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Environmental Significance Statement

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DOI: 10.1039/C9EM00492K

This paper describes a new conceptual (and parsimonious) model of pesticide transfers from agricultural land to surface waters. The model is a deliberately simplified description of a combination of the most important factors which control surface water exposure by pesticides. The model was successfully compared with (original) high frequency concentration data for metaldehyde which we collected in a small agricultural catchment in Cambridgeshire, UK. Metaldehyde is a pressing environmental problem in the UK and elsewhere because it is difficult to remove in drinking water treatment – such that concentrations in many water supply catchments challenge water quality compliance for domestic supply. The work reveals important insights about pesticide behaviour in agricultural catchments.

Environmental Science: Processes & Impacts Accepted Manuscript

A new conceptual model of pesticide transfers from agricultural land to surface waters with a specific focus on metaldehyde

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Abstract

Pesticide losses from agricultural land to water can result in the environmental deterioration of receiving systems. Mathematical models can make important contributions to risk assessments and catchment management. However, some mechanistic models have high parameter requirements which can make them difficult to apply in data poor areas. In addition, uncertainties in pesticide properties and applications are difficult to account for using models with long run-times. Alternative, simpler, conceptual models are easier to apply and can still be used as a framework for process interpretation. Here, we present a new conceptual model of pesticide behaviour in surface water catchments, based on continuous water balance calculations. Pesticide losses to surface waters are calculated based on the displacement of a limited fraction of the soil pore water during storm events occurring after application. The model was used to describe the behaviour of metaldehyde in a small (2.2 km²) under-drained catchment in Eastern England. Metaldehyde is a molluscicide which has been regularly detected at high concentrations in many drinking water supply catchments. Measured peak concentrations in stream water (to about 9 µg L⁻¹) occurred in the first few storm events after application in mid-August. In each event, there was a quasi-exponential decrease in concentration during hydrograph recession. Peak concentrations decreased in successive events - responding to rainfall but reflecting an effective exhaustion in soil supply due to degradation and dissipation. Uncertain pesticide applications to the catchment were estimated using land cover analysis of satellite data, combined with a Poisson distribution to describe the timing of application. Model performance for both the hydrograph (after calibration of the water balance) and the chemograph was good and could be improved via some minor adjustments in assumptions which yield general insights into the drivers for pesticide transport. The use of remote sensing offers some promising opportunities for estimating catchment-scale pesticide applications and associated losses.

Keywords: Pesticide, metaldehyde, modelling, catchment, pore water displacement

1. Introduction

Pesticides make important contributions to maintaining crop yield and quality in modern agriculture. However, they can be transferred from land to surface waters via spray drift and a range of runoff pathways, where they have the potential to cause ecological damage¹. Furthermore, if concentrations exceed thresholds for drinking water (e.g. under the European Drinking Water Directive: 98/83/EC) they can trigger compliance issues for water companies – particularly for compounds which are difficult to remove by conventional water treatment trains^{2,3,4}. Recent examples of compounds with low removal fractions include clopyralid, propyzamide, carbetamide and metaldehyde. Even where significant removal in treatment is possible, high concentrations in raw waters may still occasionally present compliance challenges⁵. For instance, even with advanced treatment, influent concentrations of metaldehyde exceeding 0.5 µg L⁻¹ can pose a risk to compliance⁶. Metaldehyde is one of the most pressing pesticide problems for UK water companies. It is a commonly-used active-ingredient in slug and snail control products which are widely applied to arable and horticultural crops. Its environmentally-relevant properties are shown in Table 1. It has been regularly detected at high concentrations in drinking water supply catchments in the UK over the past few years^{7,8} and is particularly expensive to remove by standard water treatment processes⁹. In addition (and independently of its issues in drinking water) a ban on metaldehyde use is being considered in the UK based on its risks to wildlife^{10,11,12}. 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 which can supplement improvements in water treatment technologies and the focus has started to shift to source control options^{13,14}. Indeed, this is a requirement of Article 7 of the EU Water Framework Directive for catchments used for water supply². Such options include changing the mix of active ingredients used, where possible (including product substitution¹³) and

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changing crop rotations to reduce overall catchment-scale usage. Employing buffer zones to reduce overland flow and associated pesticide transport¹⁵, containment of accidental spills and treating farm yard runoff (e.g. using biobeds¹⁶).

In order to develop effective catchment management, it is important to understand the key processes operating along the source-pathway-receptor continuum (SPRC). For example, Tediosi *et al.*^{5,17} showed that field drains were the principal pathway for propyzamide and carbetamide transfers to surface waters in the Upper Cherwell catchment and suggested that establishing buffer zones along the edges of water courses would be ineffective as a source-control measure because they would be by-passed by field drains. Numerical models can be used to describe the complex and interacting processes operating along the SPRC, to estimate the importance of different factors in controlling pesticide losses and to explore the likely effectiveness of different catchment management measures. Many such models have taken a detailed mechanistic approach to process representation – attempting to describe how many individual processes interact to generate the overall system behaviour^{18,19,20,21,22,23}. These models represent invaluable syntheses of current understanding and can be used to explore the likely behaviour of different compounds under different soil and climate scenarios (e.g. in the surface and groundwater risk assessments required for pesticide registration in the European Union^{24,25}) and the effects of land management²⁶ or climate change²⁷ on pesticide losses. However, such models often have high numbers of parameters and are computationally demanding, which means that they can be time consuming and costly to set up and run. This is widely recognised in the model user community (but rarely, if ever, quantified) and was the rationale for the development of “meta models” (libraries of existing model results for common parameter permutations²⁸).

Although attempts have been made to employ them at the catchment scale by integrating them with catchment hydrological models such as MIKE-SHE²⁹, this is more commonly achieved via the integration of individual one-dimensional simulations of land-use and soil-

type combinations^{30,31,32}. In either case, this is rarely practicable operationally (e.g. for water companies or catchment regulators). Some conceptual catchment-scale hydrological models, such as SWAT^{33,34} and INCA³⁵, also have the capability of predicting pesticide transport and have been used with some success^{36,37,38}. However, they are often, themselves, not straightforward to set up and run outside of the research environment.

