OP-FTIR: a Versatile and Powerful Technology for Measuring Multiple Gaseous Compounds

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Permanent installation of OP-FTIR
CRYO-CYL
CHART

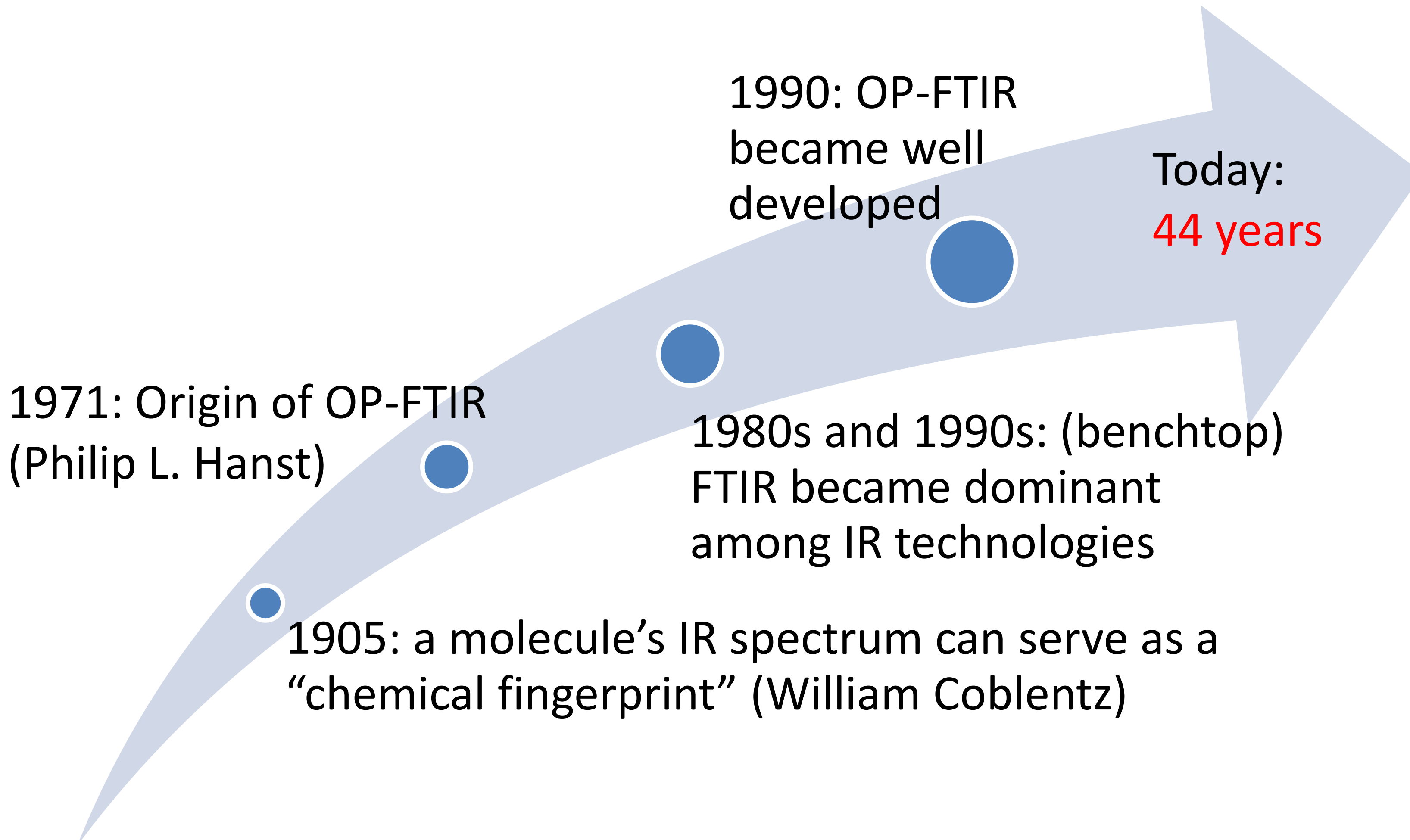

Portable FID and PID
KEPB
蘋果即時


IR camera
滅火器
蘋果即時

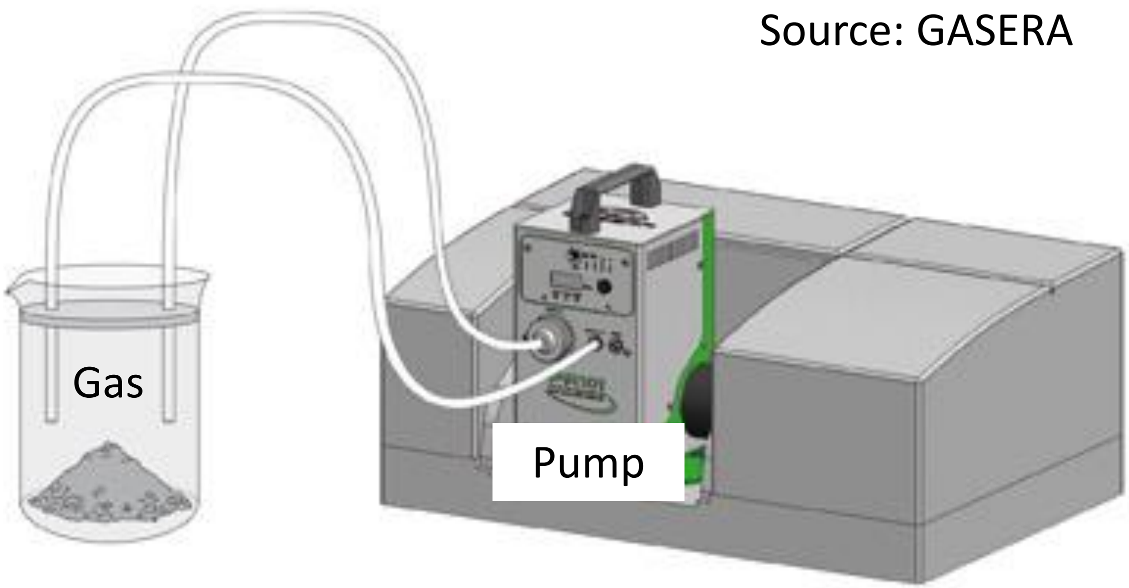
Outline

- Background
  - Brief history; Instrumentation
- Capabilities and Limitations
- Applications in Different Areas
- Highlights of Select Projects
  - Edmonton and Fort McKay
- Conclusions & Future Work
  - Links to Alberta

