The effects of *sampling, handling,* and *analysis* on measured MMHg concentration in estuarine sediments

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RMP MMHg Data Needs

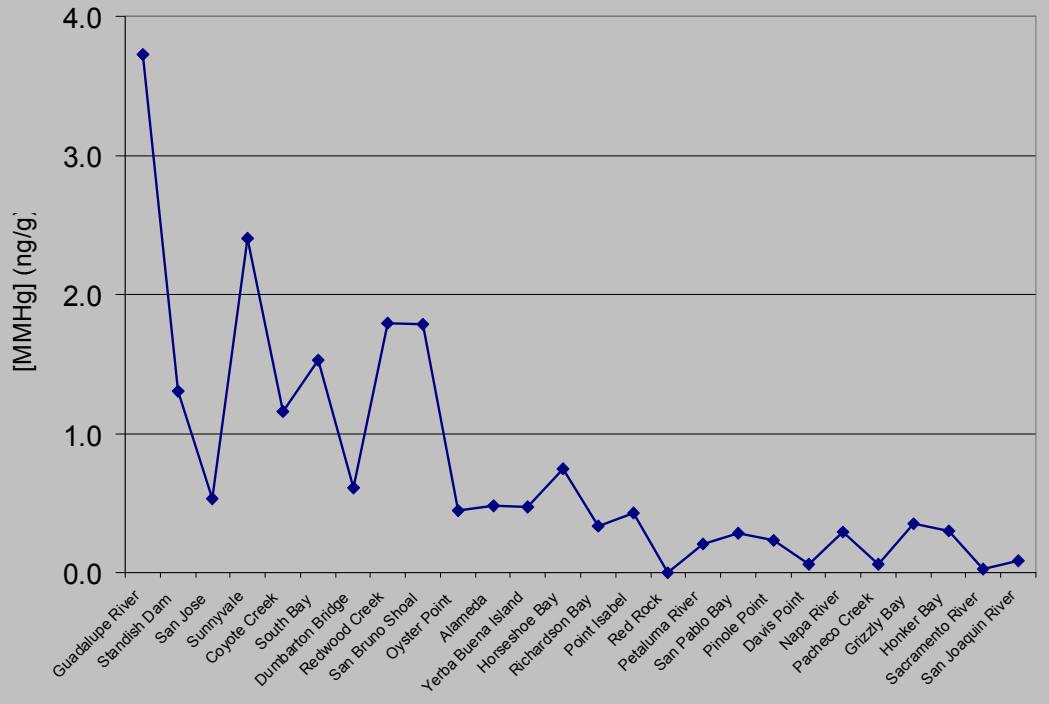
- Representative
  - Of the portion available to biota
  - Without excessive cost (many many dupes)
- Accurate
  - Minimize artifacts of sampling or handling
  - Minimize bias in analysis

