Development of a novel graphene-based passive air sampler towards bridging mercury monitoring gaps in South Africa

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The need for mercury monitoring

- SA ratified the Minamata Convention in 2019 but there is progress toward more consistent monitoring efforts
- Some prominent Hg sources in SA and impacted zones with little to no monitoring
- There is a large reliance on inventories that become progressively outdated
- The most recent inventory list is from 2011
- Release to air and land are highest
- Largest contributors to air are combustion of coal and primary metal production

- Draft regulations were put forward and updated at the end of 2023 by the Minister of Forestry, Fisheries and the Environment [1]
- Regulations have provision for the phasing out of Hg-added products and processes with some export restrictions
- These still do **NOT** provision for anthropogenic releases to air from other sources like burning of coal
- This motivates the need for more airborne concentration data to inform future regulations with respect to air

[1]: DEA (Department of Environmental Affairs), Republic of South Africa, (2011). Inventory of Mercury Releases in South Africa. [online] UNEP (United Nations Environment Programme). Available at: https://www.unep.org/resources/report/inventory-mercury-releases-south-africa, [Accessed 03 July 2024]

Atmospheric mercury sources in South Africa

- Releases to air from coal-fired power plants is a prominent source

- There is a high density of operating coal burning power stations in the upper North-Eastern provinces

- There is also a presence of ASGM

Other mercury sources

Other sources include but are not limited to:

- Chlor-alkali production – an incident led to exposure in 1998 [1]
- Fluorescent lighting
- Skin lightening practices
- Waste incineration
- Burning of biomass – “veld fires”

[1]: Oosthuizen, Jacques and Albertyn-Christie, Carol and Fu, Shih-Ching, (2008). South Africa's Minamata, an Analysis of the Thor Chemicals Saga 1989 – 2020. *Social Science Research Network*, 12, 1-10

Current monitoring efforts

Active

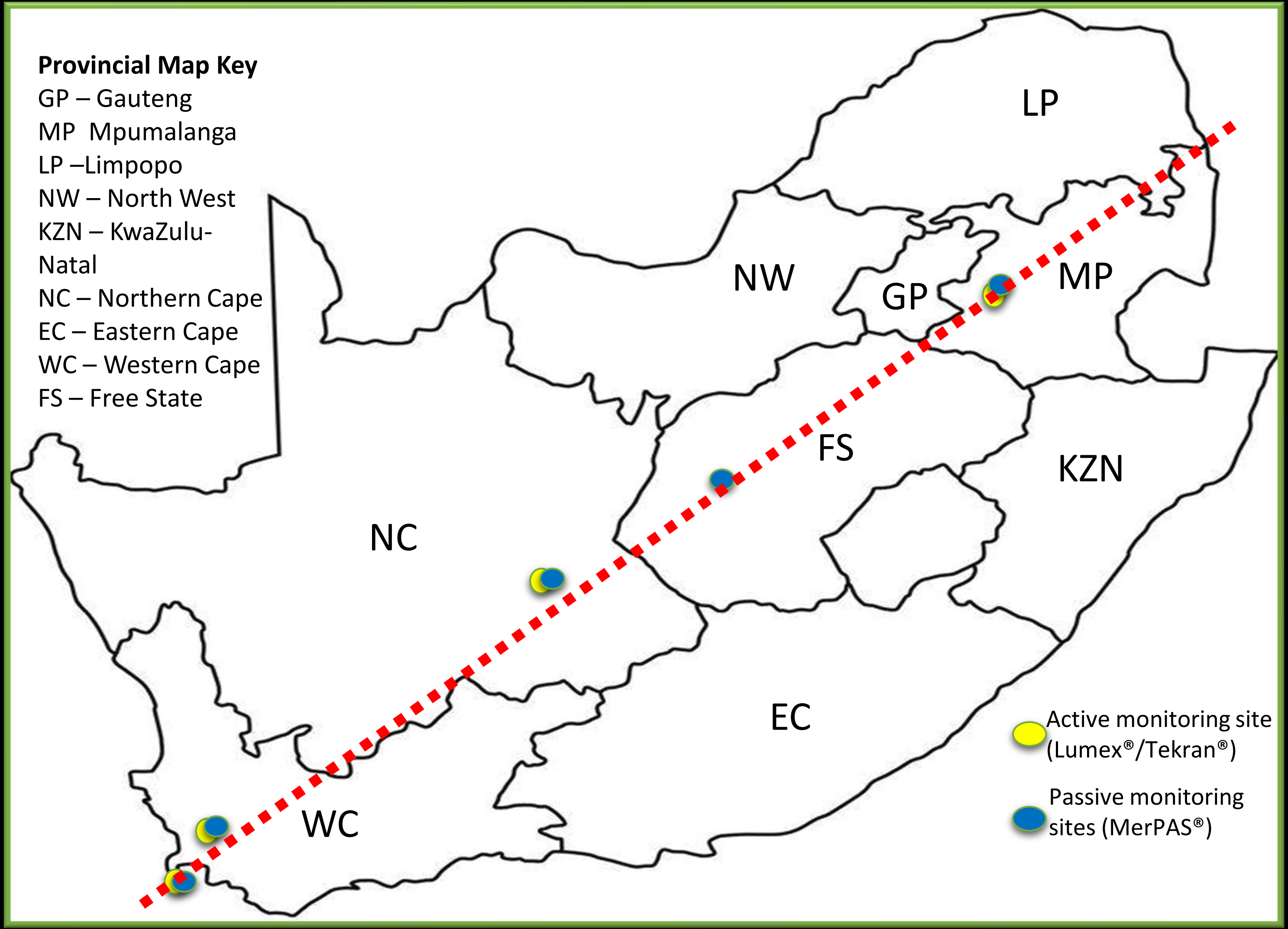
- Active monitoring with Lumex® or Tekran® instruments
- Continuous monitoring is conducted at 4 sites across South Africa – De Aar, Cape Point (GAW), Witbank and Welgegund
- Measurements at the Global Atmospheric Watch Station (GAWS) is the longest standing active data set in SA (since 1995)
- Other active sampling with gold amalgamation traps began on a small scale (2 sites) in 2023

