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On the potential of on-line free-surface constructed wetlands for attenuating pesticide losses from agricultural land to surface waters

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Abstract

Pesticides make important contributions to agriculture but losses from land to water can present problems for environmental management, particularly in catchments where surface waters are abstracted for drinking water. "On-line" constructed wetlands have been proposed as a potential means of reducing pesticide fluxes in drainage ditches and headwater streams. Here, we evaluate the potential of two free-surface constructed wetland systems to reduce pesticide concentrations in surface waters using a combination of field monitoring and dynamic fugacity modelling. We specifically focus on metaldehyde, a commonly-used molluscicide which is moderately mobile and has been regularly detected at high concentrations in drinking water supply catchments in the UK over the past few years. We also present data for the herbicide metazachlor. Metaldehyde losses from the upstream catchment were significant with peak concentrations occurring in the first storm events in early autumn, soon after application. Concentrations and loads appeared to be minimally affected by transit through the monitored wetlands over a range of flow conditions. This was probably due to short solute residence times (quantified via several tracing experiments employing rhodamine WT – a fluorescent dye) exacerbated by solute exclusion phenomena resulting from patchy vegetation. Model analyses of different scenarios suggested that, even for pesticides with a relatively short aquatic half-life, wetland systems would need to exhibit much longer residence times (RTs) than those studied here in order to deliver any appreciable attenuation. If the ratio of wetland surface area to the area of the contributing catchment is assumed to be a surrogate for RT (i.e. not accounting for solute exclusion) then model predictions suggest that this needs to be greater than 1% to yield load reductions of 3 and 7% for metaldehyde and metazachlor, respectively.

1. Introduction

Pesticides make important contributions to maintaining crop yield and quality in modern agriculture. However, pesticide losses from land to surface waters have the potential to cause ecological damage if their concentrations exceed effect thresholds for key taxa (Brock et al., 2006). Furthermore, they can represent major problems for water companies abstracting for domestic supply. The European Drinking Water Directive (80/778/EEC, amended 98/83/EC) sets limits for drinking water supplies of 0.1 µg L^{-1} for any individual pesticide and 0.5 µg L^{-1} for all pesticides at the point of supply (effectively in water leaving treatment works for distribution). A significant fraction of most pesticides in raw waters can be removed by the treatment processes commonly employed by water supply companies. However, some active ingredients are more difficult and/or expensive to remove. Recent examples include clopyralid, metaldehyde, propyzamide and carbetamide which are commonly applied to arable crops. Furthermore, even where significant removal is possible, high concentrations in raw waters may still occasionally present compliance challenges (e.g. Tediosi et al., 2012). Metaldehyde (a commonly-used molluscicide) has been regularly detected at high concentrations in drinking water supply catchments in the UK over the past few years (Kay and Grayson, 2014; Lu et al., 2017) and is particularly expensive to remove by standard water treatment processes (Rolph et al., 2018). The UK water industry is coming under increasing pressure from regulators (e.g. the Drinking Water Inspectorate and the Environment Agency) to find alternative solutions to supplement improvements in water treatment technologies and the focus has started to shift to source control options (Mohamad Ibrahim et al., 2019). Indeed, this is a requirement of Article 7 of the EU Water Framework Directive (EC 2000) for catchments used for water supply (Dolan et al., 2014). Possible mitigation strategies include employing buffer zones to reduce overland flow and associated pesticide transport, taking more care during sprayer fill-up and washdown operations, treating farm yard runoff (e.g. using biobeds: Cooper et al., 2016), changing the mix of active ingredients used, where possible (including product substitution: Mohamad Ibrahim et al., 2019) and changing crop rotations to reduce overall catchment-scale usage. Many of these options will involve increased costs to farming and should, therefore, be justified by a sound understanding of the processes contributing to pesticide loss from the farm, as well as demonstrating efficacy. For example, establishing edge-of-field buffer zones will be of little use if, as we have shown in the Upper Cherwell catchment (Tediosi et al., 2012), the main pathway for pesticide transfer from land to water is via field drains – which can effectively short-circuit riparian zones.

In cases where it is difficult or undesirable to effect land use change or to reduce application rates, it may still be possible to reduce concentrations in the receiving surface water network by constructing attenuation features in fields or in ditches (Newman et al., 2015). Natural and man-made wetland habitats are well known to provide efficient removal of organic materials, nutrients and metals (e.g. CEH, 2001; Newman et al., 2015) via a combination of sorption and biodegradation before they are released into the natural drainage network or reach water supply reservoirs. Ponds and free-surface wetlands are open areas of shallow water which can be used for temporary storage of excess water during storm events. If the storage period is long enough, relative to the removal rates operating within them (e.g. degradation by microbes, volatilisation, sorption to sediment or uptake by vegetation), such features can be effective for removing pollution from surface water runoff (Gregoire et al. 2009). A number of mesocosm studies have indicated that constructed wetland systems do have the potential to dissipate a range of pesticides (e.g. Moore et al., 2000), and there is some evidence that such systems may also perform effectively at the field scale (Schulz and Peall, 2001; Moore et al., 2002; Moore et al., 2009; Passeport et al., 2013), although this evidence is rather limited. There is, therefore, a need to investigate the potential for reducing pesticide transfers from land to surface waters using field- and ditch-scale mitigation features (typically vegetated free-surface constructed wetlands). In this paper, we assess the utility of such features for attenuating pesticide transport from land to surface waters with a specific focus on metaldehyde using a combination of high frequency monitoring and numerical modelling.

2. Methods

2.1 Monitoring

The behaviour of metaldehyde and metazachlor in two existing on-line (in-stream) free-surface constructed wetland systems was investigated at Hope Farm in Knapwell, Cambridgeshire, UK (Figure 1). The farm occupies 181 ha on calcareous clay loam belonging to the Hanslope soil series (Cranfield University, 2017). Metaldehyde is applied via a bespoke hopper mounted on the back of a quadbike – most frequently in the August post-harvest period. Metazachlor, a herbicide used to control grass and broad-leaved weeds in arable crops, is applied via spraying in late August. The two monitored systems (located to the north and south of the farm) have a free water surface (FWS) with emergent vegetation. Vegetation cover is seasonal and is dominated by reeds (Phragmites australis) and bulrushes (Typha latifolia) which start growing in spring (March onwards) and die back in late autumn (October-November). The winter period is characterised by progressive stem decay which may result in reduced flow resistance. At the south site, two wetlands with bank-full surface areas of 242 and 322 m^2 (see Table 1) have been placed in series (about 114 m apart) on a small stream (catchment area: 3.9 km^2) which drains land which is not under the control of Hope Farm: South Wetland 1 and South Wetland 2 (Figure 1; Figure 2), located upstream and downstream respectively. At the north site, a single constructed wetland with a bank-full surface area of 262 m^2 (North Wetland, Figure 2) has been excavated on a drainage ditch (see Table 1 for details). This feature drains a catchment of approximately 0.66 km^2 containing four fields. At the downstream end, a bund has been constructed which outflows via a pipe (37 cm internal diameter). This means that the flow regime on this system is intermittent (i.e. the wetland only flows when water levels exceed the level of the outflow pipe).

FIGURE 1 HERE

TABLE 1 HERE

Monitoring was conducted in a number of storm events and under base flow conditions over one autumn-winter period (August-December 2014). At each feature, gauging structures (a combination of flat plate 60° V-notch weirs and Washington State College Design Venturi flumes) were established on the inlet and outlet to measure discharge. Water levels (stage) were measured using a combination of pressure transducers (Mini-Divers: Van Essen Instruments, Netherlands) and ultrasonic devices (AV2150 submerged probe: Teledyne-ISCO, Lincoln, NE, USA). A tipping bucket rain gauge was installed locally (603 m from the South Wetland 2 outlet and 1059 m from the North Wetland outlet) for hydrological modelling and data interpretation. Water samples were collected using a combination of manual grab sampling and ISCO 6712 automatic samplers (Teledyne-ISCO, Lincoln, NE, USA). The automatic samplers were used to collect samples every 8 hours. Where possible, samples were typically analysed within a week of sample collection. In this case, samples were kept in the dark at 4℃ before analysis. Instrument issues meant that some samples needed to be stored for several weeks. In this case, samples were either refrigerated (maximum storage time 3 weeks) or frozen. Possible losses of pesticides by sorption or degradation during sample storage were evaluated via a stability study. Briefly, pesticide standards were added to wetland water in polyethylene plastic bottles at nominal concentrations of 0.2 to 10 $\mu g\ L^{-1}$, incubated at either 4℃ or -20 ℃ and analyzed over a period of 112 days. No significant sorption was observed in the filter membrane and losses of all pesticides were below 3%

(refrigerated samples) and 10% (frozen samples), suggesting that stored samples were stable (see Ramos et al., 2017 for full details). Samples were analysed for five pesticide active ingredients (metaldehyde, propyzamide, metazachlor, carbetamide and quinmerac) using a novel LC/MS-MS method. Only data for metaldehyde and metazachlor are presented here, as examples, but similar outcomes were observed for the others. The paper by Ramos et al. (2017) details the method and the quality control measures which were implemented. Briefly, the method employed a Waters Alliance 2695 liquid-chromatography system coupled to a Quattro premier XE tandem quadrupole. A Kinetex C18 column (5 µm 150 × 2.1 mm, Phenomenex, UK) thermostated at 60 °C was used for chromatographic separation with a flow rate of 0.3 mL min^{-1} and an injection volume of 50 µL. The mobile phase consisted of ultra-pure water with 0.1% acetic acid and methanol with 0.1% acetic acid. Electrospray ionization was performed in positive mode. The mass spectrometer was operated under multiple reaction monitoring focussed, for metaldehyde, on a reaction with precursor and fragment ions of m/z 198.9 and m/z 66.9, respectively, as recommended by the Environment Agency (2009). Basic environmentally-relevant properties of metaldehyde are shown in Table 2. Data for the herbicide metazachlor are also presented in this paper and this compound was analysed simultaneously using the same method. Method Limit of Detection (LoD) and Limit of Quantification (LoQ) for both metaldehyde and metazachlor were 0.09 and 0.3 µg L^{-1}, respectively. These are high compared with the 0.1 µg L^{-1} EU limit for drinking water (80/778/EEC, amended 98/83/EC) but are adequate for monitoring concentrations in headwater catchments where concentrations during runoff events are often considerably higher.