An alternative approach is to construct much simpler conceptual representations of the system – i.e. to deliberately over-simplify the description of key processes and to omit processes which are considered to be unimportant in driving the overall system response. Such models include Brown and Hollis³⁹ and developments thereof^{40,5,3} in which pesticide transport is conceptualised as a displacement of a fraction of pesticide-rich soil pore water by rainfall which is then mixed with pesticide-poor water from elsewhere in the soil profile and from untreated parts of the catchment. Similar philosophical drivers were used to justify the development of other conceptual pesticide transfer models by Zanardo *et al.*⁴¹. These conceptual approaches have been employed in operational exposure models for pesticides. For example, CatchIS (<https://www.catchis.com>) which has been used by several UK water companies, is based on the Brown and Hollis³⁹ displacement concept.

One problem with using rainfall to drive pesticide displacement^{39,40,5,3} is that no pesticide transport from the soil is predicted after the end of the storm event. However, it is common to observe elevated pesticide concentrations in drainage water during hydrograph recession, long after the end of rainfall¹⁷. In this paper, we re-formulate the basis of the pesticide displacement concept in terms of soil water movement without introducing a major increase in model complexity. The new model was used to describe the behaviour of metaldehyde in a small catchment in Eastern England with high frequency monitoring data, as an example.

Table 1. Environmentally-relevant properties of metaldehyde. 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 EFSA⁴², 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 time. * refers to the range of soil DT_{50} ⁷. The DT_{50} value reported in the Pesticide Properties Database⁴³ is 5.1 days.

K_d (L kg ⁻¹)	K_{OC} (L kg ⁻¹)	K_{fOC} (L kg ⁻¹)	Sol (mg L ⁻¹)	$Soil\ DT_{50}$ (days)*	K_{AW}
0.23	240	38-149	188	3.17 - 223	1.43x10 ⁻³

2. Methods

2.1 Hydrological Model

The model considers a set of soil and land-cover combinations. Each soil-type and land cover combination is assumed to behave in the same way and the hydrological and pesticide concentration response at the catchment outlet is assumed to be an area-weighted average of the predicted responses for the individual combinations⁴⁴. In each soil, a single root zone store of constant depth (z , cm) is considered. The water balance of this store is

$$\frac{\Delta S}{\Delta t} = P + I - ET_a - q - q_{OLF} \tag{1}$$

where S is the total profile water storage (mm), P is the precipitation (mm h⁻¹), I is the irrigation rate (mm h⁻¹), ET_a is the actual evapotranspiration rate (mm h⁻¹), q is the vertical drainage (e.g. to field drains) out of the soil profile (mm h⁻¹), q_{OLF} is overland flow due to soil

saturation only (mm h^{-1}) and Δt is the model time step (h). Note that irrigation is not typically employed on arable crops in the UK and was assumed to be zero in all the model runs reported here. Interception loss by the crop canopy is not considered explicitly and infiltration excess overland flow is assumed to be unimportant. The latter assumption is unrealistic in general but probably holds approximately for many humid temperate soils under most conditions, where infiltration rates generally exceed rainfall intensities except when soils are very wet and for very high magnitude events⁴⁵. Even where infiltration excess overland flow is a significant process, flow paths may not always be connected to the stream channel network and re-infiltration may still lead to losses via field drains⁴⁶. ET_a is assumed to be equal to the reference evapotranspiration rate (ET_o) at high soil moisture content but the ratio ET_a / ET_o falls away linearly to zero at the permanent wilting point (S_{WP}) as the total profile soil moisture content drops below a threshold, S_T . This implicitly assumes that the potential ET rate for an individual crop and crop growth stage is equal to ET_o (i.e. the crop coefficient is equal to unity), although we recognise that this will not always be the case⁴⁵. ET_o can be either be imported or calculated from temperature using the Hargreaves equation⁴⁷. Drainage from the soil profile is assumed to be vertical. A simple gravity flow approximation under unit hydraulic gradient is adopted^{48,44}:

$$q = K(\theta) \quad (2)$$

where $K(\theta)$ is the unsaturated hydraulic conductivity (mm h^{-1}) at average profile volumetric water content (θ , $\text{cm}^3 \text{ cm}^{-3}$), which is calculated using the the Mualem-van Genuchten equation⁴⁹:

$$K(\theta) = K_{sat} \cdot \theta_*^{0.5} \cdot \left[1 - \left(1 - \theta_*^{\frac{1}{m}} \right)^m \right]^2 \quad (3)$$

where K_{sat} is the saturated hydraulic conductivity (mm h^{-1}), m is an empirical shape factor describing the soil water retention curve and θ_* is the dimensionless water content (0 to 1) given by

$$\theta_* = \frac{\theta - \theta_{WP}}{\theta_S - \theta_{WP}} \tag{4}$$

where θ_S is the average profile water content at saturation ($\text{cm}^3 \text{ cm}^{-3}$) and θ_{WP} is the average profile residual water content ($\text{cm}^3 \text{ cm}^{-3}$), assumed here to be the storage at the permanent wilting point (i.e. the water content at 1500 kPa tension). Both θ_S and θ_{WP} will depend on the pore size distribution (and indirectly on soil texture). Measured estimates are available for many soil series in the UK (<http://www.landis.org.uk/data/natmap.cfm>). Below the soil profile, drained water is assumed implicitly to reach the stream instantaneously via the tile drain network (i.e. no travel time delay is considered). Although this will clearly not be the case in reality, this assumption is tolerable at the hourly time step because travel distances are typically < 300 m and most drain velocities are likely to be > 0.1 m s^{-1} ⁵⁰. All fields are assumed to be “hydrologically similar” and no account is taken of systematic spatially-dependent variations in throughflow or overland flow (e.g. due to increased near-surface water content in topographic hollows⁵¹. Although such variations may result in “source areas” with increased potential for pesticide transfers from land to water⁵², such effects are likely to be reduced where tile drains are present because the water table is maintained below the surface.

