Air Measurements
Passive air sampling

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Why should we measure mercury in the air?

- A global pollutant that can have local impacts
- Long range transport from source regions
- Local emissions
- Deposits into ecosystem
- Uptake by tree foliage

<u>Does the Caribbean emit mercury*?</u>

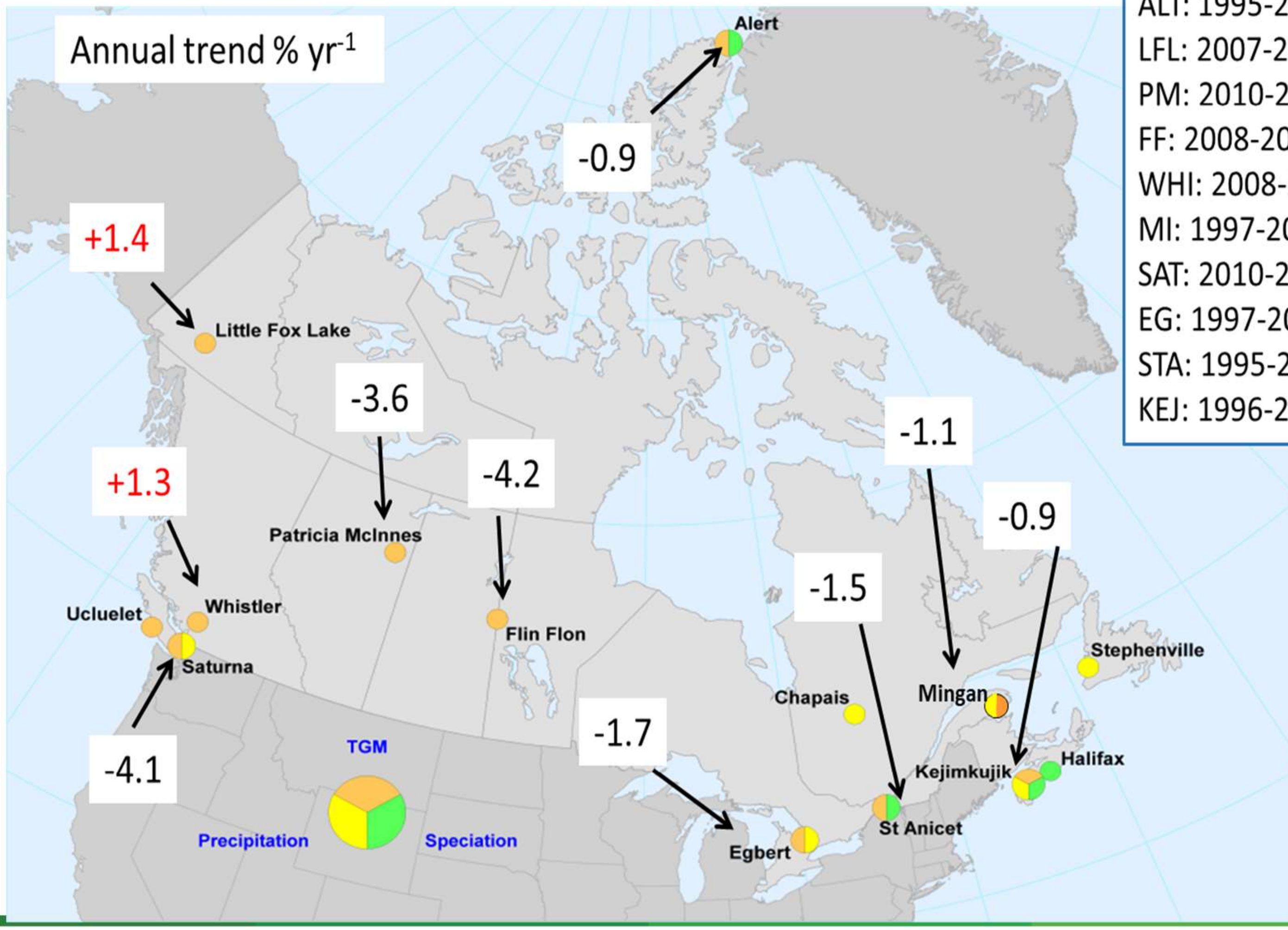
Central America and the Caribbean account for

- 2% of global emissions
- 31% of the global emissions of ASGM
- Increase in non ferrous mining
- Decrease in coal burning emissions 19% in Caribbean

* From 2015 inventories in the 2019 GMA report

Air monitoring of mercury reveals trends

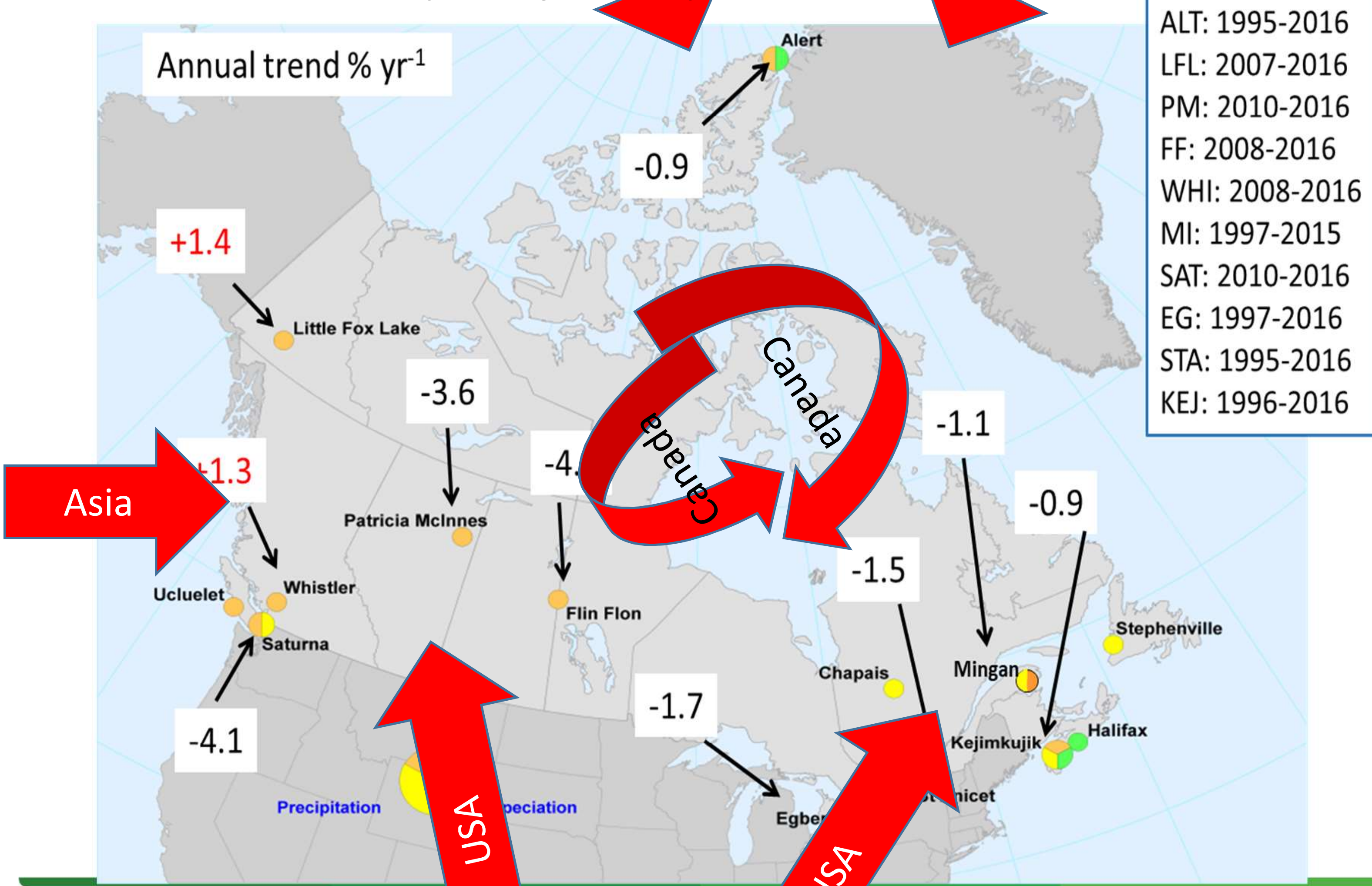
Canada is a net recipient of mercury



ALT: 1995-2016
LFL: 2007-2016
PM: 2010-2016
FF: 2008-2016
WHI: 2008-2016
MI: 1997-2015
SAT: 2010-2016
EG: 1997-2016
STA: 1995-2016
KEJ: 1996-2016