FIGURE 2 HERE

TABLE 2 HERE

2.2 Dye tracing

A number of dye tracing exercises were conducted on each feature under different conditions (see Fox et al., 2000 and Whelan et al., 2007 for examples). In each exercise, Rhodamine WT was injected as a pulse upstream of the inlet of each feature to ensure that the tracer was cross-sectionally well-mixed and, hence able to fully describe solute transport. The breakthrough curve of the dye was monitored by measuring fluorescence with instruments installed in-situ at the inlet and outlet of the feature. We employed two approaches to modelling solute behaviour in the studied wetlands: (1) the Aggregated Dead

Zone (ADZ) model of Beer and Young (1983) and (2) maximum entropy deconvolution (Sonnenwald et al., 2015) to determine solute Residence Time Distributions (RTDs) for each system under different conditions. The “non-parametric” (empirical) RTD is the theoretical distribution of solute in a system in response to an instantaneous input (Levenspiel, 1972) and makes no a priori assumptions about how the system operates (Stovin et al. 2010). Both the ADZ and RTD reveal insights into the mixing characteristics of the studied systems such as the identification of “short-circuiting” phenomena. Incomplete mixing can reduce the effectiveness of wetland features for pesticide mitigation by reducing contact with degrading micro-organisms or sorption sites.

2.3 Numerical Modelling

A mathematical model was constructed to describe the fate and transport of pesticides in free-surface wetland systems. This provides an explanatory framework for interpreting the findings from the monitoring work and laboratory studies. It also allows the understanding gained from the project to be extrapolated to implementation scenarios (e.g. to predict the effectiveness of different ratios of catchment area to treatment size [surface area and volume]) for different assumptions about pesticide-specific properties.

The model was a dynamic adaptation of the steady-state QWASI model (Mackay et al., 1983) and has recently been applied to investigate the behaviour of volatile methyl siloxanes in an Arctic lake (Krogseth et al., 2017). The processes represented by the model are shown in Figure 3. The mass balance equations for pesticide in water and sediment can be written:

$$\frac{dM_w}{dt} = E + f_{IN}.D_{IN} + f_a.D_a - f_w.(D_r + D_v + D_Q + D_{SS} + D_{WS} + D_{dep}) + f_s.(D_{SW} + D_{res}) \qquad (1)$$

$$\frac{dM_s}{dt} = f_w.(D_{WS} + D_{dep}) - f_s.(D_{SW} + D_{rs} + D_b + D_{res}) \qquad (2)$$

where M_w (mol) is the pesticide mass in the water column, M_s (mol) is the pesticide mass in the sediment, E (mol h^{-1}) is direct emission to water, f_w is the pesticide fugacity in the water column, f_a is the pesticide fugacity in air, f_{IN} is the pesticide fugacity in inflowing water and f_s is the pesticide fugacity in sediment. The D values represent the magnitudes of chemical transfer or transformation with subscripts as follows: IN is inflowing water, a is air to water transfer, r is reaction in water, v is volatilisation, Q is advection in outflowing water, SS is suspended solids advection in the outflow, WS is diffusive exchange between the water column and the sediment, dep is the deposition of contaminated sediment, SW is diffusive exchange between the sediment and the water column, rs is reaction in sediment, b is burial and res is sediment resuspention. Fugacity (f) is the medium-equivalent to partial pressure in the gas phase (which is the reference fugacity) and is related to concentration via the general relationship:

$$C = f.Z \tag{3}$$

where Z is the fugacity capacity (mol m^{-3} Pa^{-1}). For air, Z_{air} is simply calculated from temperature (T) as

$$Z_{air} = \frac{1}{R.T} \tag{4}$$

where R is the gas constant. For the other compartments Z is expressed in terms of partition coefficients at equilibrium. This means that by writing the mass balance equations in fugacity form, rather than in concentration form, thermodynamic gradients (i.e. the direction and magnitude of phase disequilibrium) are incorporated automatically via differences in fugacity (phases are in equilibrium if they have equal fugacities). All fugacity terms have units of Pa and all D values have units of mol Pa^{-1} h^{-1}.

FIGURE 3 HERE

Model equations were solved numerically using Euler’s method with a time step of 0.1 hour. Scenarios for free-surface wetland deployment were developed and treatment effectiveness assessed.

3. Results and Discussion

3.1 Monitoring: South Wetland

Examples of monitored discharge and metaldehyde concentrations in the inlet of SW1 and the outlet of SW2 are shown in Figure 4 for the Autumn and early Winter (August-November) 2014. Conditions over this period were slightly wetter than the seasonal average for this part of the UK (total rainfall 1st of August to 31st of December was 335 mm compared to a long-term average of 262 mm for this period reported in nearby Cambridge: https://en.climate-data.org). The maximum daily rainfall in the monitoring period was 34 mm d^{-1} which is relatively high. Two early storm events (14 and 26 mm d^{-1} with maximum intensities of 10 and 5.4 mm h^{-1}) on the 14th and 25th of August 2014 generated peak discharges of 46 and 78 L s^{-1}, respectively and resulted in elevated concentrations of metaldehyde. Application dates for metaldehyde in this catchment are unknown because most land is not part of Hope Farm. However, we know that Hope Farm applied metaldehyde in accordance with agronomic recommendations on the 19th of August, so we can assume that most application in the wider South Wetland catchment will have occurred around this time. In the second of these events inlet metaldehyde concentrations peaked at about 9 μg L^{-1}. It is worth reiterating that metaldehyde is applied as solid (wheat-based) pellets which act as bait for slugs. This means that metaldehyde may be leached from the recently-applied pellets by these early rainfall events, as pellets do not typically disintegrate rapidly. Thereafter, concentrations responded to subsequent events in October and November but not to the same levels. This is because the later events occurred several weeks after the main application period so a significant fraction of metaldehyde would have broken down in the soil. Similar "exhaustion" responses of concentrations to a series of storm events have been observed for propyzamide and carbetamide in the Cherwell catchment (Tediosi et al., 2012; 2013). Although the increase in concentration starts early on each storm event (i.e. concentrations increase with increasing discharge), concentrations continue to increase after peak discharge (i.e. during hydrograph recession). This suggests that pathways for metaldehyde transport to the stream are slower than those for bulk water transport. This is consistent with the fact that metaldehyde is applied in pellet form and, thus needs to move from the pellets to the soil prior to displacement from the soil. It is also consistent with the fact that only a small mass of pesticide is required (both in relative and absolute terms) to elevate concentrations significantly. Simultaneously, it is supported by the general insight from tracer studies which have been conducted elsewhere that, in most catchments, the biggest contribution to stream flow is from the displacement of "old" (pre-event) water which has been resident in the catchment from some time (e.g. Klaus et al., 2013). In most cases, this old water should have low residual pesticide concentrations.

Metaldehyde concentrations in paired inlet and outlet samples (i.e. where the outlet sample was collected within approximately one hour of the inlet sample time) in the South Wetland system are shown in Figure 5. The red dashed line shows the 1:1 relationship and the solid black line shows the best-fit linear regression. The relationship between the inlet and outlet concentrations was strong ($R^2 > 0.9$). Moreover, most of the points fall close to the 1:1 line suggesting that the outlet concentrations were similar to those in the inlet and the slope of the best-fit line was (0.9) close to unity. These concentrations were also compared formally using a paired t-test to assess whether differences were statistically significant. This confirmed that there was no significant difference between them ($p > 0.01$).

FIGURE 4 HERE

FIGURE 5 HERE

3.2 Monitoring: North Wetland

Figure 6 shows daily rainfall, inflow discharge (V-notch weir) and the concentrations of metaldehyde and metazachlor (for comparison) in the North Wetland inflow and outflow between late August and early October 2014. Both the inlet ditch and the wetland were relatively dry in early August. However, the rainfall event on the 25th of August (26 mm day^{-1}) triggered a short (24 hour) hydrograph with a peak discharge of 20 L s^{-1} on the 26th. The flashy nature of this hydrograph suggests that rapid hydrological pathways such as overland flow played a significant role in this event. Soil moisture content prior to the event was low and 26 mm of rainfall is unlikely to have reduced soil moisture deficits to anywhere near field capacity. In fact, we calculate that less than 2% of the rainfall was translated into runoff, so it is unsurprising that the shallower recession curves often associated with soil drainage (evident in Figure 4 and to a lesser extent in Figure 7) are not apparent. By the end of the 27th of August (and through to the 13th of October) flow in both the inlet and outlet of the wetland were negligible, although subsequent small precipitation events resulted in some minor inflows. During this period, the North Wetland essentially behaved as a static system with no significant inlet or outlet flows.

