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Introduction

In order to demonstrate the applicability and usefulness, and to improve the acceptance of emerging and low cost tools for water quality monitoring, a number of field testing studies are being conducted in river basins. These include certain Pilot River Basins (PRBs) across Europe as part of the SWIFT-WFD project (WP5.1).

Owing to its past industrial history (including ship building in Preston docks), the Ribble estuary has often failed its Environmental Quality Standards (EQS) values for a number of metals and certain organic and organo-metallic compounds (e.g. TBT). Presently, monitoring is conducted monthly by the Environment Agency for England and Wales by collecting water samples generally at one site in the estuary.

The present study was designed to extend the assessment of tools identified and tested in WP 3.4 by demonstrating their potential for application in the various mode of monitoring (surveillance, operational & investigative) and providing reliable and representative information. Techniques were selected for:

- time-integrated measurements of concentrations of heavy metals including mercury, TBT and polar and non-polar organic pollutants at certain sites,
- the rapid mapping of pollutant concentrations and toxicity using assays based on the collection of spot samples.

Aims & objectives

This field study aims to provide additional data to support the validation and suitability of specific tools for monitoring purposes:

- Selection of tools according to identified pressure points along the estuary, historical data and EQS failures.
- Implementation of tools to demonstrate their most appropriate uses.
- Test tools that were unavailable for testing in the Eijsden trial (WP 3.4).
- Obtain a representative overview of the quality of water in the Ribble estuary.
- Collect information to be fed into other work packages including "cost of implementation" data.

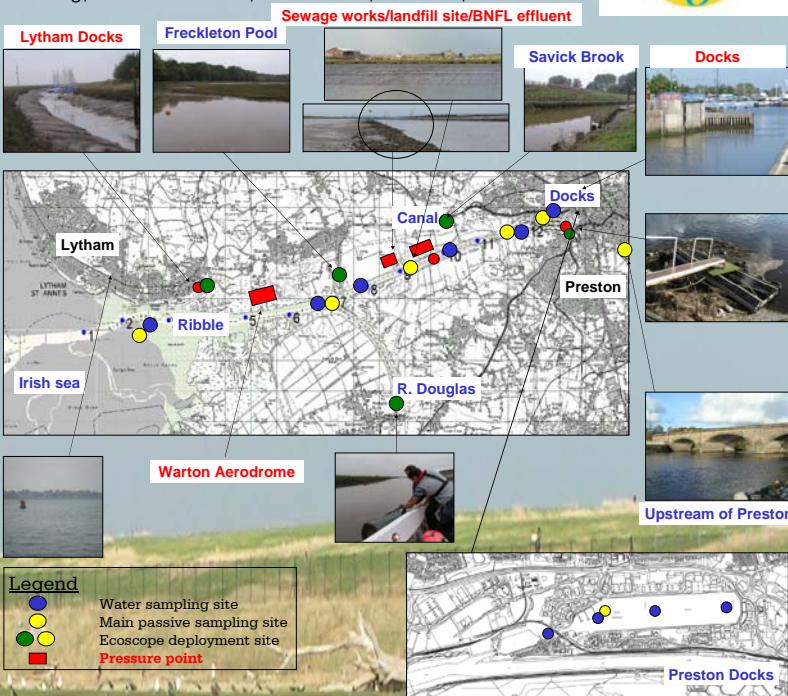
EQS failures in the River Ribble:

Metals	Cd	Cr
	Cu	Fe
	Pb	Zn

Organo-metallics	TBT

The Ribble estuary

- 10 miles long with fast tides (4 knots)
- Alternating freshwater & seawater due to tidal effects
- Significant re-suspension of sediment
- Contains a number of identified pressure points along the estuary



Mapping

Toxicity

GreenScreen Assay (Gentronix Ltd)
ToxAlert® (Microtox, Merck)
Palmsens/screen-printed electrodes for genotoxicity
Vitotox® test kit (Thermo)
Microbial biosensor for TBT and metals (Biolumine)
ToxScreen (Checklight Ltd)

- To characterise the identified pollution (EQS failures) using rapid on-site tools
- To detect and quantify toxicity hotspots within the estuary

Metals

Arsenic test kit (Industrial Test Systems, Inc.)
Ecoscope (including Hg & radionuclides)
Palmsens/screen-printed electrodes

