Workshop "Elements to consider when designing a Global Monitoring Plan for Mercury"
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Passive air sampling as a tool to measure mercury in ambient air: results of the pilot survey

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About PASs preparation and characterization

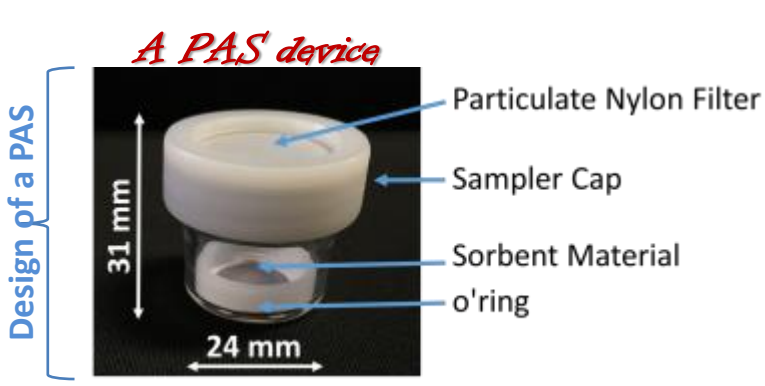
Passive sampling systems sound to be:

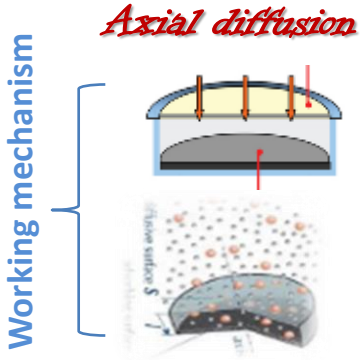
i) a **low cost strategy to quantify Hg levels in air** over different environmental locations, remote as the Polar Regions, rural and urban locations;

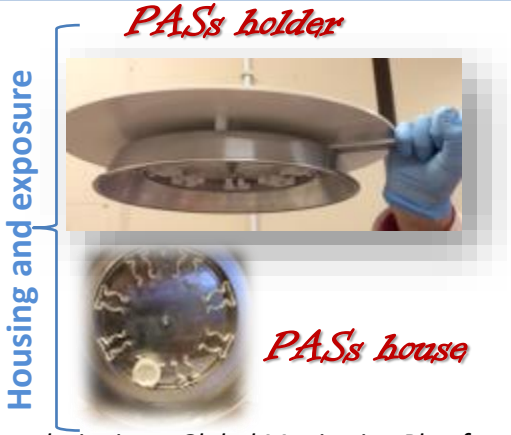
ii) compact, portable, unobtrusive, and inexpensive;

iii) able to give information about the average pollution levels over time periods of few hours to weeks/months.

Novel passive samplers (PASs) of mercury based on nanostructured materials (nanoparticles of titanium oxide properly functionalized with gold nanoparticles), have been designed, developed, characterized and applied







More specifically….

The passive sampler, designed and fabricated within CNR, comprised:

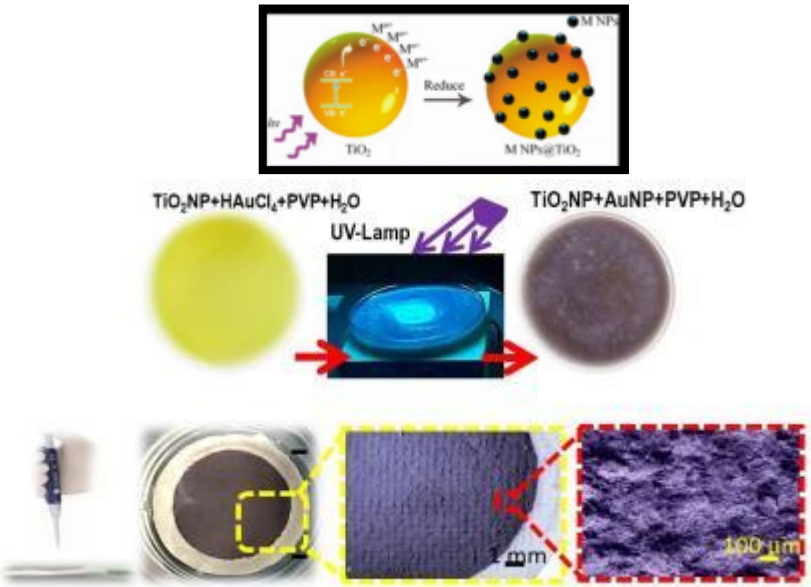
i) **a nanostructured adsorbing membrane coating a porous quartz slice,**
ii) **a glass vessel;**
iii) **a cap with a protective grid for the exposure to the environment.**

Adsorbing membrane: titania nanoparticles (≤25nm diameter) that after a suspension in an aqueous solution of PVP/HAuCl4 and UV-irradiation changed the color from white to blue-violet, resulting from a fine decoration with **gold nanoparticles (6-20 nm**). Such a functionalization occurred for the photocatalytic properties of TiO_2 (anatase).

The nanostructured suspension was deposited on a **thin quartz slices (450 µm thick, 20 mm length),** dried to 550°C and then placed into an **axial diffusive sampler** in order to be exposed firstly to air polluted with well-known amounts of Hg^0 for calibration and characterization and secondly to the atmosphere.

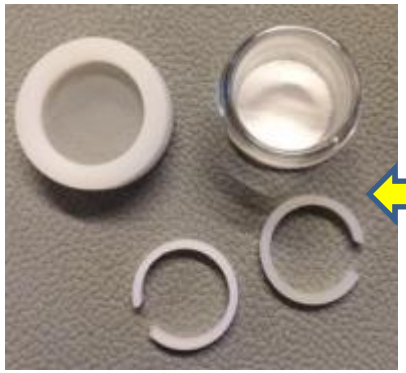
About the procedure of PAS preparation….