GAW monitoring station, Cape Point, South Africa

Passive

- Main passive sampling efforts through use of MerPAS® in collaboration with Environment Canada and the SAWS
- In tandem with active instrument locations, MerPAS® is also deployed at De Aar, Cape Point (GAW), Witbank and Welgegund
- Many MerPAS® samplers are shipped for analysis in Canada
- 18 months of historical data is available with 3-month deployment intervals

MerPAS® deployed at the GAW station, Cape Point, 2021



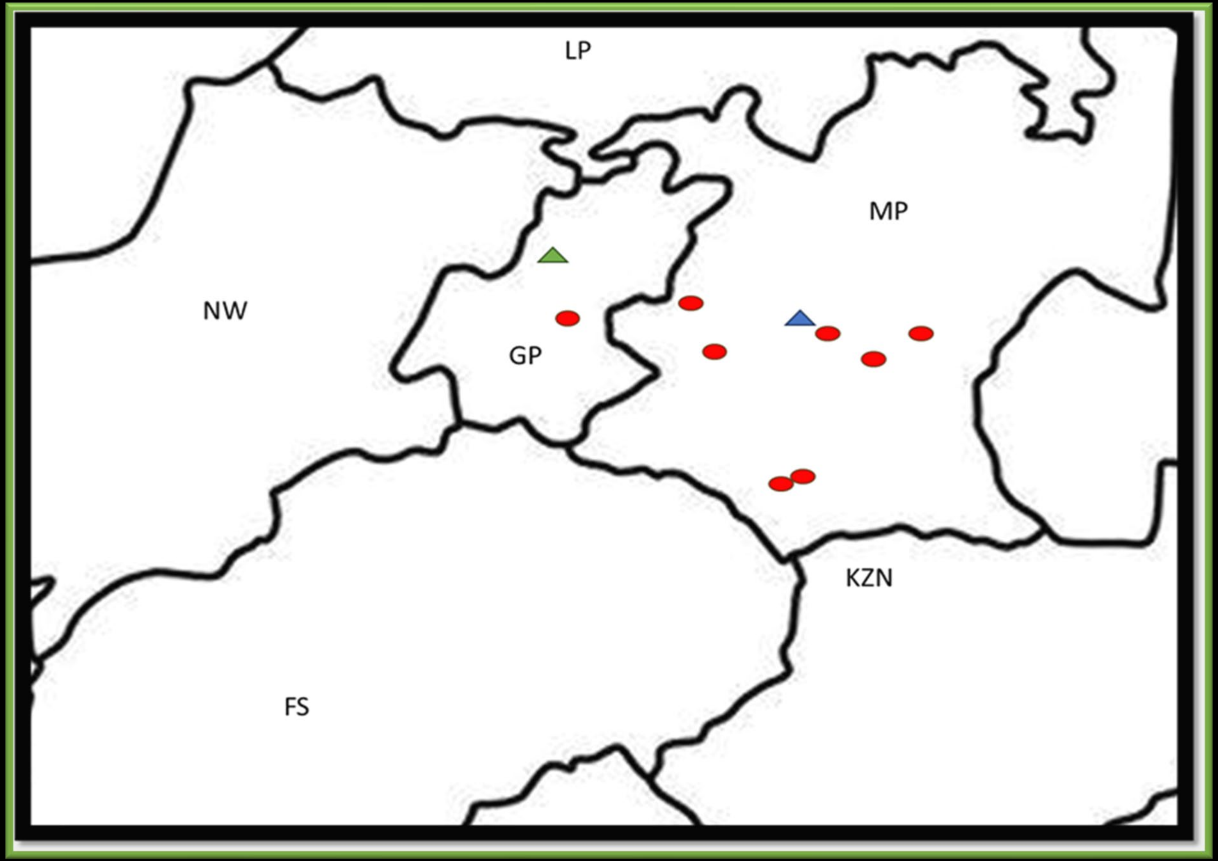
Provincial map of South Africa: current active and passive monitoring efforts

Data gaps

- Despite current efforts, there is a clear absence of monitoring in the majority of provinces
- Most sites have active monitoring alongside passive efforts – can substantiate data with both
- Current monitoring has some representation along a central line across the country but minimally around point sources
- More established background sites are also needed
- Some data gaps are present for active monitoring due to power outages
- Sites of monitoring should be chosen based on proximity to known or suspected point sources