All model equations were solved numerically using Euler’s method with a time step of 0.1 hour. A similar approach to modelling the catchment water balance has been employed successfully using daily meteorological and discharge data in other catchments at various spatial scales^{44,5,3,53}.

2.2 Pesticide Model

After application, pesticide is assumed to penetrate into a narrow layer (z_{mix}) at the soil surface (arbitrarily 2 mm³⁹) and to mix with the soil pore water in this layer. No account is taken of interception by the crop canopy, even for spray-applied pesticides. For pellet applications, such as metaldehyde, no account is taken of the lag in migration of the pesticide from the pellet to the soil or of pellet disintegration. This did not appear to make an appreciable difference to the timing or magnitude of predicted peak metaldehyde concentrations but is considered further in the discussion. Equilibrium partitioning is assumed between the sorbed and dissolved phase, such that the dissolved phase fraction (f_{diss}) is

$$f_{diss} = \frac{1}{(1 + K_d \cdot \rho_B)} \quad (5)$$

where ρ_B is the soil bulk density (kg L⁻¹) and K_d is the soil solid phase to water partition coefficient (L kg⁻¹) which is, in turn, calculated as $f_{OC} \cdot K_{OC}$, where f_{OC} is the organic carbon content of the near-surface soil (g g⁻¹) and K_{OC} is the organic carbon to water partition coefficient (L kg⁻¹). No explicit account is taken of pesticide volatilisation, although volatile losses may be captured via dissipation half-lives (DT₅₀). The concentration of pesticide in the pore water at time t (C_t) is calculated as

$$C_t = \frac{f_{diss} \cdot M_t}{V_{i,t}} \quad (6)$$

where M_t is the mass remaining in the soil at time t and $V_{i,t}$ is the volume of water in the “interactive” pore space (L m⁻²) which is defined as

$$V_{i,t} = z_t \cdot \theta_{i,t} \quad (7)$$

where z_t is the penetration depth for the pesticide (mm) and $\theta_{i,t}$ is the interactive soil water content ($\text{cm}^3 \text{ cm}^{-3}$) defined, in turn, as

$$\theta_{i,t} = \theta_t - \frac{\theta_{WP}}{2} \tag{8}$$

in which θ_t is the volumetric water content at time t (adjusted via the water balance in Equation 1). It is assumed that only half of the residual water held at tensions greater than 1500 kPa contains pesticide (i.e. pesticide is excluded from the very smallest pores due to size³⁹). The rate at which the penetration depth, z_t , is assumed to increase from its initial value of z_{mix} (2 mm) on the day of application via diffusion and advection is given by

$$\frac{dz_t}{dt} = \frac{K(\theta)}{R} \tag{9}$$

where R is a dimensionless retardation factor for each pesticide on each soil type:

$$R = 1 + \frac{K_d \cdot \rho_B}{\theta_i} \tag{10}$$

This means that there is often a gradual dilution of pesticide in the interactive pore volume over time as z_t and, hence, $V_{i,t}$ increase due to “chromatographic” advection and diffusion. It should be noted that the assumption that pesticide is assumed to reside in a single (variable) soil volume is a major departure from discrete soil solute transport models^{54,19,23}, where solute is passed from one cell to the next. Note also that no account is taken of aged sorption⁵⁵, although we recognize that in reality some pesticides do often become more strongly sorbed over time, which may influence their mobility.

The flux rate of pesticide out of the rooting zone (J , $\mu\text{g m}^{-2} \text{h}^{-1}$) is calculated as

$$J = C_t \cdot V_{m,t} \quad (11)$$

where $V_{m,t}$ is volume of pore water which is mobilized ($\text{L m}^{-2} \text{h}^{-1}$) i.e.

$$V_{m,t} = q^\alpha \quad (12)$$

where α is a fixed parameter describing the shape of the relationship between the drainage rate and the volume of pesticide-rich pore water released. Both for this catchment and (not shown) for the headwater sub-catchment of the Upper Cherwell^{5,17}, a value 1.5 for α resulted in good agreement with measured pesticide concentrations. Mobilised pesticide is assumed to be displaced out of the soil matrix and to move rapidly to field drains via preferential flow pathways in the soil and through mole drains (temporary sub-surface slots which run approximately perpendicular to the main tile drains and improve the connection between the inter-drain areas and the tile drain network), where present. This movement is not described explicitly.

The overall mass balance of pesticide in the soil is given by

$$\frac{\Delta M}{\Delta t} = E_t - J - k_{deg} \cdot M_t \quad (13)$$

where E_t is the emission (application rate) to the soil ($\text{mg m}^{-2} \text{h}^{-1}$), which is zero except at the time of application, M_t is the pesticide mass remaining at time t (mg m^{-2}) and k_{deg} is a first order rate constant to account for pesticide dissipation (i.e. degradation plus loss processes such as volatilisation which are not explicitly measured in many soil fate tests: h^{-1}). The value of k_{deg} is derived from DT_{50} values reported in the literature with correction for

temperature using the Arrhenius equation (see S1) with a value of 65.4 kJ mol⁻¹ used for the Activation Energy, as recommended by EFSA⁵⁶.

The concentration of pesticide in stream water at the catchment outlet at any time t ($C_{catch, t}$; $\mu\text{g L}^{-1}$) is calculated as

$$C_{catch, t} = \frac{\sum_{\gamma=1}^N J_{\gamma} \cdot w_{\gamma}}{\sum_{\gamma=1}^N ((q_{\gamma} + q_{OLF, \gamma}) \cdot w_{\gamma})} \tag{14}$$

where γ represents a crop and soil combination, N is the number of crop and soil type combinations in the catchment (including non-agricultural areas) and w_{γ} is the area-proportional weight of crop type and soil type combination γ . Only one soil type was considered in the study described here but the model allows for several different soils to exist in a catchment. Note also that no account is taken of travel time delays in the channel network which are likely to be short and unimportant compared with travel delays in the soil for small catchments^{51,57}. As for the hydrological model, equations were solved numerically using Euler’s method with a time step of 0.1 hour. The simple nature of the model assumptions mean that no iterations are required to achieve convergence and run time is of the order of 75 seconds for the experimental period described below on a Windows laptop with an Intel Core i5 processor. Calculations describing the hydrological and pesticide responses are performed in the same time step with hydrological calculations (which are independent) solved before those describing pesticide behaviour.

