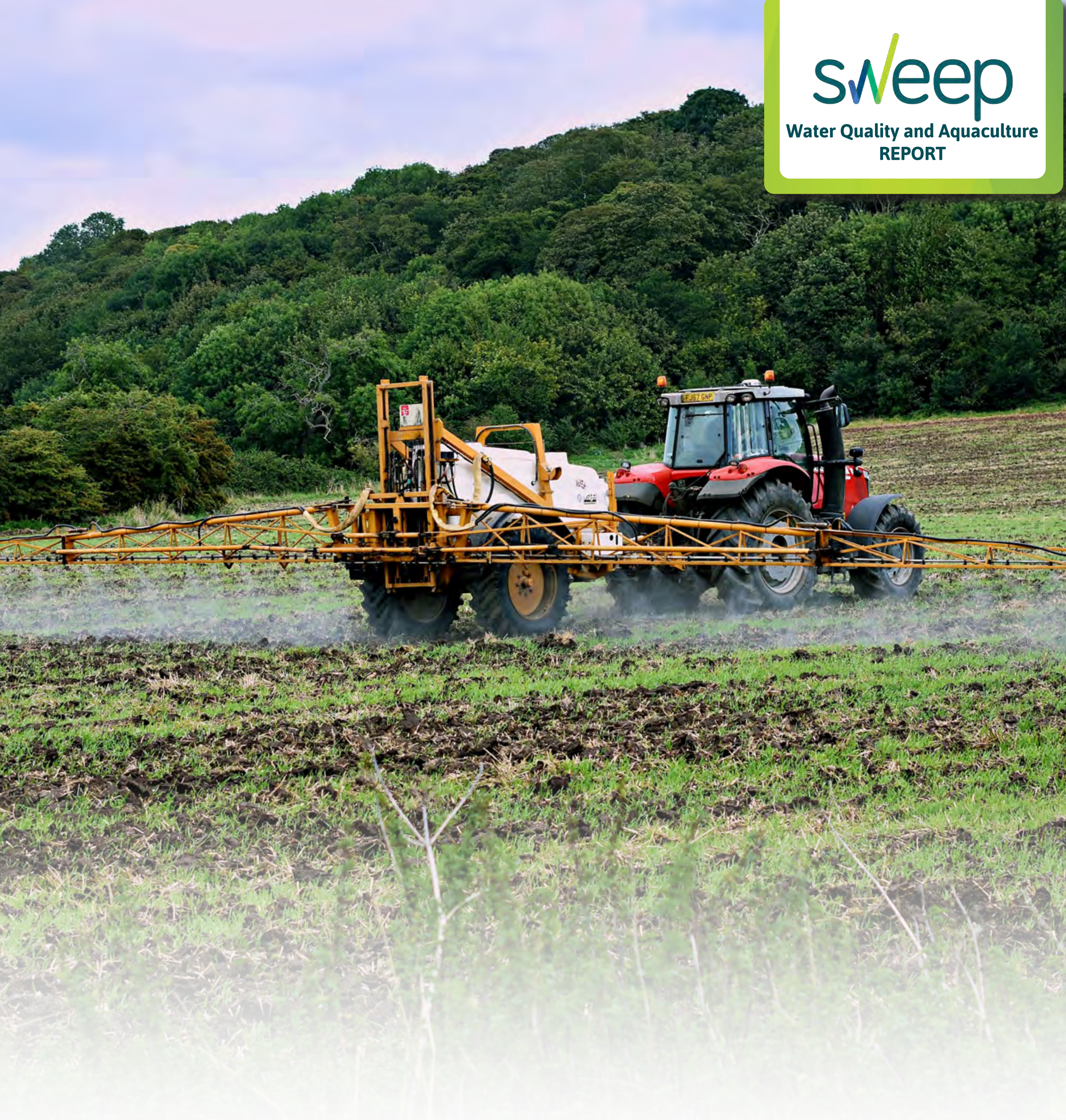
Water Quality and Aquaculture REPORT



# Acid herbicide wash-off exploration tool

## Guidance document

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# Acid herbicide wash-off exploration tool.

Guidance document

## Summary

This guidance document describes the **Acid herbicide wash-off catchment exploration tool** and details how it can be used. The tool allows users to evaluate the scale and trajectory of mobilised acid herbicides (i.e. agricultural run-off from grassland) during periods of intense rainfall and understand the potential impact on phytoplankton. It has been developed to explore these issues within the UK's South West estuaries, however the approach could be easily adapted to incorporate new catchments, chemicals and future scenarios. The tool is not intended to be a comprehensive hydrological and chemical fate model and its underpinning strengths and limitations are set out in this guidance document accordingly.

