ULTRA TRACE LEVEL POPs MONITORING IN VENICE LAGOON WATER BY LARGE VOLUME SAMPLING

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Introduction

The Environmental Ministry Decree issued on July 30th, 1999 has modified the limit value table for waste water discharge into the Venice lagoon and into the receptors of draining basin (nine rivers that pour into the lagoon) on the basis of the quality objectives concerning the Venice lagoon waters set in a preceding Decree, issued together with the Public Works Ministry earlier on April 23rd, 1999.

This legislation has immediately required the introduction of analytical methodologies little known so far, to reach detection limits as low as a thousandth of those required for drinking water quality.

In some cases, even using extremely sophisticated techniques such as HRGC/HRMS to detect organic micropollutants or ICP/MS for metals, it is not possible to reach the required detection limits. The problem can be overcome by a spur pollutants preconcentration, therefore sampling from 50 to 200 liters of water instead of the usual volumes (1 to 5 liters).

The most suitable system consist in a solids filtration stage, followed by solid phase extraction (SPE), to be realistically realised on the field, sampling directly from the water body under examination.

The system has been tested with analite-spiked samples to determine performances (recoveries and detection limits) and later moved to field practical application

Methods and Materials

The sampling system chosen was "INFILTREX II" from AXYX Environmental Systems Ltd, Canada.

It consists of an immersion device able to sample automatically, composed by a microprocessor-controlled pump, a flow-meter, a multi-stage filtration system, the extraction column an batteries that supply the energy required during the sampling.

The filtration system and the extraction column may vary as a function of the targeted analytes: organic can be filtered on glass-fibre and adsorbed on XAD2; inorganic filtration is best carried out on polypropylene and adsorbtion on a column containing 8-Hydroquinoline supported on a polystyrene resin.

The actual study was carried out on organic pollutants.

The immersed sampling device pumps the programmed volume through the filtration system to the extraction column where the soluble components present in traces are adsorbed on the resin.

The data concerning the sampled volume, the sampling start/end time, date, sampling site, and sample description are transferred from the memory of the system to the PC.

"INFILTREX II" behaves as follows: it operates submerged in water (up to 100 meters), sampling flow from 50 to 300 mL/min (depending on suspended matter), sampling volume up to 150 L (depending on suspended matter), weight: 12.5 Kg (in water 5.5 Kg), turbine flow-meter with optical reading (total accuracy 2% from 100 mL/min, calibrated against a primary standard). The trials have been carried out under the following conditions: samples with a high level of SSM; samples with a low level of SSM; and a high concentration of spiking analytes. The total number of samples was 16. Before each test a blank run was carried out under the same conditions using organic free water.
Given the need to reach the maximum sensitivity, with organics it has been decided to analyse the total particulate matter plus the absorbed sample. The filters containing the particulate have been extracted by ASE while the absorbtion column has been eluted with methanol and methylene chloride. The two fractions were joined together, concentrated and analysed according to the following methodologies:

PCDD/Fs	method EPA 1613/94
PCBs	method EPA1668/99
HCBs, PAHs (> 3 rings), POCs	method EPA 525.1

According to the methods utilised the samples have been spiked with 13-C labelled internal standards, and quantitation done calculating the RF of each native standard with respect to the corresponding labelled standard. The analyses were performed by HRGC/HRMS (high resolution mass-spectrometer set at a resolution power, RP>10,000 at 10% of the valley between two peaks).

Results and Discussion
The study has shown light PAHs contamination (not included in this study) due to XAD2 and the solvents employed.
Recoveries of the spiked compounds lied between 50% and 85%. During the study, the system stopped only once because of a defective power supply. Hence the trial has been repeated. All data concerning the on field trials will be displayed on a poster.
In summary, the lower detection limits (20 to 30 times according to the nature of the analyte and the matrix) obtained increasing the sample volume avoiding contamination due to improper sample handling and problems related to storage and shipping of large volumes. All this brings ultimately to a better sampling reproducibility and makes easier samples storage simply by removing from the device filters and absorption column. Furthermore, the device allows one to programme sampling in correspondence of a certain tide phase.
Considering the extremely low detection limits required by the Ministry Decree dated 30/07/99 and the need to produce accurate data we carried out a preliminary trial on the INFILTREX system under the different working conditions to verify the sampler efficiency toward the ability to concentrate pollutants with satisfying and reproducible yields as declared by the constructor.
To carry on sampling of such a volumes requires two technicians on the field, sampling times can be between 6 and 8 hours/sample, procedures for the spike-system cleaning, and a laboratory equipped and experienced in analysed of ultratraces.