HAZRUNOFF

PROJECT

"Integration of sensing and modelling technologies for early detection and follow-up of hazmat and flood hazards in transitional and coastal waters"

1.4.1 Assessment of sentinels and indicators

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CONTENTS

INTRODUCTION

This report details work prepared by Public Health England (PHE) in support of Work Package 1, Chemical Detection and Assessment associated with coastal and riverine environments.

During incident response it is important to have knowledge of the chemicals that have been released to aid forecasting and inform the risk assessment to protect health and the environment. In view of the diversity of chemicals used in industry and transported on rivers and seas (EEA, 2011) it is not possible to have real time sensing for every chemical. As such this work is proposed to identify real-time sensing capabilities for the most common pollution incidents and to identify proxies that can be used as an initial means of detecting other types of incidents before using laboratory analysis to fully identify and quantify pollutants.

To determine incident scale and impact it may be necessary to monitor the environment (such as air and water quality) at multiple locations utilising several types of monitoring equipment capable of monitoring a range of parameters (CEFAS, 2018). In an acute incident, concentrations of pollutants can vary considerably over a short time period, collecting data with a short averaging period generates volumes of data that require consideration and comparison to multiple standards quickly. A tool to aid the rapid evaluation of monitoring data and inform the dynamic risk assessments during the incident phase would thus need to meet the key objectives of;

- Rapid processing of raw data
- Assessment against relevant standards
- Production of clear visual outputs for rapid decision making on potential health and environmental impacts.

Oil pollution following tar leak (PHE, 2008)

METHODS

Selection of proxies and indicators

REVIEW OF INCIDENTS

Incidents involving oil and hazardous and noxious substances (HNS) in the coastal and riverine environment reported to UK Public Health bodies and environmental regulators (NRW, 2018), and to UK Maritime and Coastguard Agency (ACOPS, 2018) and international maritime bodies (EMSA, 2018) were reviewed for the period 2011-2018 and categorised by:

- pollutant (type and substance),
- location (river, lake, canal, port, marina, beach and coastal),
- principal target of impact (human, environment),
- scale (small, medium, large by estimate of release volume).

Figure 1 identifies that for the incidents reviewed (n=194) in inland waters (rivers, lakes and canals) the most common contamination incidents involved "chemicals" (predominantly involving pesticides) (30%) and blue-green algae (BGA) (23%).

