

# Comparison of Two Methods for the Measurement of Methyl Mercury Concentrations in Penobscot River Sediments

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## Introduction

Acid distillation and solvent extraction methods<sup>1,2,3,4</sup> are widely used to determine monomethyl mercury (MMHg) content in sediments. During initial phases of the Penobscot River Mercury Study in Maine, USA in 2006 – 07, both methods were evaluated for performance. A combination of results from 3 laboratories (Flett Research Ltd., Battelle Marine Sciences Laboratory and Trent University) indicated the following:

- Results from solvent extraction average ~50% lower than acid distillation (number of tested samples >200);
- CRM IAEA-405 and matrix spike recoveries were similar and good with both methods;
- Artifact generation from conversion of Hg<sup>2+</sup> to MMHg in acid distillation<sup>2,4,5</sup> is low (<0.1%) according to isotopic labeling method<sup>6</sup> and non-isotopic standard addition Hg<sup>2+</sup> spike recovery and therefore is not a major factor for higher distillation results.

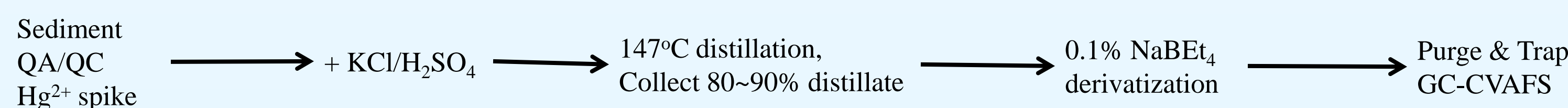
The cause of the discrepancy was unclear and therefore it was decided to test the following hypothesis: **Distillation is providing the correct methyl mercury concentrations and the application of heat and/or acid is required to release methyl mercury for accurate determination by the solvent extraction method.**

Two large well-homogenized sediment samples (one river and one estuary, taken as part of QA/QC procedures for the Penobscot Study) were used to test this hypothesis.

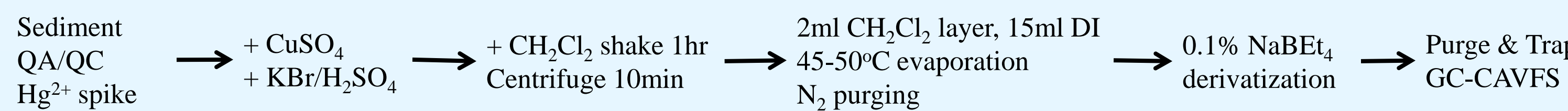
## Methods

Sediments from two sites in Penobscot River, Maine, USA were sampled in this study. ES2 was obtained from the river estuary, whereas OB2 was taken upstream from the estuary. In the flow chart below, DI is ion-exchanged pure water. KCl/H<sub>2</sub>SO<sub>4</sub> is 1.6% KCl in 8 M H<sub>2</sub>SO<sub>4</sub> solution. CuSO<sub>4</sub> is 1M CuSO<sub>4</sub> solution. KBr/H<sub>2</sub>SO<sub>4</sub> is 18% KBr in 10% H<sub>2</sub>SO<sub>4</sub> solution. CVAFS is cold vapor atomic fluorescence spectrometry, QA/QC includes MMHg matrix spike, inorganic Hg<sup>2+</sup> spike and sediment CRM IAEA405. When wet sediments were analysed, all MMHg concentration was normalized into dry weight basis, as ng/gdw.