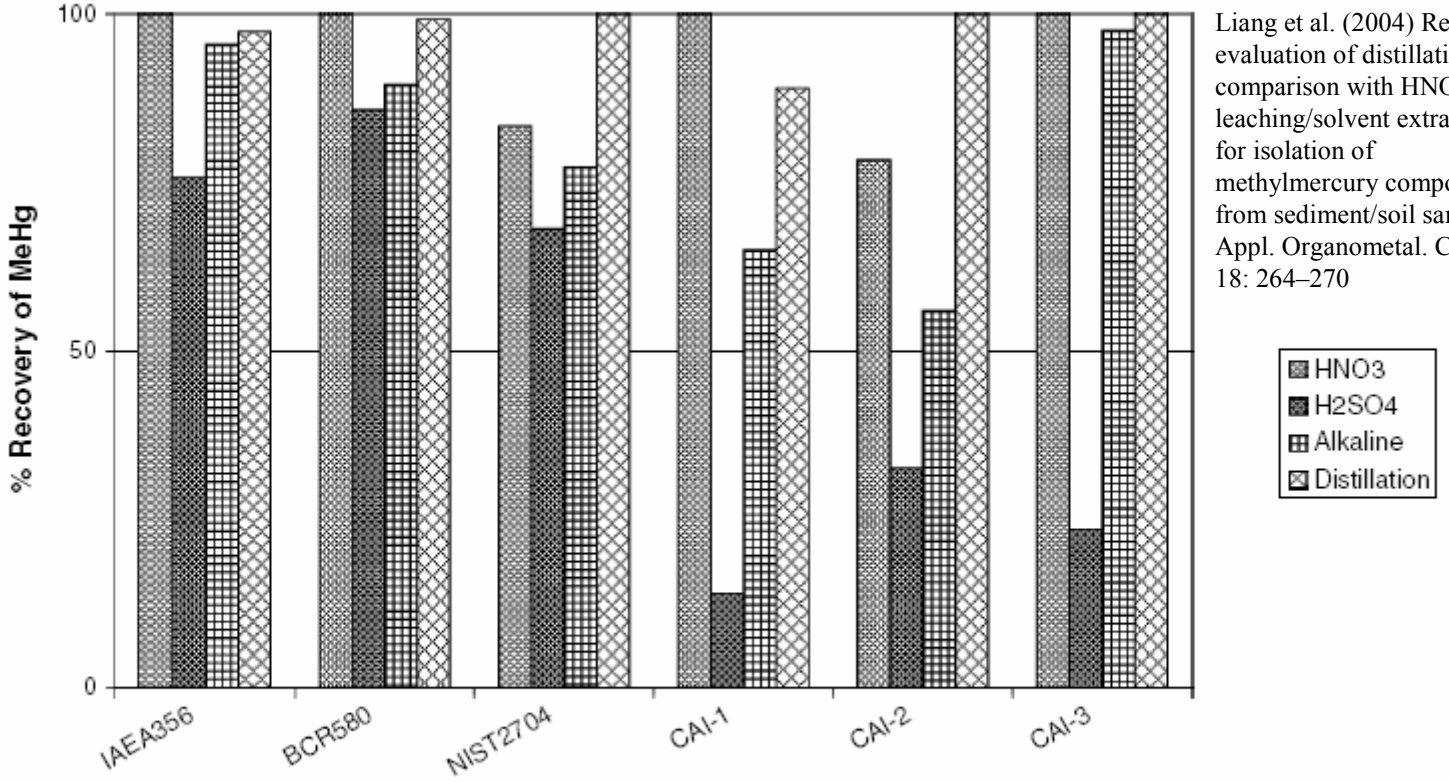
Sometimes aims work at cross purposes

Current RMP sampling and analysis procedure

- Van Veen grab
  - Triplicate grabs composited
  - 20min limit until…
- Freezing
  - Dry ice
- Storage
  - Holding time 1yr (+?)
- Analysis
  - Acid digest organic extraction

Sufficient to avoid artifacts?





Liang et al. (2004) Re-evaluation of distillation and comparison with HNO3 leaching/solvent extraction for isolation of methylmercury compounds from sediment/soil samples Appl. Organometal. Chem. 18: 264–270

Figure 1. Comparison of MeHg results in typical sediments and soils using different isolation techniques. Highest value of each sample is presented as 100% in the figure.

Method of analysis

H_2SO_4 method most common

Artifact of others or low bias?

Table 1. Samples used for investigation[a]

Sample ID	Type	Location	THg (μg g^{-1})	MeHg (ng g^{-1} as Hg)	Status
IAEA 356	Estuarine sediment	Mediterranean	7.35*	5.46*	Dry
BCR 580	Estuarine sediment	Ravenna Lagoon	132*	69.5*	Dry
NIST 2704	River sediment	Buffalo River, NY	1.44*	4.28	Dry
CAI-1	Gravel soil	TN, USA	6.85	7.52	Wet
CAI-2	Bog sediment	B.C., Canada	4.24	2.91	Wet
CAI-3	Compacted clay and gravel soil	GA, USA	5.26	2.68	Wet
CAI-4	Bog sediment	B.C., Canada	4.39	2.46	Wet
CAI-5	Bay algae sediment	FL, USA	0.117	0.207	Wet
CAI-6	Bay algae sediment	FL, USA	0.023	0.145	Wet