Air monitoring of mercury reveals trends

Canada is a net recipient of mercury



Global Monitoring has changed

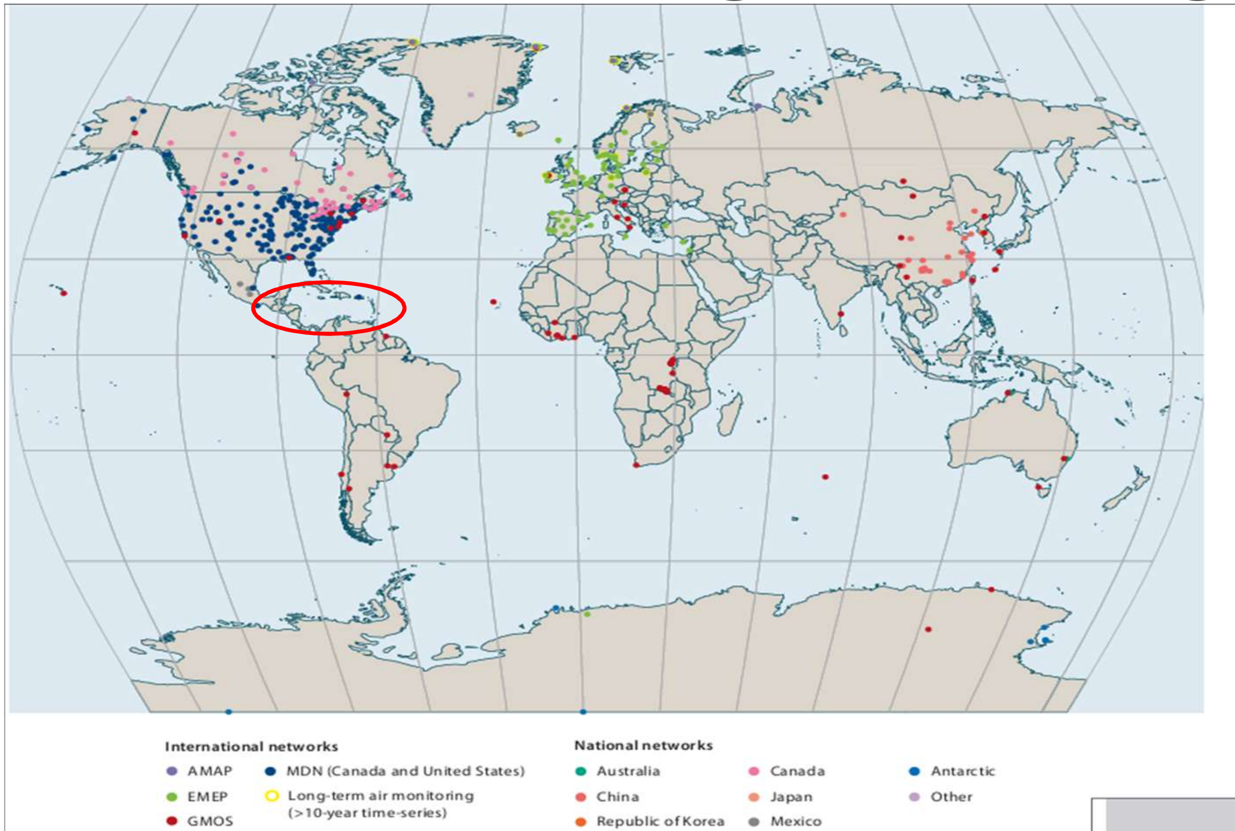
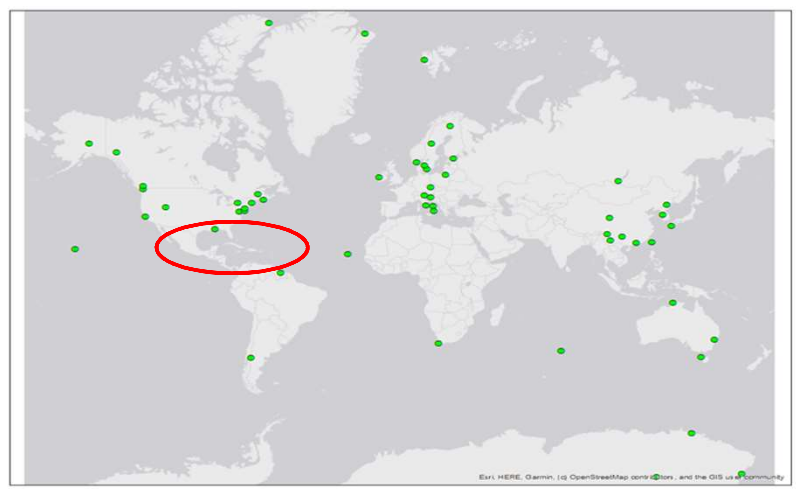


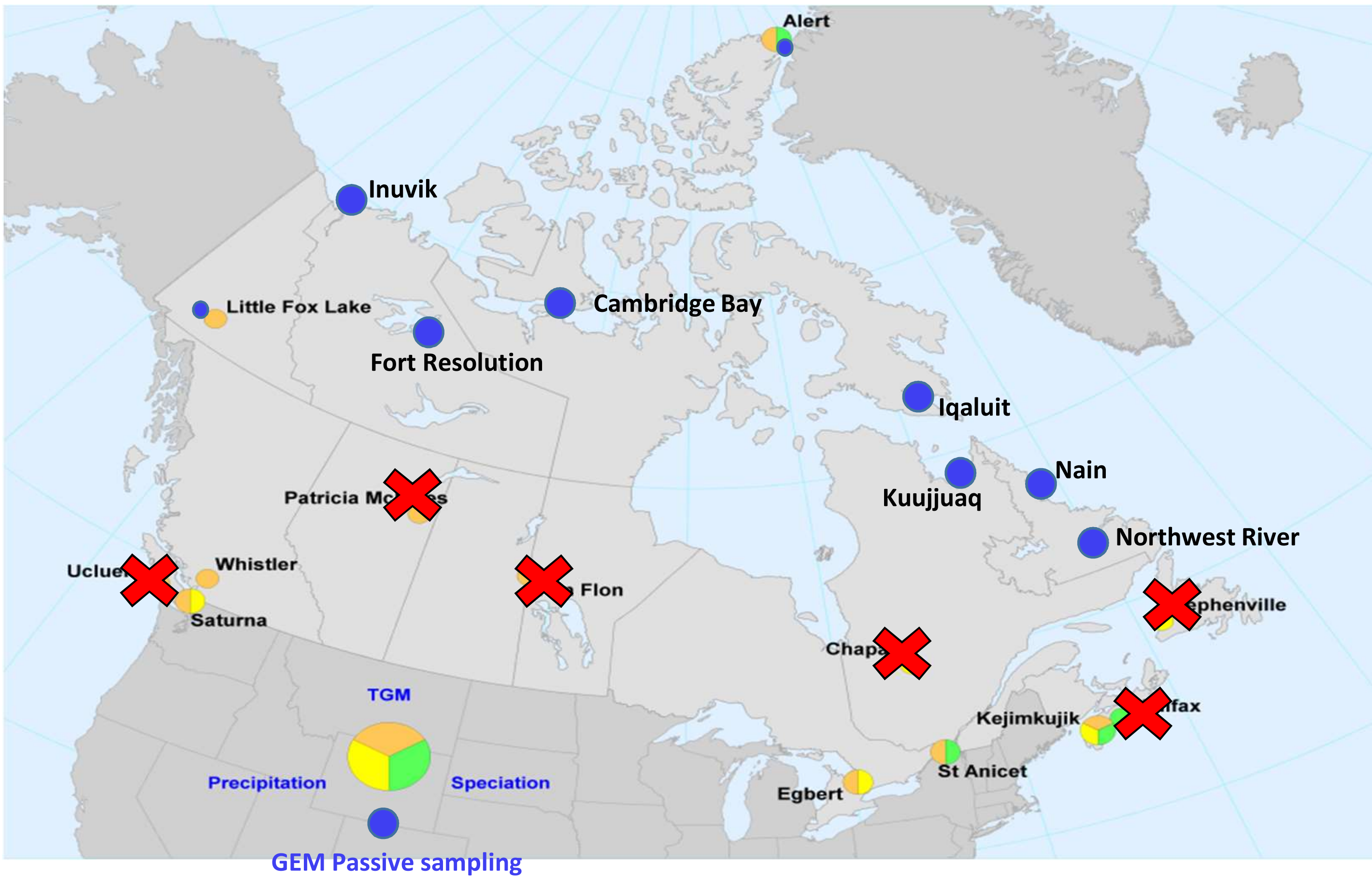
Figure 4.1 Global map of Hg monitoring networks (www.gos4m.org and metadata description therein for each regional network).