Concentrations of both metaldehyde and metazachlor in the inlet increased and then decreased sharply during this storm event. However, inlet concentrations beyond the 28th of August probably represent those in the pond behind the inlet weir and, hence, do not represent real inflows. No inlet samples were collected beyond the 6th of September. In the wetland itself (sampling point close to the outlet), concentrations of both pesticides also increased during the storm event of the 25th-26th of August (to about 18 and 150 µg L^{-1} for metaldehyde and metazachlor, respectively). However, subsequent decreases were more gradual and may have resulted from a combination of dilution caused by minor rainfall events in this period, some water turnover (high-concentration advective outflow replaced with lower concentration inflow), net sorption to sediment and in-situ losses (e.g. by degradation and or volatilisation). For both compounds, the rate of decrease in concentration to the 3rd of September was steeper than in the period thereafter. This may reflect some dilution (inflow concentrations < outflow concentrations) but may also be a result of some net sorptive losses from the water column to the sediment. Net sorption will be negligible as thermodynamic equilibrium is reached. Unfortunately, no metaldehyde data are available between the minor storm event on the 25/09/2014 and mid-October which makes full interpretation of metaldehyde behavior challenging for this system – at least in this period of static water. However, concentrations did decrease approximately monotonically from 9.4 µg L^{-1} on the 4th of September to about 7 µg L^{-1} on the 25th. The behaviour of metazachlor during this period is also worthy of comment; concentrations decreased quasi-exponentially from 54 µg L^{-1} on the 4th of September to 2.6 µg L^{-1} in early October, with a DT_{50} of 9 days. The mechanisms for this removal are still not completely understood but the exponential shape of the concentration decay suggests that some biodegradation of metazachlor may have occurred within the wetland over this period. For reference, the laboratory-derived DT_{50} of metazachlor reported for a water-sediment system (PPDB, 2016) is 20 days. Advective solute losses via water infiltration into the bed and banks of the wetland would not have changed concentration in the water remaining. This is explored in more detail in Section 3.4 on modelling.

FIGURE 6 HERE

Figure 7 shows the time series of metaldehyde concentrations in the inlet and outlet of the North Wetland, along with rainfall and discharge in the outflow, between mid-October and early December for periods when the outflow was active. As in Figure 4, concentrations in the inlet and outlet of this system were very similar (slope of regression between inlet and outlet concentrations = 1.03, $R^2 = 0.96$) and there was no significant difference between paired concentrations (paired t test $p < 0.01$). Again, similar observations were made for the other pesticides including metazachlor (slope = 1.18, R^2 = 0.86: data not shown). Thus, as for the South Wetland system, there is little or no pesticide removal in the North Wetland system for flow-active periods, even though the catchment area for this system is much smaller than that for the South Wetland.

FIGURE 7 HERE

3.3 Dye Tracing

Example fluorescence data from the inlet and outlet of South Wetland 1 is given in Figure 8. These data were collected under approximately steady state flow conditions with a discharge of 13.5 L s^{-1}. The change in peak fluorescence between the inlet and outlet is principally caused by hydrodynamic dispersion and dilution (mixing) with the existing water in the wetland.

FIGURE 8 HERE

For steady state, the theoretical (or nominal) residence time can be estimated as the quotient of the water volume and the flow rate (i.e. assuming idealised “plug flow”). For the Hope Farm wetlands, which typically have an approximate volume of 105 m^3, this yields a nominal residence time of 130 minutes for a discharge of 13.5 L s^{-1} (Figure 8). For a discharge of 5 L s^{-1} the nominal residence time would be around 350 minutes, whilst for 40 L s^{-1} it is approximately 44 minutes. However, the peak-to-peak delay shown in Figure 8 is only 25 minutes; far shorter than the nominal residence time. This discrepancy is not uncommon and reflects “short circuiting”, where a significant fraction of a tracer is retained for periods which are much shorter than the nominal residence time.

Fitting the Aggregated Dead Zone (ADZ) model of Beer and Young (1983) to the tracer data obtained in South Wetland 1 at Hope Farm suggested that solute fully mixes in only about 50% of the wetland volume, with the remainder exhibiting pure advection. Cumulative RTDs (CRTD) obtained using maximum entropy deconvolution for several dye traces obtained at Hope Farm are shown in Figure 9. This analysis shows that the maximum solute residence time in both the South Wetland systems was less than about 90 minutes for all flow conditions examined. The t_{50} (the time for half the introduced solute to pass through the wetland) was between 10 and 50 minutes for South Wetland 1 and between 10 and 20 minutes for South Wetland 2. The t_{50} of 25 minutes for South Wetland 1 at 13.5 L s^{-1} is comparable with the peak-to-peak delay of 25 minutes observed for this discharge in Figure

8. These times are significantly shorter than the nominal residence times (44 - 350 minutes for flow rates of 40 and 5 L s^{-1}, respectively). The North Wetland has a smaller catchment area so discharges tend to be lower. In addition, the outflow is controlled by the bund at the downstream end which is drained via a pipe. This creates longer residence times in this system – particularly when the outflow is limited. Values of t_{50} of 60 and 360 minutes were observed for discharge conditions of 17 and 0.5 L s^{-1} respectively, although these values were also significantly shorter than the nominal residence times for this system. Again, this implies that the mixing volume is smaller than the total volume of the wetland and suggests that more direct solute transport pathways exist, i.e. some solute is “excluded” from some zones - reflecting the complexity of processes associated with real heterogeneous vegetation (Sonnenwald et al., 2017).

FIGURE 9 HERE

3.4 Modelling

3.4.1 South Wetland System

Predictions of metaldehyde behaviour in the South Wetland system generated using the dynamic fugacity model based on QWASI (Mackay et al., 1983; Mackay, 2001; Krogseth et al., 2017) are shown in Figure 10 for the first two storm events in autumn 2014, under different assumptions of water depth and wetland water surface area. In all cases, the DT_{50} in water was assumed to be 12.2 days (i.e. the reported value for a water-sediment test in PPDB, 2016) and that in sediment was (arbitrarily) assumed to be 122 days.

The red lines show the model predictions of concentration in the outflow, the open symbols show the measured concentrations in the outflow and the green line shows the measured concentrations in the inflow (linearly interpolated to give a time-continuous curve). In all cases, the mass influx of chemical was calculated as the product of the measured influent concentration and the influent discharge. Figure 10a shows the expectation based on the best-estimate of wetland conditions at the time of monitoring (water depth, $z = 0.5$ m, water surface area, $A = 210$ m^2). There is a good match between the model predictions and the measured data – primarily because there is such a low hydraulic residence time in the South Wetland, particularly during storm events. Increasing the water depth to 1 m had little effect, although there was a slight reduction in concentrations due to increased dilution and residence time (Figure 10b). Increasing the water surface area by a factor 2, with other factors remaining constant (Figure 10c) resulted in some (again, relatively minor) additional attenuation. More significant attenuation was only really achieved (i.e. concentrations were reduced by 36%) with a factor 10 increase in surface area (Figure 10d), although most of the concentration change was due to dilution and the total mass removal of metaldehyde was still predicted to be <1%. This is largely due to the fact that even for the largest wetland volume, the nominal residence time is still very low compared with the assumed DT_{50} of metaldehyde (12.2 days). At peak discharge (69 L s^{-1}), the nominal solute residence times for these scenarios range from just 0.42 h (25 minutes) (Figure 10a) to 8.45 h (507 minutes) (Figure 10c).

FIGURE 10 HERE

3.4.2 North Wetland System

Model results for the North Wetland static period are illustrated in Figure 11 for metazochlor (a and b) and metaldehyde (c and d). In all cases, an arbitrary system temperature of 15 °C was assumed, together with an Arrhenius activation energy of 60 kJ mol^{-1} which is typical of many organic pollutants in environmental systems [Rocha and Walker 1995; Fenner et al., 2007] but which is slightly lower than the value of 65.4 kJ mol^{-1} recommended by EFSA for regulatory evaluations (https://www.efsa.europa.eu/en/efsajournal/pub/622). As for metaldehyde in the South Wetland, the initial concentration of both compounds in the wetland were reasonably well predicted by the model suggesting that the input loads (the product of discharge and measured concentrations) were accurate. In Figure 11a, standard PPDB (2016) chemical-specific parameters for metazachlor were assumed. This clearly underestimated the loss rate under static conditions in this system. In Figure 11b, the DT_{50} in water for metazachlor was reduced to 5.6 days (135 h). Although this is shorter than the apparent half-life derived from directly fitting an exponential decay curve to the data (ca 9 days), this is adjusted in the model for partitioning between the freely dissolved phase and the suspended solids and for temperature (see Whelan et al., 2015). Figure 11c shows the predicted concentrations of metaldehyde for default system dimensions and chemical properties (PPDB, 2016). Again, model performance was reasonably good in terms of the peak concentrations triggered by the storm event. However, the measured concentration data do not display first order kinetics (the initial decline in concentrations was more rapid than in the period beyond 250 h) and the model performance is, therefore, relatively weak overall and particularly in the latter part of the record. This implies that the DT_{50} adopted for metaldehyde (12.2 days) may be too low, even considering temperature adjustment, although some model assumptions (e.g. the assumption of a time-constant water volume in each scenario may explain some of the discrepancy). The effect of hypothetically changing pond surface area (by factors of 2, 5 and 10, with all other factors kept constant) on predicted concentrations in the North Wetland for the static period are also shown in Figure 11d. The increase in system volume reduces the predicted peak concentration mainly due to dilution.