A passive sampling rationale

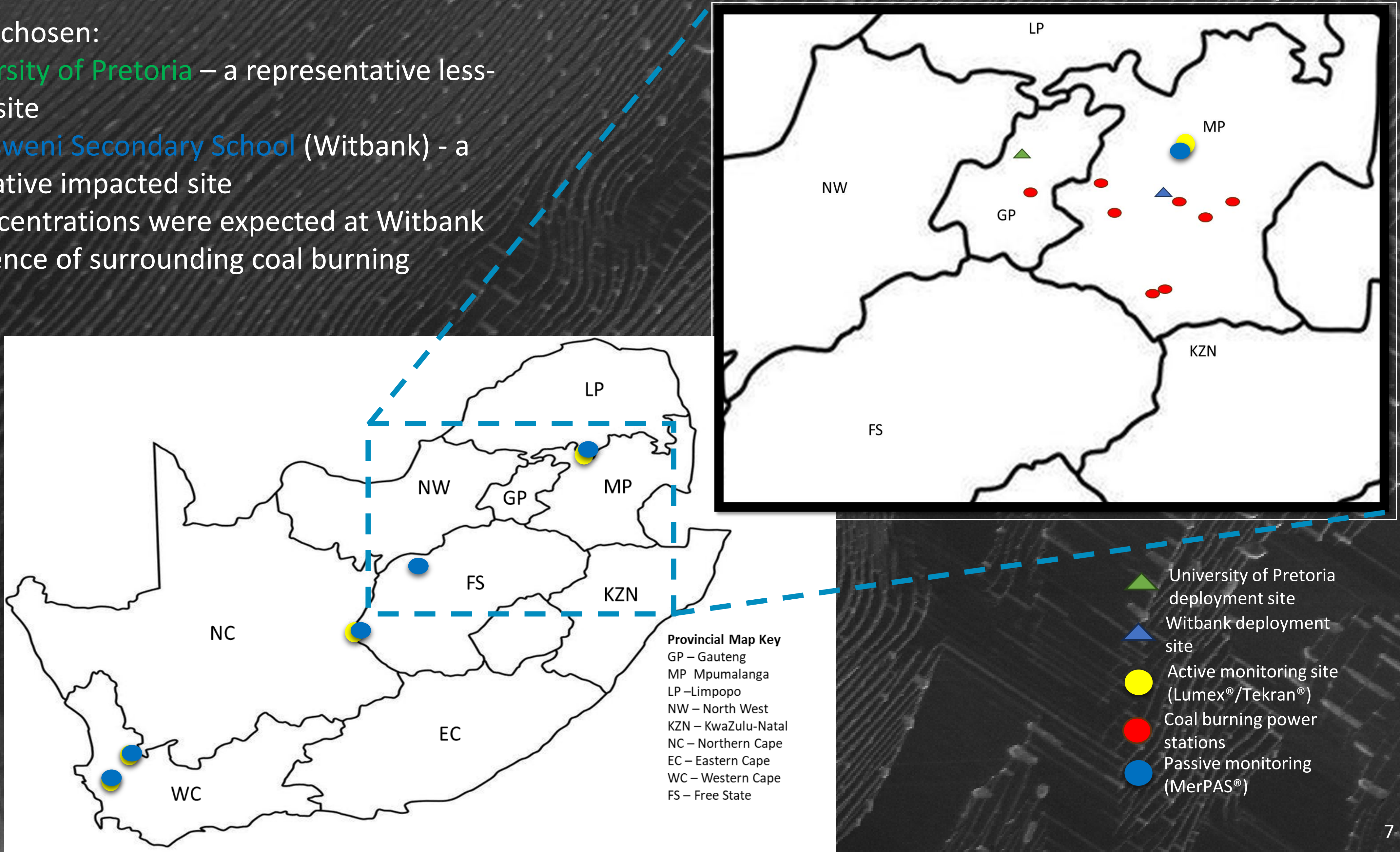
- Installation active monitoring instruments is costly
- A lack of infrastructure at remote and impacted sites can allow active sampling methods
- Passive sampling does not require the same degree of training to deploy
- Can allow for more spatial coverage at the cost of some temporal resolution
- Can be deployed near point sources, such as the high density of coal-fired power stations in the NE provinces



Geographical map showing the density of coal-fired power stations (red) around the chosen deployment sites of UP (green) and Witbank (blue)

Choice of monitoring sites

- Two sites were chosen:
  - ∆ The University of Pretoria – a representative less-impacted site
  - ∆ Elukhanyisweni Secondary School (Witbank) - a representative impacted site
- Detectable concentrations were expected at Witbank due to prominence of surrounding coal burning power stations



A novel graphene foam passive air sampler (PAS)