Method of analysis

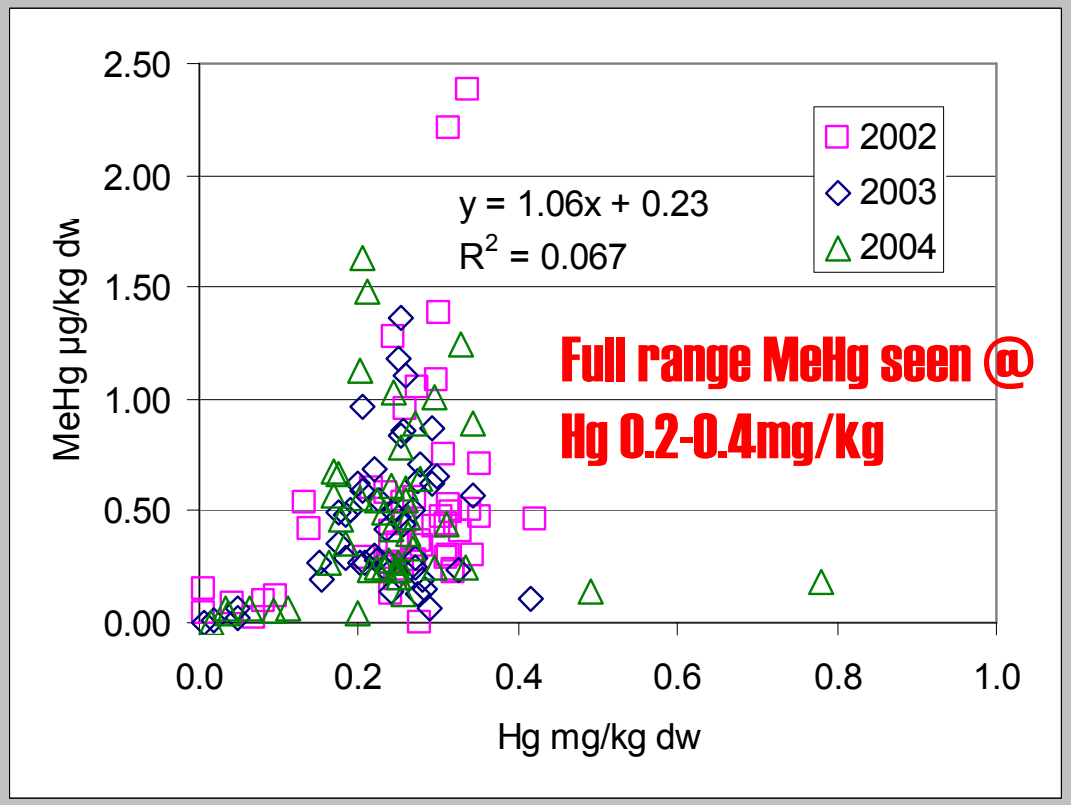
Table 2: Methylmercury in Sediment Intercomparison - Results Summary

QC Parameter	Laboratory Intercomparison Study Summary Methylmercury in Sediment				
	Laboratory A	**Laboratory B**	**Laboratory C**	**Laboratory D**	**Laboratory E**
Mean Sediment Reference Material	**2.82 ng/g** 2.6% RSD n=3	**3.31 ng/g** 5.5% RSD n=3	**6.29 ng/g** 11.3% RSD n=5	**3.41 ng/g** 9.7% RSD n=3	**3.76 ng/g** 1.2% RSD n=3
Mean Method Blank	**0.008 ng/g** n=3	**0.003 ng/g** n=3	**Not reported**	**<MDL**	**0.011 ng/g** n=3
Estimated MDL	**0.000 ng/g**	**0.002 ng/g**	**n/a**	**<MDL**	**0.011 ng/g**
z-score	**-3.585**	**-0.736**	**n/a-outlier**	**-0.155**	**1.860**
Preparation Method	**$MeCl_2$ Extraction**	**$MeCl_2$ Extraction**	**Distillation**	**$MeCl_2$ Extraction**	**$MeCl_2$ Extraction**
Analytical Method	**Aqueous Phase Ethylation CVAFS**	**Aqueous Phase Ethylation CVAFS**	**Aqueous Phase Ethylation CVAFS**	**Aqueous Phase Ethylation CVAFS**	**Aqueous Phase Ethylation CVAFS**