Water quality monitoring

Time-integrated chemical concentrations

Non-polar organic compounds

Low density polyethylene membrane (LDPE strip)
Semi-permeable membrane device (SPMD)
Chemcatcher (non-polar configuration)
Polydimethylsiloxane rod (PDMS)

Polar organic compounds

Chemcatcher (polar configuration)
Polar organic compound integrative sampler (POCIS)

TBT Chemcatcher (TBT configuration)

Metals

Diffusive Gradient in Thin film device (DGT open & restricted pores)
Chemcatcher (metal configuration)

Mercury

DGT (Hg version)
Chemcatcher (Hg configuration)

- To obtain time-integrated concentrations at sites with fluctuating conditions
- Compare data with results from spot sampling-based assays (e.g. toxicity)

Mapping with the GreenScreen Assay

The biosensor utilises a strain of the brewer's yeast *Saccharomyces cerevisiae* which has been genetically modified to express a green fluorescent protein (GFP) whenever the cell carries out repair of DNA damage. When exposed to a genotoxic chemical which causes DNA damage, the cell's natural DNA repair mechanisms are up-regulated and the cells become increasingly fluorescent. Fluorescence is measured using the YETI portable reader.

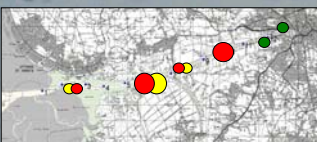


Legend

● No geno/cyto toxicity
● Genotoxicity (1 m deep)
● Genotoxicity (3 m deep)

Mapping with the ToxScreen/Metal Detector test kits

ToxScreen uses a highly sensitive variant of *Photobacterium leiognathi*, an improved lyophilization procedure, and special assay conditions to detect toxicants in water samples. When performing concurrent tests, two assay buffers are used (pro-metal and pro-organic buffer). The Metal Detector utilises freeze-dried *E.coli* carrying the luminescence system of *V. fischeri*. The test was found to be extremely sensitive to heavy metals. Bacterial and buffer reagents were mixed with the water samples into cuvettes. Luminescence was measured after 60 minutes using a portable luminometer. Toxicity is assumed when luminescence decreases by 50% when compared with clean water.

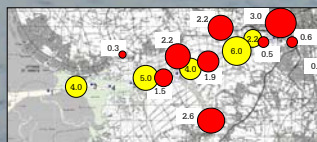


Legend

● ToxScreen (organics)
● Metal Detector
● No toxicity

Mapping with the As Low Range Kit (ITS, Inc.)

The test is based on the following reaction:
 $As_2O_3 + 12Zn + 24H^+ \rightarrow 4AsH_3(gas) + 12Zn^{+2} + 6H_2O$
 $Zn + 2H^+ \rightarrow Zn^{+2} + H_2(gas)$
Analysis is performed with a 500 ml sample. Reagents are added and after the 10 minute reduction reaction, arsine gas has converted mercuric bromide into mixed mercuric halogens changing the colour of the test pad. The strip is removed and matched to a standardised colour chart. A light yellow to brown colour change indicates that arsenic is present. The colour intensity is proportionately related to the concentration of As in the sample.



Legend

● As (18/11/05)
● As (19/10/05)
0.2 Concentration (µg/L)

Preliminary conclusions

- Fieldwork was successfully conducted according to the plan above and data analysis is on-going
- The application of the GreenScreen and ToxScreen assays for the detection and mapping of cyto/genotoxicity and toxicity (from metal or organic contaminants), respectively, revealed potential water quality problems that may require further investigation
- The GreenScreen assay demonstrated the heterogeneity of the genotoxicity levels in Preston docks with higher genotoxicity being observed closer to the entrance of the docks and with depth. This shows stratification of the water in the docks and this higher toxicity may be due to presence of contaminants in the bottom sediments
- The ToxScreen/Metal Detector tests showed different degrees of toxicity along the estuary possibly associated with metals contamination. Toxicity of some samples was also observed when using the "pro-organic" buffer. The Ribble has failed a number of EQS for metals, but not for organics, these results appear to show that toxicity may also be linked to organic contamination.
- Mapping of the estuary with rapid on-site tools, such as the Arsenic Low Range test kit for metals, allows comparison of metal concentrations between sites, while longer-term monitoring using passive sampling devices may provide data on concentration levels in a continuously fluctuating and impacted environment

The SWIFT-WFD field trial was part of a larger investigation