Background

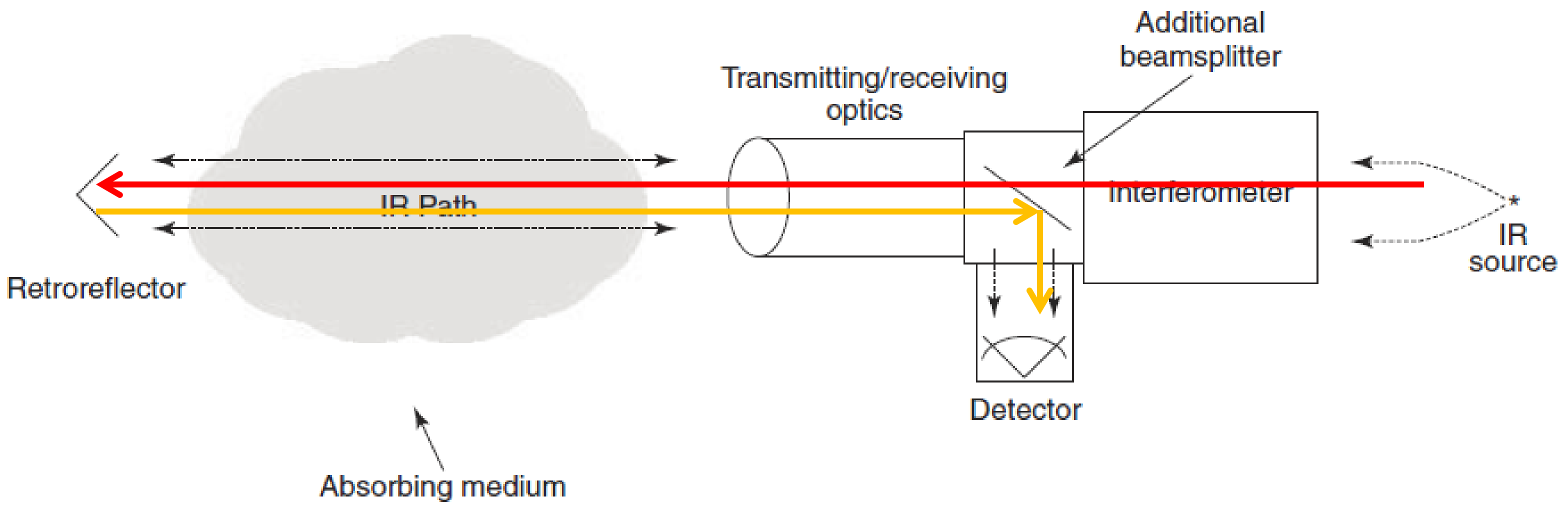

1905: a molecule’s IR spectrum can serve as a “chemical fingerprint” (William Coblentz)
1971: Origin of OP-FTIR (Philip L. Hanst)
1980s and 1990s: (benchtop) FTIR became dominant among IR technologies
1990: OP-FTIR became well developed
Today: 44 years

Background (cont'd)



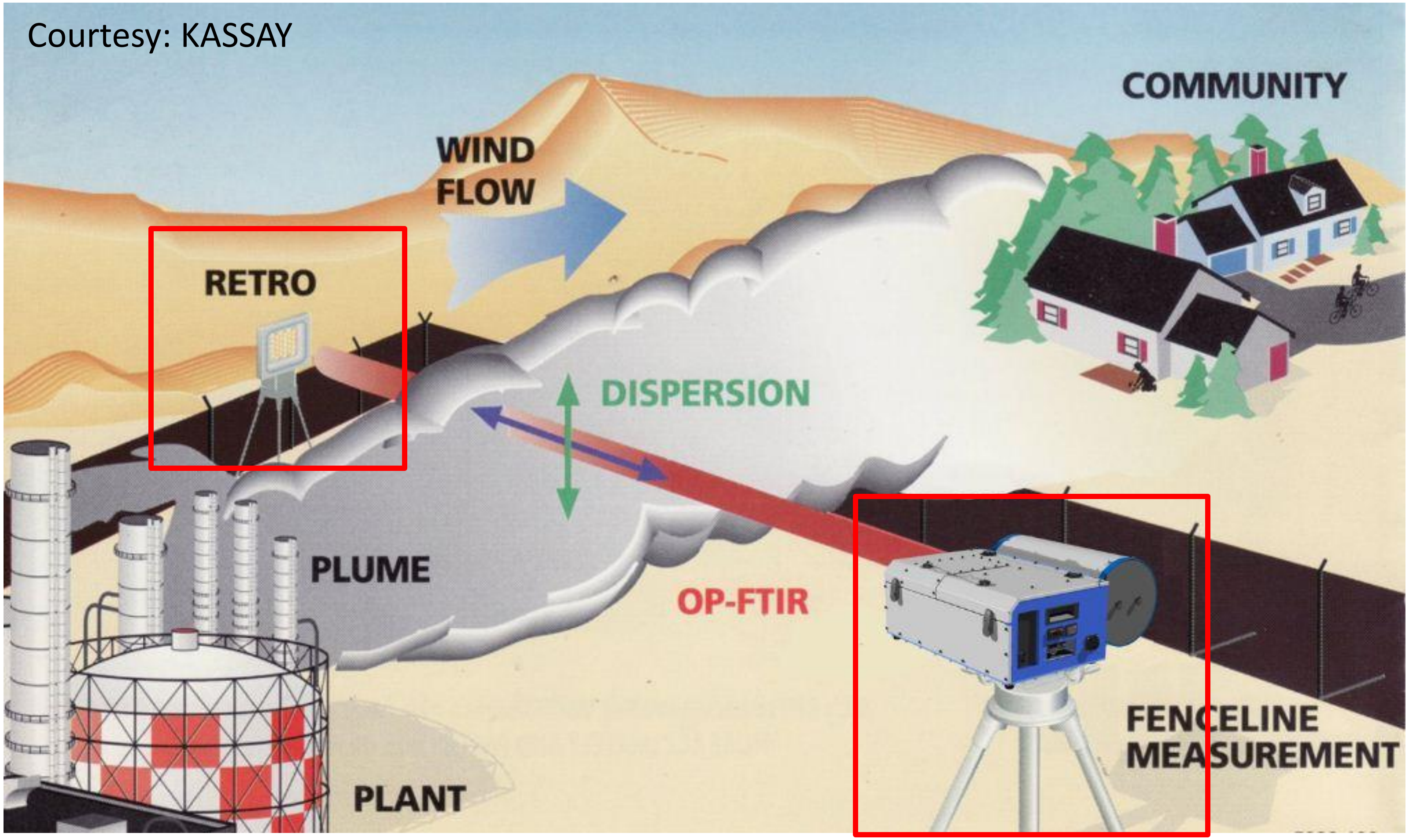
A picture of a benchtop (extractive) FTIR

Background (cont'd)