All chemicals were purchased from Sigma-Aldrich, quartz slice filters (Whatman) were 450 μm thick with a porosity of about 2 μm



The suspension was vortexed and deposited on the quartz slices, then dried to 80°C, and before being placed and sealed into the analyst sampler, it was subject to a thermal desorption at 550°C within a customized oven under a clean air flow in order to remove any trace of mercury absorbed during preparation.

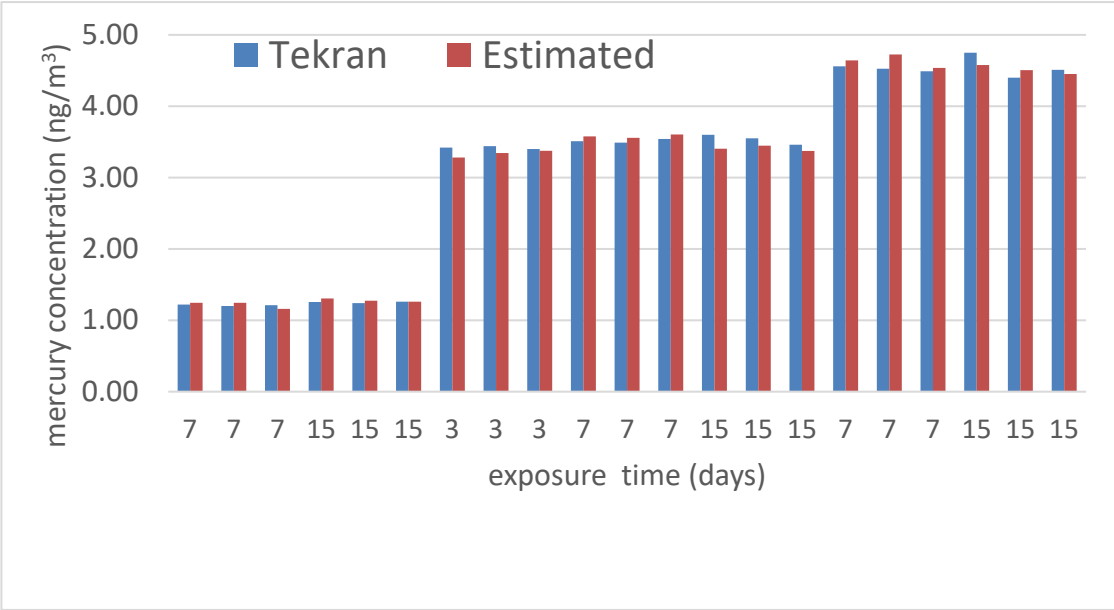
- ✓ Carefully washing of each component in HCl aqueous solution and then in ultra-pure water.
- ✓ Storage in a glove-box under purified air

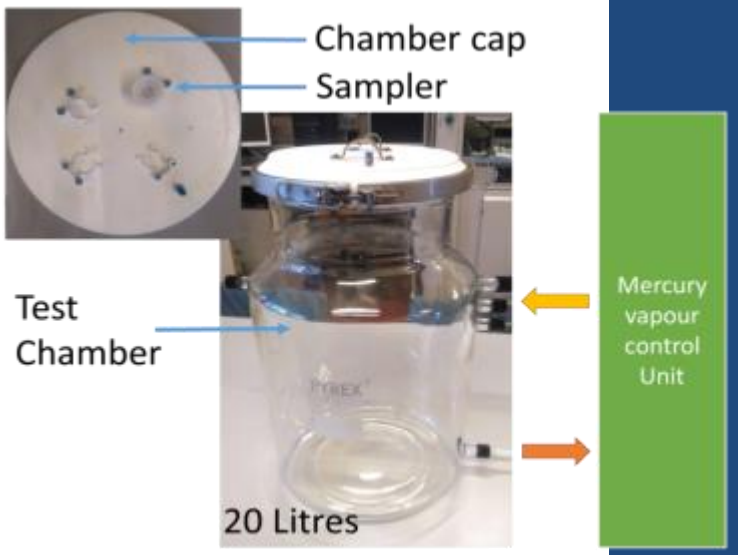


About the SR calculation in laboratory….

The novel Hg passive samplers have been firstly tested in the CNR labs and planned to share them among the selected GMOS sites in different environmental and meteorological conditions, then a detailed plan of sampling campaigns using the passive samplers have been developed for all GMOS sites involved.

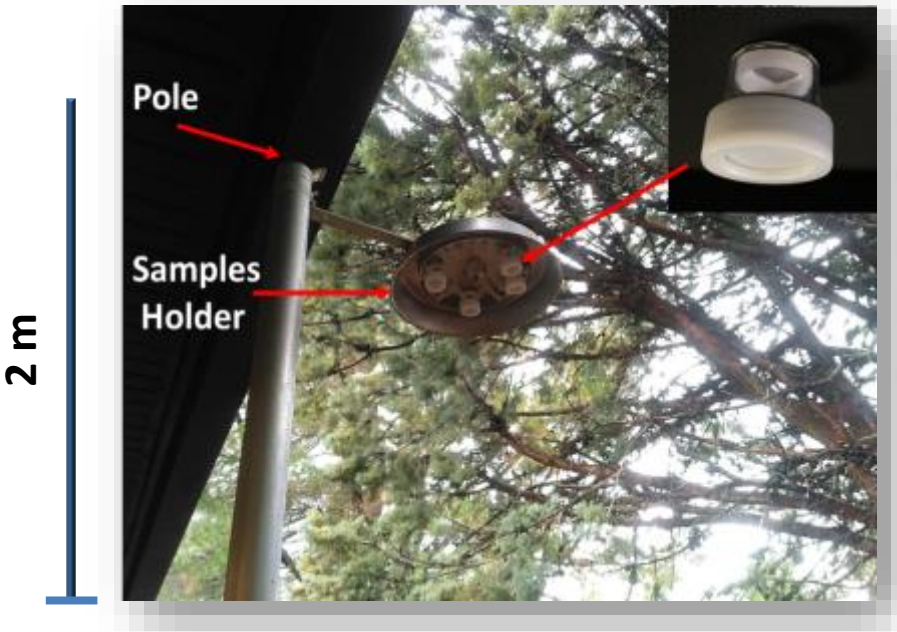
Three different samplers (PAS) were placed in the chamber and were exposed to three concentration values of ≈1.2, 3.5 and 4.5 (ng/m^3) in different time of exposure (3,7 and 15 days, respectively). Each sampler was completely desorbed from Hg^0 before and after each exposure to Hg^0 vapor in air. From each experimental run we have got two significant data: the total adsorbed mercury mass (ng) and the exposure time (days). Using these data, we have been able to calculate the sampling rate value by the Fick law.