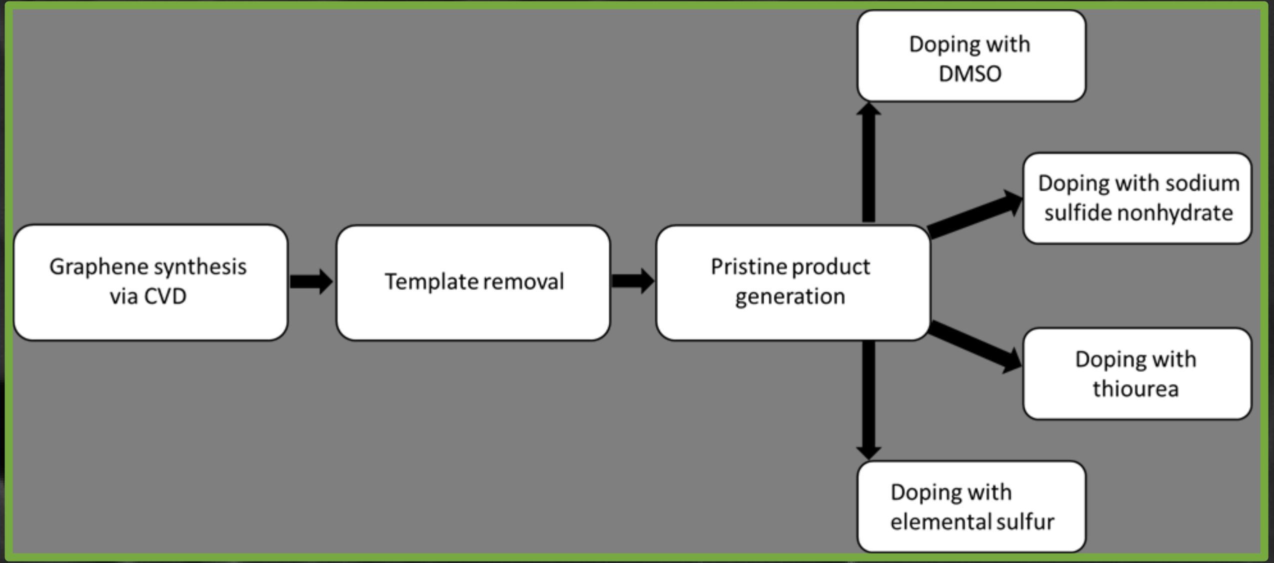
Sorbent choice: Graphene foam

- Carbonaceous sorbents have been used for Hg capture in aqueous and air matrices
- The sorbent surface can be chemically modified to improve affinity for airborne Hg species
- Has an inherently large surface area and porous structure – ideal sorbent
- Graphene is thermally stable and regenerable – reusability is promising
- Used in a radial PAS design to be compatible with the Radiello® diffusive bodies and to increase uptake rates

A novel graphene foam passive air sampler (PAS)

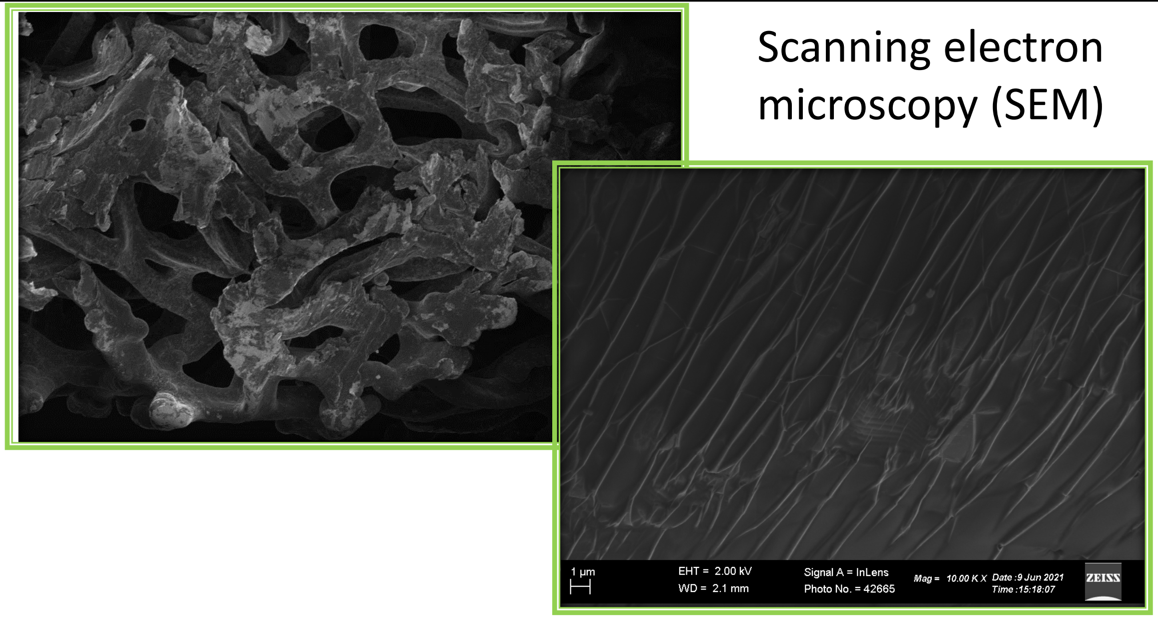
Sorbent preparation

- Pristine graphene foam is catalytically synthesised by chemical vapour deposition (CVD) on a metal support
- Further derivatized with various S sources and methods and then characterized
- S sources include: DMSO, Na_2S and thiourea and elemental sulfur
- Very low final mass ≈17 - 36 mg per sampler
- Final product can fit into PAS design as a Radiello®-sized cartridge