This tool and guidance document were developed under the NERC-funded South West Partnership for Environmental and Economic Prosperity programme (**SWEEP**) as part of the project on **Water Quality and Aquaculture** which seeks to evaluate the effect of water quality on the viability of bivalve aquaculture in South West England's estuaries.

### Key findings

1. We have developed a simple logic chain risk assessment tool designed to evaluate relative risk from acid herbicides washing off agricultural land due to intense rainfall.
2. The approach is easily adaptable to incorporate new catchments, chemicals and future scenarios. Full explanation on how to achieve this is built into the risk assessment spreadsheet.
3. The **main utility of the tool is as a simple, high-level analysis, engagement and exploration tool**. It is intended as an initial strategic level approach, applied by an expert with understanding of its limitations, as such we have designed our tool to be easily adaptable for future adjustment and application.
4. We emphasise that this report and associated spreadsheet tool are only suitable as a high level and relative risk assessments. The approach is not calibrated or validated to provide reliable absolute values for pesticide concentrations.

For more information and details of the spreadsheet tool, please contact Dr Ross Brown (Ross.Brown@exeter.ac.uk).

# Introduction

## Why evaluate acid herbicides?

The toxicity of acid herbicides in the aquatic environment is generally considered to be low; however, the ubiquity of potential sources within South West England's river catchments, where such a large proportion of the total catchment area is managed grassland (which are commonly treated using acid herbicides), warrants a risk assessment of simultaneous and widespread pollution incidents triggering acute toxicity events within estuaries.

Of pertinence to the SWEEP South West England Aquaculture Study is the possibility that these events could negatively impact the phytoplankton food sources supporting bivalve populations, hindering growth or leaving shellfish susceptible to disease.

## Report structure

We evaluate the acid herbicide risk assessment through examining a series of questions relating to the likelihood and magnitude of pollutant sources, pathways and receptor impacts.

- What are the key acid herbicides applied to the catchments?
- What are key transmission pathways?
- Can contaminant reach estuary?
- How much contaminant is applied?
- How much contaminant is mobile?
- How much contaminant washes off?
- What concentration could the contaminant reach in estuary?
- What is impact on phytoplankton?
- How can future scenarios be included within the tool?

# What are the key acid herbicides applied to the catchments?

The predominant active ingredients in acid herbicides applied to manage grassland include 2,4-D, Clopyralid, Fluroxypyr, MCPA, Mecoprop and Triclopyr. Applications exist in a wide range of formulations for both agricultural and domestic treatments. These acid herbicides are generally soluble, highly mobile, and persistent following application, resulting in a potential risk of treatments causing damage to the aquatic environment.

| | 2,4-D | Clopyralid | Fluroxypyr | MCPA | Mecoprop | Triclopyr |
|---|---|---|---|---|---|---|
| Water-sediment DT50 (days) | 18.2 | - | 34.7 | 17 | 141 | 29.2 |
| Water phase only DT50 (days) | 7.7 | 148 | 10.5 | 13.5 | 92 | 24.8 |
| Adsorption ($K_f$) | 0.7 | 0.071 | 1.2 | 0.94 | 1.54 | - |
| Application mobile in water (%) | 59% | 93% | 45% | 52% | 39% | - |
| Adsorption ($K_{foc}$) | 39.3 | 5 | 68 | 74 | 59.8 | - |
| Algae acute 72-hour $EC_{50}$, growth (mg $l^{-1}$) in freshwater[1] | 24.2 | 30.5 | 49.8 | 79.8 | 16.2 | 181 |

Table 1: Characteristics of predominant acid herbicides used within South West England (data from the University of Hertfordshire and IUPAC PPDB).

# What are key transmission pathways?

The mobility and persistence of acid herbicides results in a risk of treatments entering watercourses and being transported into estuaries. The two main sources of contamination are agricultural and domestic application.

## Agricultural application

Agricultural application of acid herbicides is typically undertaken to manage broad leaf weeds on managed grassland within two crop spraying windows: late spring and late autumn. Each field is typically treated once every four years, meaning it is reasonable to assume 25% of managed grassland will be sprayed annually.

[1] We have used the acute freshwater $EC_{50}$ as a relative measure of toxicity due to data availability, but assess impact using the acute saltwater values, which are typically lower.

Agricultural pathways include:

- Rainfall events mobilising and washing off water-phase contaminants in field runoff following application and transporting sediment-phase contaminants into watercourse through soil erosion.
- Groundwater flow transporting water-phase contaminants to watercourses.
- Spray drift directly depositing application to field drains or watercourses.
- Poor preparation and washdown procedures leading to chemical losses from steadings to watercourses.
- Dumping or poor storage practices.