From the experiment results we have calculated the medium value of sampling rate that was **0.0142 (m^3/day)** with a very low standard deviation (SD) of **0.000429**.

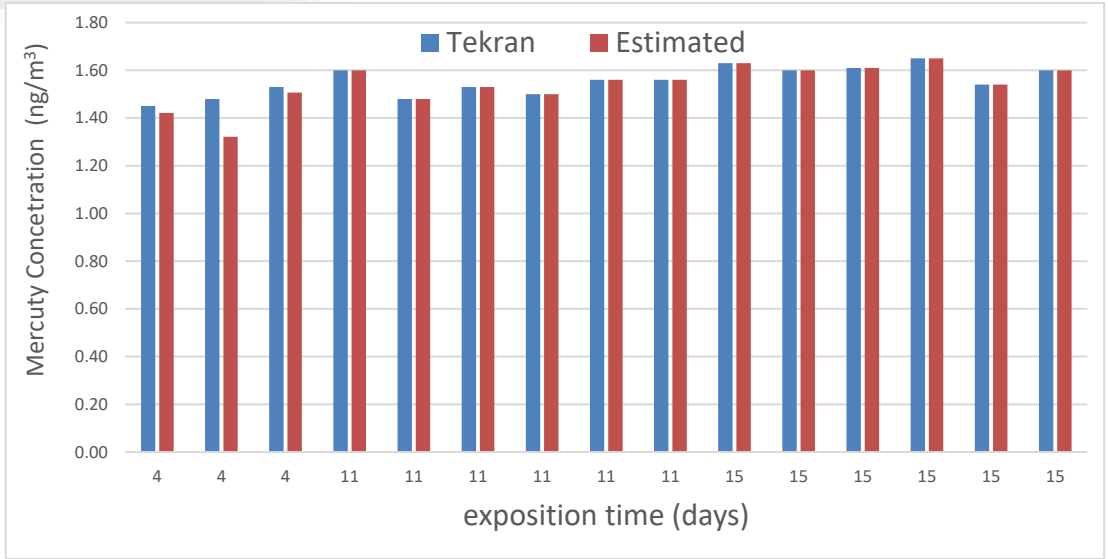
About the SR calculation outside….



PASs were exposed to wind speed of about 8 Km/h ± 5, a temperature vale of 25 °C with excursion values of ± 15 °C (day/night) and a relative humidity value of 45 RH% with max excursion values of ± 25%.

The samplers were exposed for 4, 11, 15 days and the outdoor mercury concentration was in the range of 1.45-1.63 (ng/m³).

Mean value of the sampling rate was **0.0149 m³/day** with a SD of **0.000732**.



About each box for the GMOS campaign….

Passive Sampling Materials

Each box comprises **N. 1 shelter** and **N. 1 complete passive sampling set**.

Each sampling set includes **up to N. 6 bags**, labeled with sequential numbers, holding the samplers required for a 6-week monitoring campaign.

Specifically each bag contains a well defined couples of samplers individually kept under vacuum:

- **Bag 1**: N. 4 couples of under vacuum (u.v.) passive samplers (A1-A2, B1-B2, C1-C2, Blank 1-Blank2)
- **Bag 2**: N. 1 couple of u.v. passive samplers (A3-A4)
- **Bag 3**: N. 2 couple of u.v. passive samplers (A5-A6, B3-B4)
- **Bag 4**: N. 1 couple of u.v. passive samplers (A7-A8)
- **Bag 5**: N. 2 couple of u.v. passive samplers (A9-A10, B5-B6)
- **Bag 6**: N. 1 couple of u.v. passive samplers (A11-A12)

Each passive sampler is kept in a vacuum bag and each vacuum bag comprises:

- ***N.4 self-locking clear plastic bags***;
- ***N.1 sealed glass vessel (PASs)***;
- ***N.1 open-cap mounting a diffusive barrier***

About each PAS serial code….

An alphanumeric code is reported onto each passive sampler and on each vacuum bag for identifying, according to the following scheme:

S2-C2-0316

Specifically, **S2** is a tag related to the **sampling site** (named as S0, S1, S2, S3, S4, S5, S5, S6, S7, S8, S9 respectively).
C is a tag related to the **exposure time**:

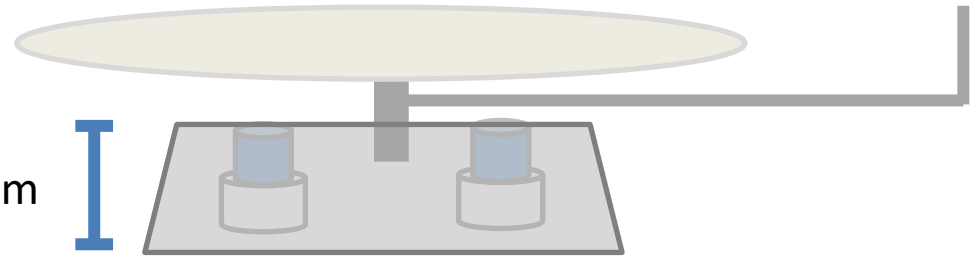
- all the samples named as **A** will be kept exposed to the air for **1 week**;
- all the samples named as **B** will be exposed for **2 weeks** and finally
- all the samples named as **C** will be exposed for **3 weeks**.
- The samples named as Blank (1 and 2, respectively) will be kept exposed throughout the sampling campaign, but tightly closed.