What once looked pretty good …

Now needs a little



Air Monitoring in Canada



Currently used technology

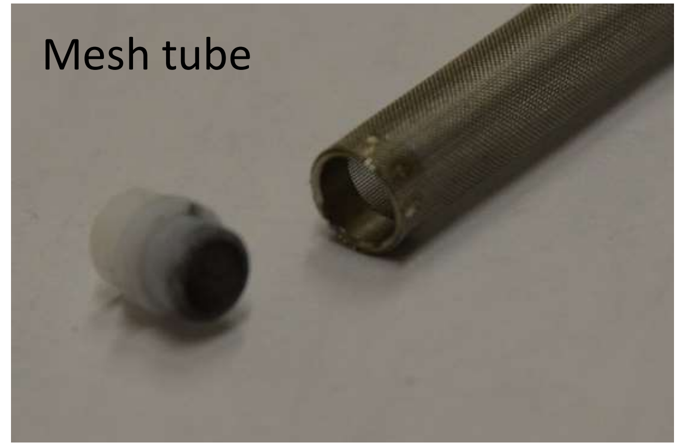
- Automated instrumentation
- Tekran instrument 2537+++
- Collects samples every 5 minutes
- *In situ* measurements
- Excellent results, gold standard
- Requires power and UHP Ar gas
- Requires indoor facilities
- $55K 1 instrument, 1 site
- Not always practical

✓ A need for new and other technology

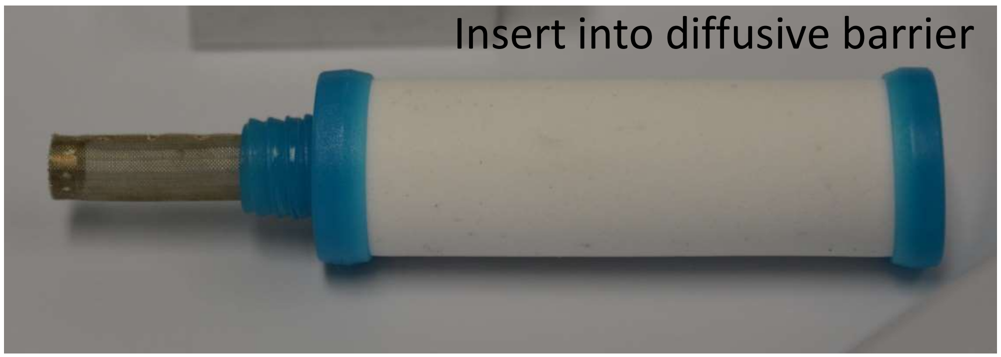
Passive air sampling technology

- New mercury sampling technology
- Developed at UTSC (Canada)
- New passive air sampler MerPAS
- Global pilot study
  - Deployed at 25+ countries around the world
  - Deployed at 55 different sites
- Uses carbon as trap
- Collected on site, sent to lab for analysis

Carbon



Mesh tube



Insert into diffusive barrier

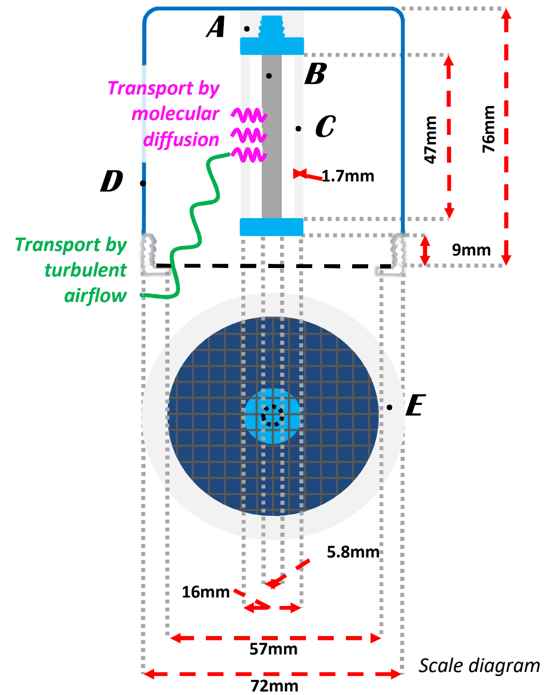
Insert into case

Open to air

Deployed

The Sampler

- Based on diffusive uptake of GEM and accumulation onto activated carbon sorbent.
- After deployment, activated carbon is analyzed for Hg
- Concentration is calculated using a calibrated sampling rate.



A. **Screw cap**

B. **Sulphur Impregnated Activated Carbon Sorbent**

C. **White Radiello® diffusive barrier**

D. **Polyethylene terephthalate (PET) protective shield**

E. **Polypropylene (PP) lid with mesh screen (PP)**

McLagan, et al., ES&T Lett (2016), 3(1), 24-29.

Why use PASs?

- Cheap
- Easy to use
- Easy to transport
- No electricity of gases
- High number, concurrent deployments
- Personal exposure sampling
- Remote sampling

How it works

Concentration derived from sampling rate of the system

Sampling rate was derived from automated instrument (gold standard)

Concentration derivation equation:

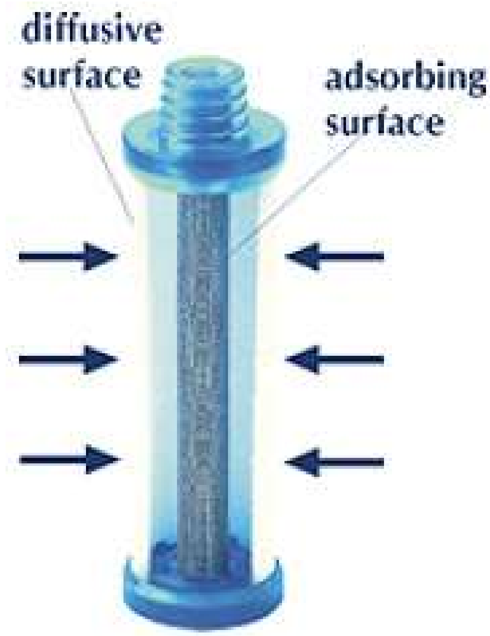
gaseous Hg concentration (ng m^{-3})

sampling rate (m^3 day^{-1})

$$C = m / (SR * t)$$

mass of sorbed Hg (ng)

deployment time (days)