### 1. DISTILLATION with KCl/H<sub>2</sub>SO<sub>4</sub>



### 2. REGULAR SOLVENT EXTRACTION with KBr/H<sub>2</sub>SO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub>

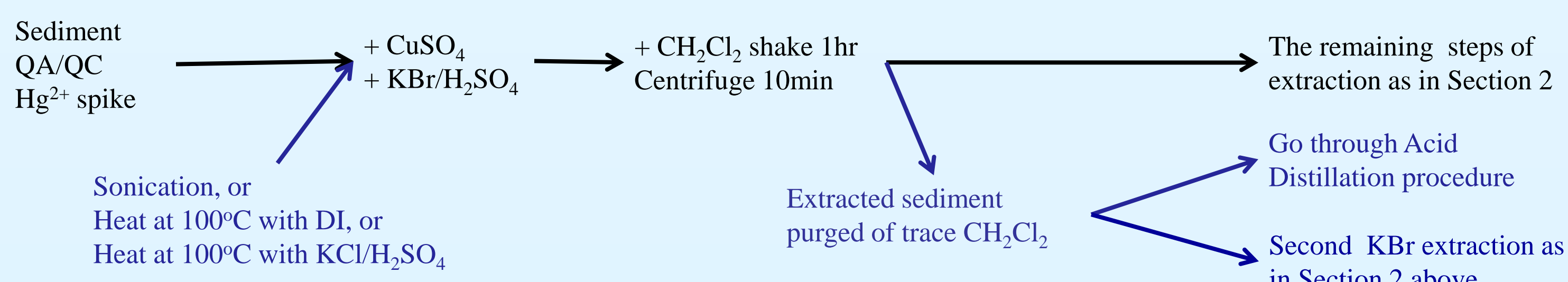


### 3. MODIFICATIONS of the REGULAR SOLVENT EXTRACTION

#### 3.1 Distill the previously extracted sediment

#### 3.2 Extract the previously extracted sediment

#### 3.3 Sample pretreatment with 100°C heat and DI OR 100°C heat and KCl/H<sub>2</sub>SO<sub>4</sub> OR Sonication

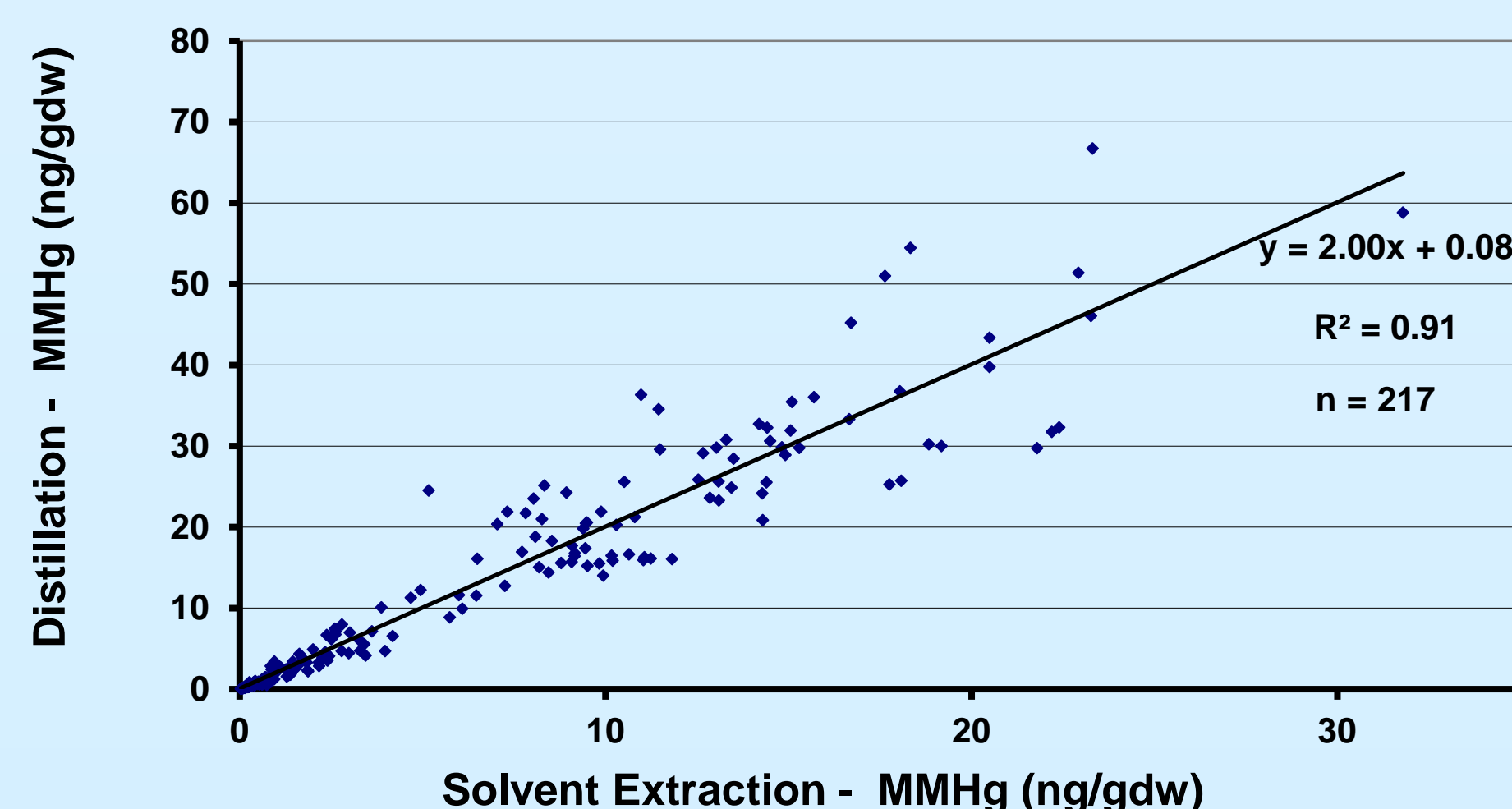


### 4. INORGANIC Hg<sup>2+</sup> SPIKE CONVERSION TO MMHg

For each experiment above, External Hg<sup>2+</sup> spike was included to evaluate the MMHg conversion. Hg<sup>2+</sup> spike is more than 1000 X MMHg concentration measured from Acid Distillation.

## Results

1. Some of the Penobscot River Mercury Study data that prompted the present investigation. All results corrected for spike recovery. Acid distillation recovered MMHg at an average of **2.13 times** of that recovered by solvent extraction.



