

A prospectus for compliance sampling of CECs and other trace organic compounds in effluents and outfalls of POTWs: Application of sampling lessons from the California Ocean Plan using integrative passive sampling and snapshot sampling technologies for trace and ultra-trace compounds.

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ABSTRACT

INTRODUCTION:

USEPA, under its legal authority to regulate the management of the nation's waters for beneficial uses, has developed and/or adopted sampling and analytical processes for compliance monitoring, since the inception of the Clean Water Act (CWA). Most of the sampling and analytical methods have been modeled after conventional pollutants whose concentrations are amenable to detection by snapshot sampling processes including twenty-four hour composites (C-24) and grab sampling; and whose toxicities may be detected by chronic and/or acute outcomes. However, many compounds with environmental concentrations at trace levels (ug/L or lower concentrations) are not amenable to measurement with these methods, although they are increasingly implicated in ecological and population outcomes in the nation's water environment. These classes of compounds which include personal care pharmaceuticals, endocrinally active compounds, and others are increasingly described as CECs. The toxicological significance of these substances makes it imperative that reliable sampling and analytical methods be developed for managing their environmental impacts. This poster summarizes the following:

- 1. The successful uses of a volume integrative sampling technologies SPMD as a robust and reliable alternative for sampling wastewaters for trace compounds in the California Ocean Plan Table, followed by laboratory analyses using approved EPA methods for compliance and resource management purposes.
- 2.A comparison between C-24 sampling methods and SPMD in resolving the detection of the California Ocean Plan Table B Compounds.
- 3.SPMD and POCIS provide data from a time-weighted average basis providing corresponding basis for evaluating human and environmental health objectives of the California Ocean Plan Tabler B compounds.
- 4. The California Ocean Plan Table B compounds compares with many CECs for their trace concentrations and modes of ecological impacts, which are measured over generations of environmental exposure.

BACKGROUND

Compounds of Emerging Concern (CEC) usually present at *trace* and *ultra-trace* concentrations in the environment, and are therefore undetectable by EPA approved methodologies when preceded by snapshot sampling technologies. Therefore they remain unregulated though their presence has been documented in various drinking water sources, wastewater effluent-dominated streams, and their effects have been demonstrated among several aquatic and amphibian species.

With advances in analytical methods (GC/MS; HPLC) the limiting effects of snapshot sampling technologies can be eliminated with the use of validated integrative sampling technologies including SPMD, and POCIS.

OUTLINE OF PROCESS:

- Deployment within facility to ensure access, security and to measure sampling temperature, flow and standard conditions.
- Flow rate: 1.5 liters/minute;
- Temperature 21° +/-1°C through duration; Duration: 30 days.
- Sample extracted, dialyzed and ampoulated by EST, St. Joseph Mo.
- List of Analytical methods used:
- EPA SW8081B/8082A; EPA SW8270D; EPA SW8260B and EPA 1613.
- Results presentable in Time-Weighted Averages.

METHOD

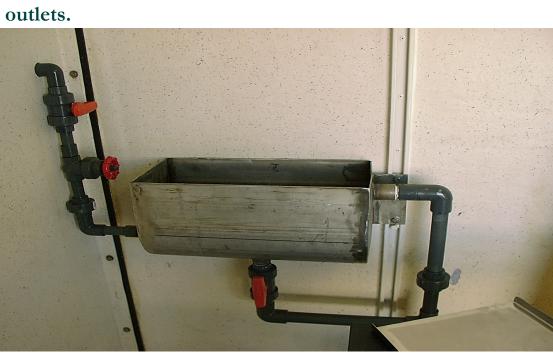
SPMDs were passively deployed in a sampling trough along the effluent discharge line within the facility and prior to reaching the Ocean to maintain security and assess temperature and sampling conditions at all times.