Small wind and air temperature correction, meteorological data is useful to have

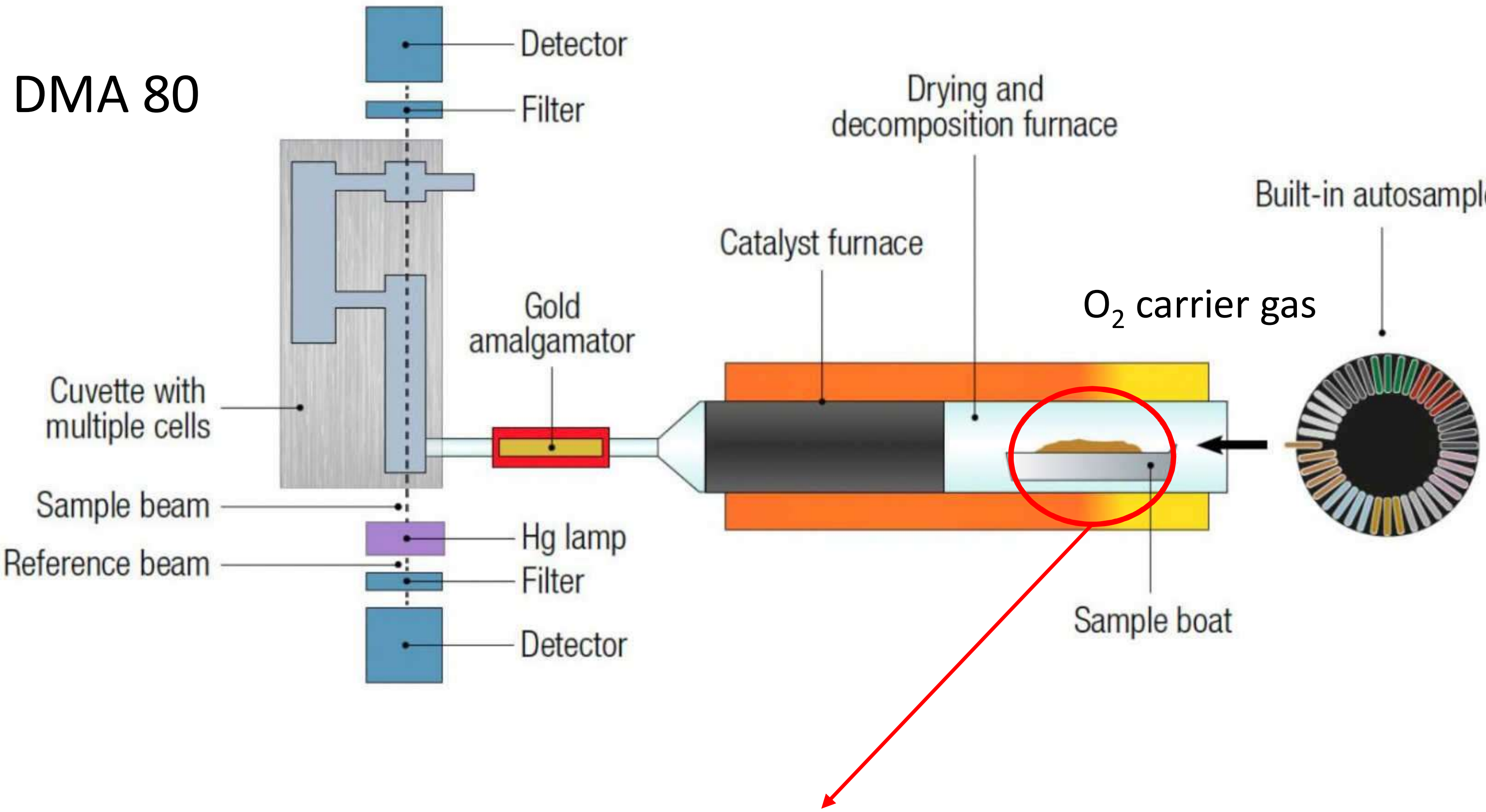
Analysis

- Samples brought back to lab
- Carbon is weighed
- Carbon is analysed for Hg content
- Direct Mercury Analyser (DMA)
    - Thermal decomposition (750^{o}C)
    - Amalgamation to gold trap (900^{o}C)
    - Atomic absorption spectroscopy

- High S content of carbon requires additives to not ruin catalyst
- EPA Method 7473 (or 1631)

Sample analysis

DMA 80



Carbon into quartz boat

Add Na_2CO_3 (Some add to catalyst as well)

A field intercomparison of three passive air samplers for gaseous mercury in ambient air

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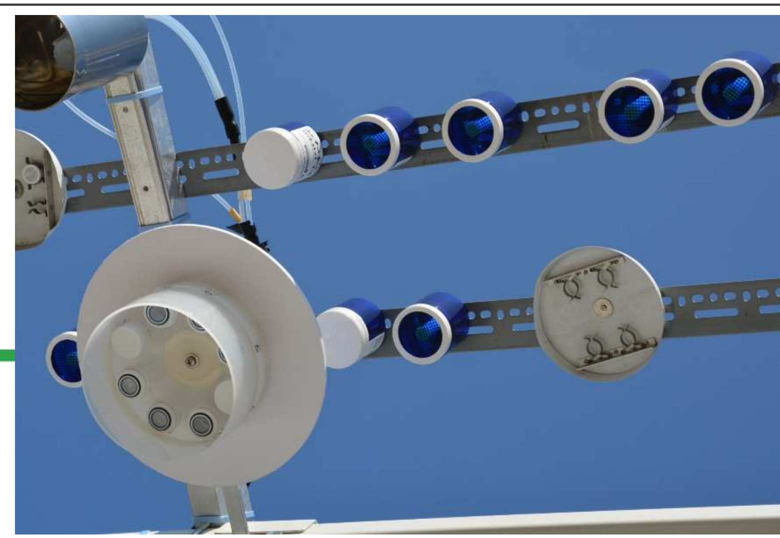
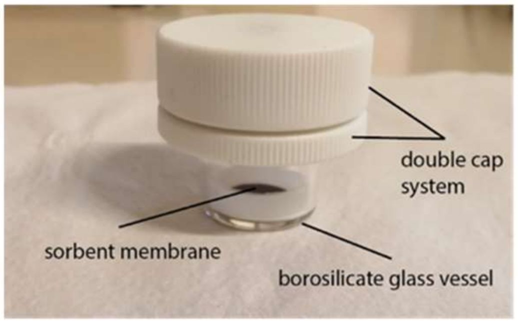
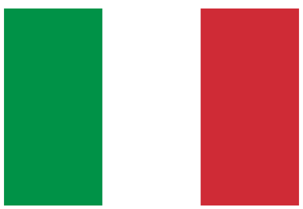
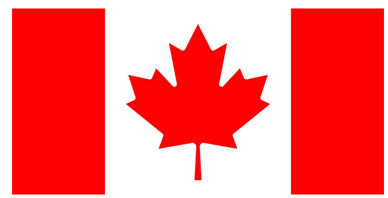


Intercomparison of 3 passive air sampling methods for TGM/GEM

CNR-PAS Macagnano et al., 2018	**IVL-PAS** Wängberg et al., 2016	***Mer*PAS®** McLagan et al., 2016a
		







Summary of key metrics investigated

	*Mer*PAS	IVL-PAS	CNR-PAS
MDL (ng)	0.16	0.25	0.13
LOD (2 weeks) (ng m^{-3})	0.10	0.59	0.67
LOQ (2 weeks) (ng m^{-3})	0.34	1.98	2.16
LOD (12 weeks) (ng m^{-3})	0.02	0.10	0.11
LOQ (12 weeks) (ng m^{-3})	0.06	0.33	0.36
Replicate precision (%) (before blank correction)	3	9	7
Replicate precision (%) (after blank correction)	4	15	14
Concentration bias n = 22 (%) (relative to Tekran)	+6.5	+8.2	-2.8
Absolute discrepancy n = 22 (%) (relative to Tekran)	6.5	12.5	19.2
Linear uptake over 12 weeks	Yes	Yes	Yes

Things to note:

- All samplers showed excellent linearity
- SR of CNR-PAS and IVL- PAS very similar at both locations
- CNR-PAS and IVL- PAS similar performance
- CNR-PAS smallest bias to Tekran
- All samplers performed better in Italy than Canada
- More refinement of SR may be required

***Mer*PAS® is best in**

- **Lowest LOD**
- **Highest precision**
- **Best accuracy**
- **Higher sampling rate due to radial vs axial design**
- **Leads to higher uptake and less impact from blanks**

Canada

Within the Minamata Convention, there is a need for global air monitoring

…but little appetite for a global network

Fill in the gaps with passive air samplers through a concept of

"network of networks"

Creating a Network of Networks

Expand currently operating networks to include mercury passive sampling

➢ No truly global air mercury monitoring network

- Use current infrastructure
  - Mercury networks
  - Air monitoring networks
  - Passive sampling networks

Canada initiated a pilot study in 2019 to demonstrate a proof of concept for use of passive sampling and a combination of networks

…hope it catches on!

