Remote atmosphere sampling and storage for mercury and very low level trace metals

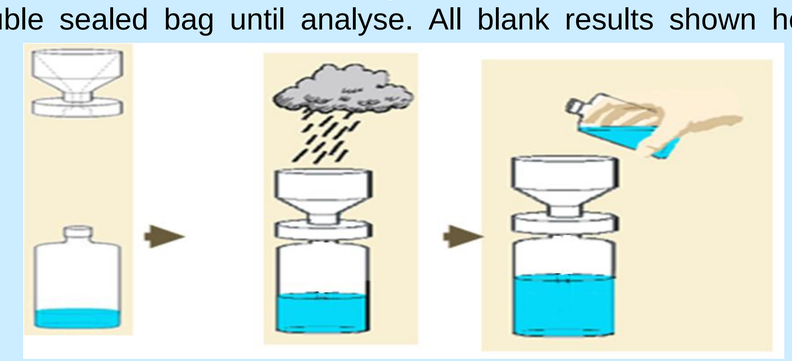
Sylvain Triquet, Elisabeth Bon Nguyen, Alexie Heimburger, Rémi Losno

Introduction:

A lot of studies have shown the difficulty to collect and preserve trace metals in wet deposition samples. Windom and al. (1991) have shown that chemical contamination have compromised measurement in seawater for many years. Benoit and al. (1997) explained the same difficulties in freshwater. Chemical contaminations compromise measurements by increasing original concentrations. Also targeted metals may escape from the sample by absorption, evaporation or diffusion. Mercury is one of the most difficult metals to preserve because Hg is ubiquitous in ambient air as gaseous. The choice of the sampling flask (Amina et al. (1999)), the preservative reagent used, and the cleanup sampling material (Gasparon and al. (1998)) can influence the quality of analytical results. The behavior of mercury storage is completely different compared to other trace metals. Sampling in remote areas induce large delays before analysis (more than 6 month in our case) that considerably enhance contaminations. We present here methods applied to cleanup sampling materials for ultra-trace dissolved metals, including mercury, adapted for long-term storage.

Total atmospheric deposition metal trace method sampling used:

Total deposition is collected using Teflon PTFE machined funnels with a 12 cm diameter. A bottle containing storage solution is screwed at the bottom of the funnel. All this system stands 2 m high at the top of a 10 cm diameter PVC tube secured with Kevlar ropes. After sample collection, the system is rinsed with 60 ml of the storage solution. Next, the bottle is firmly closed and stored in a double sealed bag until analyse. All blank results shown here are experimental field blank.

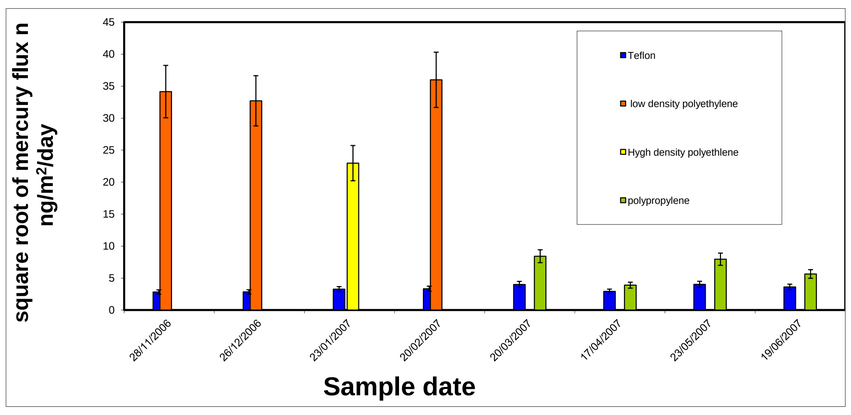


Sample collection protocol

Collector rinsing (Kerguelen island)