Results from May and July 2007 Sediments, all core depths included

2. Trace level isotopic Hg labeling experiments showed 0.01% to 0.04% inorganic Hg<sup>2+</sup> converted into MMHg while high level non-isotopic Hg<sup>2+</sup> spike experiments showed 0.07% conversion occurred in the distillation of Penobscot River sediments, vs 0.03% found in extraction. The artifact MMHg determined by isotopic labeling procedure was less than 2.4% of the MMHg value determined by the distillation method.

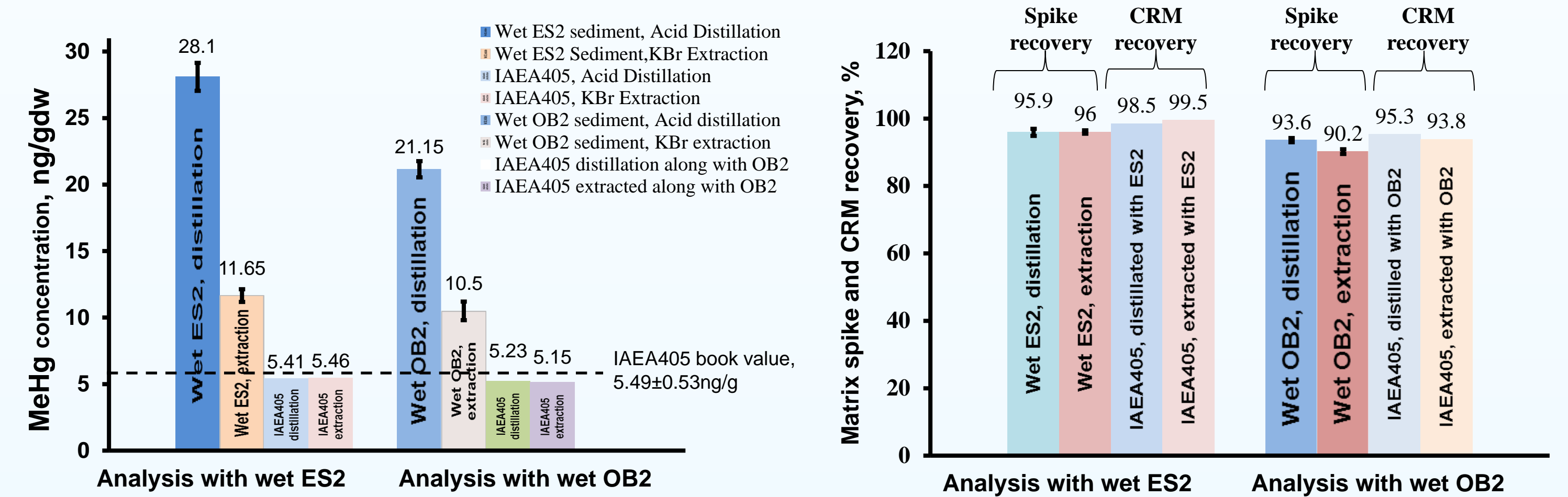
Sample Station	Sample Description	Ambient THg*, ng/gdw	Ambient MMHg, ng/gdw	Average <sup>200</sup> Hg methylated (artifact), %
OV5 (n=3)	freshwater	51	0.72	0.01
OB2 (n=3)	tidal river	1022	25.0	0.02
OB4 (n=6)	tidal river	1078	15.1	0.03
ES2 (n=6)	estuary	1622	27.3	0.04