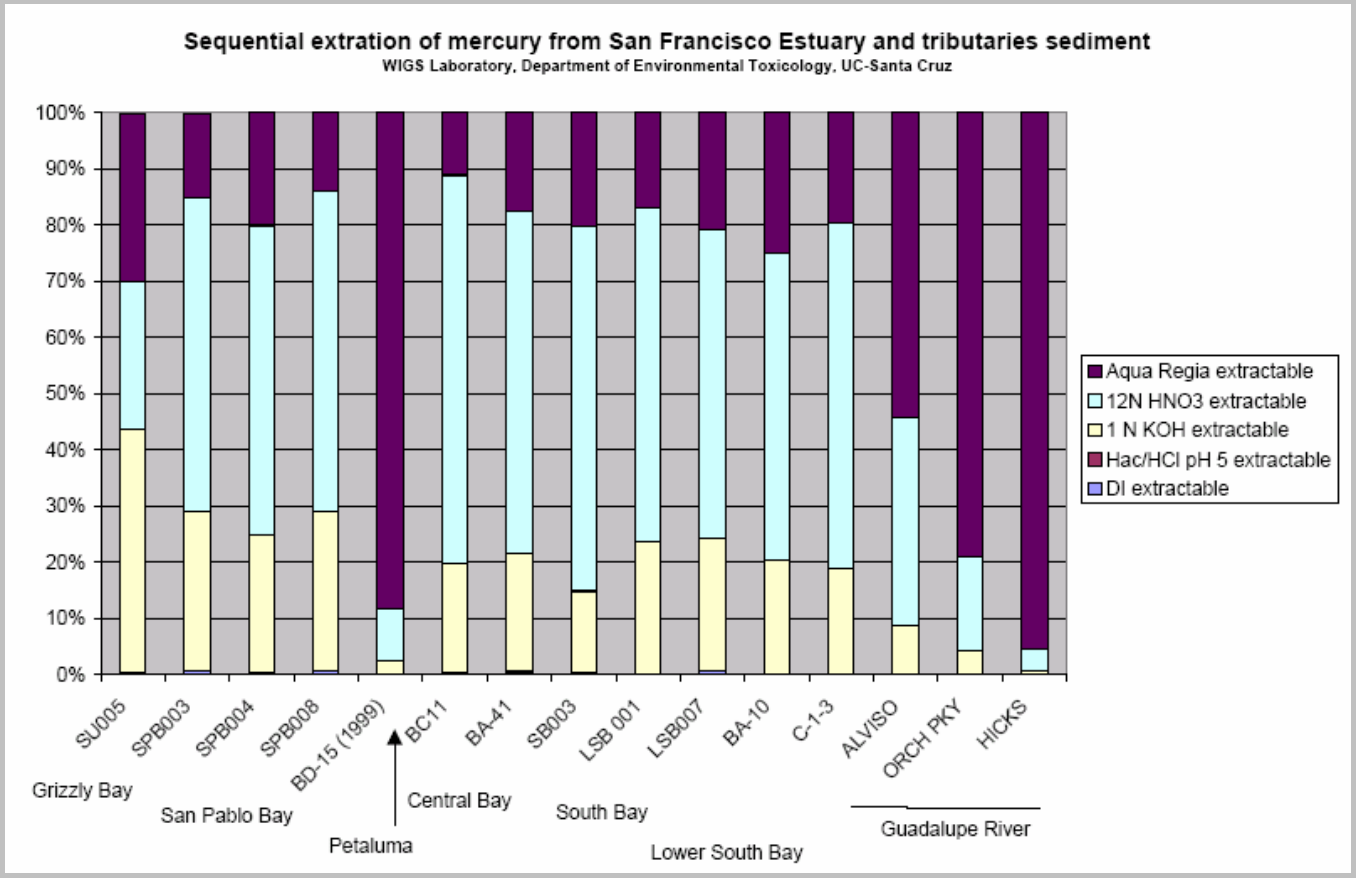
Note: Referee Laboratory is designated as Laboratory B
Results from Laboratory C have been excluded as outliers

The California Bay-Delta Authority Mercury Studies Quality Assurance Program Intercomparison

Not All Hg Equally Methylated



Reactive Fractions: KOH and Below?



Proposed Study Elements

- Sample handling & compositing (~40%)
  - Chill vs freeze, composite vs small subsample grabs
- Analysis (repeat Liang in marine sed ~10%)
  - Distillation, sulfuric, nitric, or basic extraction
  - Repeats of some RMP (sulfuric) & CRM samples
- Reactive/bioavailable Hg (~50%)
  - $SnCl_2$ reduction or sequential extractions a la Bloom
  - Evaluate whether Hg lability has any correlation to methylation

Items to investigate: Discussion

- Sampling
  - Compositing, discrete sampling, minicoring
    - Easy to implement, not technically difficult, but real sediment is 'messy'
- Handling
  - Freezing, flash-freezing, wet sieving in field
  - Storage and freeze drying
    - Also applies to total mercury
  - Processing under N_2?
    - May be difficult to implement, requires investment in equipment
- Analysis
  - Analytical methods comparison?
    - Distillation/acid-organic method/isotopic methods
    - UCSC can set up multiple methods of separation and detection
  - Effect of porewater content on analysis?