Global passive project - sample deployment

Send pail of equipment to each site

- 3 samplers (2 samples /1 blank)
- Instructions
- Mounting equipment
- Gloves, tape, pen

- Shipping is paid for
- Samples left out for 3 months – seasonality
- Once sampled, send to ECCC for analysis

Standard Operating Procedures

Sample collection

Environment and Climate Change Canada | Environnement et Changement climatique Canada

Mercury Passive Sampler

Standard Operating Procedures

Purpose

We are trying to determine how much mercury is in the air in the Arctic by using this new Passive Air Sampler (PASs). The PASs are designed to absorb mercury so that we can determine how much is in the air. With this information we can determine if levels of mercury in the air are going up or down.

In the kit (pail) are 3 PASs: 1) the 2x "***Sample***" PAS is installed on a post, fence or bracket to sample the air for 3 months and 2)The "***Blank***" PAS is included and is treated like the sample, but not left out to sample the air.

The ***Sample*** PAS is placed in a downward direction on the post to sample the air and the ***Blank*** PAS is handled like the Sample PAS where it is brought out, briefly exposed to the air and then sealed up again.

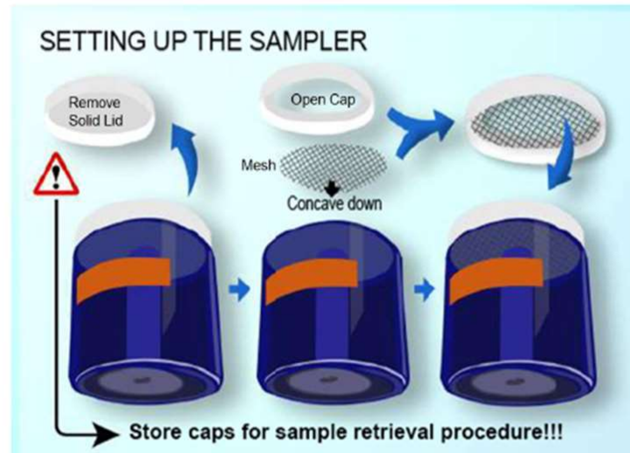
Check that your kit is complete:

- ✓ 3 blue samplers in ziploc bags
- ✓ 3 open caps and 3 screens
- ✓ 4 zip-ties, 2 H clips
- ✓ 1 metal bracket
- ✓ 1 roll of yellow tape
- ✓ 2 pair of nitrile gloves
- ✓ Instructions
- ✓ Sharpie

Prepare the Blank and Sample PAS

- Put on provided nitrile gloves
- Remove all 3 PASs from Ziploc bags (retain ziploc bags)
- Remove the tape from around lids of all 3 containers
- Remove the lids from both ***Sample*** and ***Blank*** PASs
- Replace the lids on both the ***Sample*** and ***Blank*** PAS with the open cap and black mesh (the curve of the mesh should face into the sample container)
- Label the *Start Time* and *Site* on the ***Sample*** and ***Blank*** with a permanent marker