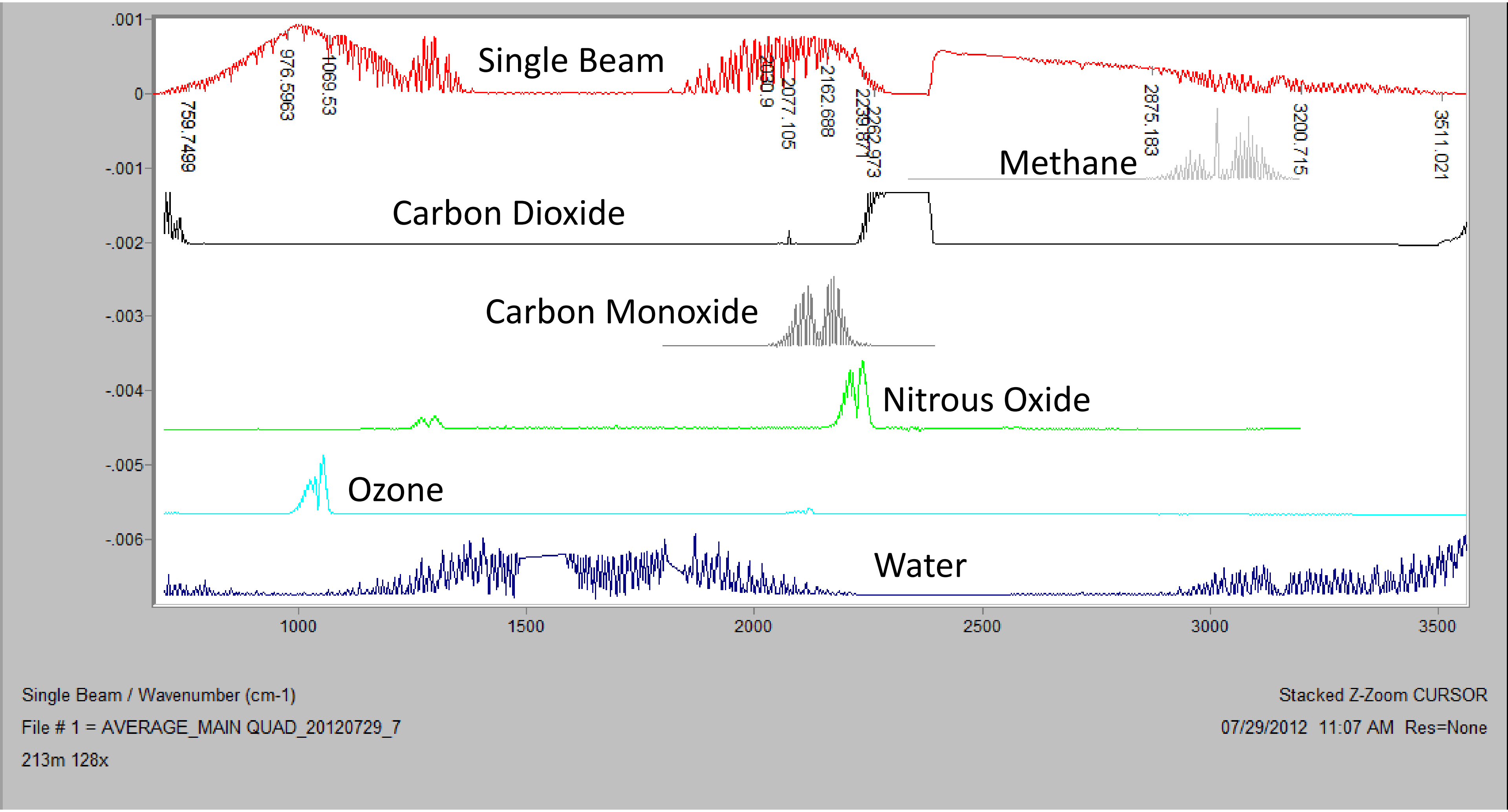


Schematic of a monostatic OP-FTIR spectrometer (Russwurm and Childers 2002)

Background (cont'd)

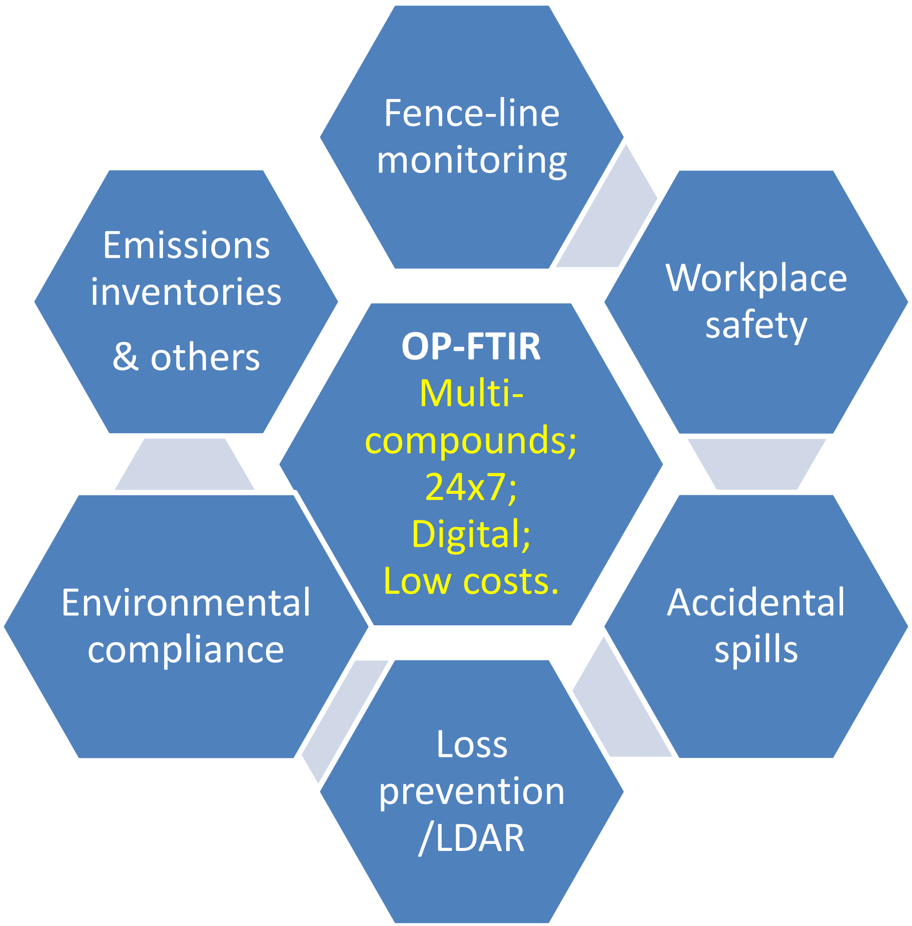


- A typical configuration of air monitoring using OP-FTIR



- IR absorbance spectra ("chemical fingerprints") of 6 select compounds in clean air

Capabilities & Limitations



- About 110 example compounds (U.S. EPA, 2011)

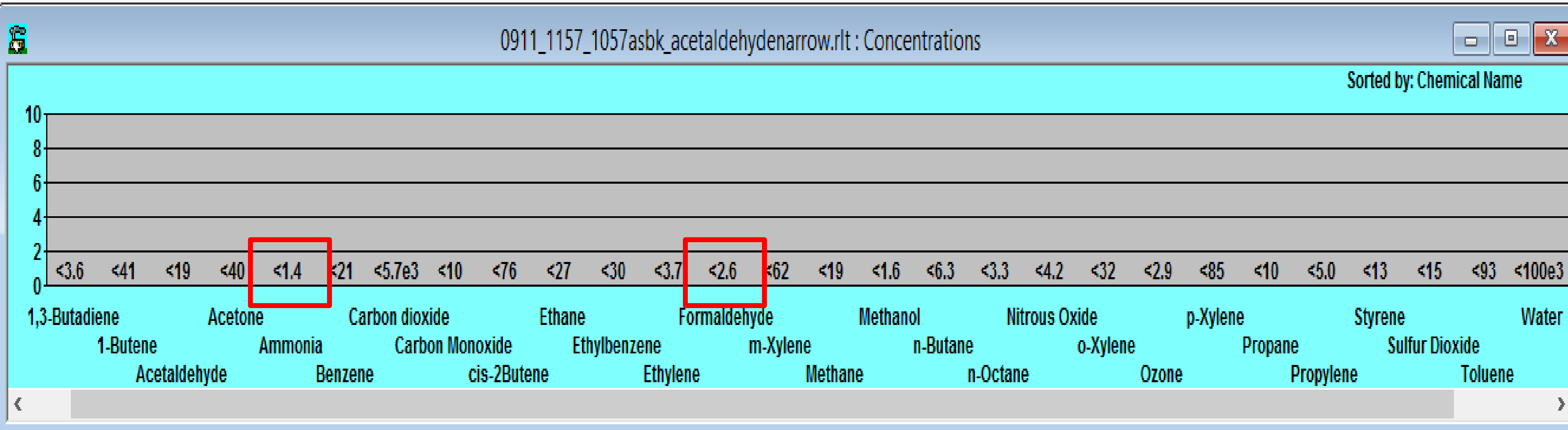
Table 2-1. Example List of Compounds Measured by FTIR Open-path Systems