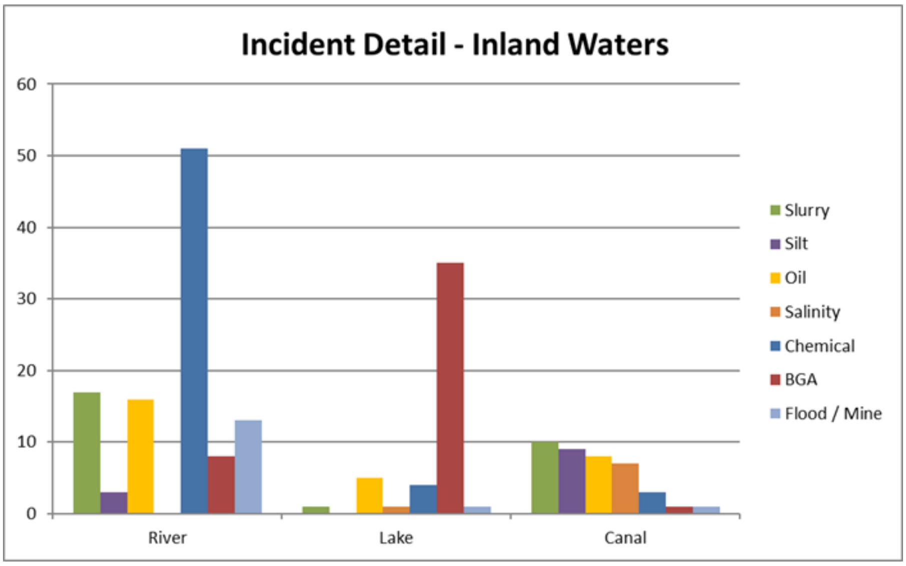


Figure 1: Inland water incidents

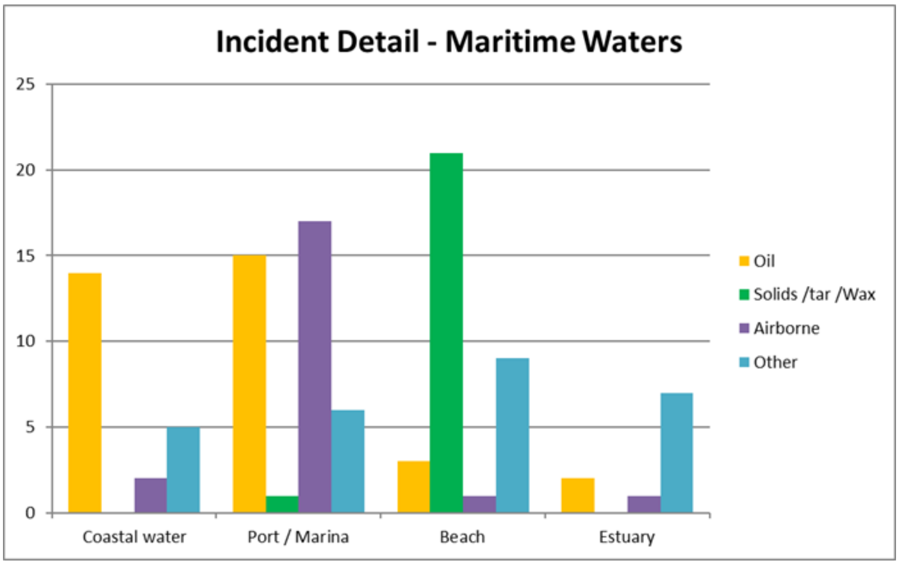


Figure 2: Maritime water incidents

Figure 2 identifies that for the incidents reviewed (n=100) in maritime waters (coastal, ports/marinas, beach and estuaries) the most common contamination incidents involved oils (35%), beached tars / waxes and airborne (predominantly combustion) pollutants (20%).

The overall review also demonstrates the prevalence of incidents in specific environmental locations, reflecting the priorities of the agencies recording the incidents and physico-chemical-biological characteristics of the contamination.

From the review of incidents, it was possible to identify 6 groups of pollutant incident type as the most frequent (Table 1). From these incident types, indicator species or proxy substances were identified that could be; monitored in the field, used to be representative of the presence and concentration of the pollutant and have an applicable exposure standard or guideline.

Table 1 Pollutants involved in incidents and potential indicators/proxies of contamination.

Pollutant incident type	Pollutant*	Indicators/proxies*
Slurry	Ammonia, TOC	Ammonia, turbidity
Oil Spill	TPH, VOC	BTEX (Benzene)
Chemical	Various including pesticides	pH, PAH, conductivity, DO
BGA	Toxin	Cells, DO
Palm Oil / Wax	VFA, TPH	DO, BTEX, pH
Flooding	TOC, turbidity, salinity, metals	pH, DO, turbidity, conductivity
* (TOC – Total Organic Carbon, BTEX – Benzene, Toluene, Ethylbenzene and Xylene, DO - Dissolved Oxygen, TPH – Total Petroleum Hydrocarbons, VOC – Volatile Organic Compounds, VFA – Volatile Fatty Acids, PAH – Polyaromatic hydrocarbons.)		

Review of earlier work/literature review

Outputs from a review of a range of literature sources helped to inform the development of the tool. Key sources included a "Knowledge tool" developed within the EU Mariner project (DGECHO, 2017) which identified and listed past projects where detection and identification of HNS studies have been undertaken. In addition, reference was also made to recently developed UK guidance developed by CEFAS called PREMIAM (Pollution Response in Emergencies Marine Impact assessment and Monitoring) for monitoring pollution after an incident. This provides detailed practical information for the collection of samples and monitoring techniques (CEFAS, 2018).

REVIEW OF MONITORING TECHNOLOGIES

Real-time (or near real-time) environmental monitoring can be invaluable in the early stages of incident management to a rapid, clearer characterisation of the incident and to inform more detailed monitoring. However, such monitoring may be limited both in terms of the availability of equipment and the range of pollutants that can be monitored in real time (USEPA, 2003).