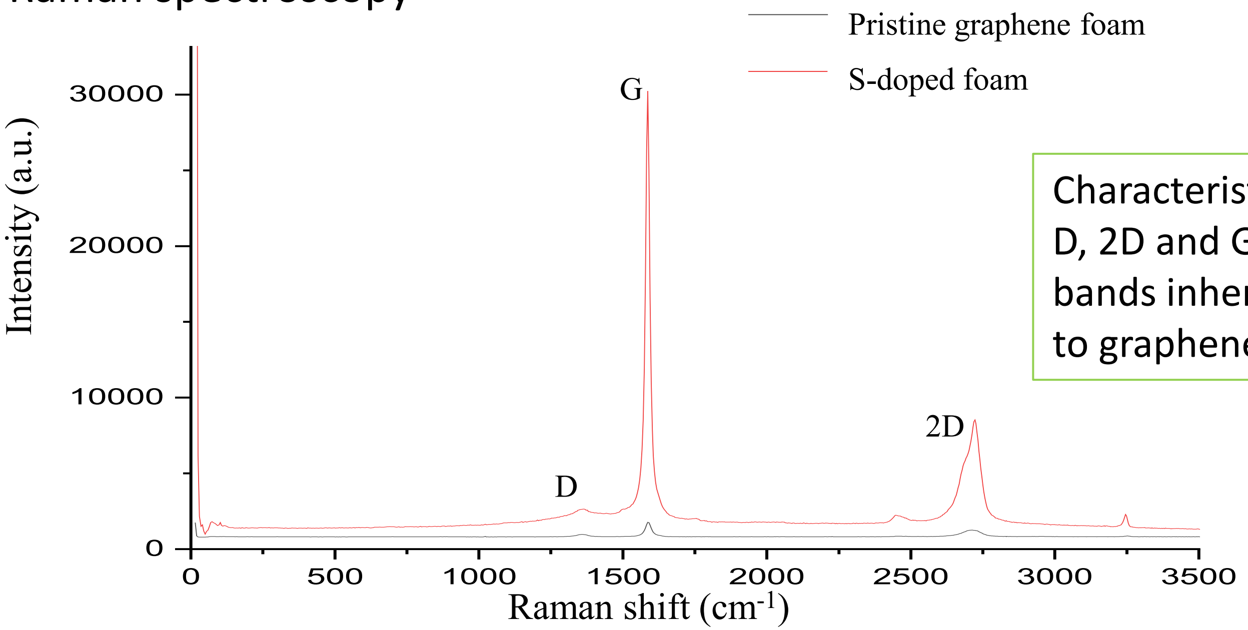


Sorbent Characterization

Scanning electron microscopy (SEM)

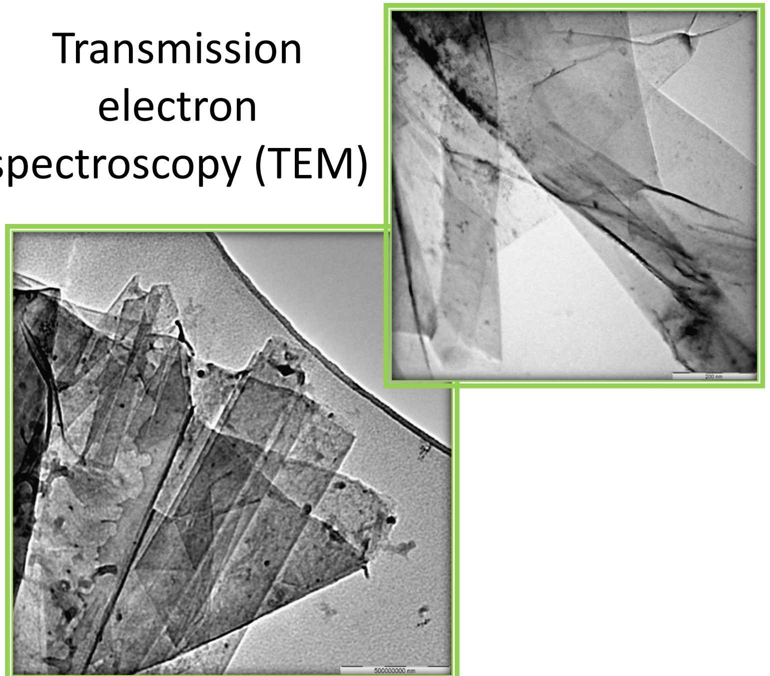


Raman spectroscopy



Characteristic D, 2D and G bands inherent to graphene

Transmission electron spectroscopy (TEM)



Surface area by Brunauer-Emmett-Teller (BET)

Specific surface areas for sorbents used in sampling

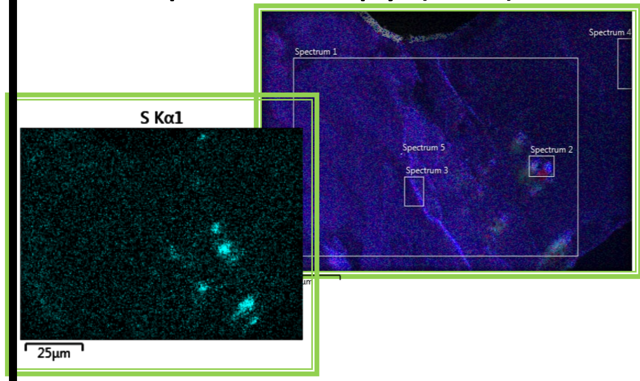
- Mean of pristine foam ~2,03 $m^2.g^{-1}$
- Mean of derivatized foams ~5,53 $m^2.g^{-1}$

Thermogravimetric analysis (TGA)

Relative mass losses upon analysis were consistent with the losses observed by TGA

- Pristine foam ~12,7% over 2 to 4 cycles
- Doped foam variants ~12,6% over 2 to 4 cycles

