Exploring unfrozen sediments potentials in trace-level organic analysis in the Santa Monica Bay, California

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INTRODUCTION

The City of Los Angeles discharges over 300 million gallons of secondary-treated industrial and municipal wastewater effluent daily from the city-owned Hyperion Treatment Plant (HTP) into the Pacific Ocean along the Santa Monica Bay (SMB) in California, USA. Residual chemicals in the effluent accumulate over-time in sediments turning SMB into a repository for chemicals hazardous to many marine organisms inhabiting the sediments. The hazardous nature of this accumulation may manifest as direct toxicity to aquatic organisms, or indirectly in wildlife and in human health by way of bioaccumulation in the food chain.

The legal permit under which HTP discharges effluent into the ocean requires monitoring the impact of the discharge on the Southern California coastal ecosystem. One component of the impact assessment is determining the levels of organic pollutants in sediments. To be successful in providing reliable data for this process, sampling sediments and sample handling should preserves the native properties of the sediment.

Anxiety exist in monitoring the ecological impact of HTP discharges due to the lack of scientific agreement about the temperature at which sediment samples should be stored . There are studies which show that freezing permanently modifies sediment structure which, in turn, alters the availability of sediment-associated contaminants. Others disagree. There is, therefore, need to determine the best temperature to store sediment samples for our needs in the SMB.

OBJECTIVES

To carry out a parallel study using split sediment samples from 17 SMB stations (Fig. 1 below) to test whether sediment refrigeration alone (i.e. skipping the freezing step during sampling and preparation for analysis) has any effect on the native levels of DDTs, PCBs and PAHs in the sediments. DDTs, PCBs and PAHs are legacy pollutants in the Southern California bight.

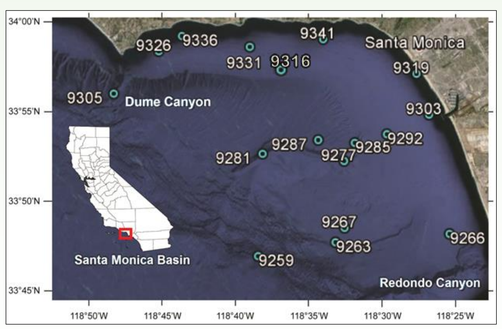


Fig. 1. Santa Monica Bay sediment sampling stations.

MATERIALS & METHODS

Sample collection and preparation

Sediment samples (17) were collected from SMB stations (Fig. 1) and divided into two halves; one half was stored at 4°C for extraction at different times (Supplementary Materials available) and the other half, frozen at -20°C until extraction.

About 5.00 g of each sediment sample (3.00 g for PAHs) was thoroughly mixed with an equal amount of diatomaceous earth, spiked with surrogate compounds and extracted with a 1:1 (v/v) CH_2Cl_2/acetone solvent mixture, purified using a Florisil packed column, eluted and concentrated to 5 mL (1 mL for PAHs) prior to instrumental analysis.

Instrumental analysis

DDT and PCB congeners analyses were performed using a GC/ECD; PAH analysis was carried out using a GC/MS. The levels of 7 DDTs, 41 PCBs and 24 PAHs were then compared in the split samples.

Quality assurance

Our laboratory participated in a Inter-Laboratory Comparison Exercises (ILCE) and passed the tests before field samples were analyzed. ILCE involved analyzing, in triplicates, reference materials NIST SRM 1944 and SR0326.

Data preparation

The levels of all the PCB congeners or the PAHs detected in each sample were summed up for data analysis. For DDTs, individual levels of the DDT derivatives (2,4'-DDT; 4,4'-DDT; 2,4'-DDE; 4,4'-DDE; 2,4'-DDD; 4,4'-DDD and 4,4'-DDMU) were above MDLs in 16 of the 17 sediment samples. Hence, the individual DDT levels used for data analysis.

Frozen/unfrozen data comparison analysis

To answer the question whether freezing or refrigeration (alone) of the same sediment samples may result in measuring the same parameters and in an equivalent manner, the levels of DDTs, PCBs and PAHs in the frozen and refrigerated split-paired sediment samples were compared using the Bland-Altman comparison approach which provided information on the strength of correlation between samples means *and* similarities of variance, together with any agreement that might exist between each pair of the entire datasets.

Statistical analyses were done using PAST, Real Statistics Using Excel and Microsoft Excel 2010 software.