\*: THg results listed here are site average of 2007 from all labs

ES2 and OB2 sediment samples used in this study have Total Hg of 892 and 1185 ng/gdw respectively, MMHg (by distillation) of 28.1 and 21.2 ng/gdw respectively. With typical 0.07% conversion found in distillation, the artifact MMHg generated (as a % of ambient) is 2.2% for ES2 and 3.9% for OB2. This artifact is not a major contributor to the large discrepancy between the two methods.

## Results (Continued)

3. Solvent extraction MMHg results on ES2 and OB2 wet sediment are about half of those determined by distillation even though Matrix Spike recoveries and CRM IAEA405 recoveries were all better than 90% with either method.



4. Sonication pretreatment of wet ES2 sample before going through solvent extraction didn't improve MMHg recovery. The MMHg detected was still half of that determined by distillation.

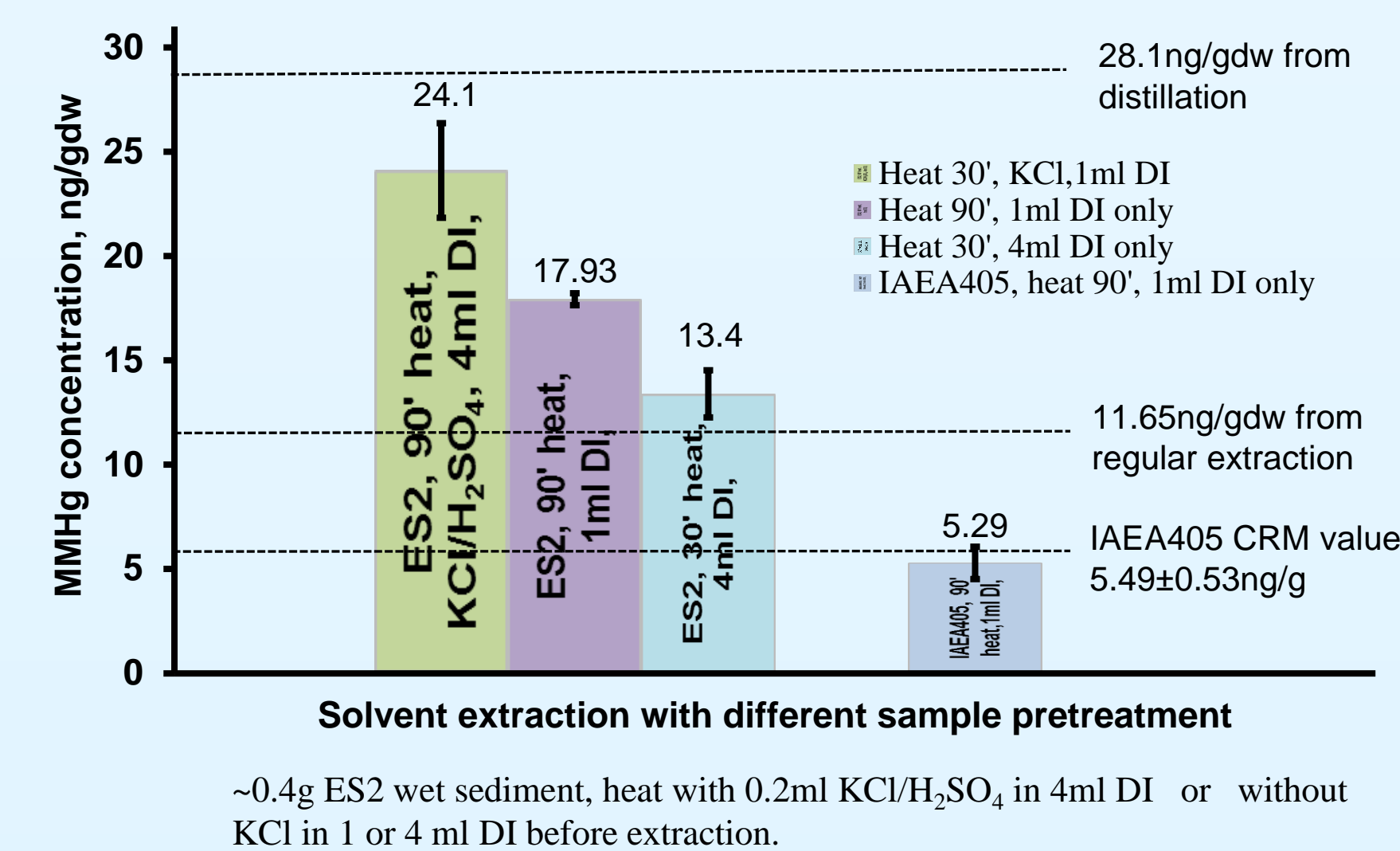
5. After a solvent extraction of wet ES2, the previously extracted sediment was distilled or went through a 2<sup>nd</sup> solvent extraction.