Species		
acetaldehyde	1,4-dimethyl piperazine	methyl mercaptan
acetic acid	**1,4-dioxane**	**methyl methacrylate**
acetone	ethane	2-methyl propene
acetonitrile	ethanol	morphaline
acetylene	ethyl acetate	nitric acid
acrolein	ethylamine	nitric oxide
acrylic acid	**ethylbenzene**	nitrogen dioxide
acrylonitrile	ethylene	nitrous acid
ammonia	**ethylene oxide**	ozone
benzene	ethyl mercaptan	pentane
1,3-butadiene	**formaldehyde**	**phosgene**
butane	formic acid	**phosphine**
butanol	furan	propane
1-butene	halocarb-11 (CCl3F)	propanol
cis-2-butene	halocarb-12 (CCl2F2)	**propionaldehyde**
trans-2-butene	halocarb-22 (CHClF2)	propylene
butyl acetate	halocarb-113 (CFCl2CF2Cl)	**propylene dichloride**
carbon disulfide	hexafluoropropene	**propylene oxide**
carbon monoxide	hydrocarbon continuum	pyridine
carbon tetrachloride	**hydrogen chloride**	silane
carbonyl sulfide	**hydrogen cyanide**	**styrene**
chlorobenzene	hydrogen sulfide	**sulfur dioxide**
chloroethane	isobutene	sulfur hexafluoride
chloroform	isobutanol	1,1,1,2-tetrachloroethane
m-cresol	isobutyl acetate	**1,1,2,2-tetrachloroethane**
o-cresol	isobutylene	**tetrachloroethylene**
p-cresol	isoprene	**toluene**
cyclohexane	isopropanol	**1,1,1-trichloroethane**
1,2-dibromoethane	isopropyl ether	**1,1,2-trichloroethane**
m-dichlorobenzene	**methanol**	**trichloroethylene**
o-dichlorobenzene	methylamine	**trimethylamine**
p-dichlorobenzene	methyl benzoate	1,2,4-trimethylbenzene
1,1-dichloroethane	**methyl chloride**	**vinyl chloride**
1,2-dichloroethane	**methylene chloride**	**m-xylene**
1,1-dichloroethylene	methyl ether	**o-xylene**
dimethylamine	**methyl ethyl ketone**	**p-xylene**
dimethyl disulfide	**methyl isobutyl ketone**	

Compounds in bold are EPA Hazardous Air Pollutants (HAPs) CAA -112Title 42, Chapter 85, Subchapter I, Part a U.S. Code 7412 (b)

Capabilities & Limitations (cont'd)

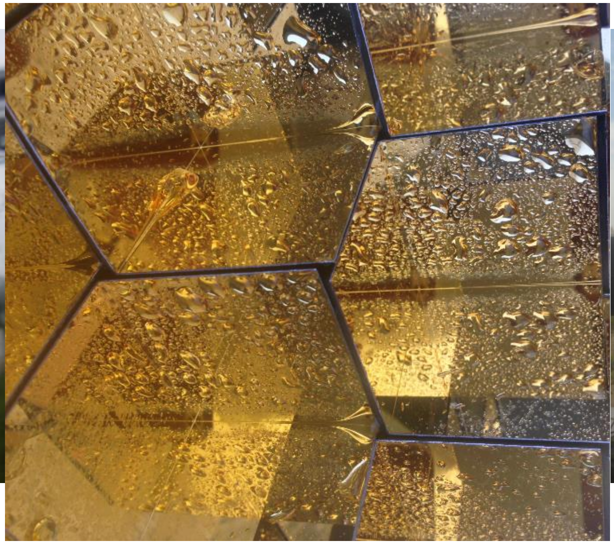
- Typical chemicals that can be measured:



- The most common criteria air contaminants: SO_x, NO_x, CO
- Volatile Organic Compounds (VOCs): n-butane, ethylene, formaldehyde, acetone, BTEX
- Green House Gases (GHGs): CH_4, CO_2
- Odour compounds: e.g., ammonia
- Detection limits: 1 ppb to tens of ppb

Capabilities & Limitations (cont'd)

Heavy rain



Water (rain/dew) on a retroreflector

Retro in heavy dust

- Unsuitable ambient conditions could cause signal and data loss in field studies

Applications in Different Areas

- Industrial areas
  - Upstream Oil & Gas Production (Segall et al. 2009); (Hashmonay 2012): Alkanes, BTEX, methanol and CH_4
  - Petrochemical Complex (Chan 2006): 39 air toxics including toluene, benzene and chloroform
  - Paint manufacturing plant (Lin et al. 2008): 7 VOCs (toluene, m-xylene, p-xylene, styrene, methanol, acetone, and 2-butanone)
- Urban areas (Grutter et al. 2003); (Hong et al. 2004)
  - Trace gases over Mexico City: CH_4, CO, propane, acetylene and ethylene
  - Ozone & VOCs in a park surrounded by heavy traffic roads: O_3, NH_3, CH_4, CO and 26 VOC species

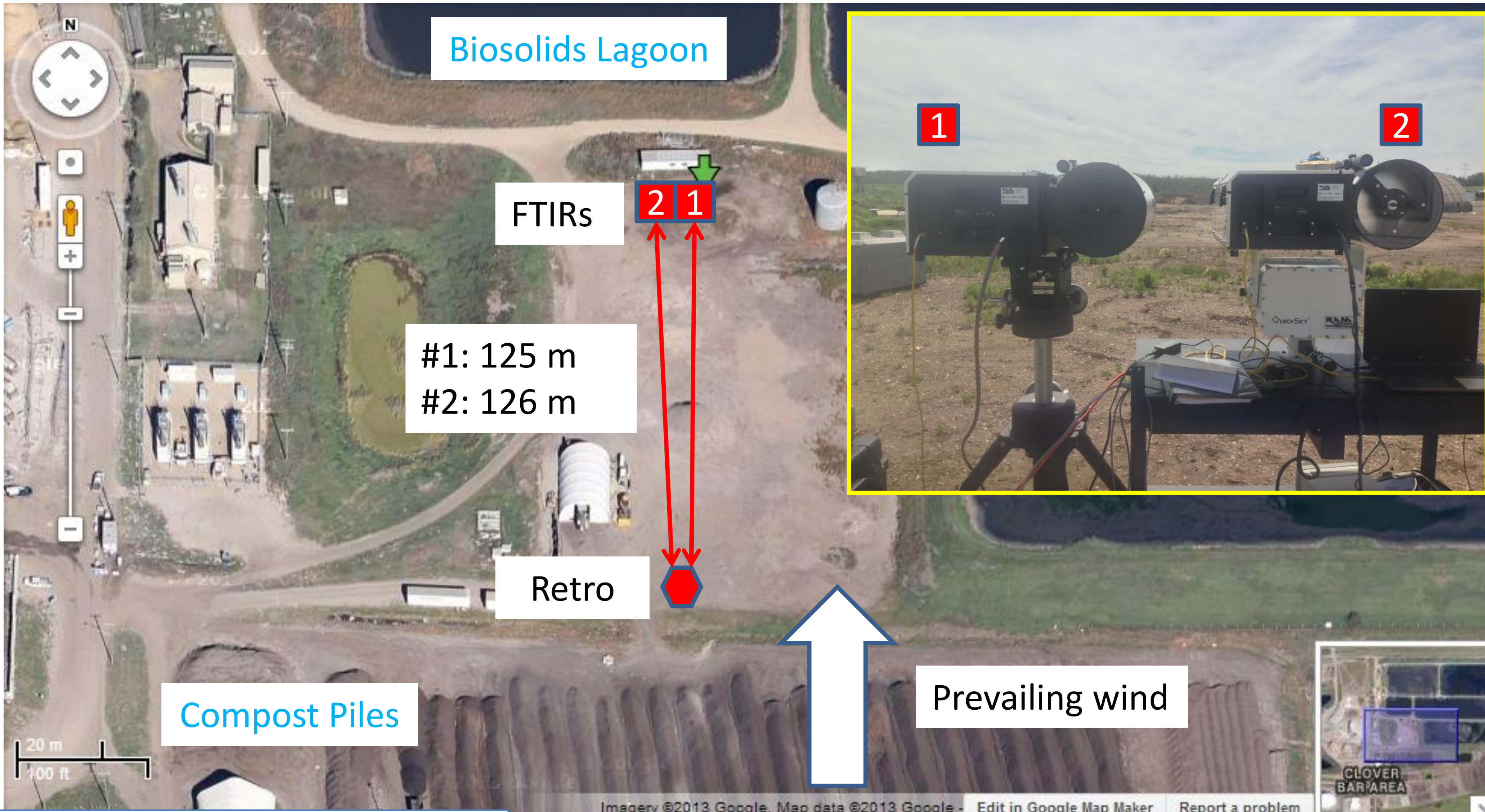
Applications in Different Areas (cont'd)