2.3 Monitoring

The model was applied to describe the behaviour of metaldehyde in a small surface water catchment in Cambridgeshire, UK (Figure 1) over one autumn-winter period (August-

December 2014). The catchment outlet is on Hope Farm in Knapwell. The area has low topography (41-78 m aod). The catchment area shown in Figure 1 was delineated from a 5 m gridded digital elevation model (UK Ordnance Survey Terrain 5 Data). However, the south of the catchment is cut off from the rest of the catchment by the A428 - an elevated main highway (dashed line in Figure 1b). The area south of the highway has been developed into a new residential and industrial zone which has its own drainage away from the catchment. Excluding this zone, reduces the catchment area from 3.9 to 2.2 km² and the latter area was used in all subsequent analysis. Soils in the catchment are dominated by clay loams belonging to the Hanslope soil association⁵⁸ and are extensively under-drained (see Supplementary Information S2). Only one soil type is, therefore, considered in the modelling described here. Field drainage was widely implemented in this part of the UK during the period 1960-1990, supported by major subsidies which encouraged almost all arable farms with heavy soils to invest in drainage⁵⁹. Our assumption is that all the arable land in the catchment is under-drained. Details of the monitoring set up, sampling protocol and analytical methods employed are given in¹⁴. Briefly, stream discharge was measured with a stainless steel Venturi flume, with stage measured every 1 minute (averaged to hourly for modelling) using a Mini-Diver pressure transducer (Van Essen Instruments, Netherlands) in a stilling well, calibrated against water level in the flume. A tipping bucket rain gauge was installed locally (ca 500 m from the flume) collecting data every 5 minutes which were summed to hourly intervals. Temperature data for the calculation of ET_o and for adjusting K_{DEG} was obtained from the baro-logger used to correct the in-stream stage for atmospheric pressure variations. Water samples were collected every 8 hours using an ISCO 6712 automatic sampler (Teledyne-ISCO, Lincoln, NE, USA).

Figure 1. (a) General location of Hope Farm, Cambridgeshire; (b) Catchment area and elevation map for the catchment derived from UK Ordnance Survey Terrain 5 Data (5 m gridded digital elevation model). The triangle denotes the catchment outlet. Blue lines were derived using flow accumulation over a threshold in ArcGIS Spatial Analyst. The dashed line shows the location of the main A428 highway.

Where possible, samples were analysed within a week of sample collection. In this case, samples were kept in the dark at 4 °C 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 µg L⁻¹, incubated at either 4 °C or -20 °C 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 stable⁶⁰. Samples were analysed for metaldehyde using LC/MS-MS⁶⁰. Method Limit of Detection (LoD) and Limit of Quantification (LoQ) 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.

Metaldehyde is typically applied in wheat-based pellets to a variety of arable crops (principally autumn sown crops such as winter wheat and winter oil seed rape) via a bespoke hopper mounted on an all-terrain vehicle – most frequently in the post-harvest period (August-September). In this study, data on metaldehyde application rates and timing for the whole catchment are unknown because most land is not part of Hope Farm. Applications were, therefore estimated based on land-use/land-cover (LULC) in the catchment, which was assessed using remote sensing. A cloud free mosaic of the catchment from the Sentinel-2 mission was created in Google Earth Engine (GEE) for the period 1st July 2016 to 31st August 2016 (Figure 2a). The mosaic created contains the 50th percentile value for all Sentinel-2 bands for each cloud free image covering the target period. The code for creating this mosaic is available in Google Earth Engine's code editor (<https://code.earthengine.google.com/>) under 'Examples → Datasets → COPENICUS S2'. GEE is a freely accessible web-based platform that can be used to access and process large cloud-based repositories of remotely-sensed data. GEE has greatly reduced barriers to accessing and processing remotely sensed data since its release in 2010^{61,62}. Sentinel-2 is a constellation of two polar-orbiting satellites in sun-synchronous orbit which uses passive sensors to collect surface information in the visible, near infra-red and shortwave infrared bands at a maximum spatial resolution of 10 m.

The boundaries delimiting different LULC classes within the study area, north of the A428 highway (Figure 2b) were determined through visual interpretation of the cloud-free mosaic and digitised as shapefiles in QGIS 3.6.¹⁶³. The target LULC classes were arable fields, woodland and pasture/grassland. Farm buildings and tracks were not included in the LULC

assessment. The classification of the digitised boundaries was checked against the Centre for Ecology and Hydrology’s Landcover Map 2015⁶⁴ and the total area of each LULC class determined for entry into the pesticide model.

Figure 2. (a) Sentinel-2 Mosaic of the catchment displaying visible bands (b) Land use categorisation.

The analysis suggested that approximately 75% of the catchment draining to the outlet was used for growing winter arable crops at the time of sampling. We assumed that metaldehyde was applied to 50% of this area in a single application at the standard label rate of 0.18 kg ha⁻¹. The timing of application (which could be important for pesticide availability and loss from soil) is also uncertain. 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 catchment will have occurred around this time. We assumed that the timing of application was distributed as a (discrete) Poisson distribution over (arbitrarily) approximately two weeks around this date (corresponding to $\lambda = 7$ days). This is illustrated in the Supplementary Information (Figure S1).

A one-at-a-time sensitivity analysis (see Supplementary Information, S4) suggested that the model was most sensitive to DT_{50} . Although the model was also moderately sensitive to the application rate, model fits were much better controlled by DT_{50} . For metaldehyde, several aerobic DT_{50} values have been reported ranging from 3.17 to 223 days⁷. The value reported in PPDB⁴³ is 5.1 days but elsewhere the best-estimate value reported is higher (e.g. Kollman and Segawa⁶⁵ give a value of 180 days). Here, the effect of a range of values on predicted exposure were explored using the PPDB value as a baseline value which was then adjusted by factors of 2 and 3. Beyond a factor of 3, further increases in DT_{50} achieved no increase in model performance.

