Field test of the TOXSWA model: comparison of simulated and observed chlorpyrifos in water, sediment and macrophytes in four stagnant ditches

Paulien Adriaanse, Maarten Braakhekke et al,
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Overview

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3. TOXSWA model description
4. Model parametrization and results
5. Optimization procedure and results
6. Discussions and conclusions

1. Introduction

TOXSWA describes processes in mechanistic way

Used for
(i) pesticide regulation to assess risks for aquatic and sediment ecosystems (NL: 1999, EU: 2003)
(ii) research

Few studies to test: reality is reflected satisfactorily ?

Here field test: overspray of four ditches,
measured: *c*(time) and process parameters of chlorpyrifos in lab experiments with site-specific material

2. Outdoor ditch experiment

8 May 1990: single treatment of chlorpyrifos, intended concentrations 35 µg/L (ditch 6 and 9)

and 0.7 µg/L (ditch 4 and 10)

Water

Depth-integrated water samples at five distances in each ditch (40 m) at nine points in time up to 129 days post-application

T and pH measured every 15 min

2. Outdoor ditch experiment

Macrophytes

Ditch cover of three main spp. estimated at four points in time

Biomass measured at 1 m^2

Shoots with chlorpyrifos sorbed to it sampled at eight points in time up to 129 days post-application

Elodea nuttalli

Chara globularis

Ranunculus circinatus

2. Outdoor ditch experiment

Sediment

Sampled in two macrophyte-free segments at six points in time up to 129 days post-application

Chlorpyrifos analyzed in four layers:
0-1 cm, 1-3 cm, 3-6 cm and below 6 cm

In addition, pH, bulk density, organic matter content and volume fraction of liquid measured in four layers

2. Outdoor ditch experiment

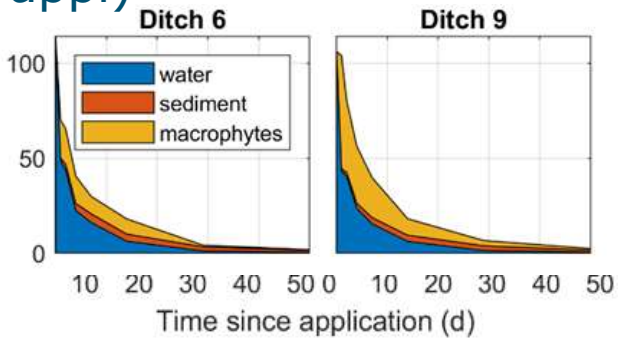
Results

Daily mean pH: 7.5-9.8
(-> degradation rate k_{wat} depends on pH)

Biomass macrophytes: 200-670 g/m^2 ditch bottom
(-> relatively high)

Mass distribution:
in water: 43-49% applied chlorpyrifos (1 d post-appl),
macrophytes: max. 20-60% (1 d post-appl)
and sediment: 3-5% (7-14 d post-appl)

observed



3. TOXSWA model description

Main processes

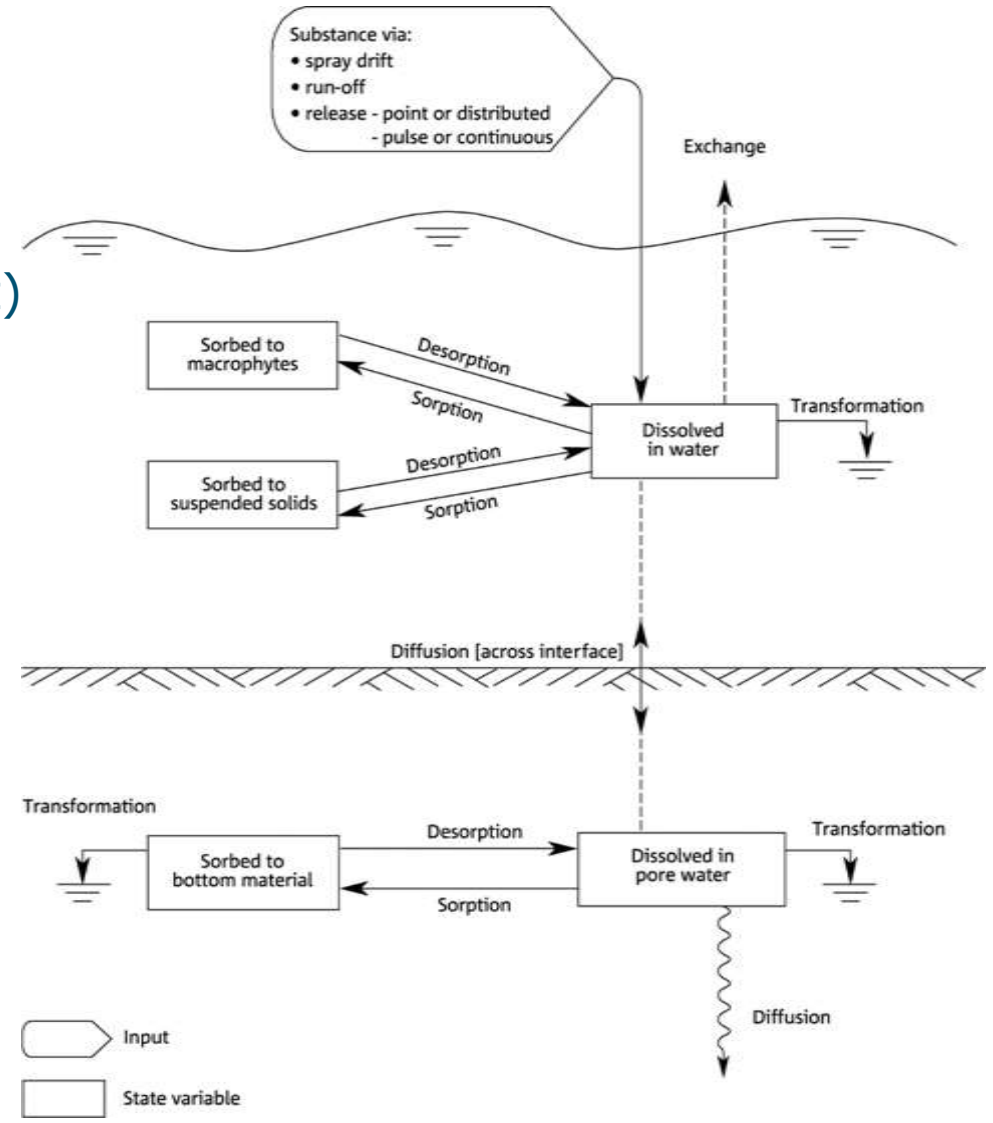
degradation (water, sediment)