Sample Type	MMHg detected in Sediment by Distillation, ng/gdw	MMHg detected in sediment by KBr extraction, ng/gdw	MMHg detected in previously KBr solvent extracted sediment (converted to equivalent MMHg concentration in dry sediment)	
			Distillation, ng/gdw	KBr Extraction, ng/gdw
Wet ES2	28.1	12.4	7.61	2.23
Wet ES2 with MMHg spike		42.55	7.35	4.13
IAEA405 (5.49±0.53 ng/g)	5.41	4.48	0.31	0.40
Hg <sup>2+</sup> conversion to MMHg	0.07%	0.03%	0.08–0.16%	<0.01%

The distillation of previously extracted sediment detected 7.61 ng/gdw MMHg, indicating a significant amount of MMHg remained after extraction. On the other hand, the distillation of previously extracted sediment which contained a matrix spike found a similar amount of MMHg (7.35) as in the unspiked sample. This indicated the aqueous based MMHg in matrix spike is easily extracted into CH<sub>2</sub>Cl<sub>2</sub> (>90% recovery was found) whereas ambient MMHg in ES2 is poorly extracted.

### 6. Heat pretreatment of sediments at 100°C prior to solvent extraction

#### 6.1 Heat ES2 wet sediment with KCl/H<sub>2</sub>SO<sub>4</sub> OR in DI only



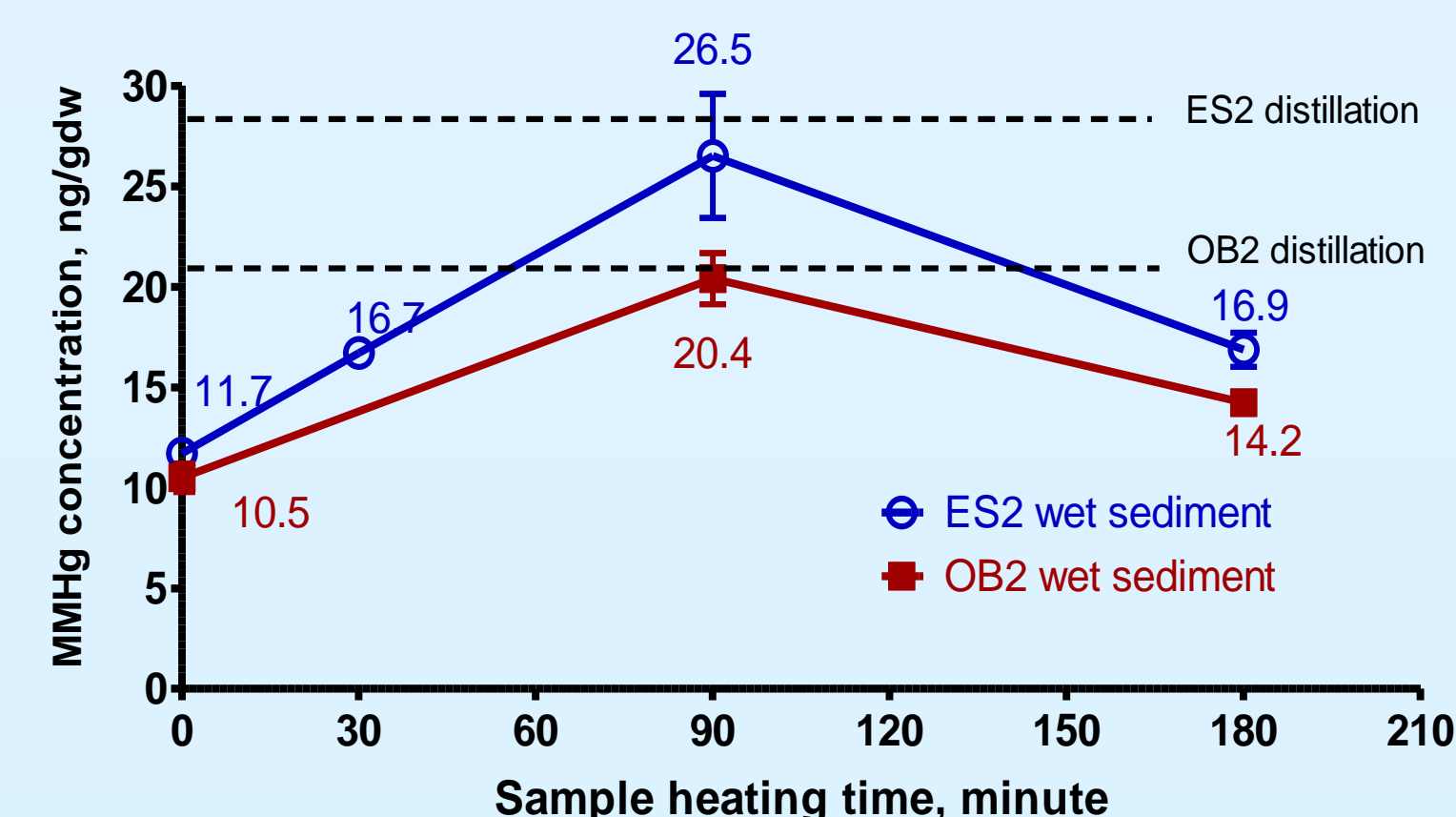
• The matrix spike and CRM recoveries were good.

• MMHg solvent extraction recovery was highest when sediment was pretreated with heat @ 100°C with KCl/H<sub>2</sub>SO<sub>4</sub>.

• If preheated in DI only, MMHg detected were higher than regular KBr/CH<sub>2</sub>Cl<sub>2</sub> extraction, but still significantly lower than that from distillation.

• The MMHg conversion from Hg<sup>2+</sup> with this heating process was 0.07%.