To identify capability and capacity within the monitoring marketplace, PHE attended industry events, met with environmental regulators and equipment manufacturers and reviewed scientific papers, industry literature and earlier projects. A database of monitoring companies and their capabilities has been compiled to identify gaps in the current industry capability to provide real-time, in-situ monitoring of the indicator/proxy substances identified by the incident review. For the study reported here, the work focussed on detection of pollution in water, although the same approach can be applied to pollutants air.

WATER MONITORING

The review of incidents identified slurry/sewage, oil hydrocarbons, blue-green algae, other organic chemicals (largely pesticides) and solid tar/wax (Table 1.0) as the most frequently occurring substances reported. Potential proxy/indicator substances for these incidents were identified as ammonia, turbidity, BTEX, pH, PAH, conductivity and DO. The surveyed market currently supports real-time monitoring of all the proxy/indicator substances. Monitoring and identification can be achieved through optical, fluorescence, photometric, non-dispersive infrared sensor, mid infrared, electrochemical, microfluidic lab-on-chip and ion selective electrode methods.

Deployment of fluorescence water quality analyser (Chelsea Technologies Group 2018)

AIR MONITORING

The review of incidents identified the primary pollutants of concern as particulates and gases and potential indicator/proxy substances as PM10, NO2, SO2, CO2, CO, VOC, H2S, Dioxins and Furans. The market currently supplies the capability to undertake real-time, in-situ environmental monitoring for all the substances identified except dioxins and furans (EA, 2018). Detection techniques include light-scatter, electrochemical cells, photo-ionisation detectors, photo-metric infrared, UV scatter and light absorption techniques.

SOIL AND SEDIMENT MONITORING

The review of incidents identified some substances released or mobilised during water incidents that have the potential to lead to land contamination such as hydrocarbons, pesticides, solid tars/waxes. Monitoring and identification can be achieved through optical, fluorescence, photometric, non-dispersive infrared sensor, mid infrared, electrochemical, immunoassay, photo-ionisation detector, X-ray fluorescence and ion selective electrode methods. Alternative sample delivery and/or preparation are required for solids compared to liquids; however, the market survey suggests suppliers support this application.

Interpretation of Results – Application of Standards and Action Limits

When monitoring for community exposure and assessing risk to the population, public health standards should be applied. In the absence of public health standards, health agencies may decide to derive conservative standards based on occupational health standards, toxicological data and situation. As occupational health standards are aimed at healthy adult workers standards derived from occupational limits will need to account for vulnerable population such as the elderly and children by incorporating uncertainty factors.

WATER QUALITY STANDARDS AND GUIDELINES

Results are analysed and interpreted against standards, considering a range of impacting factors and based on the established conceptual model and human health standards and guidelines. It is important that data are in the right form for comparison to relevant standards i.e. to reflect the relevant averaging times used by the standards e.g. 24 hour means, running means etc. There are a range of standards suitable for application to chemical incidents where contaminants may reach concentrations detrimental to health. The standards can be factored into emergency planning for protective actions, such as; do not consume water or swim. Standards can also be used for longer term community / population effects when for example setting policy decisions. The drinking water standards and guidelines are more conservative and reflect chronic ingestion as the pathway of exposure. It is important that the derivation of guidelines and standards (and their averaging periods) are understood before their use.

A range of water quality standards and guidelines were identified that can be applied to incident management. European standards and guidelines for drinking water quality are principally derived for the protection of health and are based upon chronic (lifetime) exposure as well as aesthetic factors. These are often based upon policy decisions and appear as national or international standards in member states (Europa, 1998). In addition, the WHO provides health-based guidelines for water quality based on chronic exposure (WHO, 2011) and in the UK suggested no adverse response levels (SNARLs), (developed commercially for the water supply industry) for acute risks from drinking water (WRC, 2018). Values are typically presented as milligrams or micrograms per litre of water.