Energy-dispersive X-ray spectroscopy (EDS)



Other characterization includes X-ray photoelectron spectroscopy (**XPS**) and Fourier Transform Infrared Spectroscopy (**FTIR**)

Sampler deployments

The final, assembled graphene foam PAS prototype

- Deployment dates
1. UP: May – Nov 2022 and Nov – Mar 2022
2. Witbank: July – Oct 2022 and Oct 2022 – Feb 2023
- Three sorbent derivatives and pristine foam were all deployed
- Both sites adapted on 2nd deployments to increase sampler data set

Elukhanyisweni Secondary School, Witbank

- Two full deployments over ~6 and 3 months respectively
- Deployment alongside MerPAS® on second deployment
- Six coal burning power station(s) within a 50 km radius of site

Department of Chemistry roof, University of Pretoria

- First, a proof-of-concept study
- Then a full deployment alongside MerPAS® ~ 3 months
- One coal burning power station within 50 km radius of site

Analysis

- Hg quantitation achieved by cold vapour atomic absorption spectroscopy (CVAAS) on a DMA-80 *evo* tricell
- Method validated by participation in a global interlaboratory proficiency testing scheme orchestrated by the National Institute for Minamata Disease (NIMD) and the United Nations Regional office for Asia and the Pacific (UNEP ROAP), determining Hg_{total} content in hair samples
- Calibration with aqueous matrix-matched standards and a minimum of six points
- Detection limits (LoD) and quantitation limits (LoQ) of 0,0828 and 0,2509 ng Hg achieved, respectively
- Method traceability with NIST 2962c bituminous coal reference material

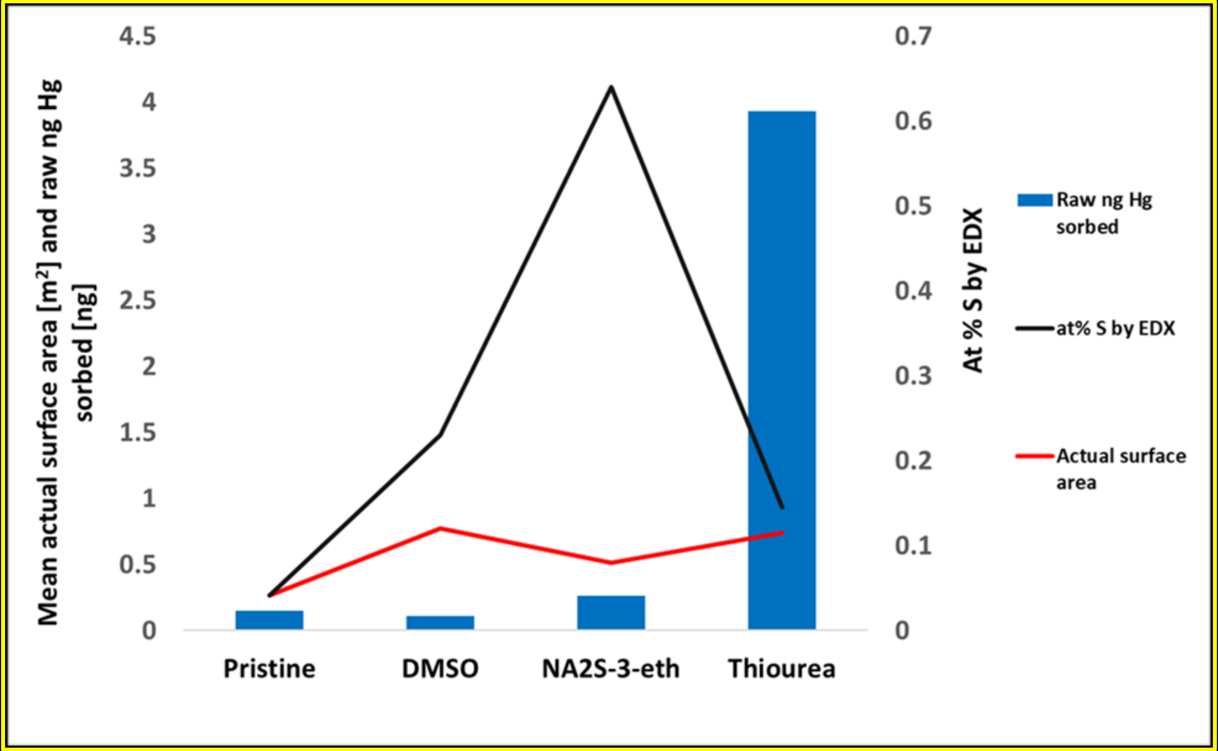
- Sorbent is thermally desorbed directly without sample preparation
- Unlike MerPAS®, Na_2CO_3 addition step is omitted – S content is low
- Local production and analysis increases data turnaround, without need for export for analysis – assists in reduced costs of monitoring compared to imported alternatives
- Desorption studies show that most detected mercury was removed after two successive analyses

Results of deployments

- Lumex® active air concentration data over the deployment period was used to calculate a preliminary sampling rate
- MerPAS® collected significantly more Hg, however, considering the mass difference (mg of graphene vs g of AC), the low responses seem reasonable
- Sampling rates for graphene sorbents are similar but lower than the activated carbon in the MerPAS®
- Calculated air concentrations were comparable to MerPAS® except for one graphene foam sampler but are low compared to expected ambient levels such as that at Cape Point (~1-1,5 ng/m^3).

