Time Integrative Passive sampling combined with Toxicity Profiling (TIPTOP): an effect based strategy for cost-effective chemical water quality assessment

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TIPTOP hypotheses

Hypothesis 1:
Risk assessment based on toxicity profiles of complex mixture is
- toxicologically more relevant
- ecologically more relevant
- more protective

than risk assessment based on individually, target-analyzed compounds (Fig 1).

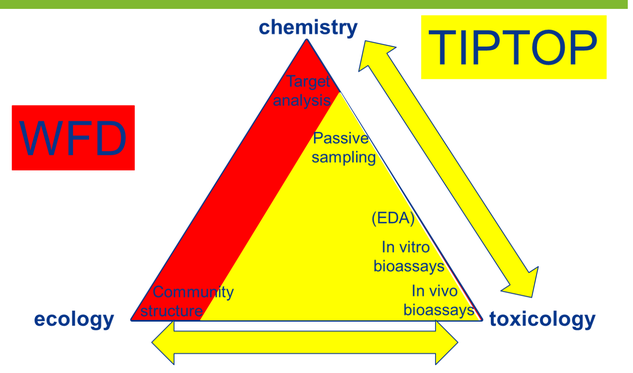

Figure 1: TRIAD approach for chemical water quality assessment in relation to the Water Framework Directive (WFD) and the TIPTOP strategy

Hypothesis 2:
For chemical status monitoring, a combination of time-integrative passive sampling and toxicity profiling is more cost-effective than target-analysis of a continuously expanding suite of individual compounds in grab-samples.

TIPTOP objectives

1. Passive sampling at well-defined WFD sites and in WWTP effluents
2. Toxicity profiling of extracts using mechanistic in vitro bioassays and ecologically relevant in vivo bioassays
3. Collecting and determining compound concentrations in passive samplers and in water
4. Making ecologically relevant interpretations of chemical concentrations and toxicity profiles
5. Evaluating the TIPTOP strategy by SWOT analysis, comparison to similar approaches and suggestion of improvements and validity tests;
6. Proposing a protocol for combined passive sampling and toxicity profiling, which is cost-effective, technically feasible, and acceptable

Passive sampling at WFD sampling sites

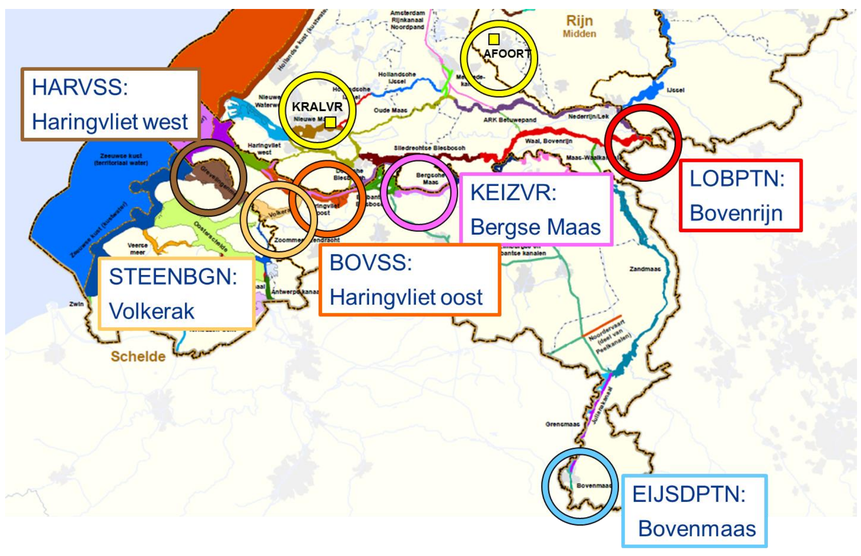

Figure 2: TIPTOP sampling sites include six well-defined WFD sites in the Dutch Delta, of which five in a downstream gradient of River Meuse. Each WFD sampling site represents a different water body with a matching color on the map. WFD sampling sites are benchmarked against effluent from two WWTPs (yellow).