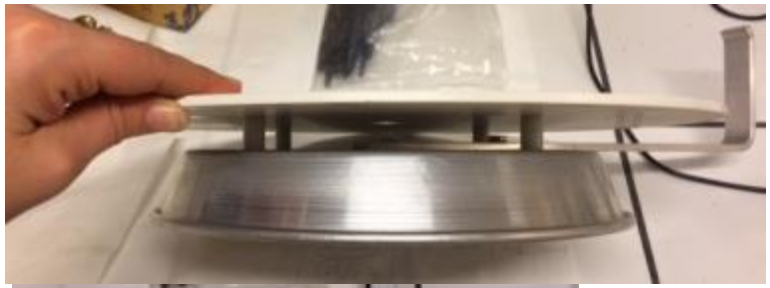
The final 4 numbers (here reported as 0316) are related to the passive batch fabrication.

The number following the label C (i.e. C2) is a serial number related to the sequential sampling within the scheduled sampling procedure.

About the adopted shelter…

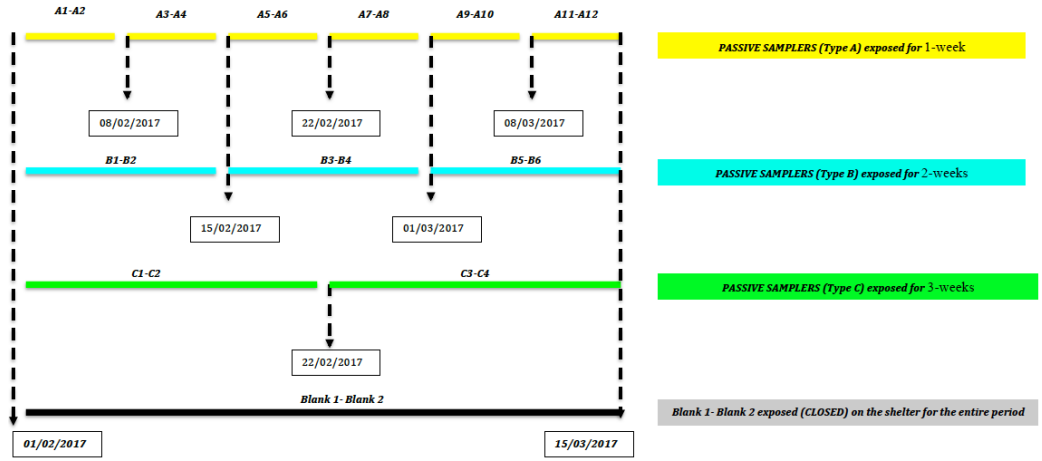
The shelter comprises N. 8 labelled seats to keep up to 8 PASs (A-A, B-B, C-C, and Blanks1 and 2).





When the sampling site has been selected, the shelter should be tied to a pole or a tree by a plastic clamp about **2 meters high**.

About the 1st campaign….

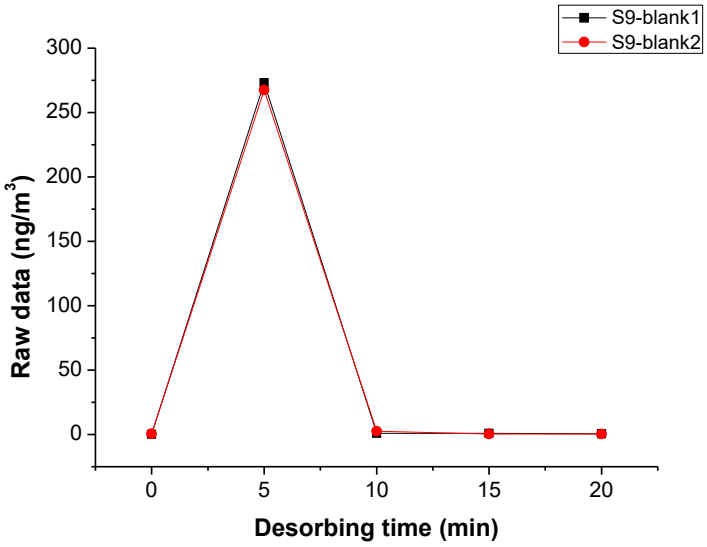


First campaign
(February-March 2017)

Carried out and completed in:
- Mongolia
- Ghana
- India
- China
- Italy
- Argentina
- South Africa
- Japan
- Russian Federation

→COSTA RICA (na)

PASs desorption procedure

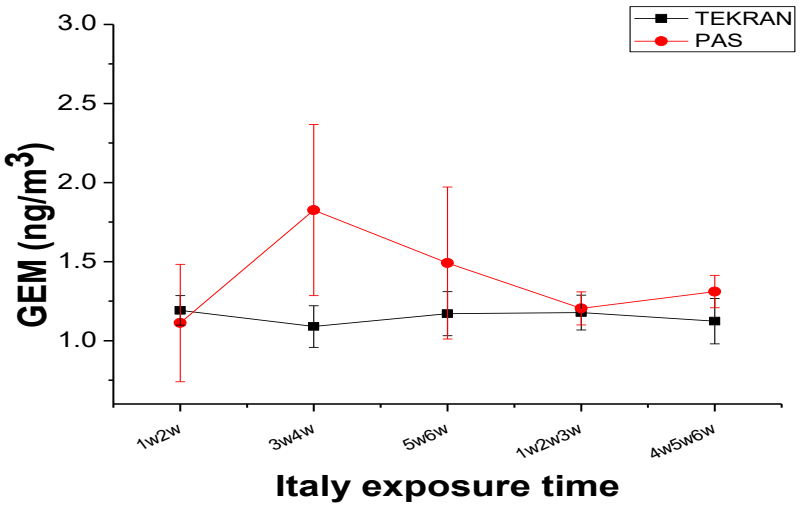


10 min at 550°C under clean air (1L/min)

