

## Electronic Supplementary information

### Re-evaluation assessment of a large volume sampling (LVS) system for the determination of petroleum hydrocarbons and their stable carbon isotopes in the deep sea waters.

Imma Tolosa<sup>1\*</sup>, Carlos Guitart<sup>1,2</sup>, Marianela Mesa-Albernas<sup>1,3</sup>, Carolina Funkey<sup>1,4</sup>, Roberto Cassi<sup>1</sup>

<sup>1</sup>International Atomic Energy Agency – Environment Laboratories, 4, quai Antoine 1er, MC 98000, Monaco

<sup>2</sup>Current address: c/Espiga 6B, 08027 Barcelona, Spain.

<sup>3</sup> Current address: 28 bis , Avenue de l'Annonciade, MC 98000, Monaco.

<sup>4</sup>: Current address: University of Hawaii at Manoa, 1950 East-West Road, Honolulu, HI 96822, USA

\* Corresponding Author

### XAD-2 Amberlite resins: cleaning and blanks

The commercial pre-cleaned XAD-2 Amberlite resin (100 g with a bed volume of about 100 mL), was soaked successively in 200 mL of MeOH followed by 200mL of MeCl<sub>2</sub> corresponding to the solvents of the extraction procedure, before being packed in the Teflon columns. These initial extracts that had a “yellowy” color were analyzed to check out the potential interferences showing high amounts of interfering compounds in gas chromatography. Thus, led to the classical procedure of the Soxhlet apparatus to clean the XAD-2 resins. During 4 days, about 200g of resin was placed in the Soxhlet and extracted with a solvent mixture of MeCl<sub>2</sub>:MeOH (2:1) with 8-12 cycles per day with a solvent change every 2 days. This cleaning method decreased the traces of the targeted compounds, the PAH compounds and aliphatic hydrocarbons to an acceptable range. Another combination of solvents (proposed by U.S. EPA) is to use MeCl<sub>2</sub> followed by MeOH, which seems to have the advantage of using the MeCl<sub>2</sub> extract to check the compounds background (“background level”) of the resin, plus leaving the resin in MeOH for storage and ready for packing. As, these Soxhlet procedures are excessively time consuming and expensive, a third study was performed by testing a “soft” cleaning by using the glass balloon were the 100 g of XAD-2 are weighed before packing. Thus, the XAD-2 resin in the balloons was sequentially soaked (statically) with MeCl<sub>2</sub> for 48h and followed by MeOH for 48h. Afterwards, the XAD-2 resins were column packed and solvent eluted for testing the blanks. This cleanup procedure resulted to be a good compromise among the other cleanup alternatives, achieving an acceptable degree of cleanness for this XAD-2 resins. Finally, after the elution process of the targeted analytes ( $V_n = \sum 1-8$ ), a final volume of MeCl<sub>2</sub> (100 mL) was added to the column and recovered separately to verify the mass background of the targeted compounds and surrogates in the XAD-2 SPE columns. This corresponds to the check-ups on the eluted columns and were labeled as the 9<sup>th</sup> elution volume ( $V_n=9$ ).

The major mass background interference found for the target analytes in the commercial XAD-2 resins were for aliphatic hydrocarbons rather than PAHs. Over the experiments, the concentration of aliphatic compounds in resins blanks and procedural blanks were always present, thus it appears that the resins were continuously leaching aliphatic compounds. The Fig. S1 shows the absolute mass obtained for each individual target compound in the XAD resins after the use of different cleaning methods (Soxhlet and soft passive cleaning), as well as obtained from the post-elution step ( $V_n=9$ ) used to control the resin background level in the SPE column. It was noticed that after several column elution processes and reuse the columns, the average mass

background for the aliphatic hydrocarbons in the resins was lower than for new cleaned resins. On the contrary, the average mass background for PAHs is initially lower, but after a number elution processes the quantity of PAHs remaining in the resins exceeds the initial background (except for the case of naphthalene and other volatile compounds which have the same or higher levels, thus these are ubiquitous and potential contamination compounds). In conclusion although the commercial XAD-2 resins are sold as pre-cleaned (SUPELPACK-2SV, Supelco), for the purpose of the present methodology (trace analysis) this resin contains a sufficient mass of the targeted chemical compounds to raise the background level of the procedural blank of the method. Further, the use of the resins (through column load and elution processes) also favours that deuterated PAHs will be carried over, and thus, the quantities of target analytes and their surrogates should be tested in order to reuse the columns.