Standards are also derived for water as an amenity. Acute and sub-chronic guidelines are also produced for water quality including in the EU MAC-EQS (environmental quality standards - maximum allowable concentrations), EU AA-EQS (environmental quality standards - annual averages) (WFD, 2000). A summary of the standards for the proxy/indicator substances is presented in Table 2.

Palm oil deposit, Tenby, UK (Pembrokeshire County Council, 2018)

Table 2 Water quality standards and guidelines for use during incidents.

		BTEX	PAH	Conductivity	pH	Ammonia	Total Pesticides
		µg/l	µg/l	µS/cm at 20°C		mg/l	µg/l
EU Drinking water standard		1*	0.1				0.5
WHO drinking water guideline		10*					
EU Environmental Quality Standards AAs	Inland surface waters	10*					
	Other surface waters	8*					
EU Environmental Quality Standards MACs	Inland surface waters	50*					
	Other surface waters	50*					
UK Private Water Supply Regulations (indicators)	Max Min	1*		2500	9.5 6.5	0.5*	

AIR QUALITY STANDARDS

Typically, air quality standards are expressed as 1 hour, 24 hour and annual average concentrations and are derived to be protective of the most vulnerable groups. The World Health Organisation provides a range of health based international air quality guideline values, derived for chronic exposure (WHO, 2005). As with water, guidelines also exist for acute exposure to harmful airborne substances. The US Environmental Protection Agency have produced acute exposure guideline levels (AEGLs) (USEPA, 2018). These define guidelines to be protective of human health from once-in-a-lifetime, or rare, exposure to airborne chemicals for short periods of between 10 minutes and 8 hours.

LAND QUALITY STANDARDS

Standards for land contamination are covered by national and international policy based upon chronic human health risks or risks to ecosystems e.g. UK soil guideline values, Dutch soil and sediment intervention values and USEPA minimal risk levels. These are typically reported as mg/kg and derived using chronic exposure models often for specific end-uses and are dependent on background concentrations (DEFRA, 2012).

Chemical containers recovered for safety by Fire Service (PHE, 2007).

RESULTS

A tool was developed to rapidly review and assess data from water analysers during incidents. Based on an approach developed by Public Health England (EA, 2018a) for air quality incident response and using commonly available software (Microsoft Excel) the tool takes data exported from water quality monitors and makes comparisons against health and environmental standards. The tool was assessed against data exported from monitors deployed during incidents in the UK (Table 3).

Table 3: Monitors used to test the beta rapid assessment tool

Manufacturer	Device	Technique	Parameters*	Source
YSI	YSI6000 and YSI EXO	Electrochemical	Conductivity pH Total dissolved solids	NRW
Chelsea Technology	V-Lux	Fluorometer	Benzene Pesticides Polyaromatic Hydrocarbons	Chelsea Technologies
*further parameters can be determined using post capture data processing for the V-Lux device.				

The tool operates by automatically processing the most recent 7 days of data, providing a red, amber, green indication compliance with the most stringent standard identified and a graphical representation of the data.

The templates (figures 3 and 4) compare data to relevant standards and to colour coded alerts to indicate any potential pollution events. The user can select the appropriate standard to consider in their assessment, based on the environmental location of the sample (effluent, fresh water, saltwater) and the receptors (human, ecological).

A graph of key pollutants is automatically generated following the processing of data to show trends and flag any peaks for each parameter during the monitoring period.

Incident/Location: 18.05.2018 Llyn Brianne

Summary of % within each alert banding, e.g. % red is % below red (lower) + % above red (upper)

	Cond µS/cm	Sal psu	TDS mg/L	pH	dO mg/l	Ammonium mg/l	Turbidity NTU
%Green	100.00	100.00	100.00	0.00	29.02	87.05	51.34
%Amber1	0.00	0.00	0.00	100.00	41.96	0.00	19.64
%Amber2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
%Red	0.00	0.00	0.00	0.00	29.02	12.95	29.02

Graphs:
X axis is days of month
for most recent data

Colour coding - use lower bounds where low values should alert, use upper values, when higher values should alert, some e.g. pH uses both