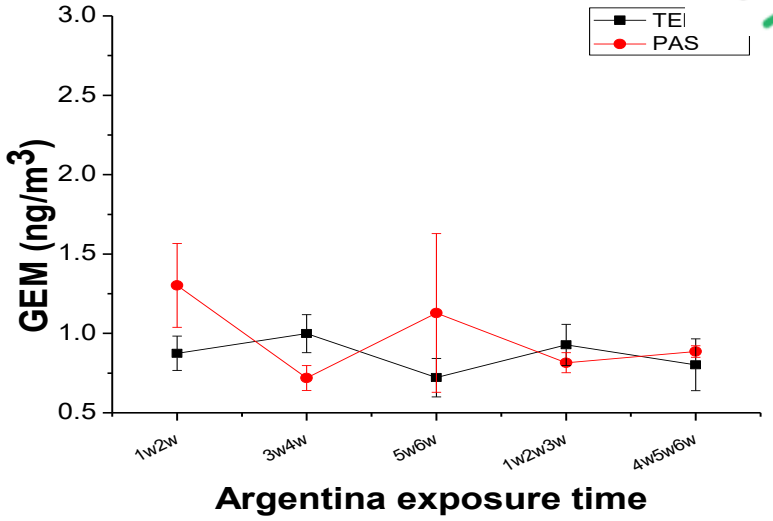
About the 1st campaign….

First campaign
(February-March 2017)