The most significant potential pathway leading to transmission of acid herbicides is a wash-off generating rainfall event triggering catchment scale contribution of recently applied chemicals. Smaller and more gradual inputs are likely to be related to leaching of eroded topsoil and groundwater flow; however, this is unlikely to reach the scale and magnitude of a widespread contamination event.

The smaller scale, improbability of simultaneous inputs, dispersed spatial application and need to deviate from well-established standard practices means that this study assumes compliant standard practice from landowners within catchments, therefore discounting risks associated with poor or negligent chemical handling and treatment. Although significant at a local scale, this type of malpractice is also less likely to be significant at a catchment scale, relative to the sort of simultaneous catchment scale input triggered by a rainfall event mobilising runoff to watercourses.

### Domestic application

Domestic scale application of acid herbicides in lawn enhancing products is also a potential pathway, predominantly through CSO spills or wastewater treatment deficiencies; However, the scale of domestic gardens is substantially smaller than the total area utilised for agricultural grassland, and as such is deemed to be a less significant risk factor.

Therefore, assuming compliant best practice, we propose that the most significant acid herbicide source and transmission pathway within South West England is a high magnitude catchment scale agricultural contamination event, caused by intense rainfall triggering field wash-off.

## Can contaminant reach estuary?

The first stage in our risk assessment determines whether the pathway is sufficient for contaminants to reach the receptor (estuary).

We determine that it is very likely any contaminant applied which washes off fields into watercourses will reach the estuary. This is based on the persistence of the acid herbicides, of which the minimum $DT_{50}$ in the water phase is 7.7 days (2,4-D). This is significantly higher than the hydraulic response time of the catchments, which is in the order of hours.

Any acid herbicides existing in the aqueous phase within surface soil which then wash-off from land are likely to the reach estuaries. This could occur if a wash-off triggering rainfall event occurs in the catchment whilst acid herbicides are available.

# How much contaminant is applied?

Dosage of acid herbicides varies across the range of available products; however, is typically within the magnitude of 1 – 2 kg $ha^{-1}$. We calculate the total amount of contaminant by multiplying the dosage (1.5 kg $ha^{-1}$) by area treated (ha).

Area treated varies year on year, however a typical managed grassland is treated with acid herbicides to manage broadleaf weeds on average once every four years. Spraying takes place in treatment windows in Spring and Autumn, which last approximately eight weeks.

For analysis, we have assumed 25% of total grassland is treated every year, and application is uniformly applied across two spraying windows.

# How much contaminant is mobile?

We assume mobile contaminants are those which exist within the aqueous phase in surface soil. This is governed by two coefficients, the ratio between the contaminant bound to soil: mobile in a water phase ($K_f$) and the proportion which is washed off.

The $K_f$ coefficient describes a default ratio of a chemical which is bound to soil versus that available in a water phase. We have converted this to a percentage of application remaining available in a water phase to calculate the total mobile contaminant.

In practice, $K_f$ is variable based on the organic carbon available within soils. For a baseline scenario we have applied the default $K_f$ value from the Pesticide Properties Database (Table 1), however for later stages of the risk assessment we also consider how contaminant availability varies along with soil carbon using the $K_{foc}$ coefficient (Table 1).

# How much contaminant washes off?

The wash off coefficient describes the proportion of the contaminant which is washed off during intense rainfall. This variable is highly dependent on the topography (particularly slope), soil type and structure, distance to watercourse and presence of interventions such as buffer strips. For strategic analysis, we applied a wash off coefficient of around 10% as a high-level estimate for our baseline scenario, based on the FOCUS soil report[2] which details a range of European case studies.

The proportion of contaminant which is washed off represents a small amount relative to the overall application, however we stress that this is under compliant best practice across a large area and the wash off from specific fields within watersheds is likely to vary significantly from the 10% assumed wash off. For comparison, 100% wash off, albeit very improbable, would contribute up to the total mobile

[2] FOCUS Surface Water Modelling Working Group. 2012. Generic guidance for FOCUS surface water scenarios. Section 2.3.2

contaminant. This does not take into account sediment bound particulates, which we assume remain in field, however significant wash off events may also mobilise sediment.

## What concentration could the contaminant reach in estuary?

To calculate contaminant concentration in the estuary, we divide the total washed off contaminant by the estuary volume at low water. This calculation assumes the relatively worst-case assumptions of the full available washed off load entering the estuary at the same time and the estuary being at low volume when this happens. However, this also assumes a uniform contaminant distribution across the entire estuary volume which in practice is likely to be governed by complex mixing. **Error! Reference source not found.** presents the resultant concentration given these assumptions.