sorption (macrophytes, sediment)

volatilization

diffusion (water-sediment, sediment)

Some ad-hoc changes to released versions for this study



4. Model parametrization and results

Measured on-site

T, pH and water depth;

Mean values bulk density, organic matter content, porosity for four layers;

Mean values of biomass (lumped three spp.).

Measured in lab with ditch-specific material

k_{wat} for initial pH 8 and 10;

k_{sed};

Sorption to *Elodea* and *Chara.*

4. Model parametrization and results

From literature

$K_{F,om,sed}$ and n (five soils, RAR, Spain, 2017);

$TC_{wat\text{-}air}$ by mass transfer coefficients in liquid and gas in Liss & Slater (1974)

with

$TC_{wat\text{-}air}$: overall mass transfer coefficient for water-air interface, based on liquid phase (m/d)

$K_{F,om,sed}$: Freundlich coefficient for sorption to sediment (L/kg)

n : Freundlich exponent (-)

4. Model parametrization and results (initial)

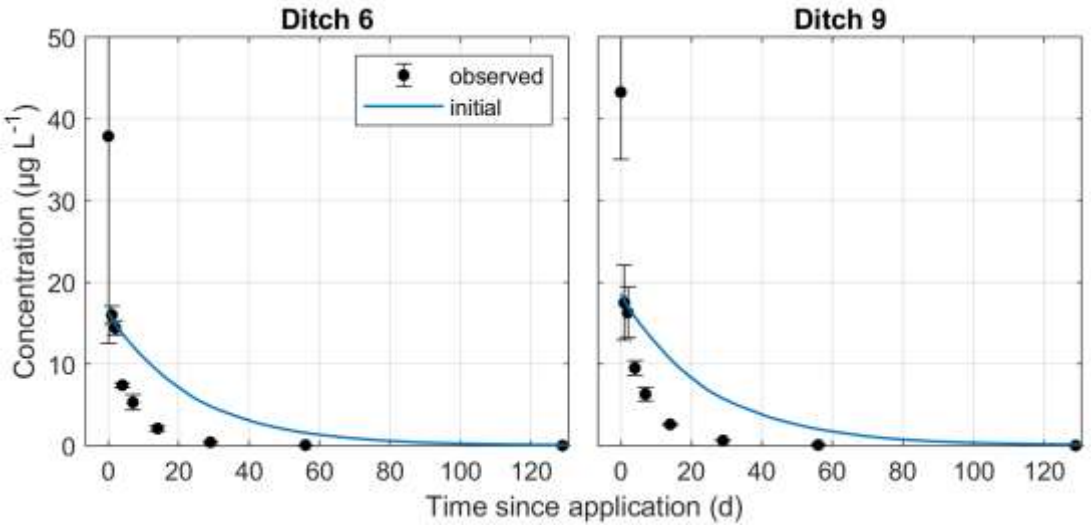
Concentration in water

Initial: concentration decline too slow
(cpf loss processes missing/underestimated)