RESULTS

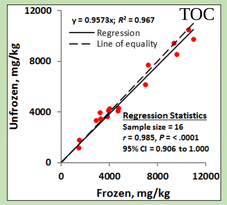
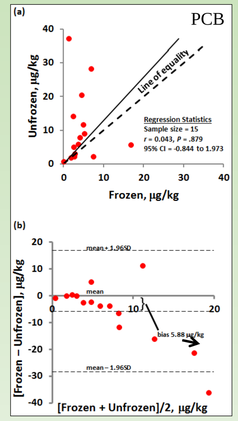


Fig. 2. Total organic carbon content (TOC) results show a high correlation (n = 16, r = 0.985, P = < .0001, 95% CI = 0.906 to 1.000) and similarity (regression plot *vs* line of equality) between frozen and refrigerated samples data suggesting little difference between freezing and refrigeration TOC data and by implication, the pollutants partitioning thermodynamics in the organic carbon-water system.

Fig. 3. (a) Scatter plots of the levels of PCB congeners in refrigerated samples *vs* frozen sediments. Regression is shown as —. Data clustering favors refrigerated samples. (b) Difference *versus* mean plot showing increasing variability (proportional error) with increasing mean, and a bias of 5.88 µg/kg towards the unfrozen samples imply that less PCBs will be detected in frozen sediments. Except for a single PCB congener outlier detected at station 9285 (shown by arrow), all data points are within the limits of agreement (mean±1.96SD).



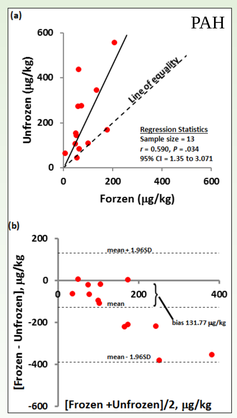
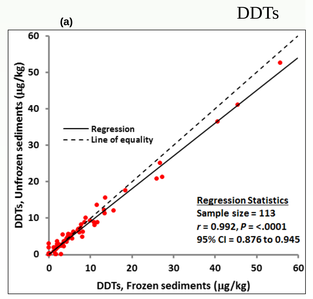


Fig. 4. (a) Scatter plots of the levels of PAHs in refrigerated *vs* frozen sediments. Regression: —. (b) Difference *versus* mean plot showing proportional errors and a bias of 131.77 µg/kg in favor of the unfrozen samples. All the data points are within the limits of agreement. The (non) effect of freezing sediment samples as found on PCB congeners above is similarly observed on PAHs.

Fig. 5. (a) A scatter plot of 113 paired concentrations of 2,4'-DDE; 4,4'-DDE; 2,4'-DDD; 2,4'-DDT; 4,4'-DDD; 4,4'-DDT and 4,4'-DDMU from 17 pairs of frozen and refrigerated SMB sediments. The line of equality is shown. Linear regression equation: Refrigerated = 0.91(Frozen), r^2 = 0.96. About 85% of the data points are below10 µg/kg where correlation is the highest.



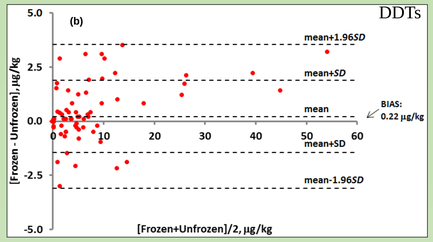


Fig. 5. (b) A difference *versus* sample mean plot of data in Fig. 4(a) showing that the frozen samples are likely to have 0.22 µg/kg more DDTs that the refrigerated sample, and that within 95% limits of agreement though, the two methods of storing samples agree (mean+1.96SD is +3.47; mean-1.96SD is -3.03).

CONCLUSIONS

In the present study, the degree of agreement between trace analysis of DDTs, PAHs and PCB congeners in frozen sediment samples and in refrigerated samples was assessed. Our results show that the two methods of handling sediment samples from SMB can substitute each other within ±1.96SD of the mean. The extra effort and cost associated with freezing SMB sediment samples can, therefore, be avoided. Variability may be remedied by adding surrogates to sediment samples immediately on collection to normalizing DDTs, PAHs and PCB congeners concentrations is recommended if freezing is unavoidable.

On a broader scale, it is tempting and erroneous to treat a current method as the gold standard against which a new method should be tested. Rather, the focus ought to be on determining if a new method and an old one can measure the same values on the same sample under the same condition at the same time (if possible) and produce the same results. This is because, when two methods of measuring unknown values are compared, as is done here, neither method will provide unambiguously accurate and precise quantitative measurement because a measurement of variables always implies certain degree of error.

REFERENCES

Otim O, 2017. Exploring unfrozen sediments potentials in trace-level organic analysis in the Santa Monica Bay, California. *Submitted*.

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