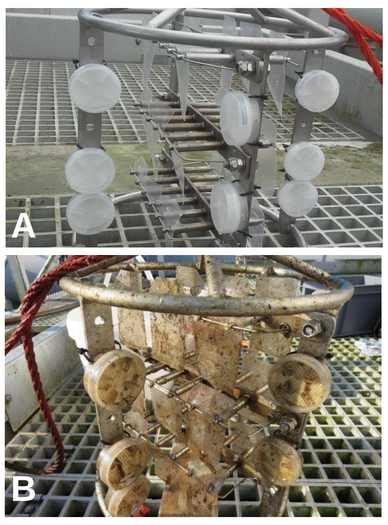

Figure 3: Passive samplers before (A) and after (B) 6-week exposure. Samplers include silicon-rubber (SR) sheets for partitioning-based sampling and Speedisks (Baker) for adsorption-based sampling.

Chemical analyses

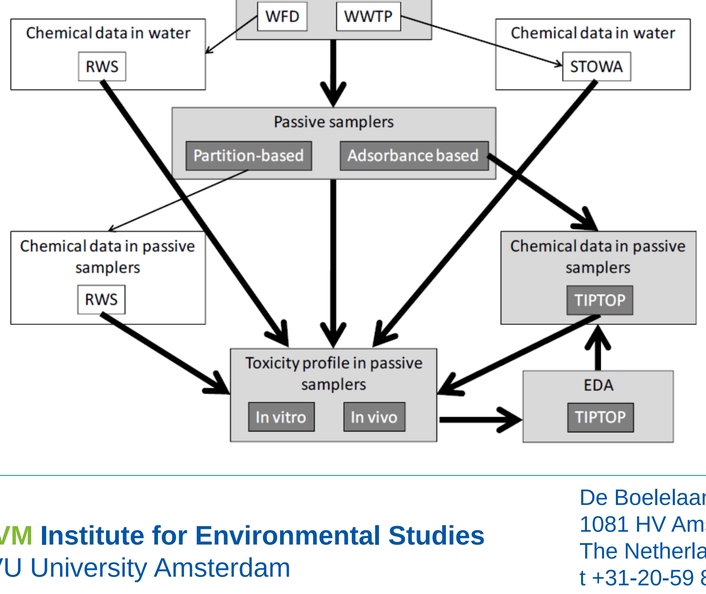

Figure 4: Overview of all chemical data available to TIPTOP. All grey shaded fields and bold arrows will be performed within TIPTOP. White fields and narrow arrows indicate the flow of additional data. Data from the WFD locations are monitored within the MWTL monitoring program. They are made available by Rijkswaterstaat (RWS) through the DONAR database. Data from the WWTP locations are monitored within the E-PRTR monitoring program. They are made available through public STOWA reports

Toxicity profiling

Sample-specific toxicity profiles (Fig. 4) will be obtained by testing the extracts from passive samplers in a battery of in vitro and in vivo bioassays.

The ***in vitro*** battery measures different mechanisms of action:
- Dioxin-like activity (DR-LUC)
- Estrogenic activity (ER-LUC)
- Androgenic activity (AR-LUC)
- Thyroid hormone mimic (TR-LUC/TTR-binding)
- AChE inhibition (Elman)
- Mutagenicity (Ames)

The ***in vivo*** battery consists of acute toxicity tests with six different species representing different taxonomic groups and trophic levels (Fig 6):

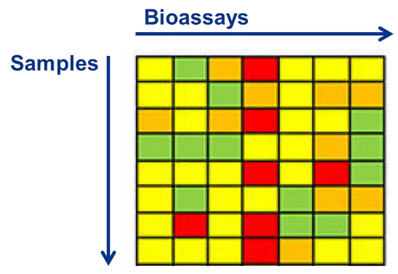

Figure 5: A toxicity profile is a toxicological "fingerprint" of a sample, indicating its activity towards a battery of biological endpoints.