Definitions

- **Sampling**
  - Removal of sediment from environment
- **Handling**
  - Storage, pre-treatment
- **Analysis**
  - Extraction and detection

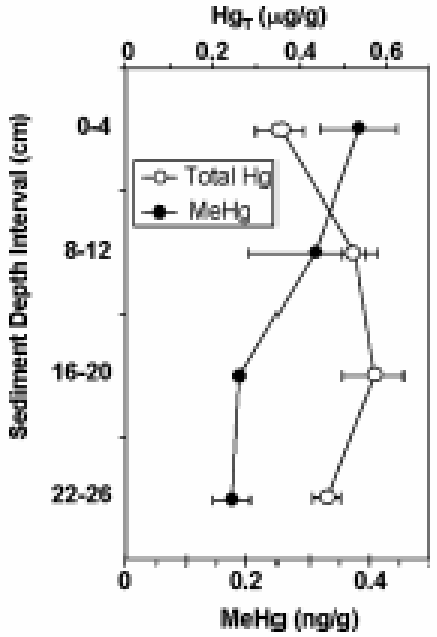
My first mercury sample, with Martha Thomas
Guadalupe River at Standish Dam, 1999

What is the problem?

- Stability of analyte
  - A balance of in situ production/degradation
  - Stable with respect to temperature, pH
  - Unstable with respect to biologic activity, light, redox agents
- Difficulty of extraction
  - Soluble in water, but likes organic material
- Artifact formation
  - Methods can make MMHg out of reactive Hg in matrix during analysis.

Sampling effects

- [MMHg] shows spatial variation
  - *Real sediment looks messier than graph*
  - *RMP samples top 0-2 cm?*
- Compositing may have an effect



Marvin-DiPasquale et al. (2003) Microbial cycling of mercury in contaminated pelagic and wetland sediments of San Pablo Bay, California. Environmental Geology, 43(3): 260-267.

Fig. 3
Sediment depth profiles of mercury (Hg_t) and methylmercury (MeHg) concentration in San Pablo Bay (CA) at site 3. *Error bars* equal one standard deviation of the mean of duplicate samples measured twice (i.e., n=4). Note different scales

Sample handling under N_2 and porewater extraction

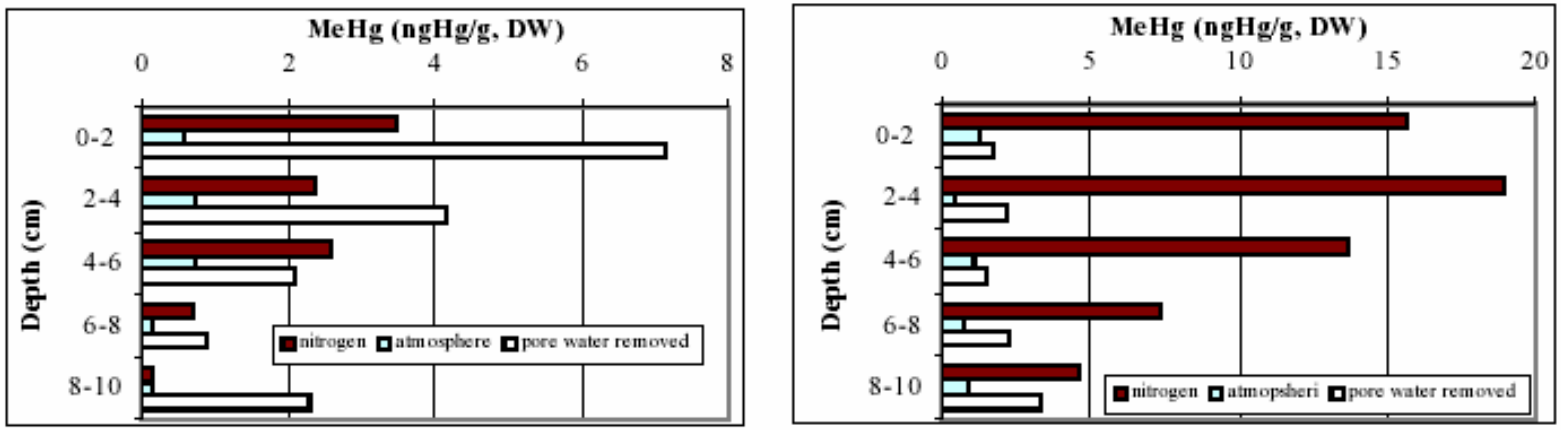
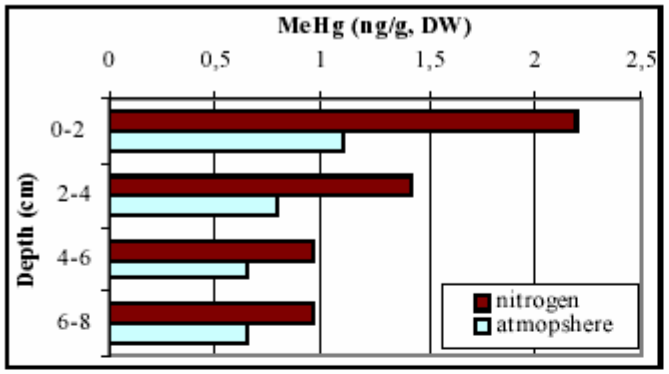
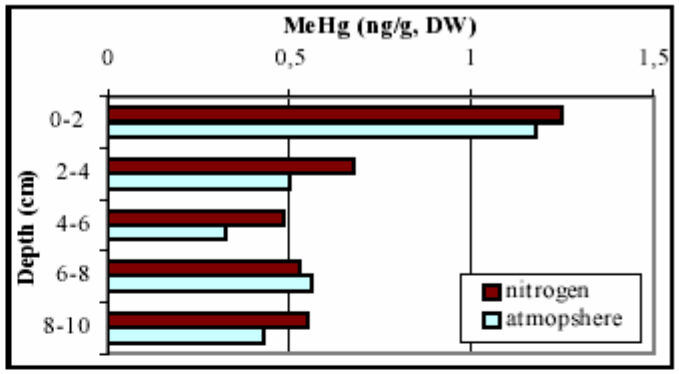


