget if they are targeted in ambient measurement campaigns. CAMEL will provide:

- A list of import mVOCs to include in future speciated VOC measurements
- Observational evidence for the times and places that reactive mVOCs will be most important
- Confirmation that OH closure is achievable if all reactive species are accounted for