FIGURE 11 HERE

The model was also applied to a period in November when the North Wetland was flowing continuously (cf Figure 7) in order to evaluate the effect of increasing wetland area on metaldehyde concentrations. The predictions are shown in Figure 12 for the default case and for increases in surface area by factors of 2, 5, 10 and 20 (i.e. A = 600, 1500, 3000 and 6000 m^2, respectively). The assumption of A = 6000 m^2 represents a wetland area to catchment area ratio of approximately 1%. This is a feasible area for a constructed wetland and is consistent with farm wetland siting for nutrient removal in Demark (e.g. Hashemi et al., 2018) and with recommendations (1–2%) by Passeport et al. (2013) for "on-line" features. Passeport et al. (2013) reported load reductions between 45 and 96% for 11 herbicides and 5 fungicides (mainly due to partly-reversible sorption) in a 1280 m^2 free surface constructed wetland serving a tile-drained catchment of 46 ha (average hydraulic retention time of about 8 hours) but this system was off-line (i.e. water was diverted from the ditch to the wetland during the post application period). As in the case of the South Wetland simulations, the modelled influx of metaldehyde was assumed to be the product of discharge and interpolated inflow concentrations. For the default assumptions, the predicted outflow concentrations match the measured data reasonably well, reflecting the similarity of the measured inflow and outflow concentrations. As the assumed wetland area increases (with all other factors remaining constant), the wetland volume and nominal residence times increase and predicted peak concentrations decrease by approximately 4, 12, 22 and 32%, respectively. However, the attenuation in metaldehyde flux is predicted to be only 0.06, 0.14, 0.41, 0.99 and 2.4%, respectively, for the default, x2, x5, x10 and x20 cases. In other words, predicted concentration changes are principally the result of dilution rather than loss processes. This is illustrated by the fact that predicted concentrations between 100 and 300 hours increase with increasing wetland surface area (i.e. the peak concentrations for increasing areas are lower but the residence times are longer so the pesticide mass remains in the system for longer). When the model was run for metazachlor, with an assumed DT_{50} of 135 h - as inferred from the static period data, these predicted reductions were 0.29, 0.60, 1.52, 3.24 and 6.84% (data not shown). For metadehyde in the x20 scenario 83% of the in-system losses were predicted to be due to degradation (D_r) and 16% due to volatilisation (D_v). For metazachlor 97% of in-system losses in the x20 scenario were predicted to be due to degradation (D_r). Net sorption to sediment is not predicted to represent a significant sink in most storm events for either pesticide. Of course, incomplete mixing would reduce residence times and, hence, reduce likely removal rates in reality.

It is widely recognised that biodegradation is often more rapid in shallow water bodies than in ones. For example, high first order rate constants (k) of 0.3 and 0.75 h^{-1} were reported for linear alkylbenzene sulphonate (LAS) in shallow streams in Yorkshire (Fox et al., 2003) and the Philippines (McAvoy et al., 2003). In contrast, lower values of k for LAS of 0.05 and 0.096 h^{-1}, respectively, have been reported in deeper rivers in Italy (Whelan et al., 1999) and Laos (Whelan et al., 2007). Similarly, in-stream denitrification rates have been inversely related to depth (Seitzinger et al., 2002). This is probably because the size of the competent microbial biomass in the water column is relatively low compared with the microbial community in biofilms attached to the wetted perimeter of the channel, which means that degradation will depend on contact time with the fixed biofilm. In shallow systems, dissolved pollutants are more likely to come into contact with the bed than in deep ones – especially if turbulence is also higher. For similar reasons, biodegradation is believed to proceed more rapidly in natural river channels compared with channels with relatively smooth (e.g. concrete lined) beds. This is because natural beds typically have a higher surface roughness and, hence, a higher surface area on bed materials for biofilm development (Boeije et al., 2000). Wetland shape can also influence performance. Carty et al. (2008) suggest that wide farm wetlands with low aspect ratio (length to width less than 2.2) tend to perform better than long and thin ones, all other factors being equal and assuming full mixing, although residence time still needs to be sufficient for the relevant treatment processes to have an effect. The wetlands investigated here have low aspect ratios (between 1.8 and 2.4) but without long residence times they were relatively ineffective.

FIGURE 12 HERE

4. Conclusions

Some pesticides present significant challenges for European Drinking Water Directive compliance in catchments used for domestic water supply. This is often the case, periodically, in catchments with a high fraction of intensive agriculture. When artificial field drainage is prevalent, drainflow usually represents a major transport pathway and this makes in-field mitigation of pesticide transfers difficult.

Free-surface wetland features are relatively cheap to install using diggers and loaders commonly available on farms and offer a potential means of attenuating pesticide transfers from agricultural land to surface waters (Passeport et al., 2013). We monitored the pesticide attenuation performance of three small free-surface wetlands with different catchment areas in Cambridgeshire, UK. Observed removal rates were relatively low – particularly during storm events, when pesticide loads were highest. A dynamic fugacity-based model of chemical behaviour in free-surface wetlands was constructed in order to provide a framework for interpreting the observed data and for evaluating different combinations of controlling factors in different scenarios. Model predictions broadly agree with measurements for the wetlands investigated (although some adjustment of chemical-specific properties was required to get a good match for the North Wetland system) and suggest that poor attenuation performance can be largely explained by low solute residence times. Dye-tracing exercises and subsequent analysis suggest that incomplete mixing (short circuiting) often occurs in the monitored wetlands, which will reduce residence times and attenuation potential. This can be exacerbated by patchy vegetation, which can promote exclusion zones for solute.

There is some potential for reducing peak concentrations and loads for relatively larger wetlands – particularly for low-discharge, high-concentration events, provided that long water residence times can be achieved. Pesticide removal for the North Wetland system was estimated to be approximately 12% for metaldehyde and 20% for metazachlor under static conditions. However, total mass removal (flux reduction) was negligible during storm events (<1%). Although predicted peak concentrations of both compounds decreased when assumed wetland surface area to catchment area ratio (R_A) was increased (cet. par.), appreciable load reduction was predicted only when R_A was greater than about 1%. Even then, load reduction was still <3% for metaldehyde and <7% for metazachlor, given a 29-fold increase in wetland area.

Overall, our data suggest that small on-line FWS wetland features may be relatively ineffective at reducing pesticide concentrations and loads during storm events and, hence, are probably not a viable approach to deliver effective catchment management of pesticide fluxes into receiving water bodies used for drinking water production. Wetland performance will improve if the catchment size is small relative to the wetland dimensions (i.e. where residence times are high). This means that a large number of such features would need to be constructed in the landscape to make an appreciable difference at the catchment scale. Wetland performance may also be enhanced by ensuring that contact between solutes and wetland surfaces are maximised – e.g. by installing baffles to enhance mixing, by designing wetlands with low water depth, segmenting wetlands into discrete basins (Scholz et al., 2007) and reducing the aspect ratio (provided full mixing can be ensured). The introduction of sorptive surface materials into the wetland may also be of value and further research is required to explore the efficacy of different materials for this purpose.

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Table 1. Details of the wetland features assessed in this study. All systems were unlined and had a natural bed consisting of approximately 15cm of organic rich fine sediment. All systems were excavated around 2000 and planted with reeds (Phragmites australis) and bulrushes (Typha latifolia) but the plants are unmanaged and the original vegetation distributions have altered over time. Water depth in each system during the winter is typically around 0.5 m.

Wetland	Surface Area (m^2)	Length (m)	Width (m)	Length: Width Ratio
South Wetland 1	242	30	16.8	1.79
South Wetland 2	322	36	18.6	1.93
North Wetland	262	28	11.5	2.43

Table 2. Environmentally-relevant properties for (a) metaldehyde (PPDB, 2016) and (b) metazachlor. K_d is the soil solid to water partition coefficient, K_{OC} is the organic carbon to water partition coefficient, K_{fOC} is the Freundlich isotherm organic carbon to water partition coefficient range derived from EFSA (2010), Sol is aqueous solubility, K_{AW} is the air to water partition coefficient (the dimensionless Henry's Law constant) and DT_{50} is the dissipation half life. W-S is water and sediment, * refers to the range of water DT_{50} in water-sediment tests derived from EFSA (2010).

	K_d (L kg^{-1})	K_{OC} (L kg^{-1})	K_{fOC} (L kg^{-1})	Sol (mg L^{-1})	K_{AW}	DT_{50} (days)		
						Soil	W-S	W-S (water)*
(a)	0.23	240	38-149	188	1.43×10^{-3}	5.1	12.2	10 - >1000
(b)	0.78	54	54-220	450	1.80×10^{-7}	8.6	20.6	49 - 384