2.4 Model Calibration, Performance and Scenarios

The hydrological model was calibrated using Monte Carlo Simulation in which the following parameters were selected randomly in a large number of iterations (1000) from uniform distributions representing the physically plausible range of values: m (0.05-0.33); θ_s (0.45-0.6 cm³ cm⁻³); θ_{WP} (0.05-0.25 cm³ cm⁻³); z (10-100 cm); δ_T (20-130 mm); K_{sat} (0.1-20 mm h⁻¹), where δ_T is S_T expressed as a deficit from saturation. Maximising the Nash Sutcliffe Efficiency (NSE)⁶⁶ was used as the model objective. Calibration was performed using 60% of the measured stream discharge data (from 1/8/2014 to 31/10/2014). Validation was performed using the remaining measured discharge data (1/11/2014 to 31/12/2014).

In addition to the NSE, model performance was assessed using the coefficient of determination (R^2) and the slope (β , proximity to unity) of the relationship between the measured and modelled discharge.

The pesticide model was not formally calibrated, although the value used for α was derived by trial and error in another catchment^{67,5} and a range of values for DT_{50} were assessed. The DT_{50} was selected as a key substance-specific parameter which is known to vary

significantly with soil properties^{68,69,70} and with the competence of the soil microbial community, which is known to be affected by previous pesticide exposure and associated acclimation⁷¹. Three metrics were used to assess the performance of the pesticide model with respect to its fidelity to measured concentrations: Root mean square error (RMSE), Nash Sutcliffe Efficiency (NSE) and the Pearson Product Moment Correlation Coefficient (*r*).

3. Results and Discussion

3.1 Hydrological Modelling

The optimal hydrological parameter set selected from the Monte Carlo calibration procedure (NSE = 0.63; R² = 0.64; β = 0.97) was as follows: *m* (0.129); θ_S (0.54 cm³ cm⁻³); θ_{WP} (0.13 cm³ cm⁻³); *z* (37 cm); δ_T (22 mm); *K_{sat}* (8.5 mm h⁻¹). We should note that there were several different combinations of parameter values which generated reasonable model predictions. This phenomenon, known as “equifinality”, is commonly observed in hydrological modelling^{72,73} and has also been observed for soil erosion⁷⁴ and multi-media environmental modelling of chemicals⁷⁵. Whilst optimal values of θ_S and θ_{WP} are consistent with the expected water retention properties of the prevailing soil type in the catchment (Hanslope: see Supplementary Information S2), the optimal value for *z* is a little too shallow to physically represent the depth of the actual rooting zone in this soil (typically 40 – 100 cm⁷⁶). The shallow optimal value for *z* was principally the result of the flashy nature of the observed hydrograph in this catchment which is a reflection of the high clay content and extensive under-drainage. In order to reproduce the steep rise and fall of the hydrograph, low total storage (shallow depth) was required, such that simulated drainage (driven by water content via the unsaturated hydraulic conductivity) could increase and decrease rapidly with moderate inputs of rainfall. The relatively low value for δ_T simply reflects the low total storage which is derived when *z* is low. The value for *K_{sat}* is high compared with the median

measured value of 1.25 mm h^{-1} reported by Kellett⁷⁶ for the Hanslope soil series but it should be noted that the model parameter is an effective value for the whole soil response which will reflect the fact that tile and mole drains have been extensively installed. The extent to which any parameter set derived from calibration is physically meaningful with respect to a highly heterogeneous reality has been highlighted by Beven⁷⁷ (and several subsequent papers). Here, we have attempted to ensure that parameter values were selected from plausible ranges and that the internal state variables (e.g. the time series of soil moisture content) were consistent with general expectations based on field observations in other studies⁷⁸. However, all parameters should be seen as “effective” and may not necessarily reflect unique or optimal descriptions of system behaviour even if model predictions for some variables (e.g. discharge or pesticide concentrations at the catchment outlet) are reasonable.

The measured and modelled hydrograph for the whole study period is shown in Figure 3, split between the calibration and validation periods. In general, the match between the predicted and measured discharge was acceptable in terms of both NSE and R^2 , although there were some systematic deviations. For example, the predicted recession curves were often shallower than those observed (particularly later on in each event) and the predicted baseflow was higher. Peak discharge during storm events was typically (although not always) overestimated for the calibration period and underestimated for the validation period. Overall, performance for the validation period ($\text{NSE} = 0.83$; $R^2 = 0.83$; $\beta = 1.04$) was better than for the calibration period.

Figure 3. Measured (red line) and modelled (black line) stream discharge for the study period. The model was calibrated for the period 1/8/2014 to 31/10/2014. The period 1/11/2014 to 31/12/2014 represents the validation period – separated by the vertical dashed line. Also shown is the hourly rainfall over the period (right axis, inverted scale). Note that measured data were not available until the 14/8/2014.

Measured versus modelled discharge is shown in Figure 4.

Figure 4. Measured versus modelled stream discharge for (a) the whole data set; (b) the calibration period (1/8/2014 to 31/10/2014) and (c) the validation period (1/11/2014 to 31/12/2014).

In both the calibration and validation periods there was some systematic deviation of the predicted discharge from the measured data, although on average the slope of the best fit line (constrained to go through the origin) was always close to unity (0.97 for calibration and 1.04 for validation). The R^2 value for the modelled versus measured data was actually higher in the validation period (0.83) than in the calibration period (0.64) and this is also reflected in a higher NSE value for the validation period (0.83) compared with the calibration period (0.63). No saturation excess overland flow was predicted over the simulation period.

Conditions during the monitoring 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 high¹⁴.