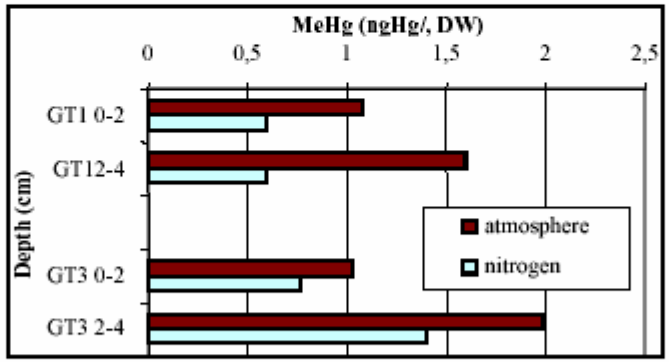
Figure 1. Concentrations of MeHg in sediments obtained during different sample preparation procedures in Minamata (left) and Fukuro Bay (right), November 2000. Left: Minamata Bay, where the total Hg concentration varies between 2 to 6 mg/kg, DW; right: Fukuro Bay , total Hg concentration varies between 7 to 8 mg/lg, DW.

Horvat, et al. (2004) The effect of sampling and sample pretreatment on MeHg concentration in coastal marine sediments. RMZ-Materials and Geoenvironment 51(3).

Sample handling under N_2







Horvat, et al. (2004) The effect of sampling and sample pretreatment on MeHg concentration in coastal marine sediments. RMZ-Materials and Geoenvironment 51(3).

Figure 2. Concentrations of MeHg in sediments obtained using different sample preparation procedures in the Gulf of Trieste, September 2003. Left: Station GT3 with total Hg concentration between 2 to 4 mg/kg and right at the station GT1 where total Hg concentration is below 1 mg/kg. The figure below shows the results obtained in duplicate cores.

Handling under N_2 and porewater extraction

Horvat et al. (2004) The effect of sampling and sample pretreatment on MeHg concentration in coastal marine sediments. RMZ-Materials and Geoenvironment 51(3).

- Marine sediment cores cut in cm slices under N_2 on-board ship
- Stored in plastic containers and kept under N_2
- Divided in lab:
  - One under N_2 throughout sample homogenization, weighing and first extraction step
  - Other exposed to normal atmosphere
- Porewater removed from some sediment core by centrifugation under N_2, then analyzed under normal conditions.

Options

- Sampling
  - Coring, compositing, grab, micro-scale sampling
- Handling
  - Wet sieving, freezing, flash-freezing, freeze drying, porewater extraction (centrifuge), inert atmosphere, holding time.
- Analysis
  - Distillation, acid digest/organic extraction (sulfuric or nitric), basic organic digest (KOH/methanol), isotopic spiking