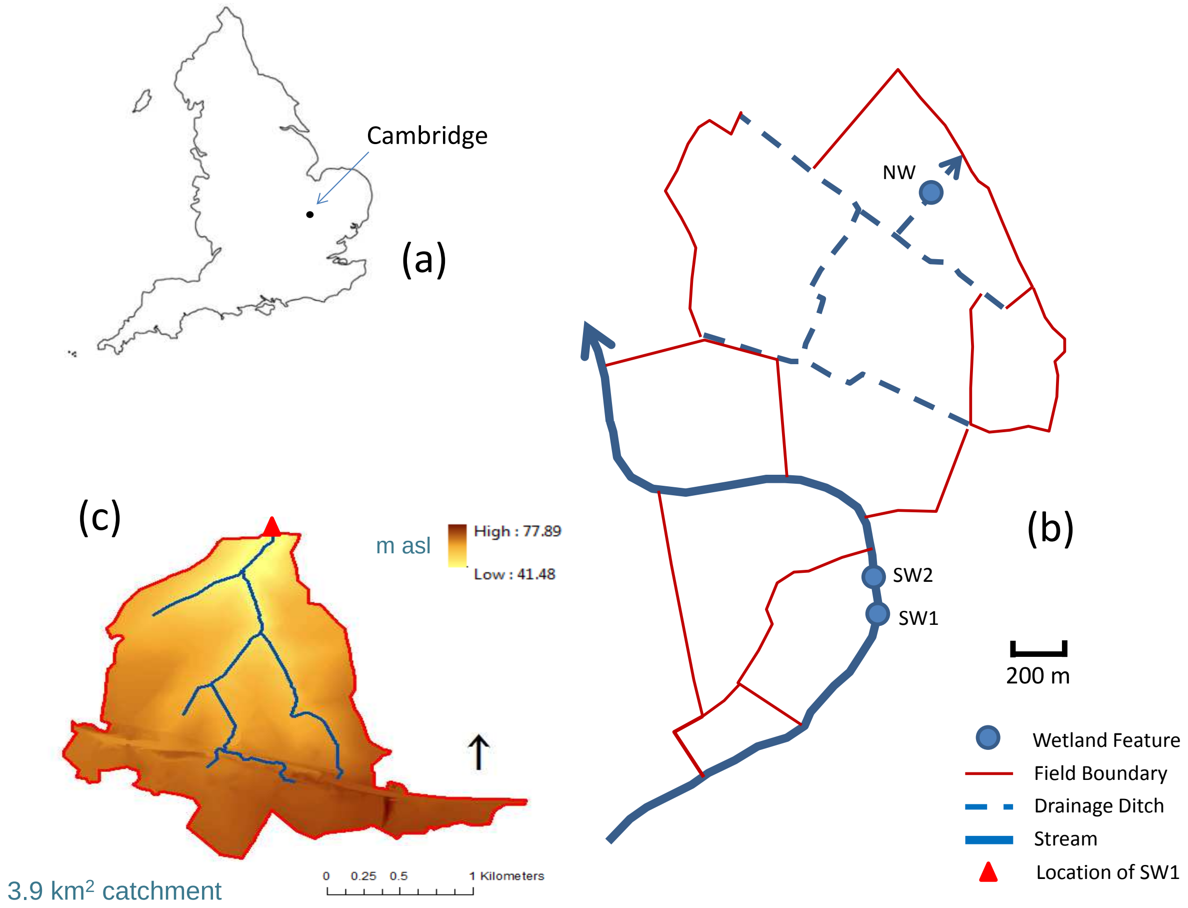


Figure 1. (a) General location of Hope Farm, Cambridgeshire; (b) The location of the monitored wetlands on the stream and drainage network (NW is North Wetland; SW is South Wetland; automatic samplers and gauge structures were installed at the inlet and outlet of each feature); (c) Catchment area and elevation map for the South Wetland system derived from UK Ordnance Survey Terrain 5 Data (5 m gridded digital elevation model).

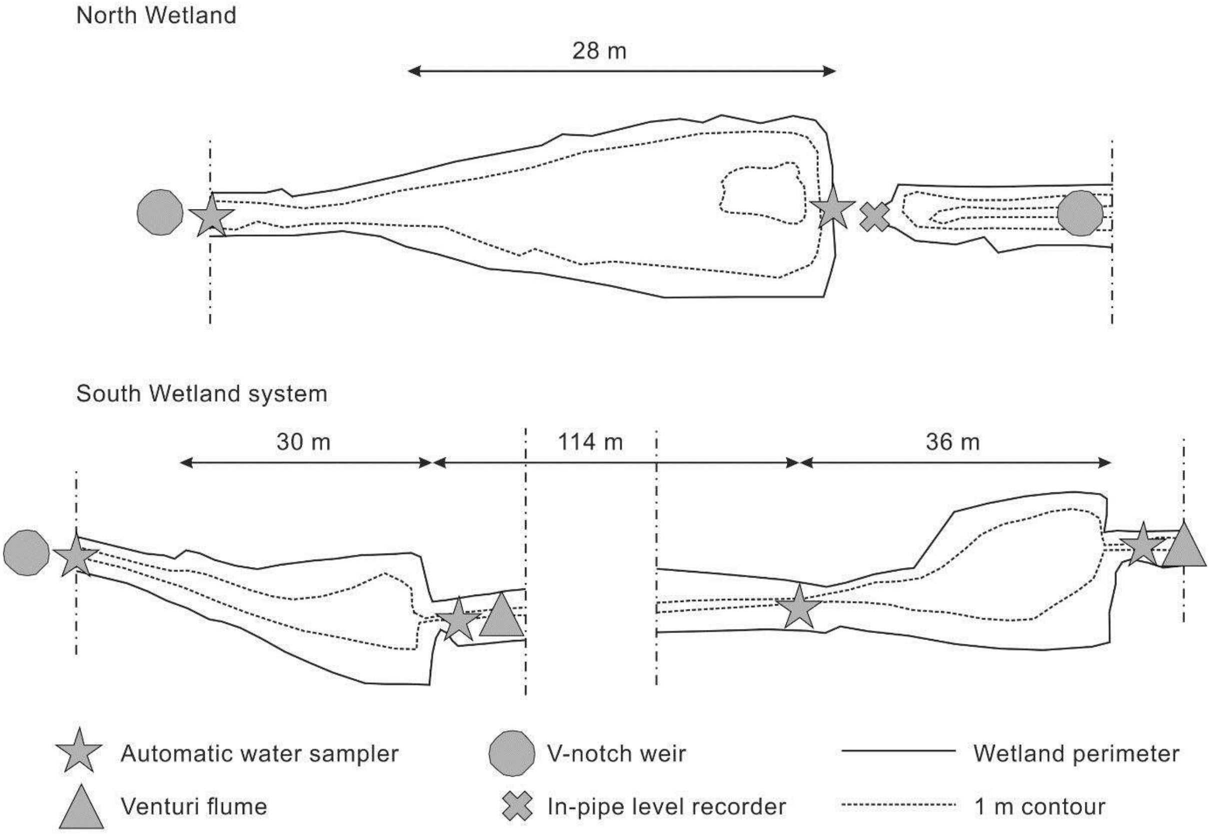


Figure 2. Detailed plans of the monitored wetlands showing the location of automatic samplers and gauging structures. The wetland perimeter represents a bank-full water level. The 1 m contours are drawn relative to a datum on the perimeter.

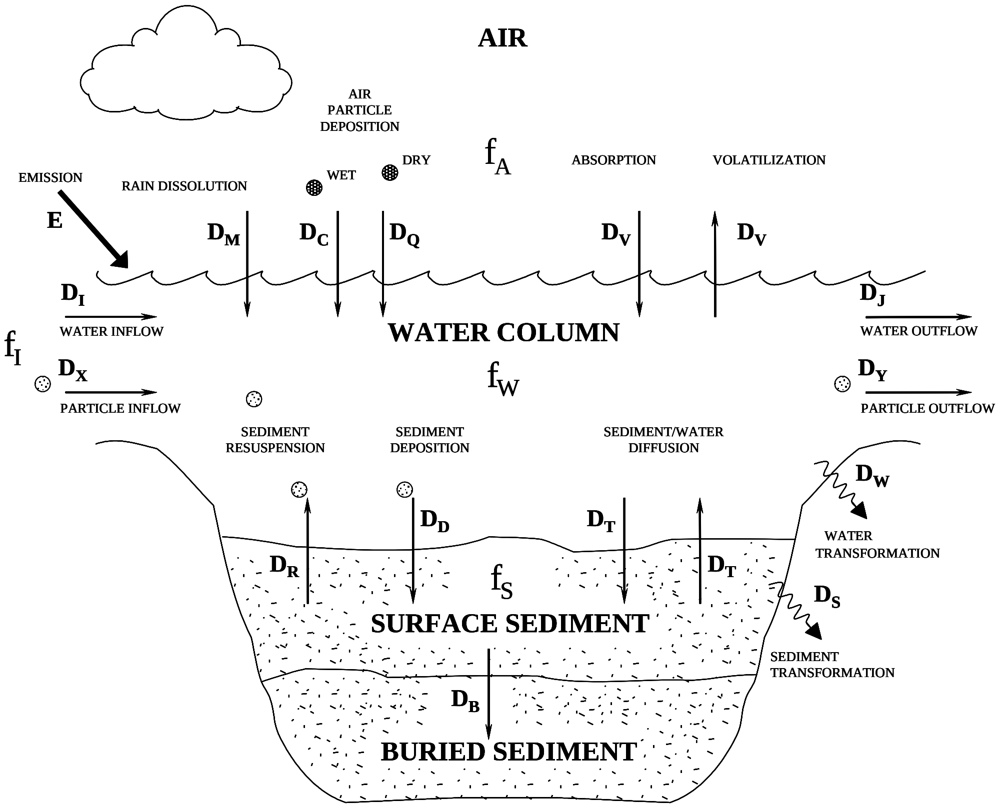


Figure 3. Schematic illustration of the processes represented by the QWASI lake model (after Mackay et al., 1983).