- Agricultural areas (Karl et al. 2007); (Bai 2010); (Bjorneberg et al. 2009)
  - Biomass burning fire: About 20 GHGs and VOCs
  - Beef & dairy cattle: CH_4
- Natural areas (Horrocks et al. 2001); (Burton et al. 2010)
  - Volcanic emissions: SO_2 & HCl
- Laboratories (Li et al. 2002)
  - Leaking gases: Methylene chloride, chloroform and acetone
- Other areas (Thoma et al. 2010) (Aneja et al. 2012) (Zhang et al. 2014)
  - Fugitive emissions from landfill applications: CH_4
  - Biosolids Lagoons: CH_4, NH_3

Applications in Different Areas (cont'd)

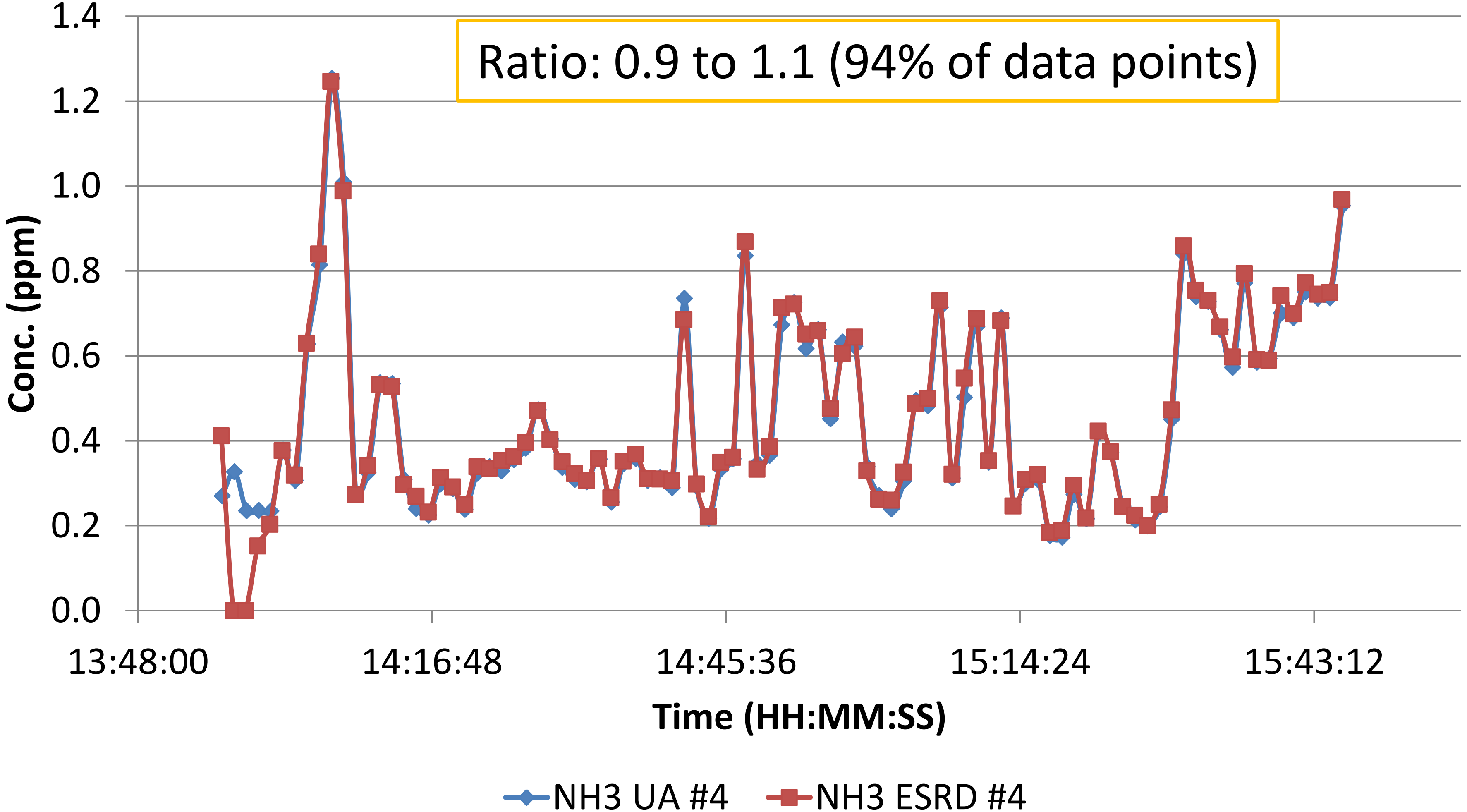
- Ongoing example projects involving OP-FTIR
  - South Coast Air Quality Management District
  - Texas A&M Institute of Renewable Natural Resources: shale gas industry
  - Pipeline industry: leak detection
  - Beijing, Taiwan and other cities
  - Alberta

Highlights of Select Projects

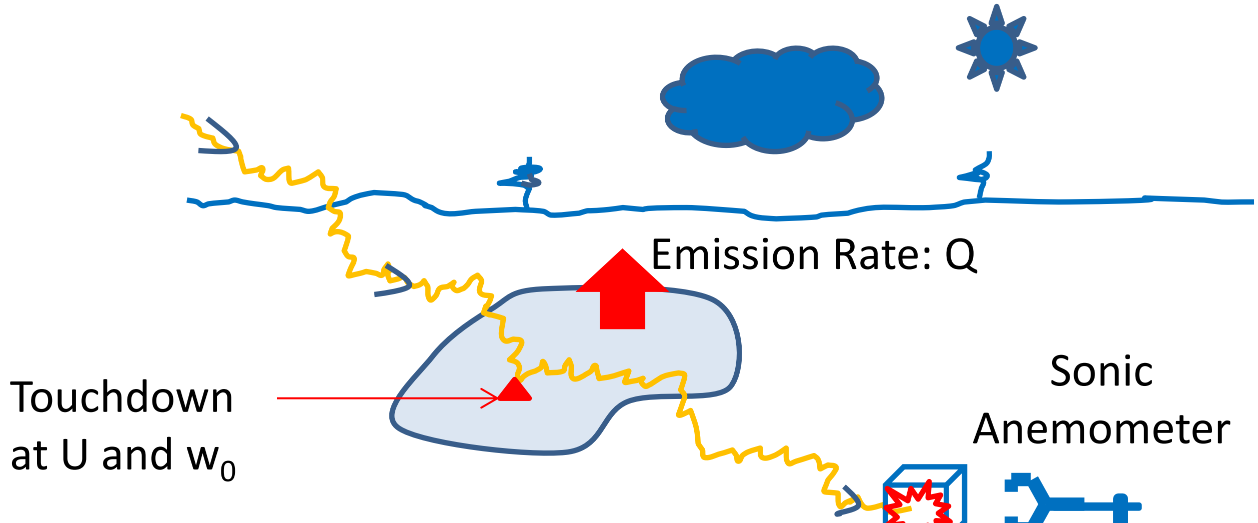


@ Compost Piles

Highlights of Select Projects (cont'd)