3.2 Metaldehyde Dynamics

Measured and predicted metaldehyde concentrations over the study period, together with the predicted pattern of stream discharge, are shown in Figure 5 for four different scenarios relating to the in-field degradation rate, developed from a baseline DT₅₀ value of 5.1 days⁴³: Scenario 1: Baseline DT₅₀ uncorrected for temperature; Scenario 2: Baseline DT₅₀ corrected for temperature; Scenario 3: Baseline DT₅₀ x 2 corrected for temperature; Scenario 4: Baseline DT₅₀ x 3 corrected for temperature. Measured versus predicted metaldehyde concentrations for each scenario are shown in Figure 6 and goodness-of-fit metrics are shown in Table 2.

The timing of measured concentration fluctuations was clearly triggered by the pattern of storm events. Two early 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 elevated concentrations of metaldehyde, peaking at about 9 µg L⁻¹. Thereafter, concentrations responded to subsequent events in October and November but not to the same levels suggesting an exhaustion of metaldehyde supply (e.g. due to degradation and dispersion) within the soil profile and or dilution. Similar exhaustion responses over a series of storm events were reported for propyzamide and carbetamide in the Cherwell catchment^{5,17}. Although the increase in concentration starts early on each storm event (i.e. concentrations increase with increasing discharge), measured concentrations continue to increase after peak discharge (i.e. during hydrograph recession). This has not been commonly reported elsewhere (e.g. Tediosi et al.^{5,17} observed that measured herbicide concentrations were approximately coincident with drainflow). Speculatively, this suggests that pathways for metaldehyde transport to the stream (at least in the first major post-application storm events) may be slower than those for bulk water transport. This is consistent with the fact that metaldehyde

is applied in wheat-based pellets which act as bait for slugs. This means that metaldehyde needs to be leached from recently-applied pellets to the soil during these early rainfall events prior to displacement to field drains. 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 in the stream 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 time⁷⁹. In most cases, this old water will be deeper in the soil profile and should have low residual pesticide concentrations. In all four Scenarios shown in Figure 5, the predicted peak metaldehyde concentrations are approximately coincident with the discharge peaks over the whole monitored period. The fact that these predicted peak concentrations consistently anticipate the observations suggests that key processes which control the early loss of metaldehyde (such as the leaching of metaldehyde from pellets or the transport of metaldehyde through the soil matrix to macropores and or to tile drains) are not well represented in the model.

In Scenario 1 (Figure 5a) predicted concentrations in late August and early September were much lower than the observed data. Predicted concentrations in later events were negligible and clearly under-estimated the observations. Including temperature correction for DT_{50} (Scenario 2: Figures 5b and 6b) improved the model fit slightly but measured concentrations were still significantly underestimated, especially in October and November. Increasing DT_{50} by factors of 2 and 3 (Scenarios 3 and 4) progressively improved the model fit in both the immediate post-application period and later. As well as making a reasonable estimate of peak concentrations, the rate of decrease in concentration during hydrograph recession was also reasonably well represented by the model. This is a significant improvement on the previous manifestations of this model^{5,3} where peak concentrations were reasonably approximated but no losses were predicted in rain-free or low-rainfall periods. The model fit also compares very favourably with other (often more complex) catchment-scale model

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predictions reported in the literature^{37,23,80,32,81,82,39} albeit, in many cases, for larger catchments and often with lower pesticide sampling frequencies.

The improved fit obtained by extending the DT_{50} to 15.3 days ($NSE = 0.44$; $R^2 = 0.36$; $\beta = 0.61$) implies that, for this catchment at least, metaldehyde is more long-lived in soil than the PPDB value would suggest. Increasing the soil DT_{50} to 20.4 days (data not shown) resulted in poorer fits overall with the measured data, particularly in the later part of the study period, when measured concentrations were notably and consistently over-predicted. However, the slope of the measured versus modelled relationship did improve due to higher predicted peak concentrations in the first two major storm events after application. Higher DT_{50} values may, therefore, be a better assumption in water supply risk assessments since the elevated concentrations predicted are more likely to cause compliance failures.

The increase in DT_{50} required for good model performance remains comfortably within the envelope of reported values (Table 1) and is more consistent with the extended period over which elevated metaldehyde concentrations have been observed in drinking water supply catchments^{7,82}. However, the longevity in metaldehyde availability for leaching loss may also have been enhanced by delayed losses from the slug pellets themselves which may depend on the integrity of the pellet matrix as well as on leaching via rainfall.

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Figure 5. Measured (open circles) and predicted (red dashed line) time series of metaldehyde concentrations over the study period for four example scenarios relating to the in-field degradation rate. (a) $DT_{50} = 5.1$ days and no temperature correction; (b) $DT_{50} = 5.1$ days with temperature correction; (c) $DT_{50} = 10.2$ days with temperature correction; (d) $DT_{50} = 15.3$ days with temperature correction. Also shown is the predicted stream discharge (right axis, inverted scale).

Figure 6. Measured versus predicted metaldehyde concentrations over the study period for the four different scenarios relating to the in-field degradation rate (see Figure 5 caption). The dashed line shows the 1:1 relationship and the solid blue line (and equation) shows the best fit regression line.

Table 2. Goodness of fit statistics for model predictions of metaldehyde concentrations at the catchment closing section and the fraction of applied pesticide which is predicted to be lost from soil to surface water over the study period for the four scenarios shown in Figures 5 and 6.

DT ₅₀ (days)	Temperature Correction	RMSE	NSE	<i>r</i>	Fraction Lost (%)
5.1	No	1.24	0.126	0.52	2.0
5.1	Yes	1.15	0.254	0.58	2.9
10.2	Yes	1.02	0.415	0.66	6.0
15.3	Yes	0.99	0.443	0.67	10.7

3.3 Loads

Catchment metaldehyde loads ($J_{catch,t}$; mg m⁻² h⁻¹) were calculated at each water sampling event via

$$J_{catch,t} = C_{catch,t} \cdot Q_t \quad (16)$$

where subscript *t* refers to the sampling event and where $C_{catch,t}$ and Q_t were either the modelled concentration and area-specific discharge, respectively, or the measured concentration and discharge. These are shown in Figure 7 for the four scenarios shown in Figures 5 and 6. As for concentration, loads were markedly underestimated by the model when DT₅₀ was assumed to be 5.1 days, except for the first major event after application. In this event, the model overestimates the measured load principally because the peak model

concentrations approximately coincide with peak modelled discharge, whereas peak measured concentrations occur after peak discharge. In all four scenarios, loads were overestimated in the initial period (until approximately the end of August 2014). Thereafter, loads were underestimated – particularly during storm events.