## What is impact on phytoplankton?

We evaluate the impact on phytoplankton through examining the estuary concentration relative to two key ecotoxicity thresholds, the predicted no effect concentration (PNEC) which is used as the current Environmental Quality Standard (EQS) and the $EC_{50}$ for the saltwater micro-algal species, *Skeletonoma costatum.*

## QA versus spot samples

We have undertaken a quality assurance of our approach through comparing indicative levels with spot samples taken across the Exe Catchment. During this analysis we find that our peak concentrations are in the same order of magnitude to peaks identified within the River Exe (0 - 10 $\mu g\ l^{-1}$); however, we caution several significant limitations with this process:

Input conditions (application rate, extent and runoff) associated with peak monitored values are unknown, so we cannot replicate these within our risk assessment. In fact, it is unlikely that the sort of worst-case application of a uniform acid herbicide immediately prior to a rainfall event would be replicated in practice.

Monitored data are from the River Exe, where dilution is much lower than we assume in the estuary.

Monitored data points are spot samples. Recent research cautions relying on spot samples for peak values due to inability to confirm whether these capture peaks, finding a 30-fold difference between spot samples and continuously monitored peak concentrations[3].

In summary, we determine that our logic chain risk assessment can provide indicative and relative values for high level comparison but cannot validate results and so do not recommend that absolute values are considered accurate.

[3] Lefrancq *et al*. 2017. High frequency monitoring of pesticides in runoff water to improve understanding of their transport and environmental impacts. *Science of The Total Environment* 587–588, p. 75-86

To maximise this utility to stakeholders we have implemented our analysis within a risk assessment tool within which variables can easily be adapted to suit future application and iteration of analysis.

## Including future scenario within the risk assessment

Due to uncertainties described in the high-level risk assessment, we consider the main utility of this analysis to be in relative comparison of scenarios, as opposed to absolute quantification of acid herbicide levels. Therefore, our risk assessment tool is easily adaptable across a range of scenarios to evaluate the relative scale and direction of change which may occur in response to catchment intervention and future conditions.

### Soil management change

Managing condition is crucial to ensure soils remain effective for environmental capital and regulation. Soil condition can be considered as a function of soil health, structure and compaction.

The organic carbon content within soils is frequently used as a proxy for health, with higher organic carbon being indicative of a healthier, more resilient and more productive soil. The organic carbon within soil is also a key controlling factor in determining the ratio of acid herbicides which bind to soil relative to acid herbicides which exist in water. This relationship is defined through the constant $K_{foc}$, which describes the relationship between organic carbon and the soils $K_f$ ratio.

We have included the effect of increasing soil heath by modifying $K_f$ based on a range of soil organic carbon levels, with a low (0.5%) and a high (5%) organic carbon scenario.

Soil condition is also affected by structure and compaction. With better managed soils demonstrating a looser structure with less compaction. We have represented this within the risk assessment through adjusting the wash off variable, with a low (5%) and a high (25%) scenario.

Different soil types, land slopes and the presence of interventions such as buffer strips can also be represented by adjusting the organic carbon and wash off variables within our risk assessment spreadsheet.

### Land use change

We represent land use changes through adjusting the crop types and area treated. For this analysis we have considered increasing and decreasing the treated area by 25% and 50% as an indicative representation of how future land use change within catchments may affect resultant pollutant loads.

Further detail could be added to land use change by simultaneously adapting soil condition variables, as described above.

### Behaviour change

Farmer behaviour change can be represented through adjusting the application schedule and quantity. The application schedule includes changing fields treated per year, number of treatment windows and fields treated before rainfall event (a proxy of treatment window length and treatment distribution). Application quantity can be adjusted through changing the dosage rate variable.

For this analysis we evaluate changes to treatment windows and dosage rate (1 kg $ha^{-1}$ and 2 kg $ha^{-1}$).

### Climate change

The predominant impact of climate change on the hydrological cycle is likely to be an increase in the intensity of rainfall events. We have represented this here through adjusting the wash off variable to represent a larger rainfall event triggering high runoff rates and washing off a higher proportion of mobile contaminant. This is a difficult relationship to define, so for an indicative example we have evaluated the impact of a 50% wash off rate.

## Conclusions

1. We have developed a simple logic chain risk assessment tool designed to evaluate relative risk from acid herbicides washing off agricultural land due to intense rainfall.
2. The approach is easily adaptable to incorporate new catchments, chemicals and future scenarios. Full explanation on how to achieve this is built into the risk assessment spreadsheet.
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