@ Compost Piles

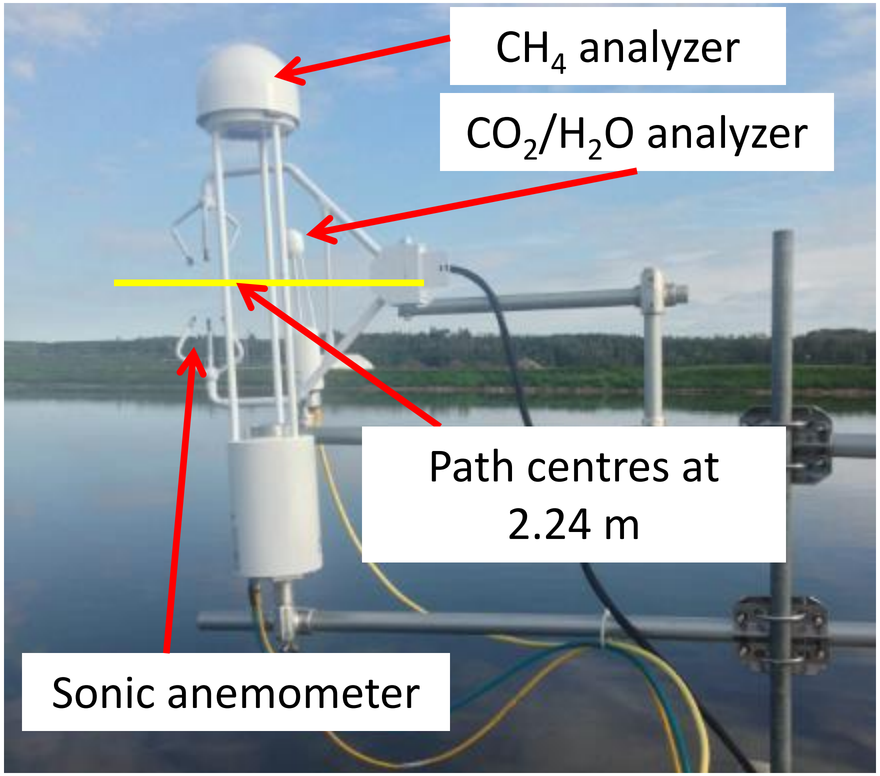


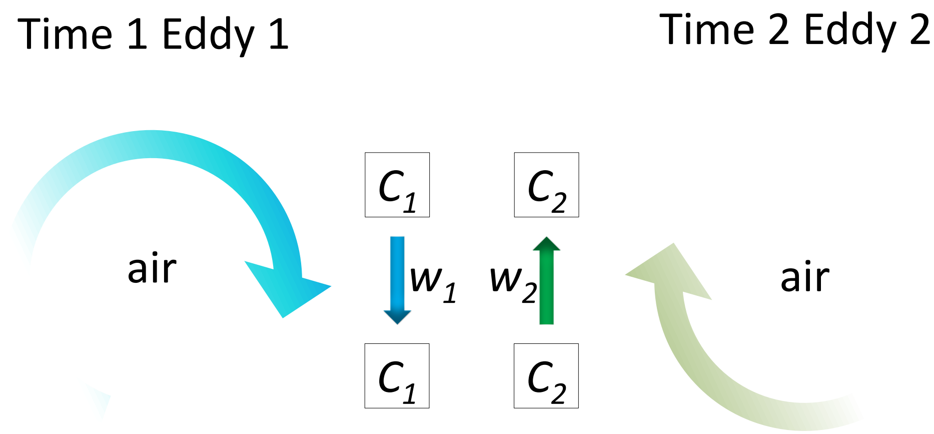
$$n \equiv \boxed{\frac{UC}{Q}} = n_t \equiv \frac{1}{N}\sum_{i=1}^{N}\frac{2U}{w_0}$$

A backward Lagrangian Stochastic model

Figure inspired by the teaching of *Atmospheric Boundary Layer* by Dr. John D. Wilson

U: mean horizontal wind speed (m/s)
C: gas concentration
N: number of particles released
w_0: vertical touchdown velocity
n_t: theoretical value of n
Software: WindTrax (Thunder Beach Scientific)





Reproduced from (Burba 2013)

The general principle is to measure

- The number of molecules moving downward and upward over time
- Travelling speeds of these molecules (Burba 2013)

$$F \approx \bar{\rho}_d \overline{w'C'}$$

- ρ_d: mean air density;
- w': fluctuations of vertical wind speed;
- C': fluctuations of gas concentration

Software: EddyPro (LICOR)

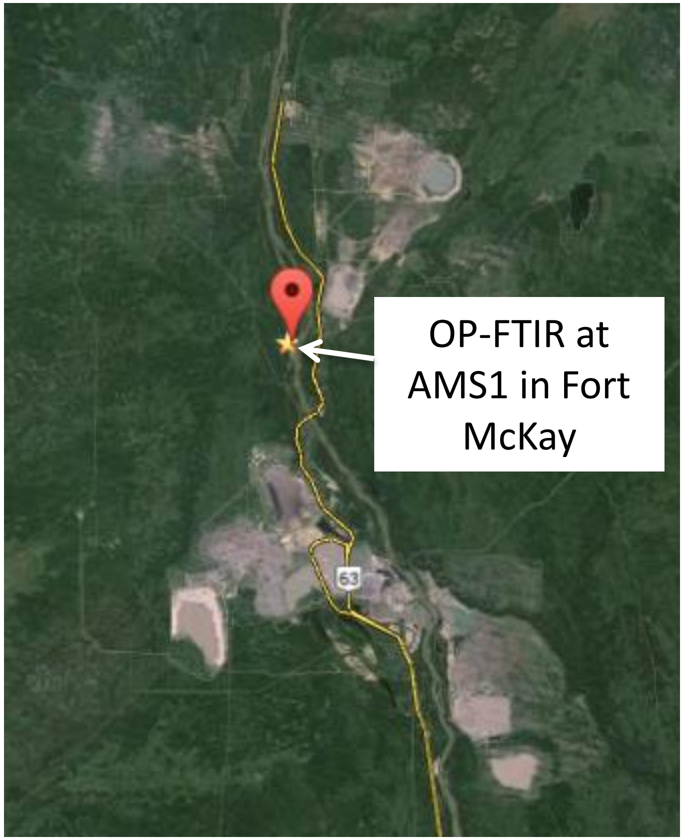
@ biosolids lagoons

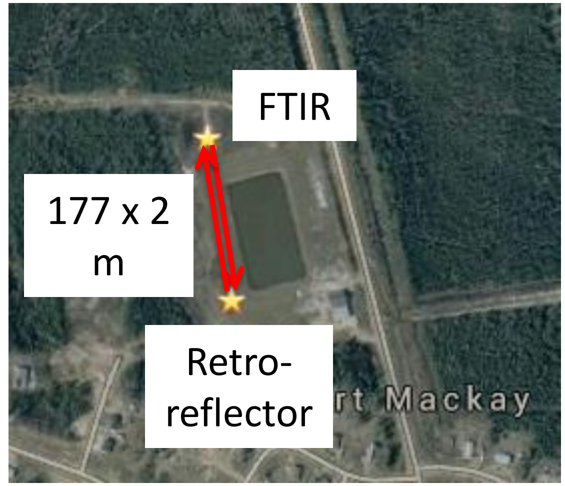
Highlights of Select Projects (cont'd)