Figure 7. Measured (open symbols) and predicted (closed symbols) time series of metaldehyde loads over the study period for four example scenarios relating to the in-field degradation rate. (a) DT_{50} = 5.1 days and no temperature correction; (b) DT_{50} = 5.1 days with temperature correction; (c) DT_{50} = 10.2 days with temperature correction; (d) DT_{50} = 15.3 days with temperature correction.

Measured versus modelled loads are compared for the four scenarios in Figure 8. Also shown are the 1:1 line (perfect agreement between the model and measured data) and the best-fit linear regression line (constrained to go through the origin), regression equation and coefficient of determination. If the performance of the model is taken as the best statistical

fit, then the model predictions for the final scenario ($DT_{50} = 15.3$ days) are clearly better than for the others. However, although the line gradient is close to unity, the R^2 value is low (only 0.19) and the cumulative flux predictions are poor. This is caused in part by deviations between modelled and measured concentration but also by errors in the predicted discharge. For the fourth scenario ($DT_{50} = 15.3$ days), the model tended to underestimate concentrations (see Figure 6d; average concentrations were 0.91 and 0.67 $\mu\text{g L}^{-1}$ for the measured and modelled data, respectively) but overestimate the load (Figure 8d).

Figure 8. Measured versus predicted metaldehyde loads over the study period for the four different scenarios relating to the in-field degradation rate (see Figure 7 caption). The dashed line shows the 1:1 relationship and the solid blue line (and equation) shows the best fit regression line.

The cumulative measured and predicted loads are shown in Figure 9. This is instructive because it illustrates clearly the tendency of the model to overestimate loads in August 2014 (even for the first two scenarios with assumed short half-lives) but to underestimate loads for later events in all scenarios except for the fourth. Total cumulative load is slightly over-predicted in Scenario 3 and markedly over-predicted (by approximately a factor of 2) in Scenario 4, despite the fact that concentrations were underpredicted on average. This is partly due to an over-prediction in stream discharge in general (equivalent cumulative curves for measured and predicted discharge are shown in Figure 10 with the cumulative prediction 22% higher than the measured value). However, more important is the fact that the model over-predicted both concentration and discharge during storm events and in the subsequent recession periods.

Figure 9. Cumulative curves for measured (dashed lines) and predicted (solid lines) metaldehyde loads over the study period for the four different scenarios relating to the in-field degradation rate (see Figure 8 caption).

Figure 10. Cumulative curves for measured (dashed line) and predicted (solid line) stream discharge over the study period.

3.4 Insight

The application of metaldehyde to soil at the label rate (0.18 kg ha^{-1}) would result in a theoretical concentration in pore water of $1696 \text{ }\mu\text{g L}^{-1}$, assuming a 2 mm initial mixing depth, an (arbitrary) soil water content of $0.4 \text{ cm}^3 \text{ cm}^{-3}$ and equilibrium partitioning between the soil solid and liquid phases (Equation 5). However, arable crops are only grown in a fraction of the catchment (here assumed to be 75%) and only a fraction of arable crops are treated (here we assumed 50%). Furthermore, the application date is assumed to be distributed over a two week period and degradation is assumed to occur continuously within the soil, which means that there will be a variable mass of metaldehyde available for leaching. If we neglect degradation, then the catchment-average near-surface pore water concentration will

be $1696 \mu\text{g L}^{-1} \times 0.75 \times 0.5 \approx 636 \mu\text{g L}^{-1}$. These assumptions suggest that only about 1.4% of the maximum pesticide mass available in the catchment needs to be mobilized in order to generate the peak concentration observed at the catchment outlet. This is consistent with model predictions of the total fraction of metaldehyde applied which is lost in catchment drainage of 10.7% over the whole monitoring period in Scenario 4 (Figure 5d). Although leaching losses will continue beyond the end of the monitoring period, these losses are assumed to be relatively minor (i.e. most losses occur in the first few weeks after application). In addition, metaldehyde can be reapplied over the growing season but in practice applications after September tend to be minimal. That said, it is possible for pesticide residues to be present in the soil as a result of historical applications (pesticides are often detected in drainage waters from fields which have not received recent applications⁸³) which may make some contribution to early losses of metaldehyde. Such losses may be enhanced if pesticides are present in the subsoil where degradation half-lives may be higher, although aged sorption and physical protection of pesticide residues in soil aggregates will tend to reduce the risk of leaching loss for such residues⁸⁴.

The model described here builds on a previous description of soil pore water displacement by rainfall³⁹ by using simple (but process-based) water balance calculations to drive predictions of pesticide transfer to surface waters. Although it is deliberately oversimplified, it is capable of describing the temporal patterns of metaldehyde concentration and (to a lesser extent) load reasonably well. Its description of hydrological response clearly ignores the details of vertical and spatial variations in soil properties and topography, water table dynamics and drain responses. Similarly, the description of solute transport is “lumped” and does not describe explicitly the detailed mechanisms of diffusion and advection in the soil matrix and advective solute transport down preferential pathways (macropores and the tile drain gravel backfill). These mechanisms are accounted for explicitly by other (one dimensional) pesticide models such as PEARL²³ and MACRO^{17,19} which have also been

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shown to describe (small) catchment scale time series reasonably well, despite ignoring topographic and edaphic complexities at this scale. This is principally because the vertical mobilization of pesticides is often the limiting step in pesticide transport at the field scale and at the small catchment scale when fields are underdrained and the drain response times during storm events are rapid¹⁷. Thus, at these scales, so called physically-based one dimensional models are also conceptual abstractions.