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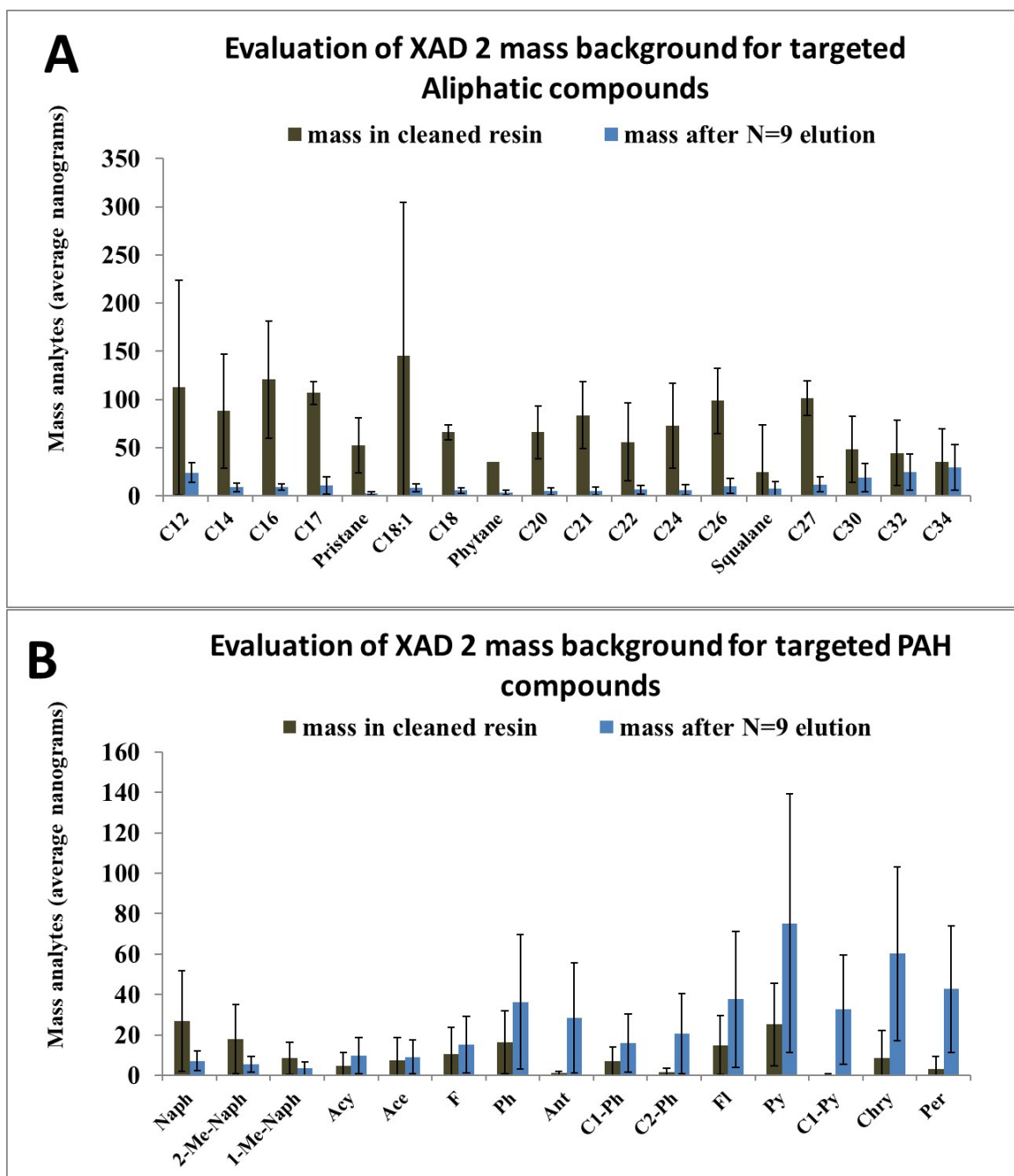


Fig. S1. Mean absolute mass background calculated after cleaning the resins and after reusing the SPE columns (from Vn=9, n=16) for A) aliphatic hydrocarbons and B) PAH compounds. The abbreviations for the compounds are defined under section 2.1 (Reagents and chemicals).