Canada

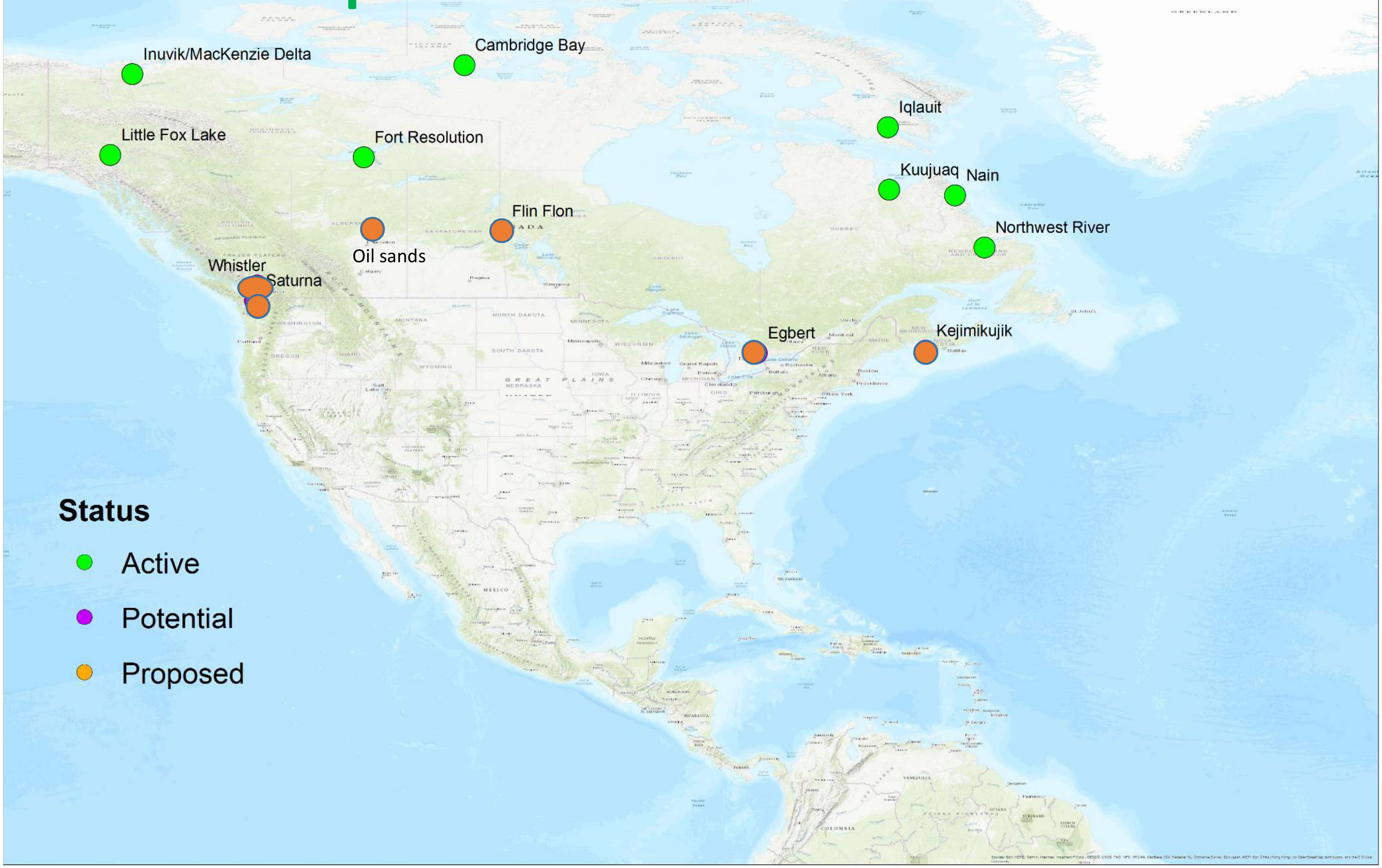


Installing the Sample PAS

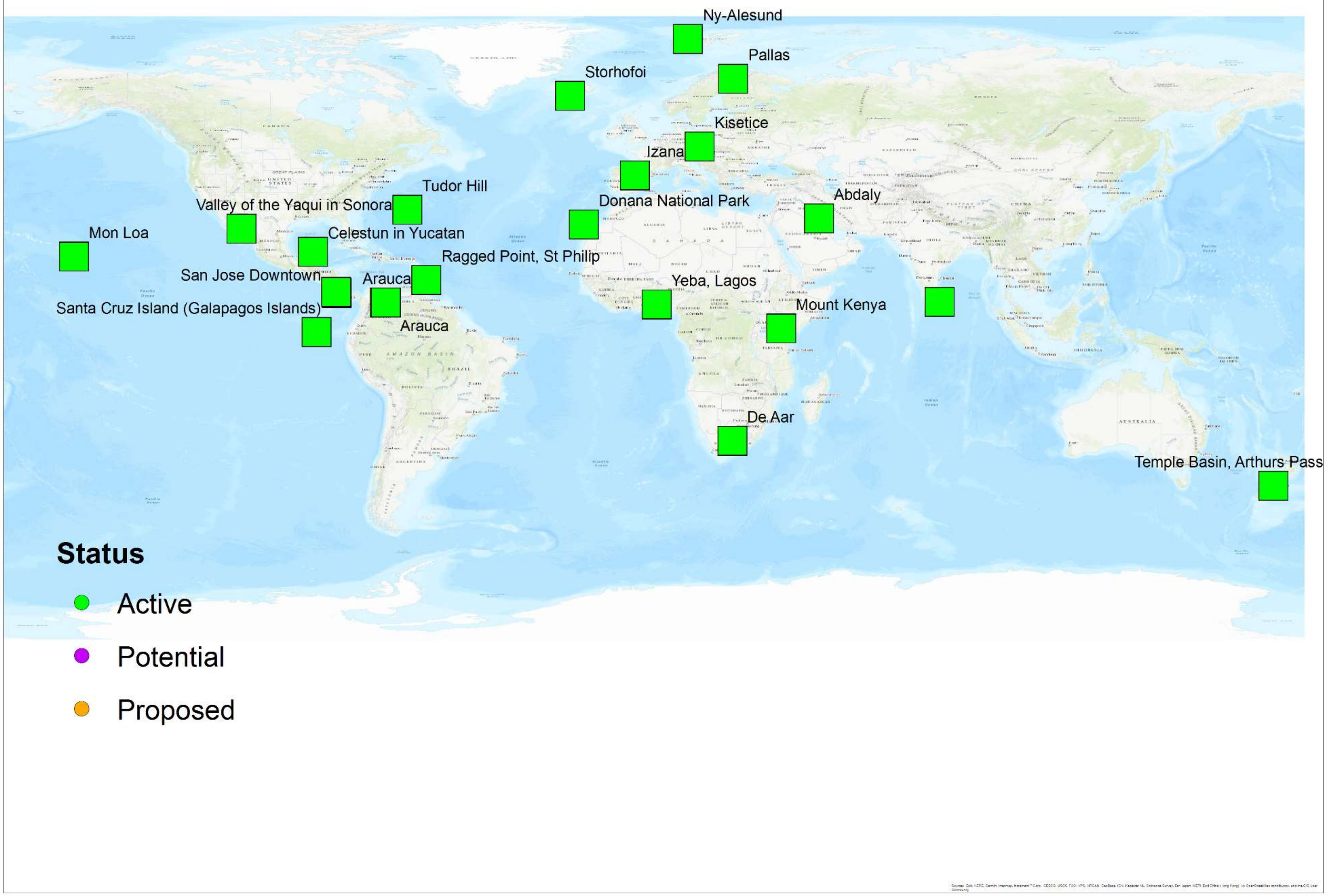
- Install the ***Sample*** PAS on a post, fence or structure using the provided zip-ties. Several zip-ties can be used to get around a large diameter post if necessary. Install the H-Clip if necessary to keep the ***Sample*** PAS pointed downward using 2 zipties (Method 1)
- Alternatively, the ***Sample*** PASs can be attached to the metal bracket using the zip-ties available in the kit. The zip-ties can be used to get the metal bracket around a post, fence or other structure. The side of the metal bracket with the two circles can be used to hold the ***Sample*** PASs as the bottom of the sampler has a small plastic screw where the lid of the screw can be removed and re-attached after the screw is put through the circle in the metal bracket. The lid of the sampler will be facing the ground (Method 2)
- Put the solid lid from the ***Sample*** back in ziploc for safe keeping until the sampler is changed
- Take a picture of the final installation