#### 6.2 Effect of different heating times on ES2 and OB2 wet sediment with KCl/H<sub>2</sub>SO<sub>4</sub>



Wet ES2 and OB2 showed similar trends of heating effect.

Comparative results from Distillation are 28.1ng/gdw and 21.2 ng/gdw for ES2 and OB2 wet, respectively.

## Conclusions

- MMHg determined by KBr Solvent Extraction underestimates the real MMHg concentration in Penobscot River sediment samples by ~50% due to low extraction efficiency. A portion of MMHg in these sediments is in a form that is different than the MMHg in standard spike solutions, making it unavailable to solvent extraction at room temperature: matrix spike recovery is good but final measurement is low. Good spike recovery does not guarantee good sample recovery.
- Pretreatment of sediment with heat, and particularly heat in the presence of KCl/H<sub>2</sub>SO<sub>4</sub>, significantly improves the solvent extraction process. Although the conversion of inorganic Hg<sup>2+</sup> is correspondingly increased, from 0.03% to 0.13%, the artifact accounts for less than 7% of the overall MMHg detected, and is only significant when THg/MeHg ratio is extremely high.
- Poor solvent extraction is matrix specific. Solvent extraction of CRM IAEA-405 is nearly complete while test sediments ES2 and OB2 extractions were only about 50%. Good CRM recovery does not guarantee good sample recovery.

## Acknowledgment

The Penobscot River Mercury Study is thanked for permitting these data to be presented here.

## References

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