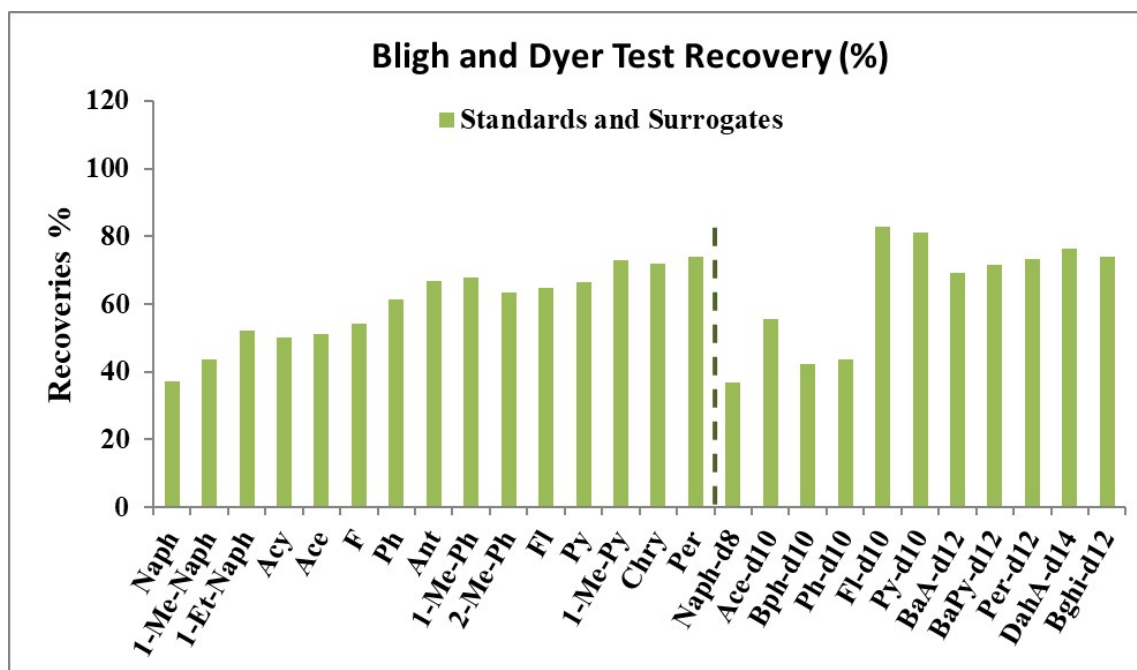


Fig. S2. Absolute recoveries (%) for PAHs for a Bligh and Dyer (B&D) liquid-liquid extraction step tested for the target compounds and deuterated surrogates. The abbreviations for the compounds are defined under section 2.1 (Reagents and chemicals).