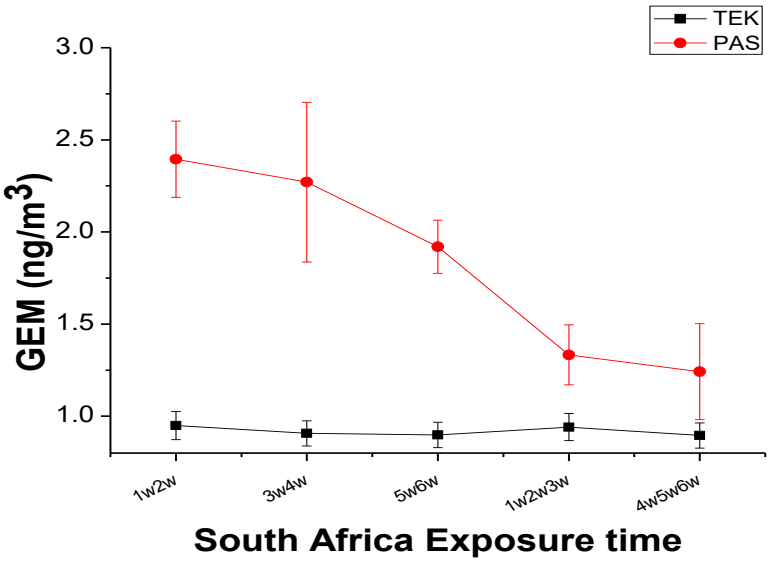
Monte Curcio - ITALY



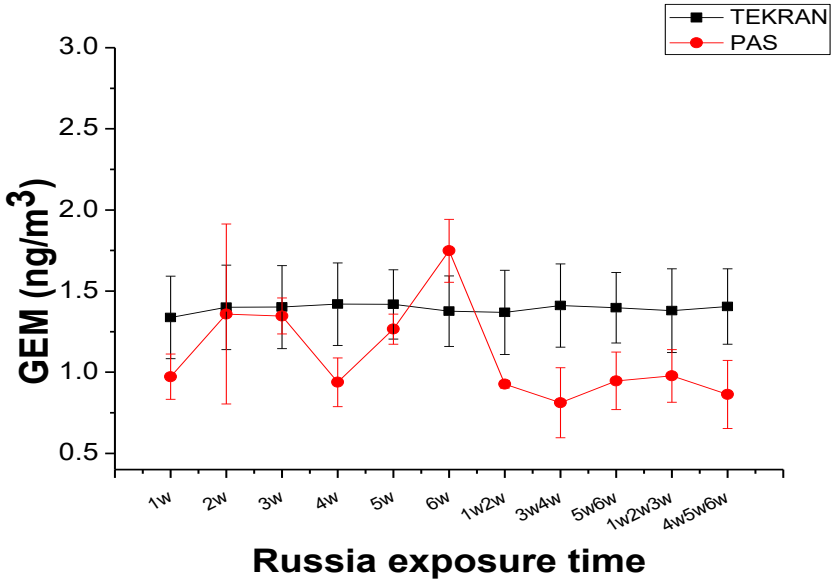
Bariloche - ARGENTINA



Cape Point - SOUTH AFRICA



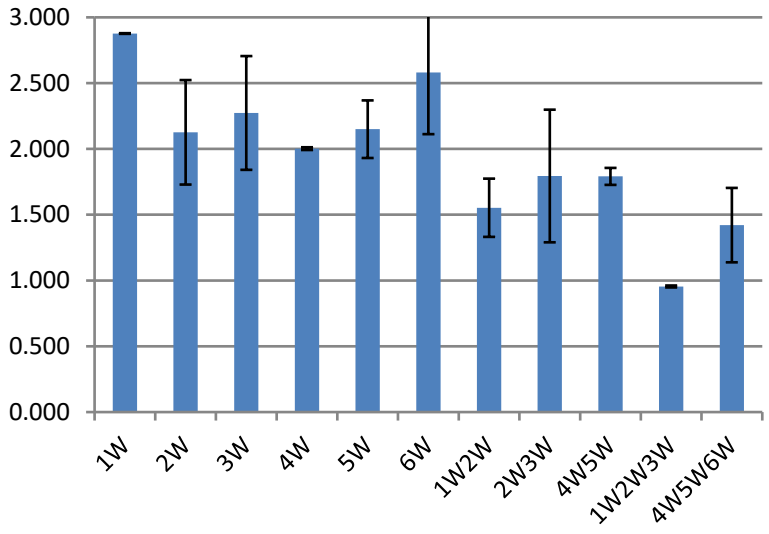
Listvyanka - RUSSIA



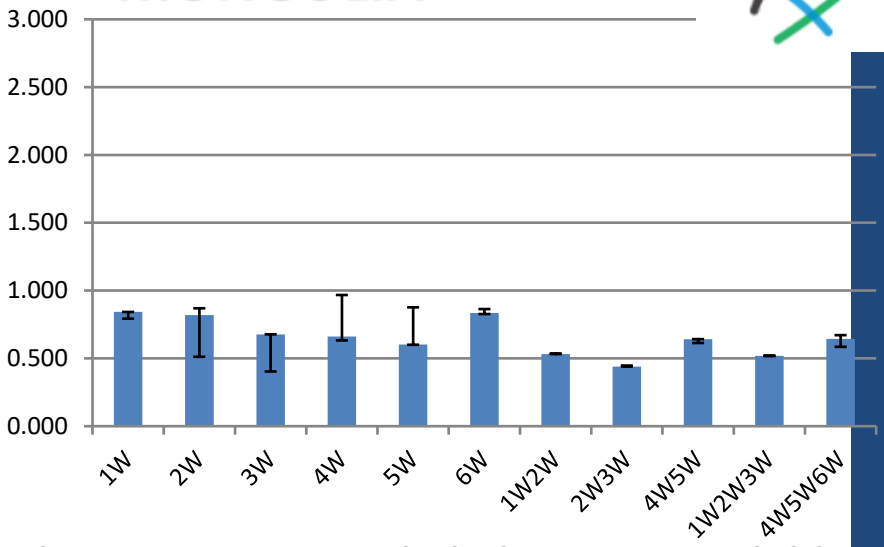
About the 1st campaign….

First campaign
(February-March 2017)

INDIA

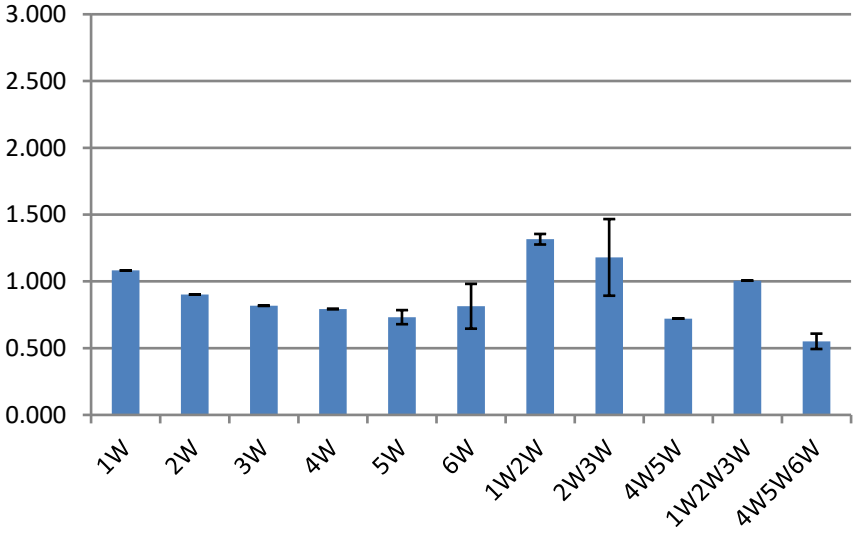


MONGOLIA

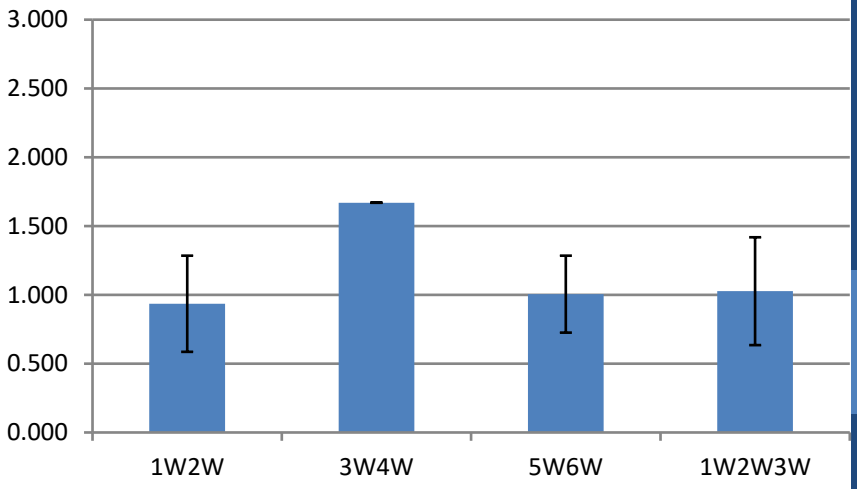


Ghana PASs: no-sealed, data not available

CHINA



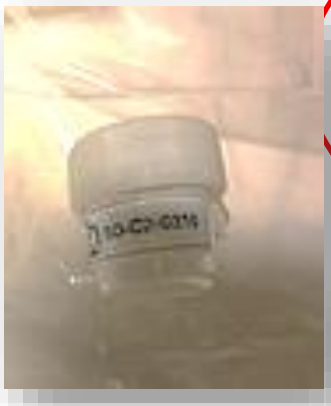
JAPAN



1st PASSIVE SAMPLING CAMPAIGN DRAWBACKS

To avoid:

- ✓ to shift of the adsorbent septum
- ✓ to partially seal samplers
- ✓ to wet samplers
- ✓ to introduce sand/powder within the samplers (by handling?)
- ✓ to expose Blanks too (no-offset)
- ✓ a partial obstruction of the diffusing barrier

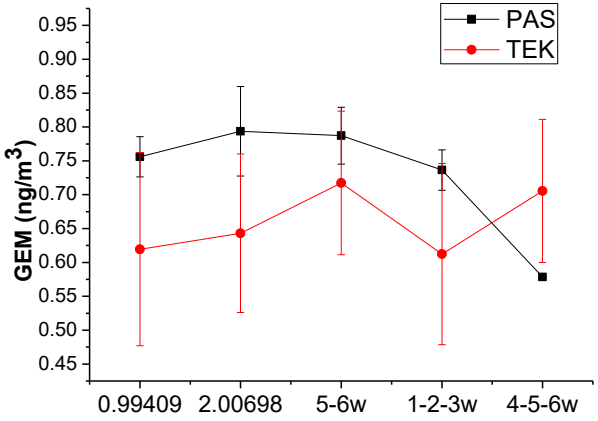


About the 2nd campaign….

Second campaign
(June-July 2017)

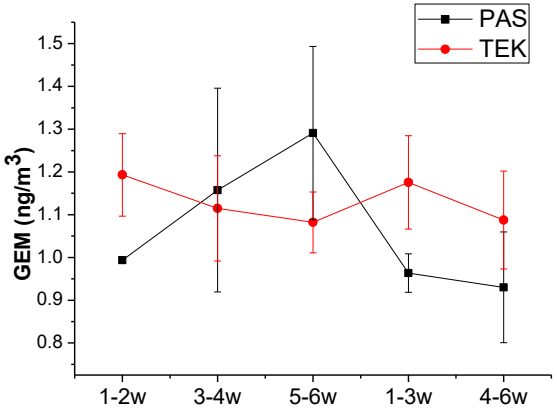
In :
- Italy
- Argentina
- South Africa
- Japan

Bariloche - ARGENTINA

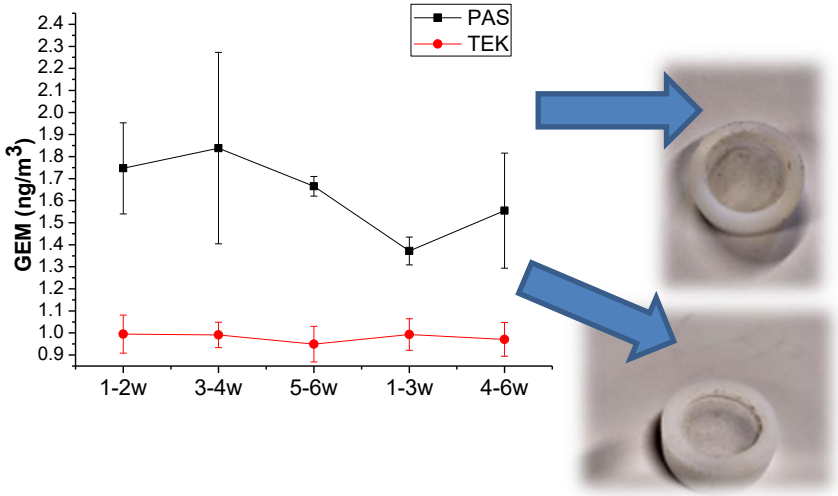


Japan had serious problems with adverse weather conditions (typhoons, hurricanes, heavy rains) thus no scheduling was respected.

Monte Curcio - ITALY



Cape Point - SOUTH AFRICA



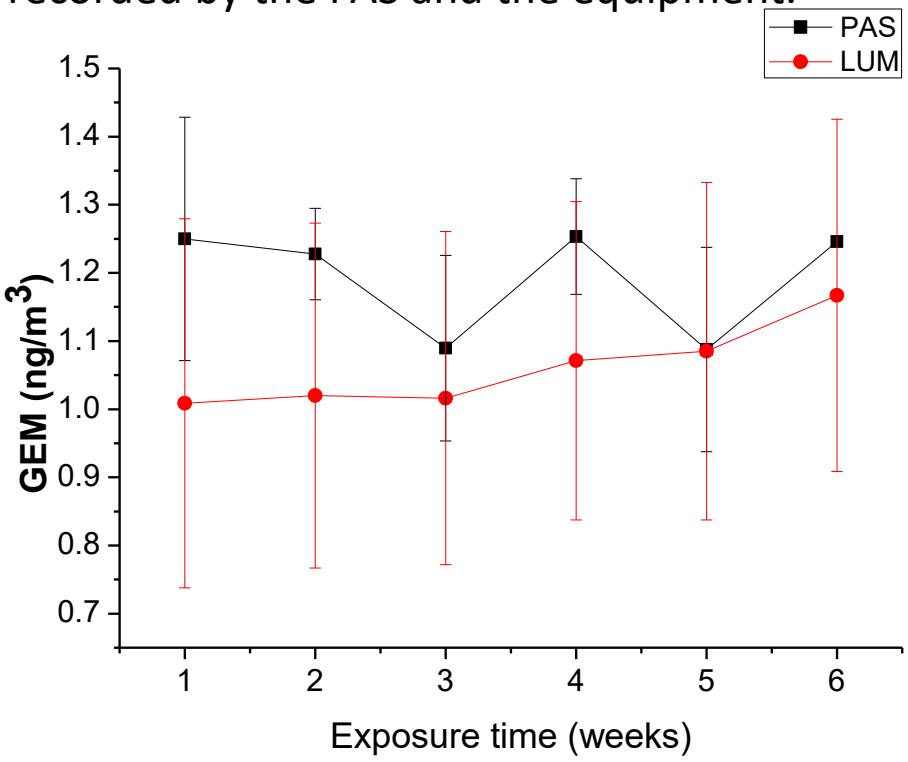
About the 3rd campaign….