- The trough shown in Figure 2. was rated for 16 gals and the inlet valve set at a flow rate of 2.5 Liters per minute for the duration of the sampling event. SPMDs may be deployed by vertical suspension in the sample stream or they may be suspended horizontally.
- The device is encapsulated in a metal canister to reduce biofouling that might otherwise occur in the natural environment. Each canister may hold up to 5 discs that are interspaced with standard spacers. The membrane area exposed to the aqueous matrix is optimized by weaving the membrane across the surfaces of porous metal plates. (See Figure 1)

Figure 1. SPMD membrane (left) and containers before placement into trough



Figure 2. Sampling trough with control valves, inlet and



HIGHLIGHTS OF RESULTS:

- Sample concentrations are meaningful within the context of Time-Weighted Averages as specified by the COP, when sampled with SPMD/POCIS integrative sampler.
- More compounds are detectable with the SPMD integrative sampler.

RESULTS

| Effluent | Sample Type | |
|--------------------------|-------------|-------------|
| COMPOUND | C-24 (µg/L) | SPMD (μg/L) |
| Acenaphthene | ND | 30 |
| Acenaphthylene | ND | ND |
| Anthracene | ND | ND |
| Benzo(a)anthracene | ND | 69 |
| Benzo(b)fluoranthene | ND | ND |
| Benzo(k)fluoranthene | ND | 19 |
| Benzo(g,h,i)perylene | ND | ND |
| Benzo(a)pyrene | ND | ND |
| Chrysene | ND | ND |
| Dibenzo(a,h)anthracene | ND | ND |
| Fluoranthene | ND | 440 |
| Fluorene | ND | 43 |
| Indeno (1,2,3-cd) pyrene | ND | ND |
| 1-Methylnaphthalene | ND | 26 |
| Methylnaphthalene | ND | 7 |
| Naphthalene | ND | 12 |
| Phenanthrene | ND | 282 |
| Pyrene | ND | 330 |
| Acenaphthene | ND | 30 |

| EPA 1613COMPOUNDS (Dioxins and Difurans and congeners) | C-24 At Lowest Limit of Resolution (10 ⁻¹² g/L) | SPMD At Lowest Limit of Resolution (10 ⁻¹⁵ g/L) |
|--|---|--|
| Total Tetra-Dioxins | 13.4 | 81.7 |
| Total Penta-Dioxins | ND | 151 |
| Total Hexa-Dioxins | ND | ND |
| Total Hepta-Dioxins | ND | ND |
| 2,3,7,8-TCDD | ND | ND |
| 1,2,3,7,8-PeCDD | ND | ND |
| 1,2,3,6,7,8-HxCDD | ND | ND |
| 1,2,3,7,8,9-HxCDD | ND | ND |
| 1,2,3,4,6,7,8-HpCDD | ND | ND |
| OCDD | ND | ND |
| Total Tetra-Furans | 9.24 | 78.2 |
| Total Penta-Furans | ND | 13.5 |
| Total Hexa-Furans | ND | ND |
| Total Hepta-Furans | ND | ND |
| 2,3,7,8-TCDF | ND | ND |
| 1,2,3,7,8-PeCDF | ND | ND |
| 2,3,4,7,8-PeCDF | ND | ND |
| 1,2,3,4,7,8-HxCDF | ND | ND |
| 1,2,3,6,7,8-HxCDF | ND | ND |
| 2,3,4,6,7,8-HxCDF | ND | ND |
| 1,2,3,7,8,9-HxCDF | ND | ND |
| 1,2,3,4,6,7,8-HpCDF | ND | ND |
| 1,2,3,4,7,8,9-HpCDD | ND | ND |
| 13C-OCDF | ND | ND |

CONCLUSIONS

- SPMD/POCIS sampling enabled more frequent quantification of trace organics in the COP Table, using standard EPA approved methods on the dialysates.
- More reliable environmental management decisions are based upon TWA than episodic measurements, in effluents.
- A prospectus for quantifying trace environmental organics including many CECs in wastewater effluents is now available.