	Cond µS/cm	Sal psu	TDS mg/L	pH	dO mg/l	Ammonium mg/l	Turbidity NTU
Red (lower)				4	1		
Amber2 (lower)							
Amber1 (lower)				6.5	5		
Green							
Amber1 (upper)	1880			9.5		0.2	1
Amber2 (upper)						0.5	
Red (upper)	2500			11		1.5	4

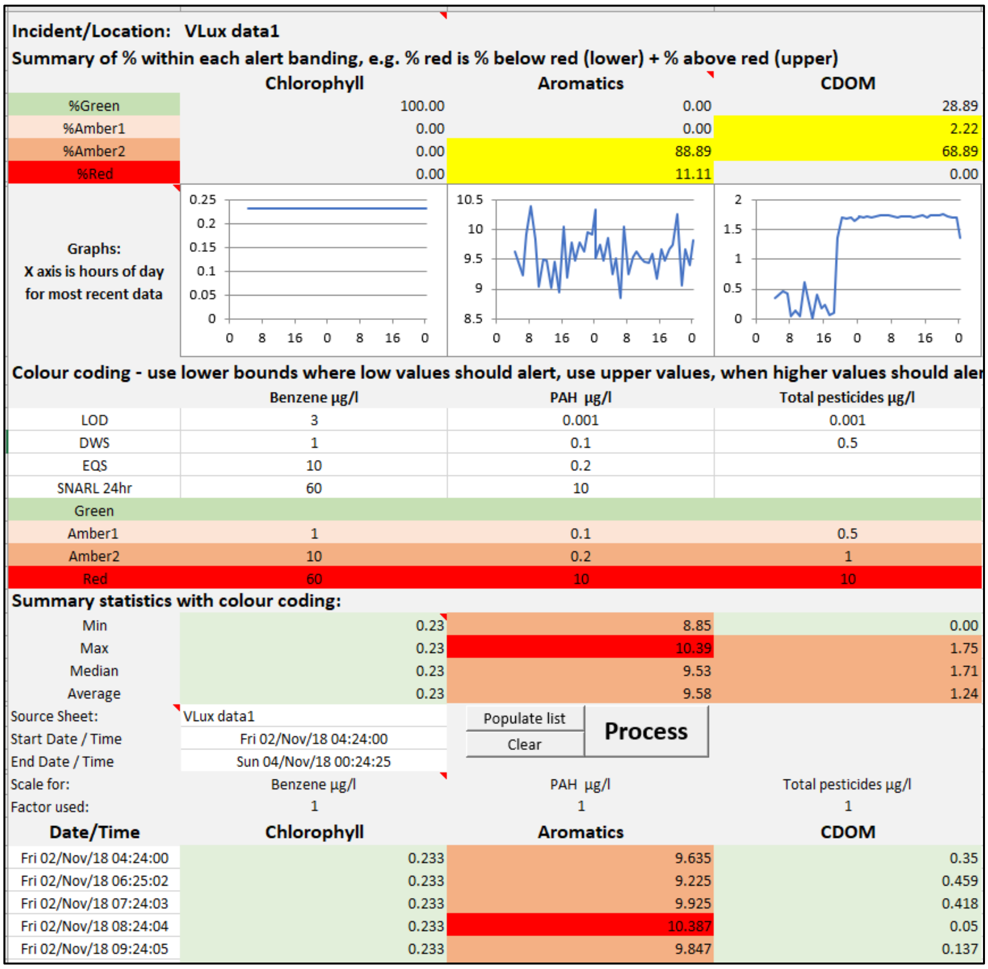
Summary statistics with colour coding:

	Cond µS/cm	Sal psu	TDS mg/L	pH	dO mg/l	Ammonium mg/l	Turbidity NTU
Min	25.20	0.02	26.00	6.27	0.02	0.20	0.00
Max	26.60	0.02	26.00	6.45	9.00	91.00	5.00
Median	25.60	0.02	26.00	6.36	4.00	0.20	0.00
Average	25.71	0.02	26.00	6.36	3.57	6.39	1.86

Source Sheet: 18.05.2018 Llyn Brianne
Start Date / Time: 07/06/2018 00:00 Trimmed to 7 days
End Date / Time: 13/06/2018 23:45
Populate | Clear | Process
Source Sheet: 18.05.2018 Llyn Brianne DO
Timebase Rows matched: 672 rows out of 672
Proportion - 100% is all times: 100.0