Participating Networks

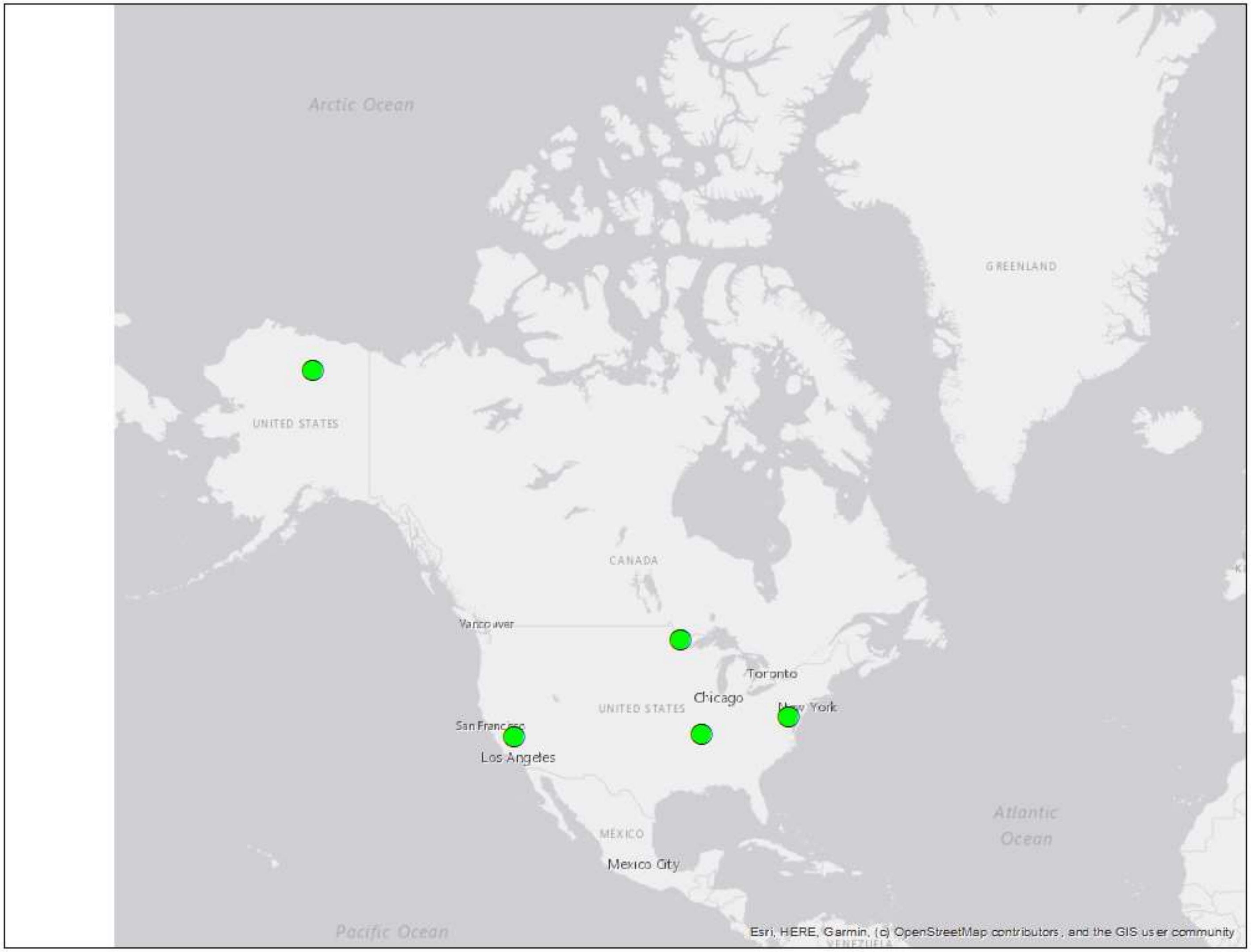
ECCC-AMM passive sites



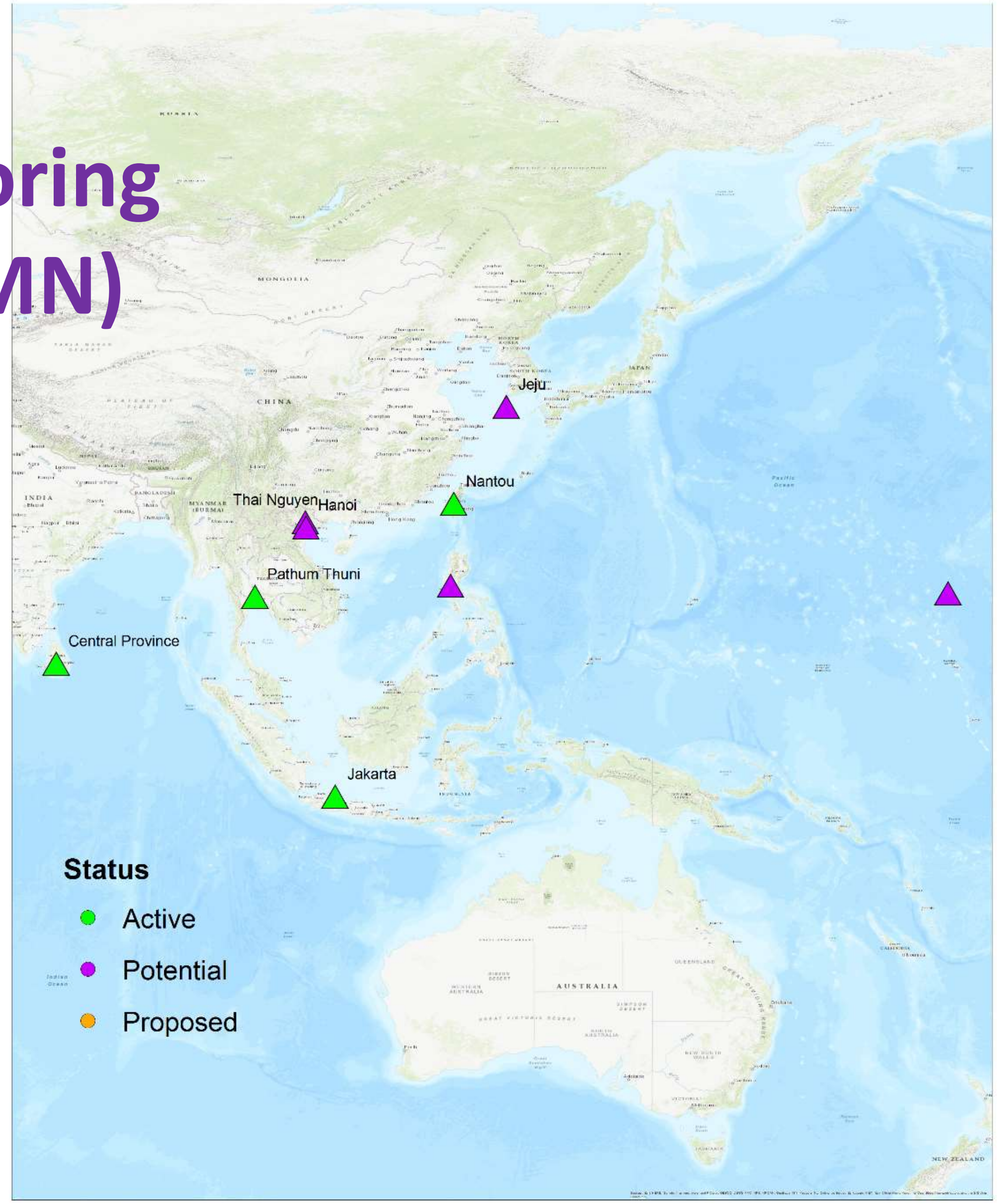
Global Atmospheric Passive Sampling Network (GAPS)



National Atmospheric Deposition Network (NADP)



Asia Pacific Mercury Monitoring Network (APMMN)