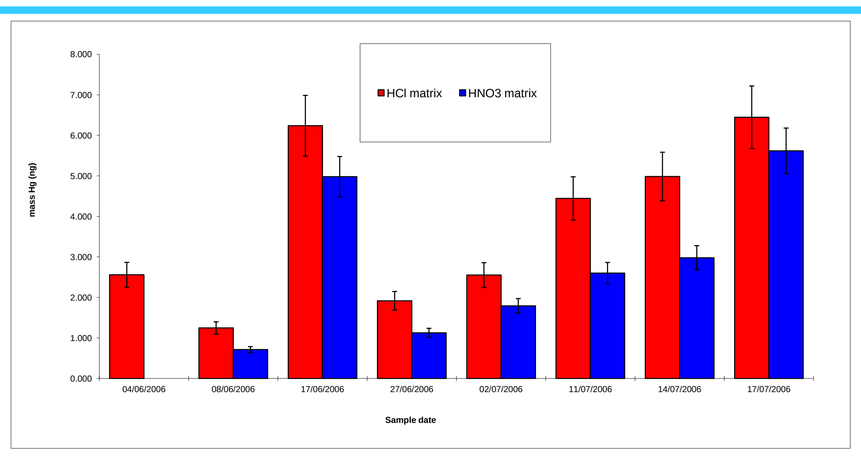
Mercury storage: Bottle material

For the choice of the bottle material, series of samples collected with each time FEP and an another material are compared. All samples are stored with ultra pure hydrochloric acid 2% v/v. **We can observe a good storage for Teflon bottles.**



Mercury storage: acid used

To test the choice of acid, series of 2 collecting samples in Teflon bottles containing hydrochloric and nitric acid (2% v/v) were compared. **We can observe a better storage with hydrochloric acid.**



Procedure of bottles decontamination

The decontamination method was performed using Cossa et al. 2003 procedure and standard EPA 1631 revision E protocol:

Hand dishwashing (dust removal)

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detergent Decon® Bath for 24 hours

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Bath of Normapur® nitric acid diluted with osmosis water (10% v/v) for one week

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Bath of Nnormapur® hydrochloric acid diluted with osmosis water (10% v/v) for one week

↓

Bottles are filed with ultra pure hydrochloric acid and ultra pure water under horizontal laminar air flux cabinets for a minimum of 3 week

Site de collecte	Mass of mercury in blanks (pg)	RSD	Approximate mass collected in each samples (pg)
Vouzon (France)	176	26%	1000
Niger (Africa)	214	No calculated	3000
Kerguelen (TAAF)	160	37%	550 for 5 samples

the storage method of environmental samples of mercury is effective enough for provides high quality measurements even with a long time between the collection and the analysis

Other trace metals storage:

Hydrochloric acid is generally used to clean bottles but **it's important to clean them with nitric acid to ensure the total removal of contamination from the surface of the bottle because ultra pure nitric acid (2% v/v) is then used to store the sample (HNO_3 matrix)** .

For the same reason, the **concentration of acid used must be higher than the concentration of the matrix.**

For cost problem, polypropylene bottles are chosen instead of Teflon material. **PP can be used if the washing procedure is strictly executed.**

Hand dishwashing (dust removal)

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detergent Decon® Bath for 24 hours

↓

Bath of Normapur® nitric acid diluted with osmosis water (10% v/v) for one week

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Bath of Nnormapur® hydrochloric acid diluted with osmosis water (10% v/v) for tow week

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Bottles are rinsed five times with ultra pure water and next filed with Suprapur® hydrochloric acid diluted in ultra pure water (5% v/v) in ISO5 clean room under horizontal laminar air flux cabinets for a minimum of 5 month

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Bottles are rinsed again five times with ultra pure water and refiled with Suprapur® hydrochloric acid diluted in ultra pure water (5% v/v) in ISO5 clean room under horizontal laminar air flux cabinets for a minimum of 4 month

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Finally, bottles are rinsed at least 6 times and dried under ISO1 horizontal laminar air flux cabinets before using

Analytical results from Kerguelen Island (Southern Ocean)

	Fe µg/L	Al µg/L
Analytical blanks	0.1	0.02
Field blanks	1.7 ± 0.35	3.9 ± 1.4

Expressed as amounts, filed blanks are never larger than 10% of the deposit quantities in any collected samples

we can say that the ultra clean washing method is validated