Deployed sorbent	N	Sorbed Hg [ng] at Witbank		Sorbed Hg [ng] at UP		Sampling rate [m^3/day x 10^{-3}]		Calculated TGM concentration in air [ng/m^3]	
		mean	%RSD	mean	%RSD	mean	%RSD	mean	%RSD
Pristine graphene	3	0.1500	39	0.0866	60	0.60	40	0.546	45
DMSO	4	0.1063	29	0.2124	127	0.33	30	0.306	23
Na_2S-ethanol	3	0.2630	40	0.1087	66	1.06	40	0.538	39
Thiourea	3	3.9280	30	0.0741	63	15.81	30	0.517	34
MerPAS®	3	29.2400	4	23.9000	11	116.74	4	0.484	4

Witbank



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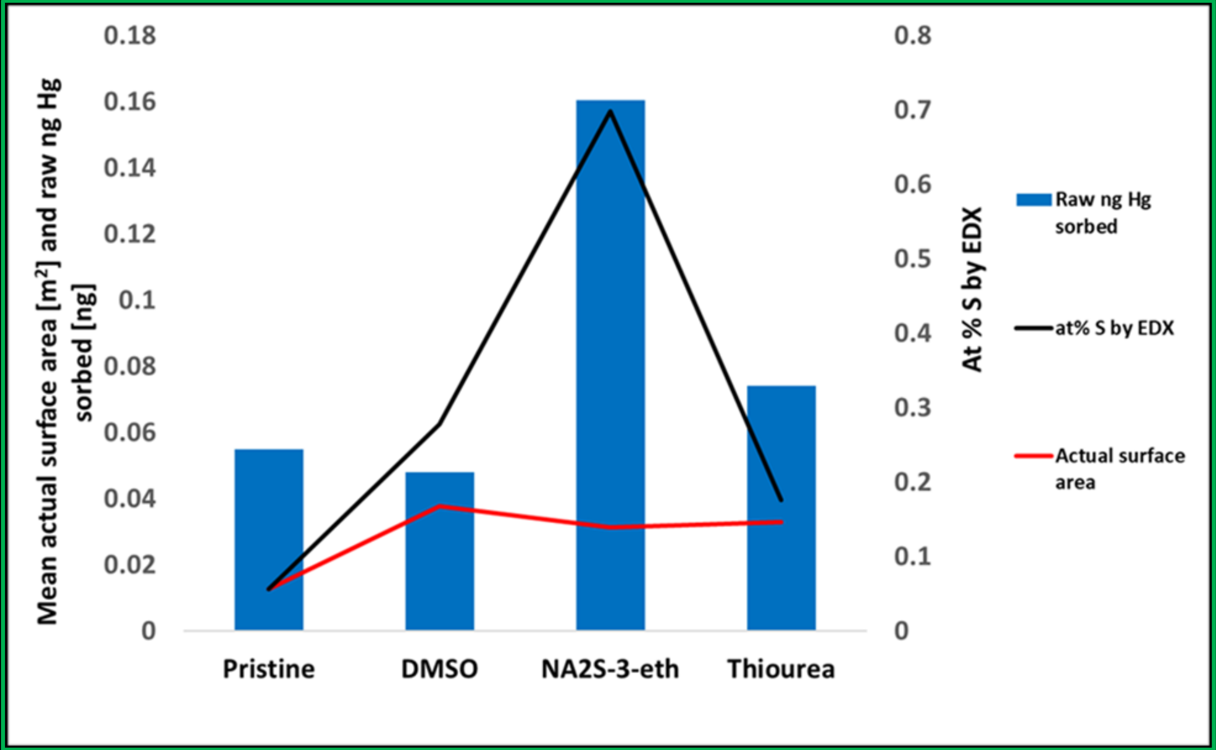
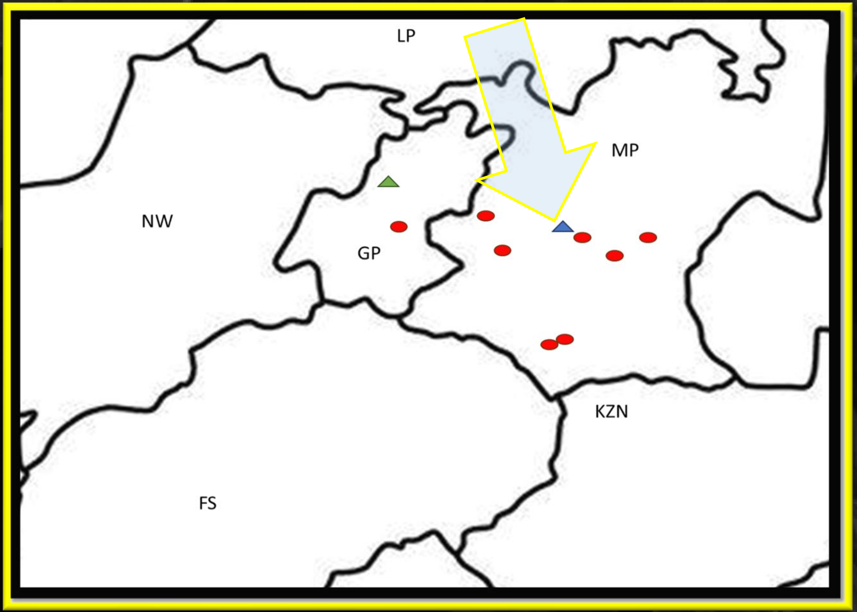
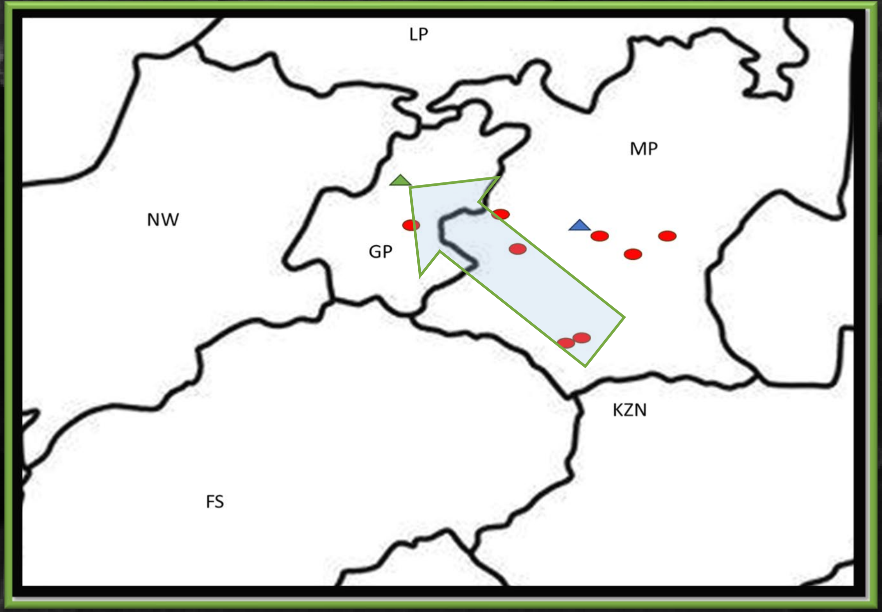
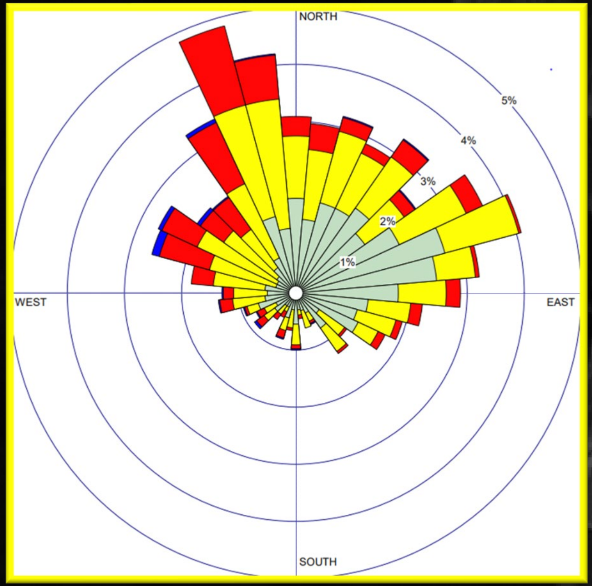