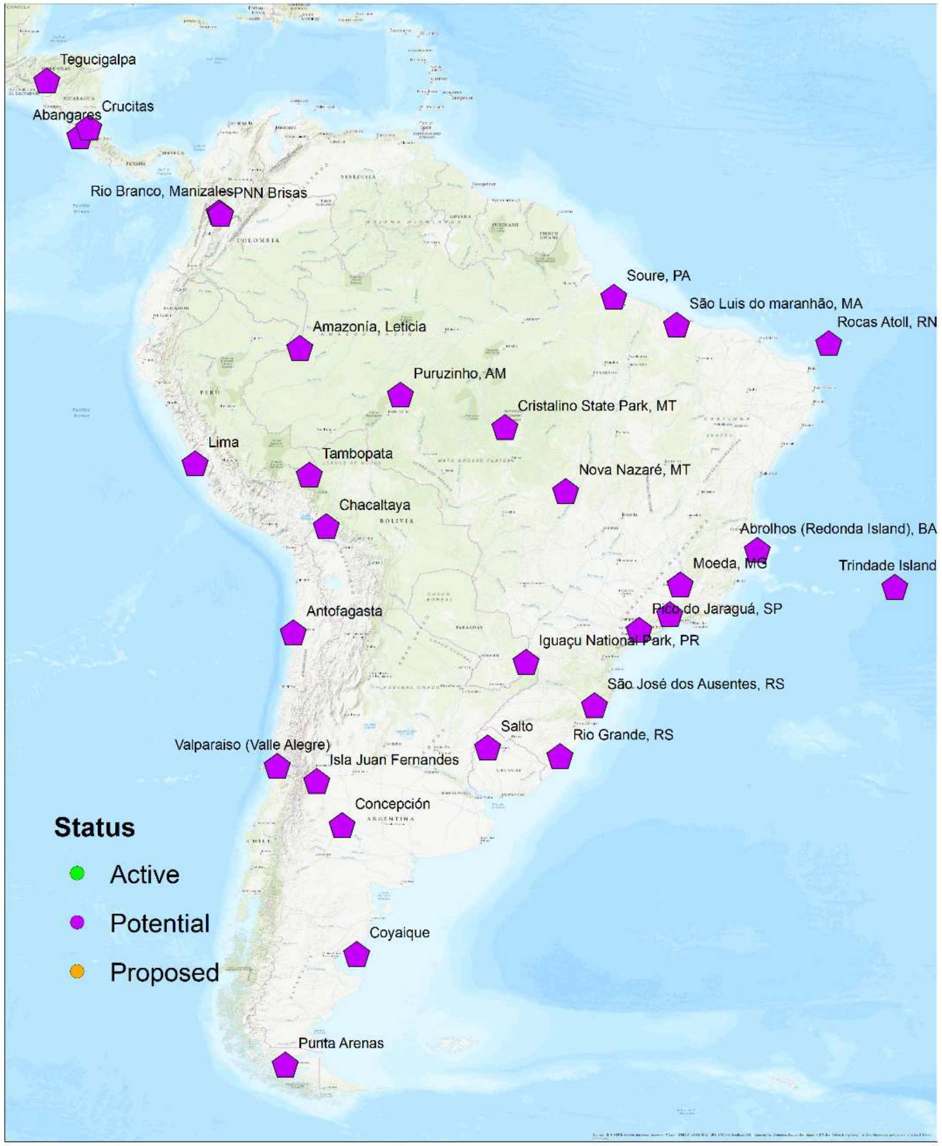


LAPAN – potential

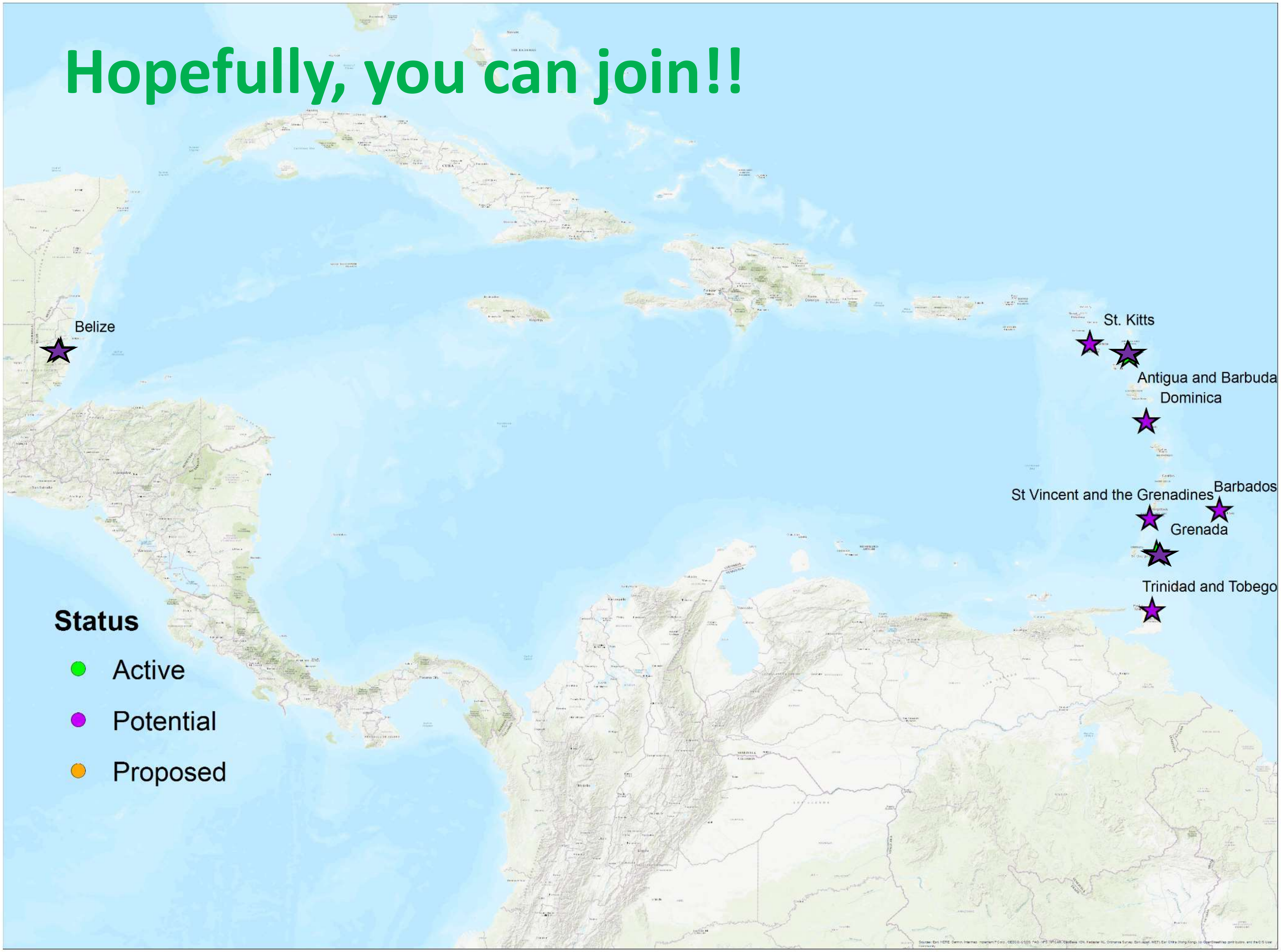
POPs network who has agreed to partake, just need to pick sites and work out details

Frank Wania did 1 year study at all these sites

We are waiting for discussions to assess what sites can be part of this project

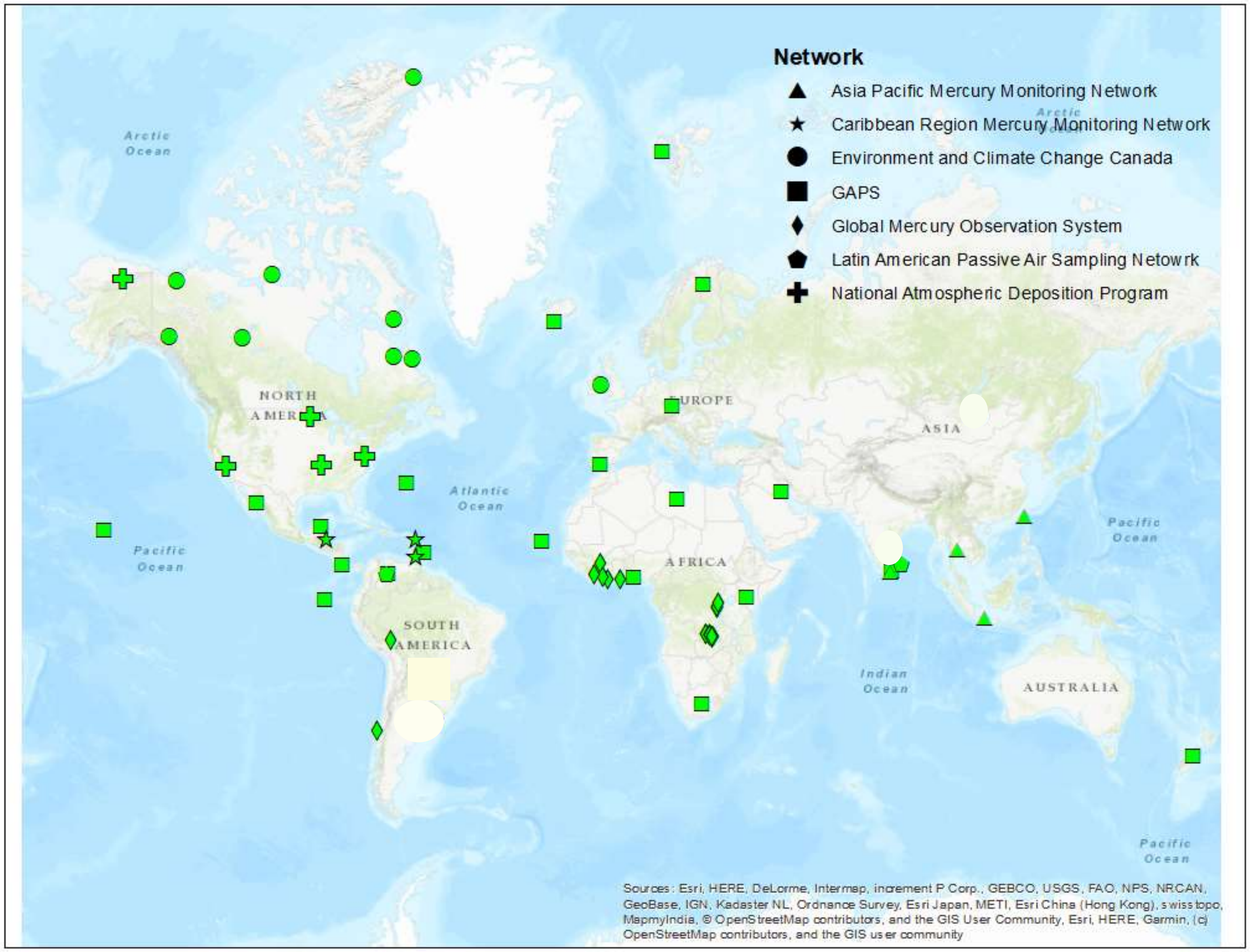


Hopefully, you can join!!



GMOS Passive air monitoring sites

Progress so far in the global pilot study



- 55 sites
- ~285 deployed
- ~ 200^{+} samples analyzed

Ultimate goals

- Engage CRMMN to sample and analyze air samples for mercury
- Provide support and information where needed
- Networks run their own samples and participate in intercomparisons
- **Use for other regional questions as desired**
- Report the data to assess inputs to the region
- Report the data for a better global picture
- Use the data collected to assess the effectiveness of the Minamata Convention

Summary

- Air monitoring is important to understand mercury inputs to the region
- New passive sampling technology can help with regional monitoring to look at overall spatial and temporal trends
- Work with CRMMN to initiate inclusion in global passive network
- Move towards CRMMN running the air program and collaborate with the global passive network

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Thank you!

Dr. Linroy Christian
Dr. David Evers

Site operators are invaluable!

Financial

- ECCC- Environmental Protection Branch – Chemicals Management Program
- ECCC - Air Quality Research Division
- Northern Contaminants Program