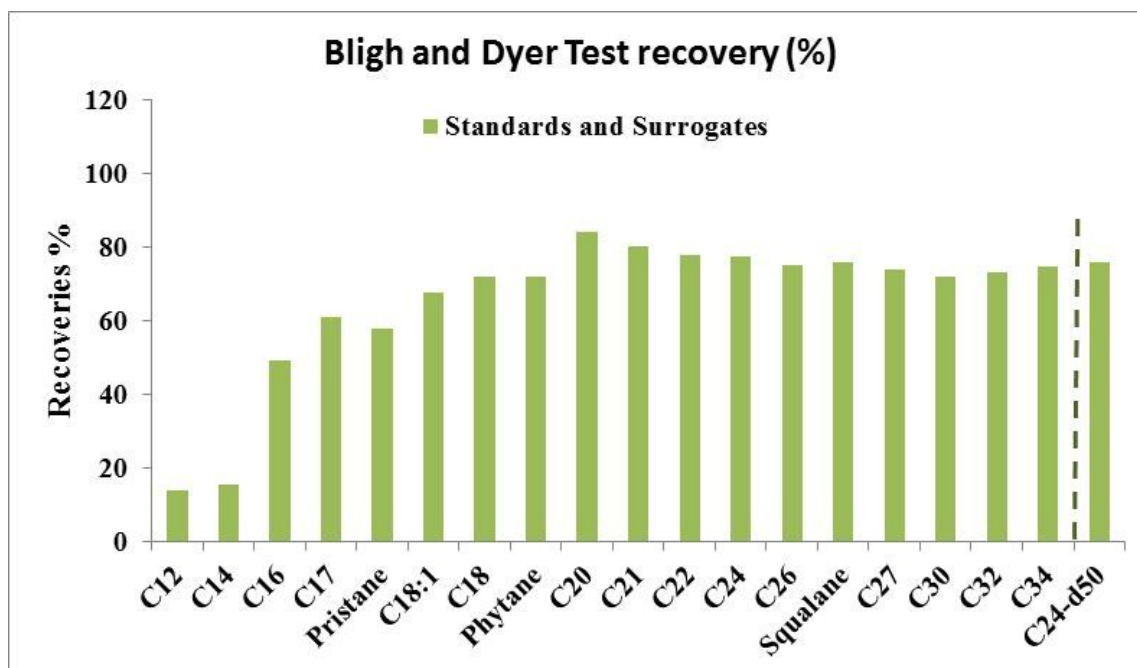


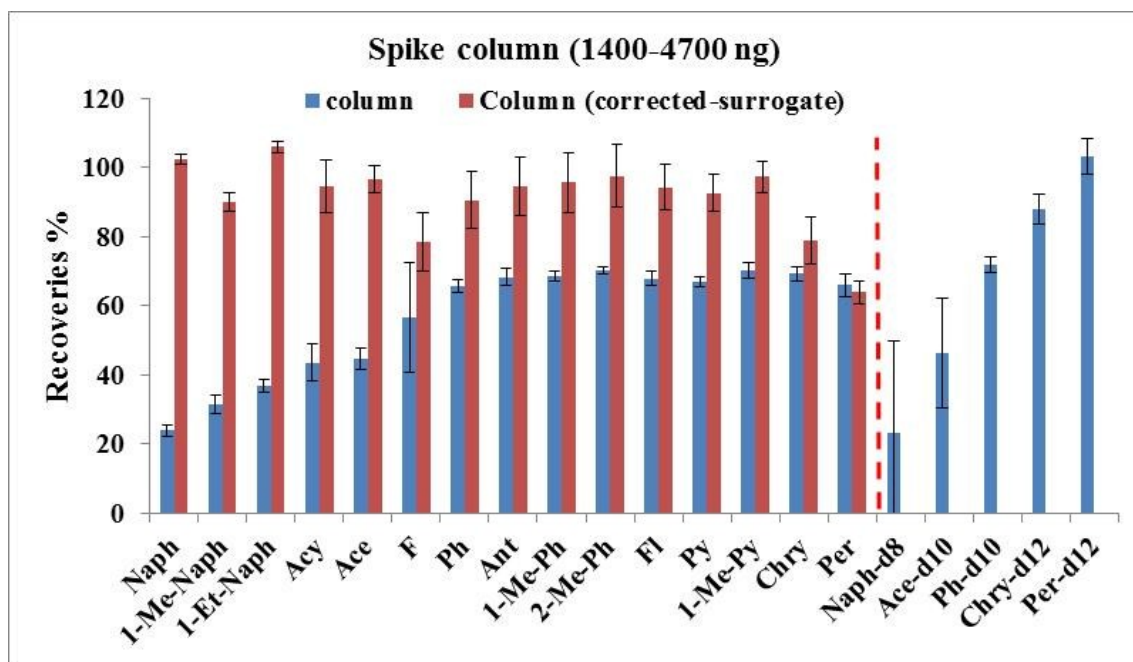
Fig. S3. Absolute recoveries (%) for aliphatic hydrocarbons for a Bligh and Dyer (B&D) liquid-liquid extraction step tested for the target compounds and surrogate deuterated compounds. The abbreviations for the compounds are defined under section 2.1 (Reagents and chemicals).



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2 Fig. S4. Complete system of columns and separation funnels.

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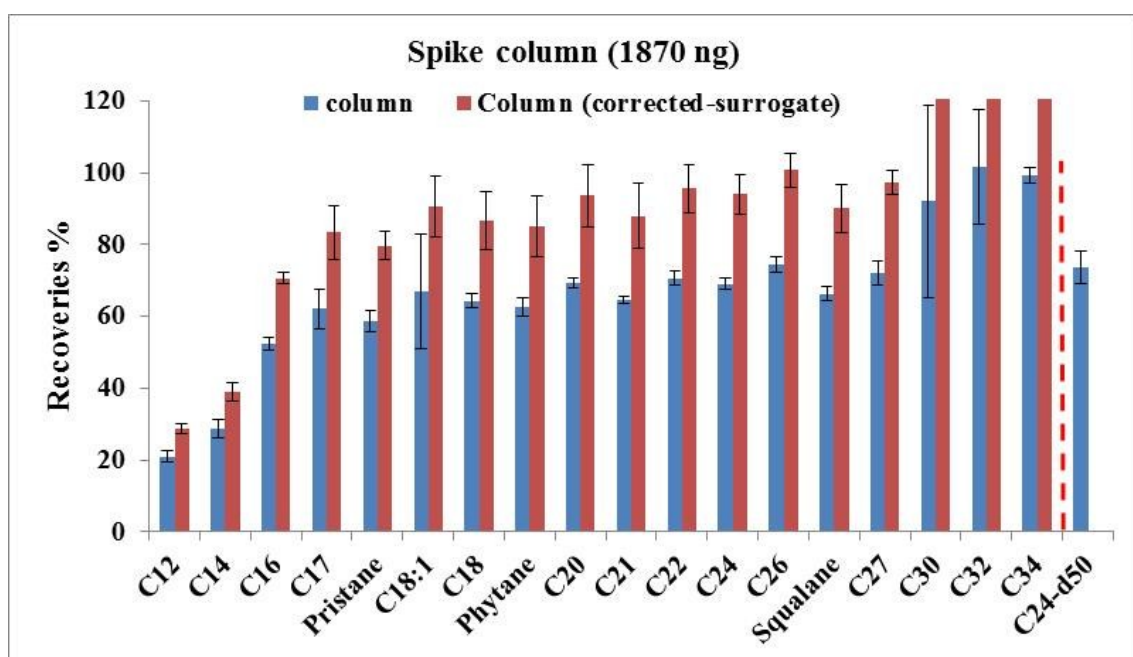