The results presented here suggest that the relatively complex vertical and lateral interactions between different pore-water domains which drive pesticide transport to the drainage network can be simplified even further to a simple displacement of a minor fraction of the near-surface soil pore water, at least in heavy and drained soils. That said, the provenance and age of the pesticide-free diluent and the actual fraction of pore water mobilised remain unknown because stream water, pore water, field drain backfill and groundwater have seldom been sampled and analysed for pesticides simultaneously. This means that most models (including this one) are likely to be ill-conditioned with respect to important internal state variables. Perhaps more importantly, the significant developments in hydrological understanding at the catchment scale which have been derived in recent years from the use of natural tracers such as the stable isotopes of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) and anionic tracers such as Cl^- , have largely (hitherto) been ignored in catchment-scale pesticide studies. These studies have shown that the hydrological response of stream water discharge to rainfall (characterised by the so-called celerity at which perturbations are transmitted⁸⁵) is often much faster than the mean transit time for water (characterised by mean water velocity). Stream water usually has a tracer signature characteristic of “old” (pre-event) water (i.e. water which has resided in the soil and or groundwater of the catchment for months, years or even decades) with relatively little contribution of “new” water (i.e. with an isotopic signature similar to rainwater). The modulation of isotopic variability in precipitation to that in streamflow is mainly due to physical mixing processes (e.g. diffusion and hydrodynamic dispersion), although fractionation has been observed to operate in some situations⁸⁶. This

implies that water storage volumes involved in solute mixing in many catchments are much larger than those required for successfully representing the hydrological response in conceptual model representations. Relatively few natural tracer studies have been conducted in drained catchments (exceptions include Granger *et al.*⁸⁷ and the irrigation study of Klaus *et al.*⁷⁹) and attempts to combine insights from natural tracer dynamics to better-understand pesticide behaviour have been surprisingly rare (see e.g. Heppell & Chapman⁸⁸ who used conductivity for event-based hydrograph separation and Stone & Wilson⁸⁹ who used Cl⁻ at the field and small head water catchment scales). Klaus *et al.*⁷⁹ applied stable isotope and Br⁻ tracing techniques to field drain systems (400 m²) which suggested that drainflow is often dominated (>80%) by pre-event water. The extent to which the water age implied from natural tracers is consistent with pesticide concentration data (which suggests that some very recently added pesticide can be transported rapidly to the surface water system via the drains) remains unknown.

Artificial field drains are installed under approximately 6.4 x 10⁶ ha (>30% of the agricultural land⁹⁰) in the UK (and a significant fraction elsewhere). These drains maintain water tables at depths which allow increased yields in heavy soils. However, they also act as conduits for the rapid transfer of water from land to surface waters and could contribute to reduced hydrograph lag times and increased peak flows (i.e. an exacerbation of flood risks). In addition, they are known to be important pathways for solute transport including nutrients and pesticides. Given the extent of field drains globally and their critical role in influencing water quality, there remains a conspicuous need to improve our knowledge of the links between water storage, mixing, water age and pesticide mobilization in drained catchments. Whilst it is tempting to attempt to describe drainflow mechanistically¹⁷, the purpose here is to deliberately simplify the processes to those which limit pesticide losses to the catchment outlet.

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. Numerical models are powerful tools for describing system behaviour, responses to meteorological drivers, land management and management interventions. They are at the heart of environmental (ground and surface water) exposure assessments required for pesticide registration in the European Union^{24,25} and in the US⁹¹. They are also used in Water Safety Plan risk assessments for drinking water supply catchments^{5,92} and for operational decision-making in drinking water abstraction⁸². However, models need to be fit for purpose with a level of complexity and parameterisation requirements which are appropriate for their intended use. In this paper, we describe a new conceptual process-based model which was deliberately designed to be simple and easy to apply whilst being able to describe metaldehyde transport from land to surface water well. The model is based on a simple but effective description of the catchment water balance combined with a prediction of pesticide displacement which is based on the predicted mass of chemical remaining in soil pore water and soil drainage predicted using the gravity flow approximation. The model was applied to metaldehyde in a small artificially drained catchment, with land use and associated metaldehyde applications estimated with the help of remote sensing. Overall performance (both in terms of peak concentrations and the shape of the chemograph recession curves) was good. Load predictions were also reasonable on average but cumulative losses were over-predicted even when concentrations were predicted reasonably well due to high coincident concentrations and discharge during events. The fact that the model performance was generally good, despite the fact that it did not explicitly include aspects of pellet disintegration, suggests that metaldehyde may leach readily from pellets – although the need to extend DT_{50} for good performance may have been due to delayed availability

caused by pellet integrity. Other deliberate simplifications, such as the lack of an explicit description of infiltration excess overland flow in the model or of topographically controlled source areas may also be responsible for some departures of the model predictions from the observed data. However, the exact effects of such omissions are difficult to ascertain at the catchment scale without specific observations of overland flow occurrence and contribution to runoff, which are difficult to make. The model has promising potential as a tool for assessing pesticide exposure in surface waters and the effect of different management regimes (e.g. crop rotation combinations, pesticide application rates and timing) – which could be particularly useful in catchments used for drinking water supply. The model results suggest that the displacement of a relatively small fraction of contaminated soil pore water can explain the observed pattern of metaldehyde concentrations at the catchment outlet. The extent to which the concepts employed here are more widely applicable to other pesticides and other catchments, particularly those with lighter soils and fewer or no tile drains is currently uncertain and should be investigated further in future work.

5. Acknowledgements

This work was jointly funded by the Chemicals Regulation Division (CRD) of the UK Health and Safety Executive (Project PS2248) and Lonza. Interpretations of the data are those of the authors and are not necessarily endorsed by the sponsors. We are grateful to the RSPB for allowing us to use Hope Farm as a study site and, in particular, the farm manager Ian Dillon. We also acknowledge Ian Bayliss and Vassia Ioannidou for help with weir and instrument installation and sample collection along with two anonymous referees for thorough and constructive feedback. None of the authors declare any conflict of interest.

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