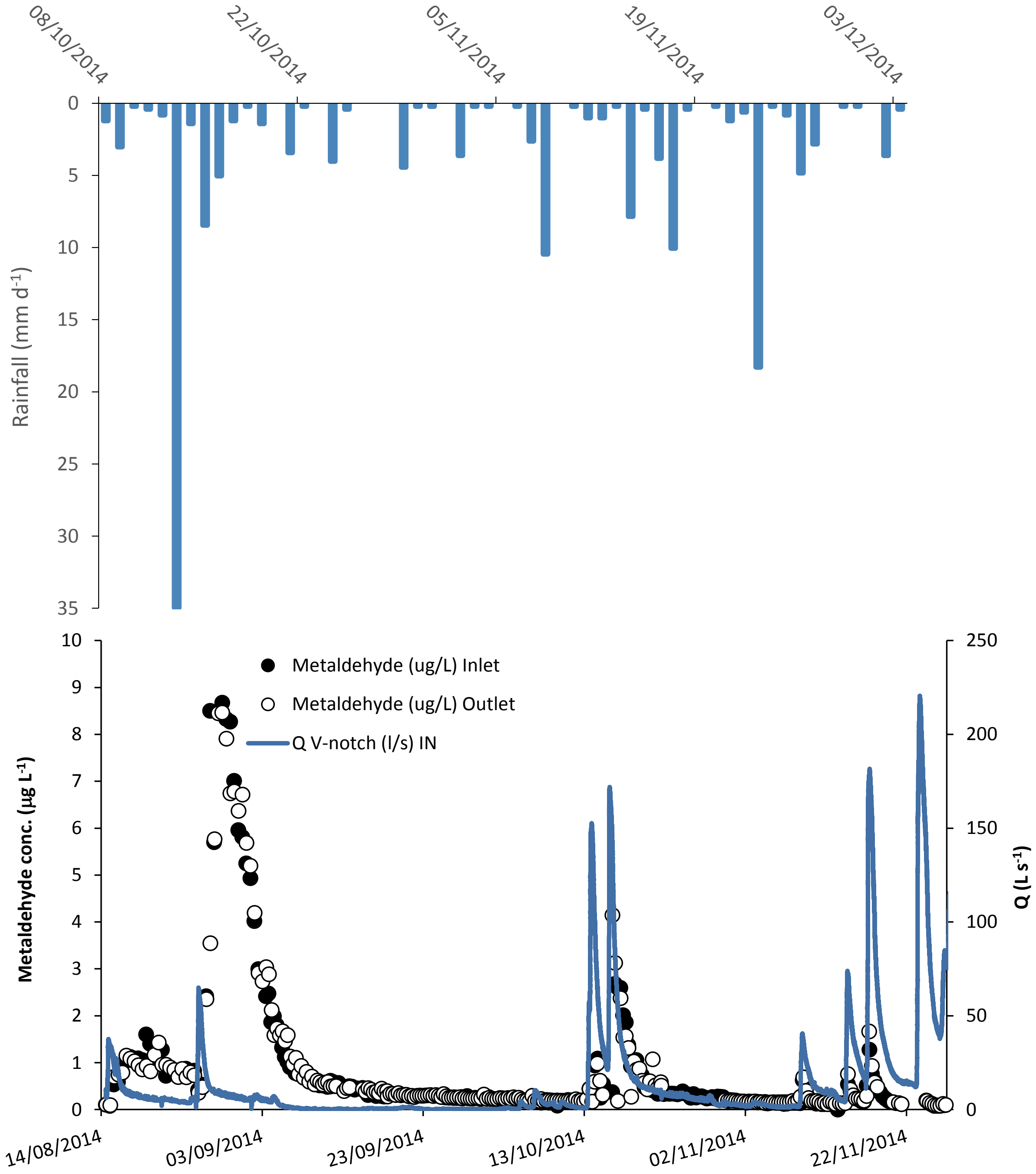


Figure 4. Stream discharge at the V-notch weir (Q, right axis) and the concentration of metaldehyde (left axis) in samples collected from the inlet (SW1) and outlet (SW2) of the South Wetland system between mid-August and early-December 2014.

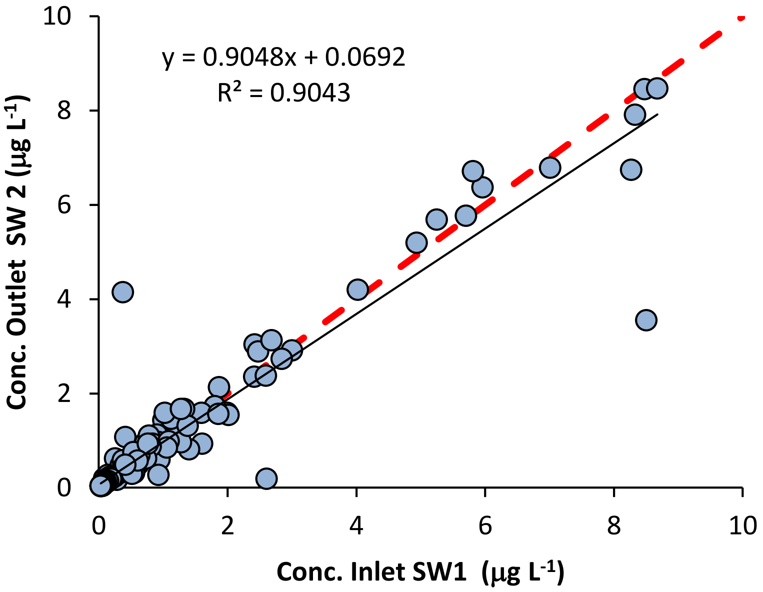


Figure 5. Comparison of equivalent inlet and outlet concentrations in the South Wetland. Dashed lines show the 1:1 relationship. Solid black lines show the best-fit linear regression (equation and R^2 values also shown).

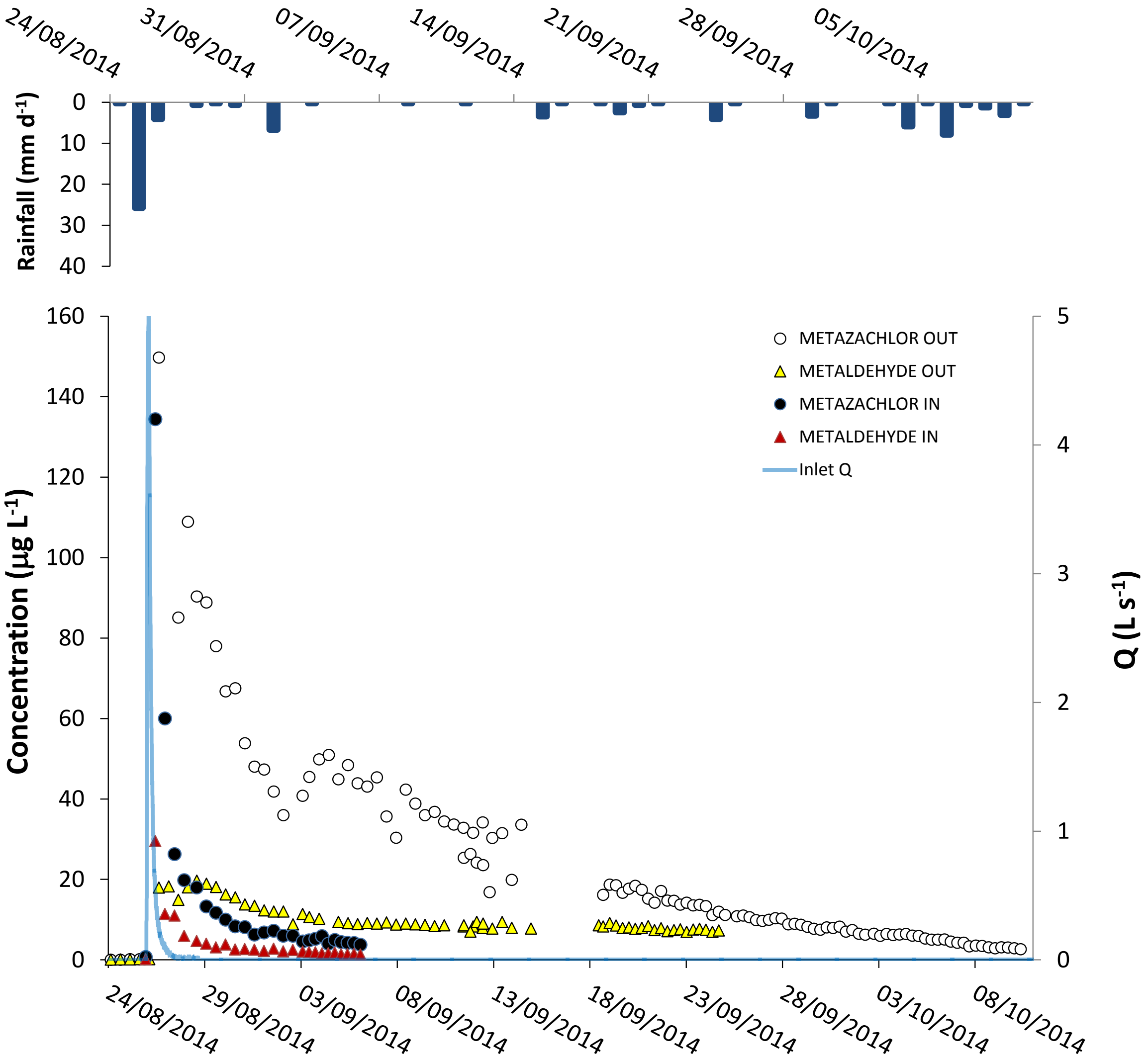


Figure 6. Inflow discharge and the concentrations of metaldehyde and metazachlor in the inlet and outlet of the North Wetland between late August and early October 2014.