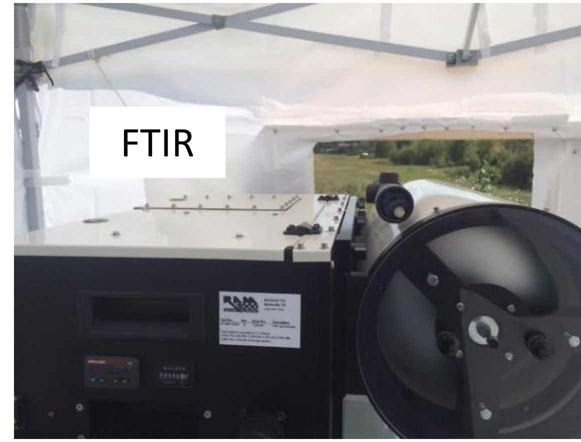
Date	Time	CH_4 IDT	CH_4 ECT	IDT/ECT
		$\times 10^{-3}$ kg/(m^2-d)	$\times 10^{-3}$ kg/(m^2-d)	Ratio
Day 3	13:30	4.66	4.18	1.11
Day 3	14:00	5.23	4.31	1.22
Day 3	14:30	4.26	3.30	1.29
Day 3	15:00	4.49	4.04	1.11

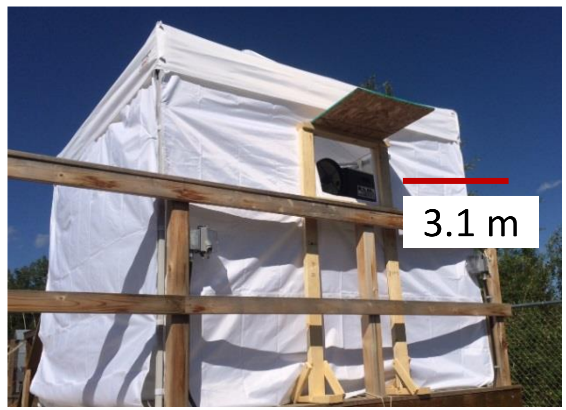
Note: IDT stands for Inverse Dispersion Technique; ECT stands for Eddy Covariance Technique.