Date/Time	Cond µS/cm	Sal psu	TDS mg/L	pH	dO mg/l	Ammonium mg/l	Turbidity NTU
Thu 07/06/18 00:00	25.3	0.02	26	6.31	4.01	0.2	0
Thu 07/06/18 00:15	25.3	0.02	26	6.3	4.02	0.2	0
Thu 07/06/18 00:30	25.3	0.02	26	6.3	4	0.2	0
Thu 07/06/18 00:45	25.3	0.02	26	6.3	4	0.2	0
Thu 07/06/18 01:00	25.3	0.02	26	6.3	4	0.2	0
Thu 07/06/18 01:15	25.3	0.02	26	6.3	4	0.2	0
Thu 07/06/18 01:30	25.3	0.02	26	6.3	4	0.2	0

Figure 3: Rapid assessment tool summary of inorganic parameters.



Incident/Location: VLux data1

Summary of % within each alert banding, e.g. % red is % below red (lower) + % above red (upper)

	Chlorophyll	Aromatics	CDOM
%Green	100.00	0.00	28.89
%Amber1	0.00	0.00	2.22
%Amber2	0.00	88.89	68.89
%Red	0.00	11.11	0.00

Graphs:
X axis is hours of day
for most recent data

Colour coding - use lower bounds where low values should alert, use upper values, when higher values should aler

	Benzene µg/l	PAH µg/l	Total pesticides µg/l
LOD	3	0.001	0.001
DWS	1	0.1	0.5
EQS	10	0.2	
SNARL 24hr	60	10	
Green			
Amber1	1	0.1	0.5
Amber2	10	0.2	1
Red	60	10	10

Summary statistics with colour coding:

	Chlorophyll	Aromatics	CDOM
Min	0.23	8.85	0.00
Max	0.23	10.39	1.75
Median	0.23	9.53	1.71
Average	0.23	9.58	1.24

Source Sheet: VLux data1
Start Date / Time: Fri 02/Nov/18 04:24:00
End Date / Time: Sun 04/Nov/18 00:24:25
Populate list | Clear | Process

Scale for:	Benzene µg/l	PAH µg/l	Total pesticides µg/l
Factor used:	1	1	1

Date/Time	Chlorophyll	Aromatics	CDOM
Fri 02/Nov/18 04:24:00	0.233	9.635	0.35
Fri 02/Nov/18 06:25:02	0.233	9.225	0.459
Fri 02/Nov/18 07:24:03	0.233	9.925	0.418
Fri 02/Nov/18 08:24:04	0.233	10.387	0.05
Fri 02/Nov/18 09:24:05	0.233	9.847	0.137

Figure 4. Rapid assessment tool summary of organic parameters.

The data processed by the tool for organic pollutants (Figure 4) uses fluorescence as a measure of aromatic hydrocarbons (Benzene and PAHs). These parameters are used by the tool as a proxy for oil (fuel and crude) and aromatic pesticides where agricultural run-off may be an issue. The monitoring data presented by this technique is in the form of fluorescence units and requires the user to set a correction factor within the assessment tool for the parameter of interest. The tool prompts users to select the parameter of interest from a drop-down menu and the correction factor is then automatically applied during processing.

DISCUSSION

The rapid assessment tool is designed for reviewing raw monitoring data and to flag results which may be indicative of a pollution incident requiring further consideration. In this way, the tool is aimed at assessing data captured during the initial phases of a pollution incident and helping to inform subsequent actions. The tool is not designed to provide the user with a detailed risk assessment but to identify potential incidents and aid rapid response.

Subsequent response may include issuing of alerts to response teams, to initiate management controls and further detailed sampling and analysis, issuing of advice to stakeholders that may be impacted such as industries, communities, recreational users etc. downstream of an incident, as well as regulators.

The fluorimetry technique was identified as appropriate for incident response due to its capability to identify and quantify organics outside of a laboratory environment. The parameters are identified from a common signal using correction factors. In practice, the manufacturer reports that the measured fluorescence can be quenched by high turbidity, this is overcome by an algorithm applied by the device. We have considered this in the rapid assessment tool to alert users for the need for further consideration.