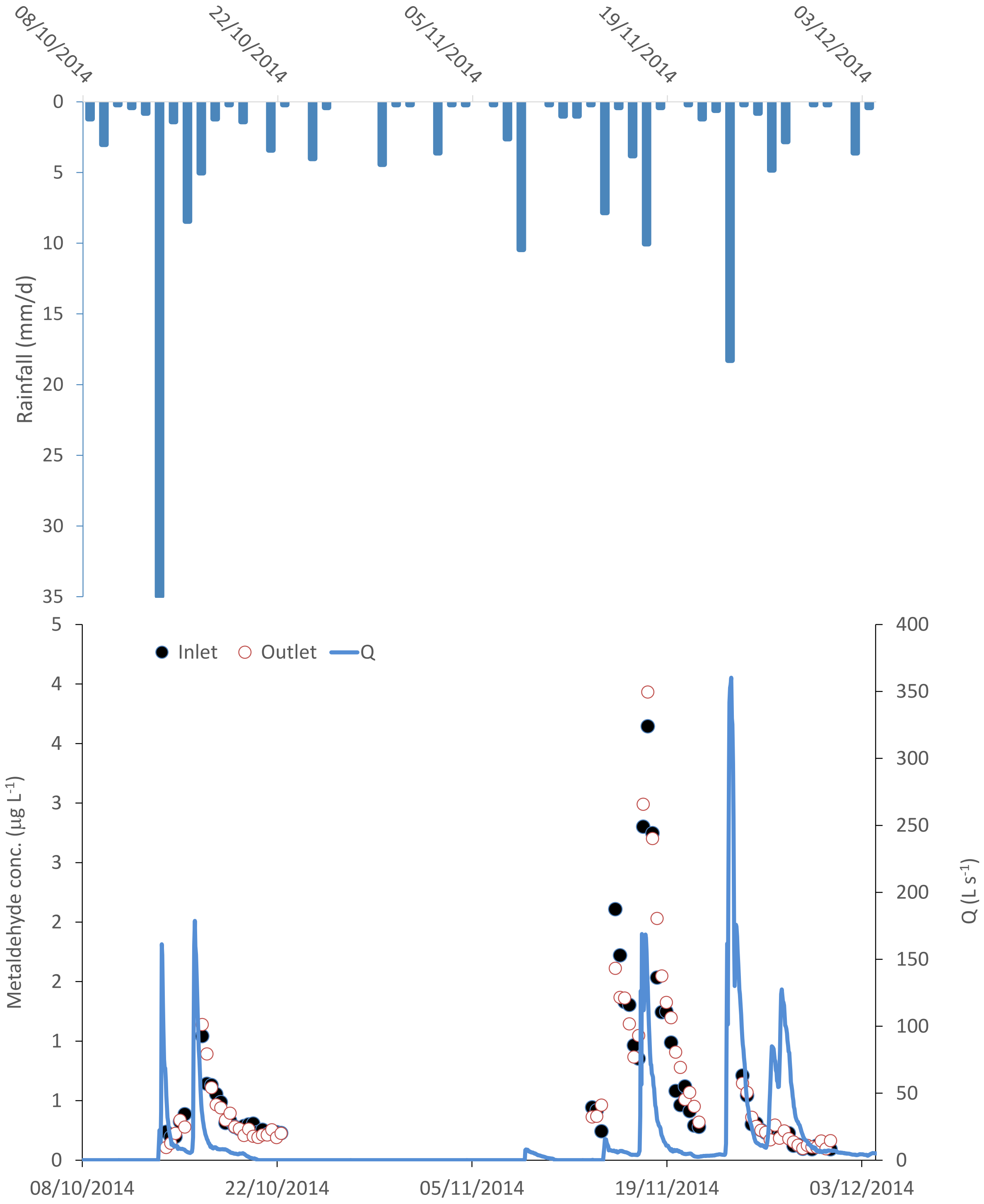


Figure 7. Stream discharge at the outflow (Q, right axis) and the concentration of metaldehyde (left axis) in samples collected from the inlet and outlet of the North Wetland system between mid-October and early-December 2014.

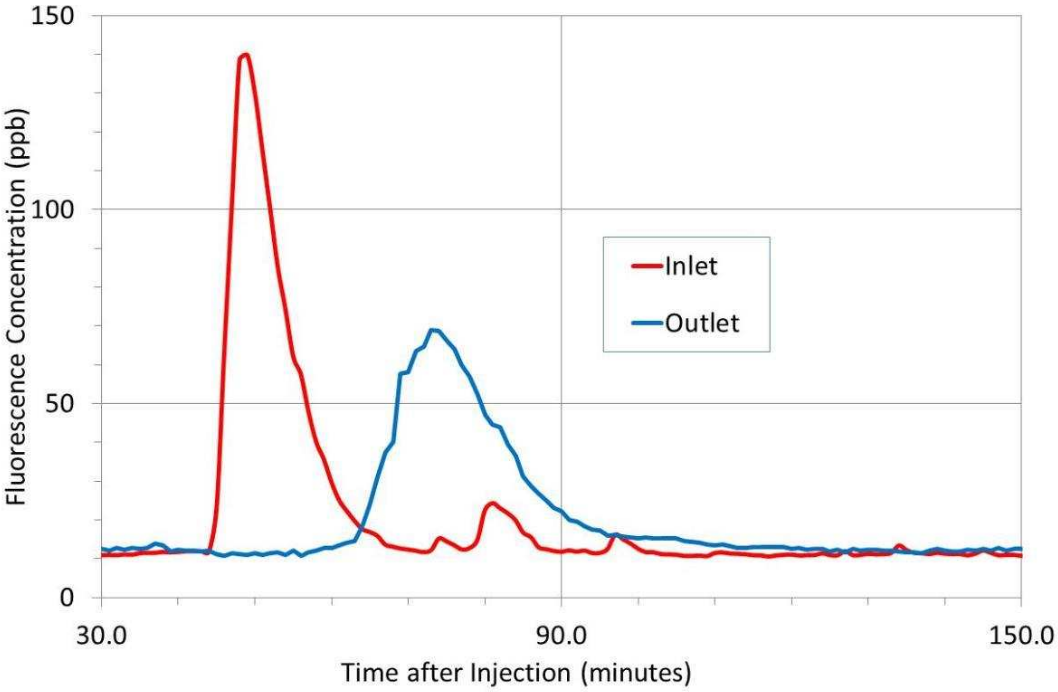
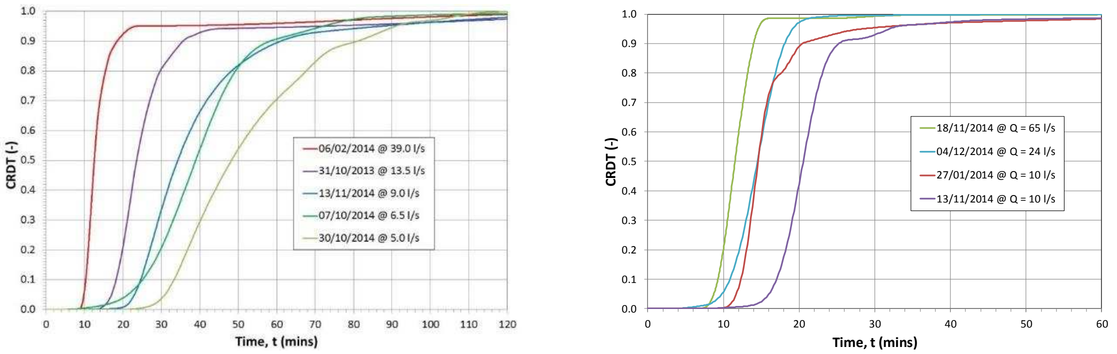
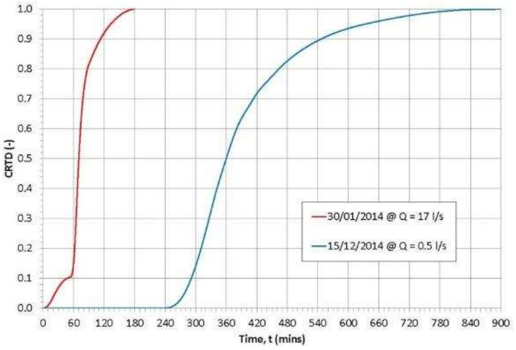


Figure 8. Example fluorescence data for South Wetland 1 for a discharge of 13.5 L s^{-1}.



a) South Wetland 1

b) South Wetland 2



c) North Wetland

Figure 9. Cumulative Residence Time Distributions for Hope Farm Wetlands (a) South Wetland 1; (b) South Wetland 2; (c) North Wetland for tracing exercises conducted under a range of different discharges in 2014.

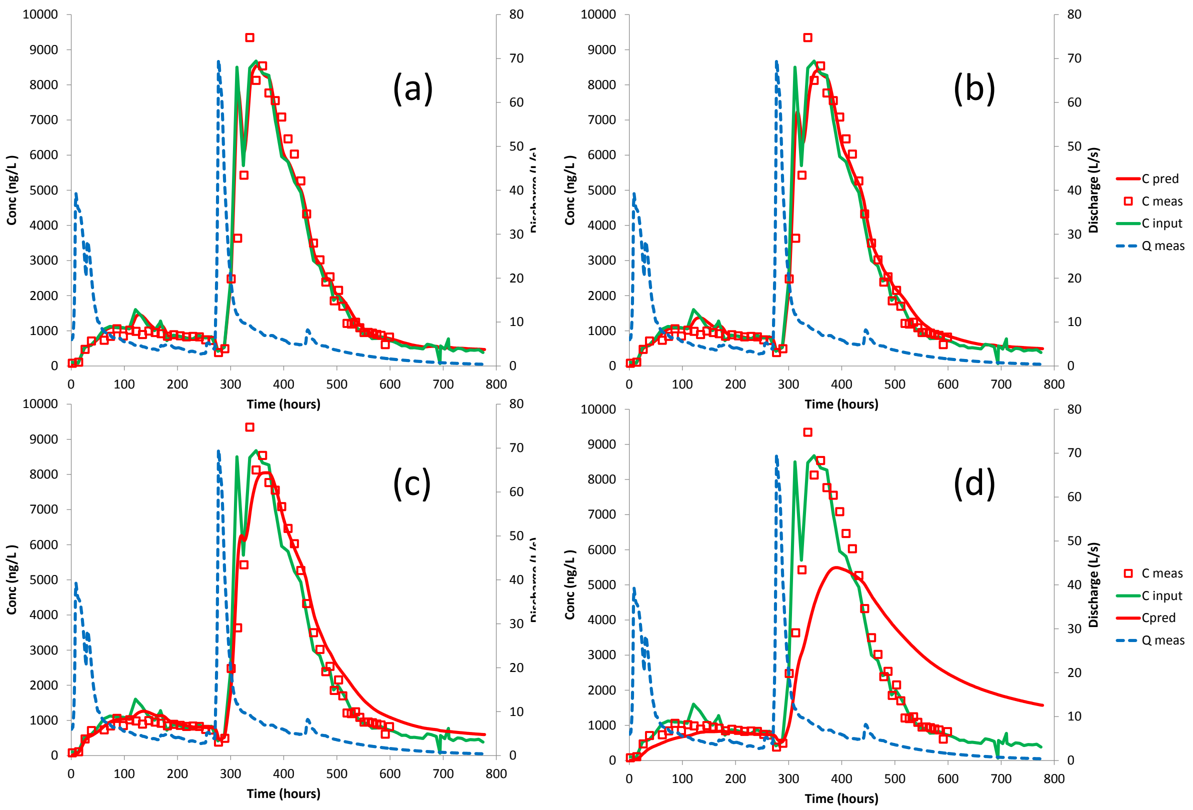


Figure 10. Predicted changes in aqueous-phase metaldehyde concentrations over time in South Wetland 1 in response to two storm events. The time scale is from 14:30 on the 14th of August. The DT_{50} in water was assumed to be 12.2 days (i.e. the reported value for a water-sediment test in PPDB, 2016) and that in sediment was (arbitrarily) assumed to be 122 days. In all cases, the dashed line is stream discharge at the outlet, the open square symbols show the measured concentrations at the outlet, the green line shows the predicted concentration at the inlet and the red line shows the predicted concentration at the outlet for (a) $z=0.5$ m, $A=210$ m^2; (b) $z=1$ m, $A=210$ m^2; (c) $z=1$ m, $A=420$ m^2; (d) $z=1$m, $A=2100$ m^2 where z is the water depth and A is the water surface area.