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2 Fig. S5. Mean absolute and corrected recoveries (%) of target PAHs standards in the retainability test (140 L) and  
 3 absolute recoveries (%) for the deuterated standards added before column elution (n=3). The abbreviations for the  
 4 compounds are defined under section 2.1 (Reagents and chemicals).

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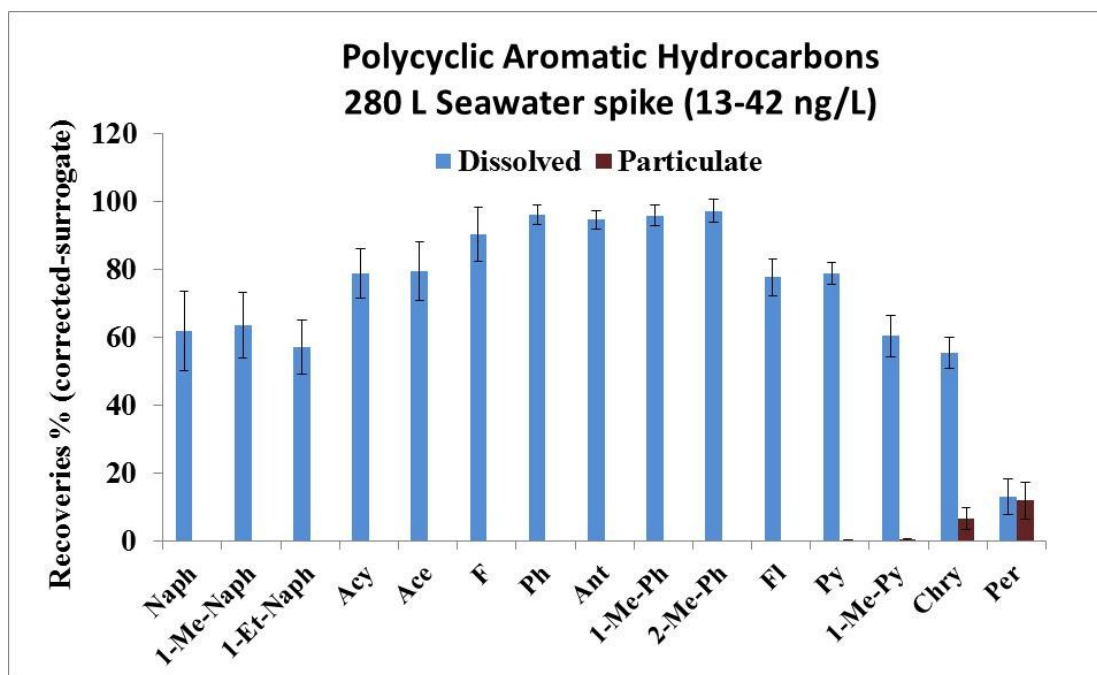


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8 Fig. S6. Mean absolute and corrected recoveries (%) of target aliphatic standards in the retainability test (140L)  
 9 and absolute recoveries (%) for the deuterated standards added before column elution (n=3). The abbreviations  
 10 for the compounds are defined under section 2.1 (Reagents and chemicals).

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2 Fig. S7. Mean recoveries (%) and SD (n=3) for the dissolved and particulate phases obtained for the PAHs at  
3 trace concentrations. The abbreviations for the compounds are defined under section 2.1 (Reagents and  
4 chemicals).

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