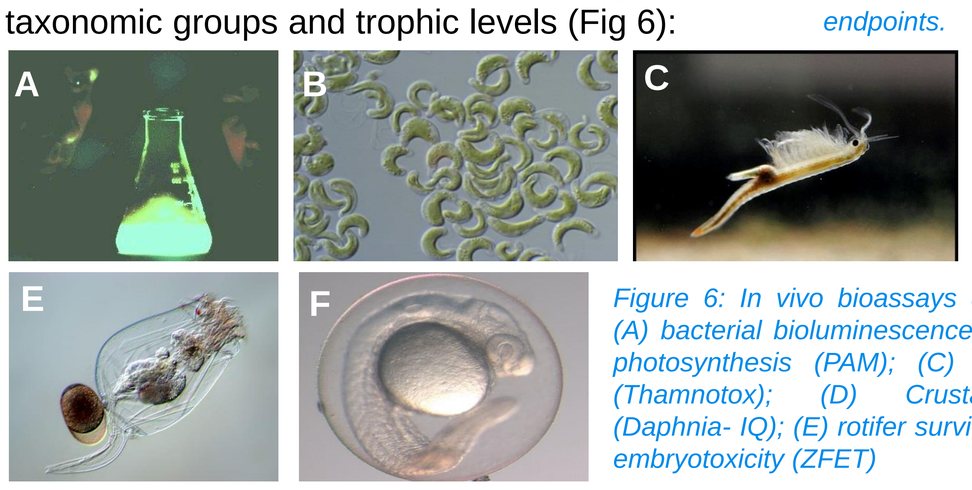

Figure 6: In vivo bioassays determine effects on (A) bacterial bioluminescence (Microtox); (B) algal photosynthesis (PAM); (C) Crustaceae survival (Thamnotox); (D) Crustaceae metabolism (Daphnia- IQ); (E) rotifer survival (Rotox); zebrafish embryotoxicity (ZFET)

Interpretation and evaluation of results

Classical approach

0. Compare concentration with EQS (compound-by-compound)
   To what extent do individual priority compound exceed their EQS?

Based on chemical data

1. Compare calculated toxicity with observed effect
   To what extent can target compound levels explain observed responses?
2. Compare concentration of narcotics with critical bodyburden (CBB)
   To what extent is CBB reached for narcotic compounds?
3. Calculate msPAF for narcotics
   How many species are potentially affected by polar and non-polar narcotics?
4. Calculate msPAF by target analyzed compounds
   How many species are potentially affected by target analyzed compounds?

Based on toxicity profiles

5. Benchmark toxicity profile surface water to WWTP effluent
   How do toxicity profiles at WFD sites compare to a positive reference site?
6. Compare in vitro bioassay responses to trigger values
   To what extent do in vitro bioassay responses exceed trigger values?
7. Determine NEC^f (chronic) using EC^f_{50} (acute) and ACR=10
   How many times should water be concentrated for chronic effects?
8. Determine msPAF based on SSD in vivo bioassays
   How many species are exposed above $NOEC_{chronic}$ in undiluted sample?

Effect-directed analysis

If chemical analyses explain only a minor part of the observed toxicity, responsible compounds will be identified by EDA (Fig 7). Demonstrating the applicability of EDA in passive samplers is especially relevant for investigative monitoring within the WFD.

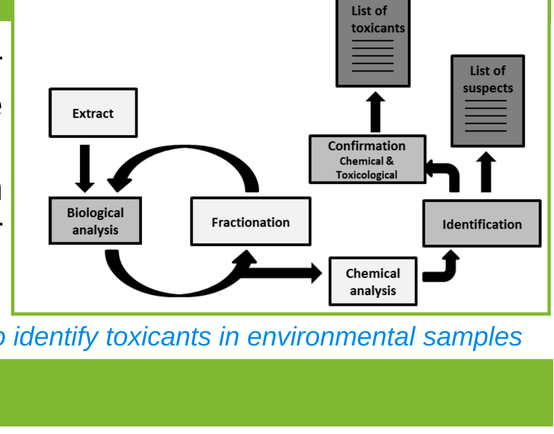

Figure 7: EDA is an iterative procedure of biological analysis, fractionation and chemical analysis to identify toxicants in environmental samples

TIPTOP evaluation

Can toxicity profiling of passive samplers be regarded as a "safety net" for chemical status monitoring? Can we characterize this net? Number and size of mazes in the net? How to reduce mazes? Price? Acceptability?

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