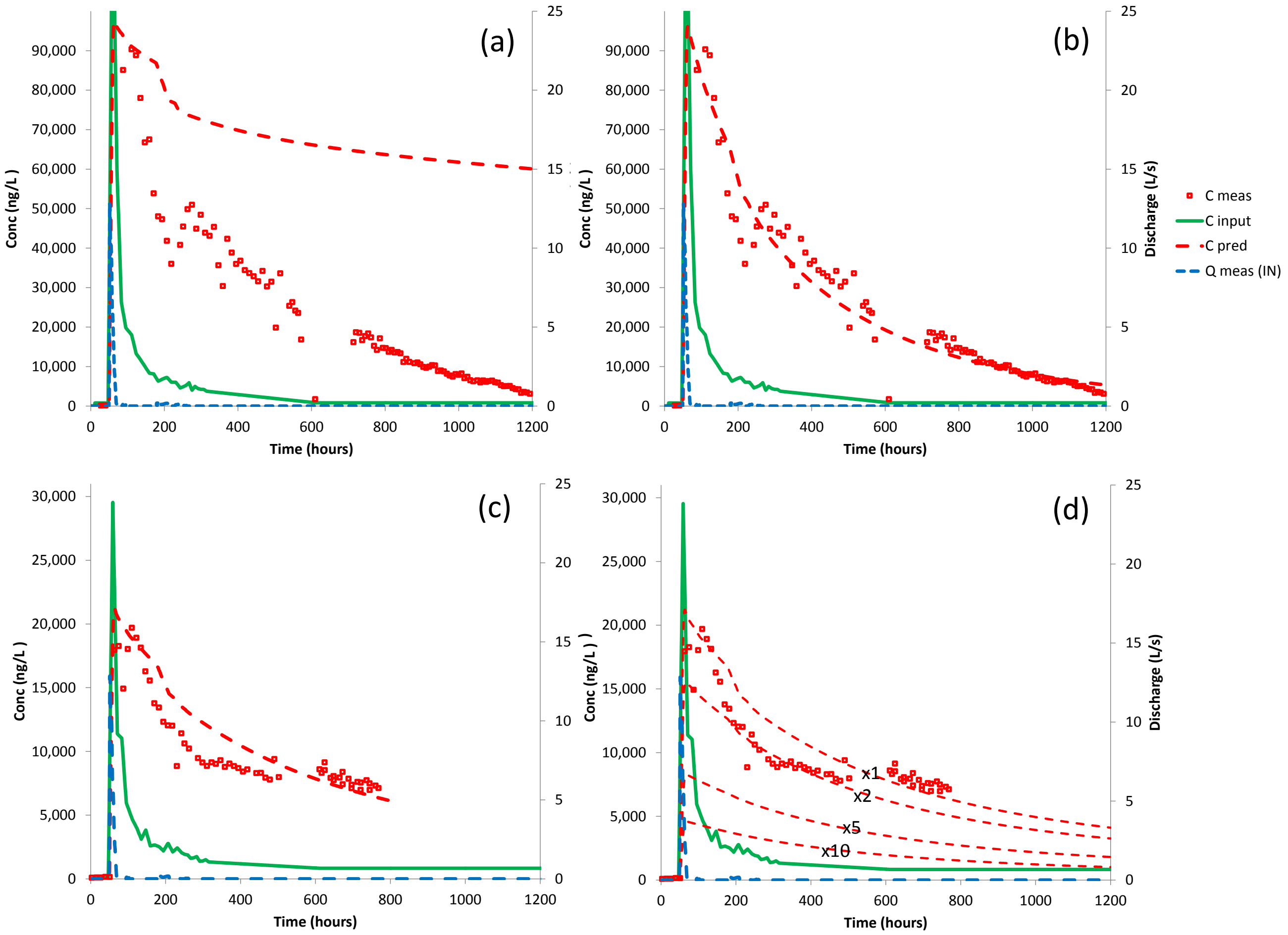


Figure 11. Predicted changes in aqueous-phase metazachlor and metaldehyde concentrations over time in the North Wetland in August and September 2014. The time scale is from 0:00 on the 24th of August. (a) metazachlor with a DT_{50} in water of 494 h (20.6 days) (i.e. reported from a water sediment test in the PPDB Pesticide Database); (b) metazachlor with a DT_{50} in water of 135 h (i.e. equivalent to an effective temperature-adjusted DT_{50} of ca 207 h [9 d]); (c) metaldehyde with a DT_{50} in water of 292 h (12.2 days). In all cases z=0.5 m and the catchment area was assumed to be 0.66 km^2; (d) metaldehyde with changes in A (x1=300 m^2; x2=600 m^2; x5=1500 m^2; x10=3000 m^2).

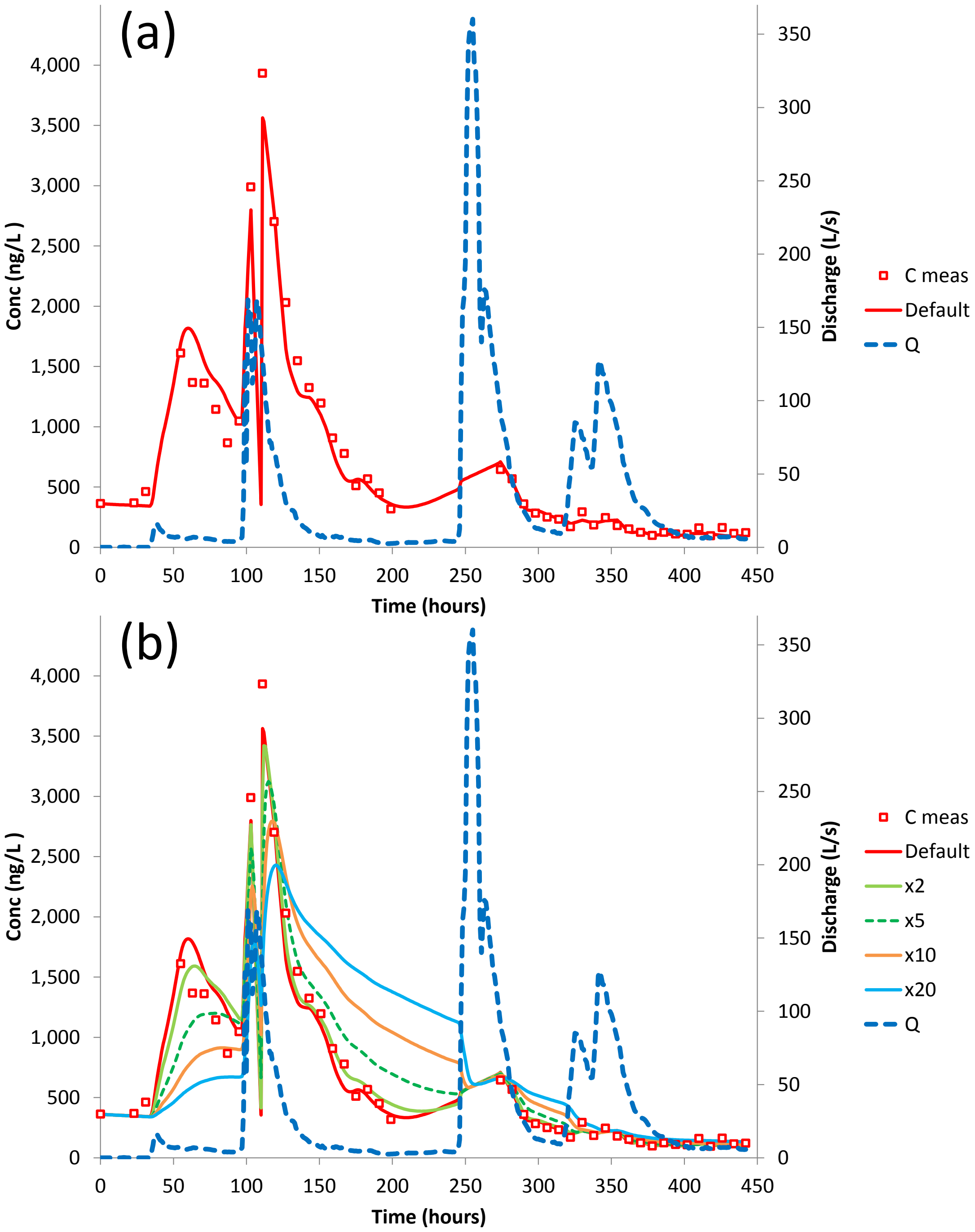


Figure 12. Measured and predicted concentrations of metaldehyde and outflow discharge (Q) in the North Wetland for November 2014. The time scale is from 0:00 on the 13th of November. (a) Default case (A=300 m^2); (b) Predictions for A = x2, x5, x10 and x20 (600, 1500, 3000 and 6000 m^2).