Third campaign
(October - November 2017)

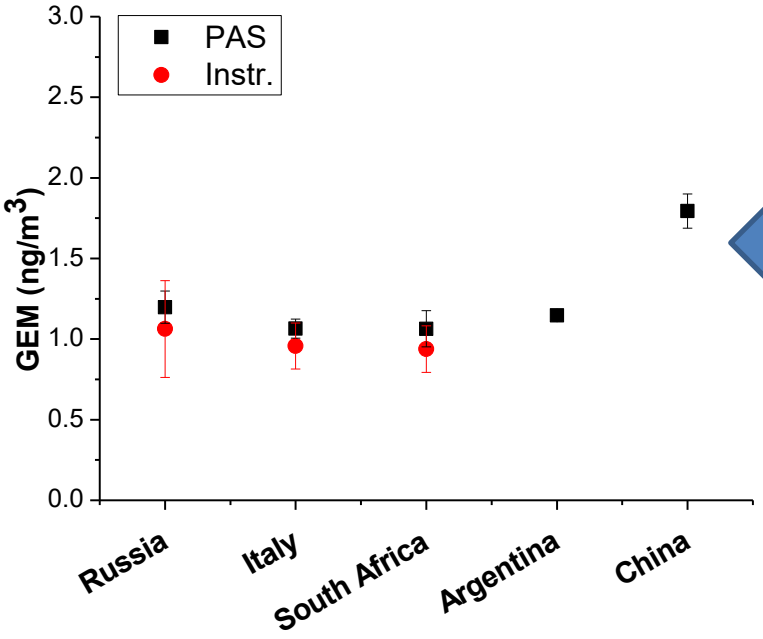
Carried out in:
- Mongolia
- Ghana
- India
- China
- Italy
- Argentina
- South Africa
- Japan
- Russian Federation
- Costa Rica (started late)

Comparison of PAS data with LUMEX data in Russia (6 weeks of exposure)

Further recommendations to close the caps well and seal them with parafilm, added in the packages, seem to have significantly reduced the difference between the values recorded by the PAS and the equipment.



About the 3rd campaign….

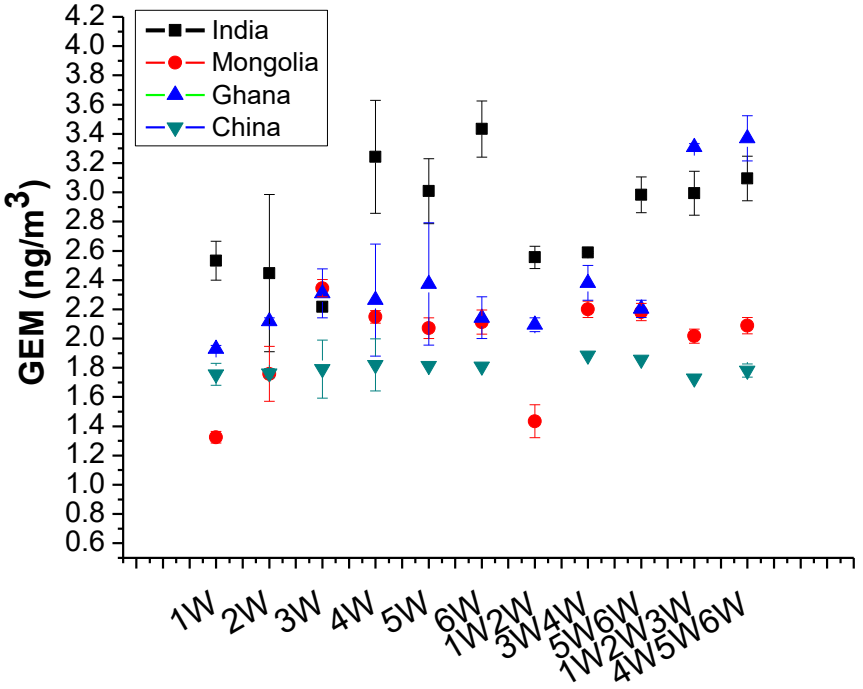


GEM mean values comparison between analytical instruments and PASs:

i) PAS values result within SD of instrumental data

ii) PAS could give infoes when electrical troubles happened on the equipment

Comparison of all the data measured by PASs after exposure to the air of N. 5 different countries in the same time for 6 weeks.



Conclusions

- PASs have been confirmed to be an alternative «low cost» strategy to get information about the amount of GEM in the atmosphere without using sophisticated equipment.
- PASs handlig and storage are key parameters on which to pay great attention to avoid incorrect data.
- The design of the shelter should be shaped according to the SOP, in order to protect better the PASs by extreme environmental conditions (sandstorms, water storms, windstorms) that alter the results with external contamination.
- The novel nano-material seems stable and well attached to the substrate (there are no material losses) as well as stable in time, since it can be exposed to the air and restored by thermal desorption for dozens of times without losing its adsorption characteristics.
- The PAS data collected in these 3 measurement campaigns have shown that it is possible to get comparable results with the analytical instrumental data, but only if the exposure, handling and storage are carried out according to correct procedures.