- Mercury captured, surface area and sulfur content show a clear trend where Hg sorbed was dependent on the surface functional groups
- The introduced sulfur is not expected to offer selectivity between Hg species
- Performance was diminished at lower ambient concentrations due to low sorbent mass
- Further characterization is needed



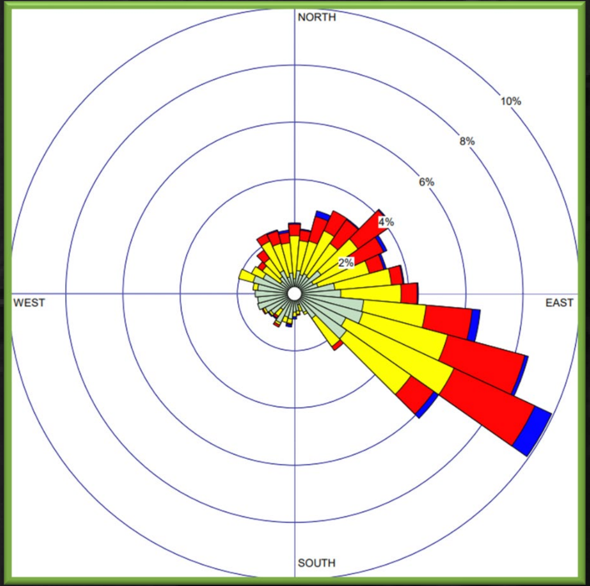
Results of deployments





For Witbank, wind patterns show mean wind direction is opposite to that of point sources – Hg still detected!

For UP, the opposite is true, lower mercury mass captured and wind speed is toward the sampling site



Witbank

University of Pretoria

Conclusions

- There has been a gradual increase in Hg monitoring data in South Africa
- The novel graphene foam sorbent shows potential for TGM capture from air
- Cost of using MerPAS® is higher, ~R1400 ($72) per single MerPAS® vs ~R300 ($15) for our novel sampler
- The low mass of the sorbent and long deployment times required infer best use at impacted sites
- The sorbent foam can be adapted to suit different applications such as badge samplers for occupational sampling
- A journal publication on this study has been submitted for review

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Thank you!