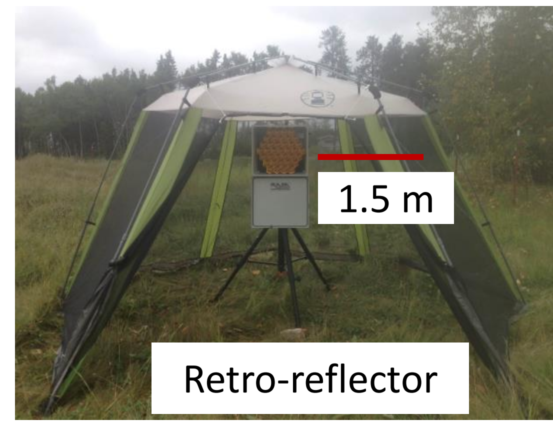
@ biosolids lagoons





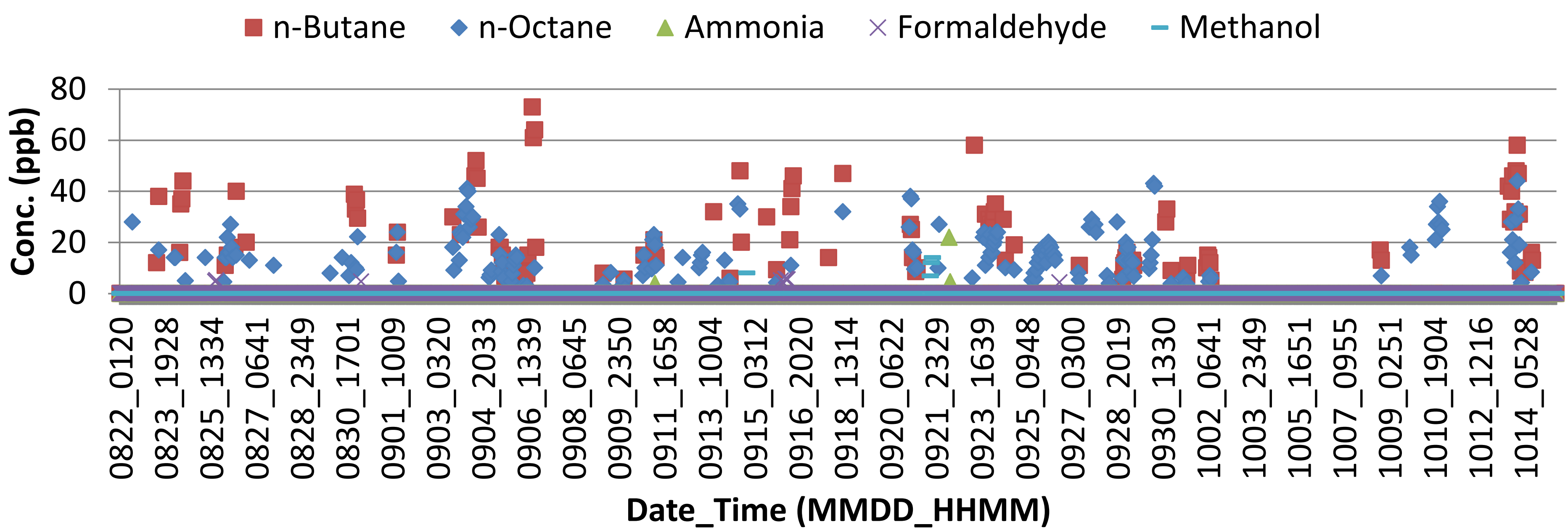






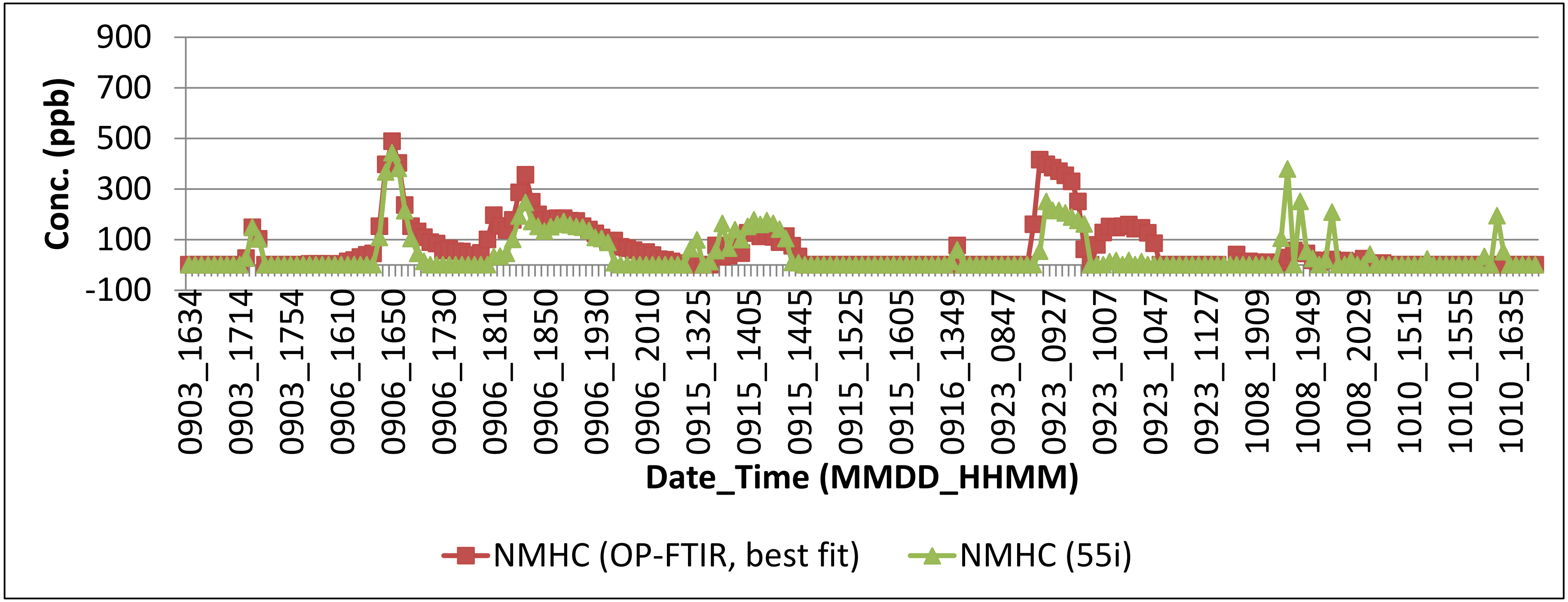
- August 22, 2014 – October 15, 2014 (54 days). Round-trip pathlength was 354 m; Sampling frequency was 1-min/sample, continuously; Heights of FTIR and retro-reflector were 3.1 m and 1.5 m, respectively.

@ Fort McKay AMS1



Compound	n-Butane (ppb)	n-Octane (ppb)	Ammonia (ppb)	Formaldehyde (ppb)	Methanol (ppb)
Min	5.2	2.1	3.8	4.3	6.9
Max	73	44	22	5.7	14
Average	24.1	16.2	10.1	5.1	10.2
Median	19	14	4.5	5.2	10
No. of Hours Quantified	109	192	3	8	4
AAAQOG (1-hour)	NA	NA	2,000	53	2,000
Total Hours	1300 (54 days)				
Total Effective Hours	1080 (83% of total hours)				

@ Fort McKay AMS1



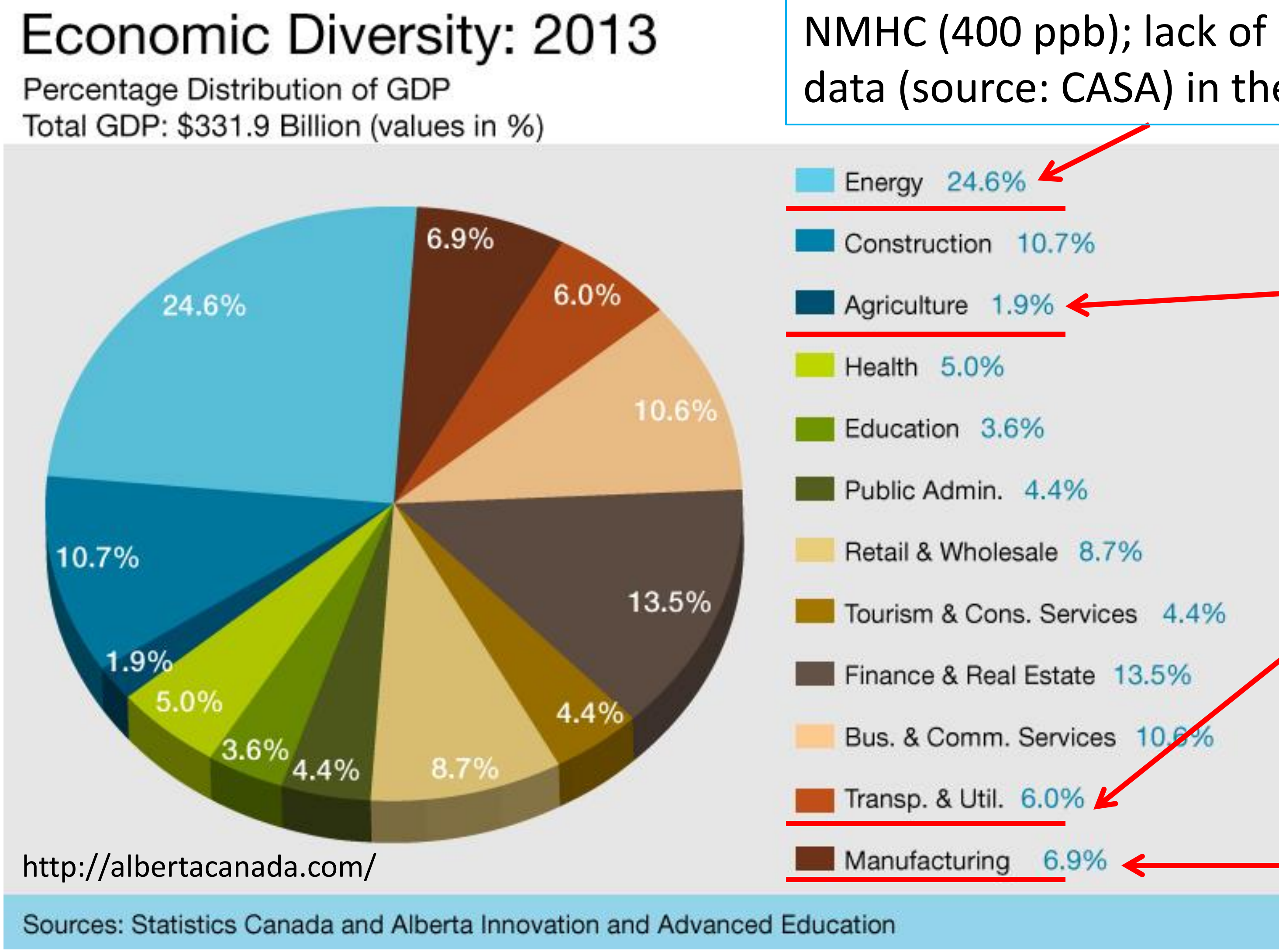
- Consistent trends of Non-Methane Hydrocarbon (NMHC) episodes between OP-FTIR and 55i (Thermo Fisher Scientific)
- NMHC by OP-FTIR = 3 x [n-butane (propane)] + 0 x [n-octane] (factor 3, propane (C_3H_8)).

@ Fort McKay AMS1

Conclusions & Future Work

- OP-FTIR projects in Alberta (and around the world) have shown encouraging results.
- OP-FTIR is a versatile and powerful technology for air monitoring and we anticipate that it would become more widely used.

Conclusions & Future Work



http://albertacanada.com/

High hourly conc. of methane (13 ppm) and NMHC (400 ppb); lack of continuous VOC data (source: CASA) in the oil sands regions

Cattle farms in southern Alberta: ammonia (precursor) and GHGs

Vehicular formaldehyde; GHGs and odour

Chemical plants in Fort. Sask. and Red Deer areas: ethylene; 1,3-butadiene; and hydrocarbons

Acknowledgement

- AEMERA (JOSM) and AESRD (Ecotrust) for the funding support
- WBEA and AITF for the field support (Fort McKay project)
- Dr. Sunny Cho for her support with the biosolids lagoon work
- Colleagues in Dr. Hashisho's lab for the field support (Clover Bar project)

- Thank you for your attention
- Questions? ☺