CONCLUSION AND RECOMMENDATIONS

Oil, pesticides, sewage, blue-green algae and solid tars/waxes are the most prevalent substances reported during in-land and maritime water incidents reported to the agencies surveyed. By identifying indicator or proxy substances for these releases it is possible to utilise real-time in-situ monitors to determine the magnitude of the incident impact.

The monitoring and sampling market provides capacity for water, air and land contamination. However, for dioxins and furans monitoring techniques currently in use rely on collection of a sample on a filter media and subsequent laboratory analysis and as such are not suitable for field deployment.

Based upon techniques used for assessment of impacts from fires, a tool was developed to rapidly assess potential pollution incidents in water environments. The tool can contribute to rapid risk assessment of potential impacts from pollutants using real-time data, informing advice, analysis and response strategies. The tool utilises existing standards and guidelines based on drinking water, bathing water and environmental quality standards and applies rapid visual alerts related to these.

The tool is intended to provide a rapid assessment of water quality and identify potential pollution incidents enabling prompt response and management. In this respect the tool has been designed to be simple to use, to quickly provide results for several days of monitoring data and provide assessment of results against relevant standards and triggers. The design also enables users to easily review the data from visual colour coded and graphical outputs, helping to inform decisions.

The tool has been tested as a beta version with data supplied by UK regulatory and commercial organisations using standard monitoring techniques. While the tool is currently designed as a demonstration of concept, receiving data from specific monitors there is potential for it to be further developed to automate the processing of data from many more monitors and techniques and using data in a range of formats.

APPENDIX A

Rapid assessment tool instructions (for use with the excel spreadsheet tool)

The spreadsheet is designed for reviewing raw monitoring data and to flag results which may be indicative of a pollution incident and require further consideration.

The aim of the tool is to provide a rapid review of monitoring data captured during the initial phases of a pollution incident in order to inform subsequent actions (alerts, sampling and analysis, pollution controls / management, risk communications). Please note it is not designed to provide the user with a detailed risk assessment.

The spreadsheet allows you to store raw data (if necessary) and will automatically process output reports.

Raw data files are added to the tool and then imported into the appropriate "Template" using the "Populate" and "Process" buttons in the Template, (or by cutting and pasting the data into designated Template cells). Please refer to the 'Quick Instructions' page for more detailed information on how to add and process data.

There are two templates; for inorganic and organic parameters. At the top of each template there are fields available to record the incident name.

On processing, the spreadsheet will generate a new worksheet (which is named using the monitoring location details specified on the template page) recording who processed the data, with a date and time stamp. A number of observations on the dataset are recorded: monitoring duration; maximum and minimum intervals between data points; and total number of data points.

The template will compare data to a range of standards and colour coded trigger values to indicate any potential pollution events. The user will need to select the appropriate standard to consider in their assessment, based on the environmental location of the sample (effluent, fresh water, saltwater) and the receptors (human, ecological).

A graph of key pollutants will be automatically generated following the processing of data to show trends and flag any peaks for each parameter during the monitoring period.

Quick Instructions

Open this workbook (the tool) and your raw data (this tool is a beta version and has been designed to work for YSI and Chelsea Technology data sets only at this time).

You may wish to keep a copy of your raw data in the same workbook as your processed output, if so:

a) Copy the raw datasheet into the tool by:

b) Selecting the spreadsheet to be imported (you can select multiple tabs while pressing and holding down Ctrl)

c) Right click on the selected sheet tab(s) and select "Move or Copy" tick the "create copy" box

d) A dialog box appears asking where to copy to, select the tool spreadsheet and "move to end" Click OK.

e) In the tool spreadsheet, click on a single sheet to be imported for processing.

To Process Data

1) Select Template – inorganic or organic
2) Press "Clear" to remove any existing data
3) Press Populate and choose data set from drop down list of existing worksheets
4) Select Process

Outputs

Processed data will be presented for each parameter in a series of graphs indicating results over monitoring period and as tables showing Min, Max, Average and Median with each cell colour coded indicating compliance or exceedance to relevant standards.

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