Note:

mismatch t=0:
instantaneous sorption
to macrophytes

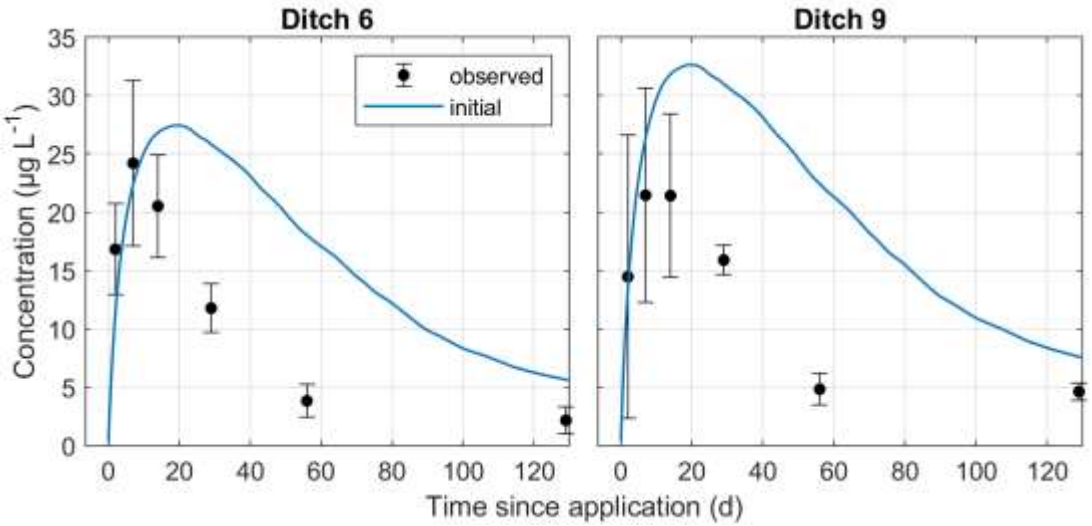
uncertainty in
measurements



4. Model parametrization and results (initial)

Concentration in 0-6 cm sediment layer

Initial: general shape OK (peak followed by decline), but decline too slow, and peak too high and too late (latter related to c_{wat})



5. Optimization procedure and results

Optimization procedure

TOXSWA run iteratively by PEST, varying optimization parameters, until minimal sum of weighted squared differences between model predictions and observations ($c(t)$ in water and sediment)

Goodness of fit

Visual assessment of $c(t)$ + residuals
R^2, coefficient of determination
(difference predicted-observed vs overall variation observations in time)

$$R^2_{\text{wat}} = 1 - \frac{\sum_{t=1}^{N_{\text{wat}}} \left(c^{sim}_{\text{wat},t} - c^{\text{obs}}_{\text{wat},t}\right)^2}{\sum_{t=1}^{N_{\text{wat}}} \left(\overline{c^{\text{obs}}_{\text{wat}}} - c^{\text{obs}}_{\text{wat},t}\right)^2}$$

5. Optimization procedure and results

Optimization parameters

no site-specific values
important for *c*(time) in water and sediment (sensitivity analysis):

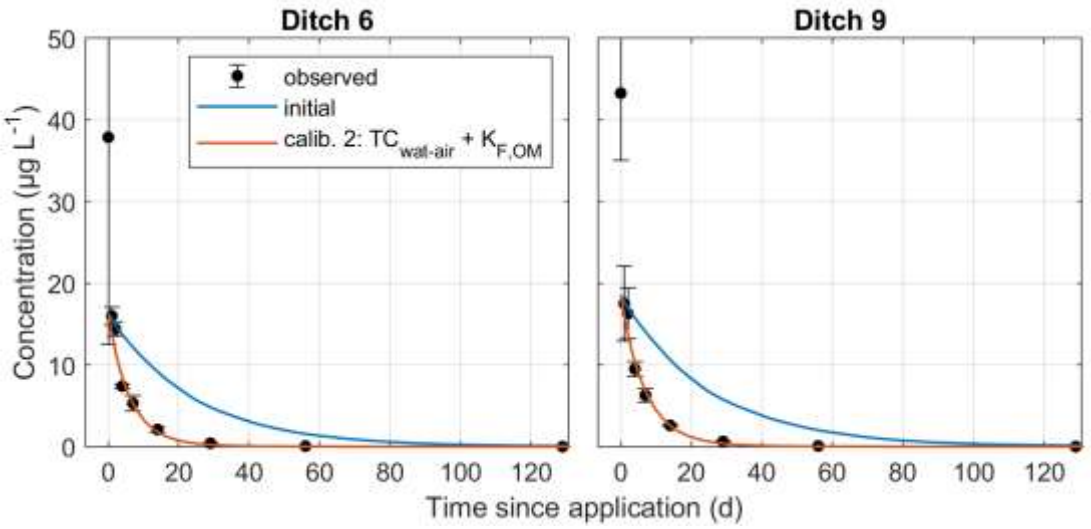
1. $TC_{wat\text{-}air}$: chlorpyrifos is relatively volatile, next
2. also $K_{F,om}$: significant sorption capacity (2072 L/kg)

5. Optimization procedure and results (calibration 2)

Concentration in water

Great improvement: faster decline in water

$TC_{wat\text{-}air}$ increase of initial 0.0311 to 0.144 and 0.099 m/d (ditch 6 and 9)

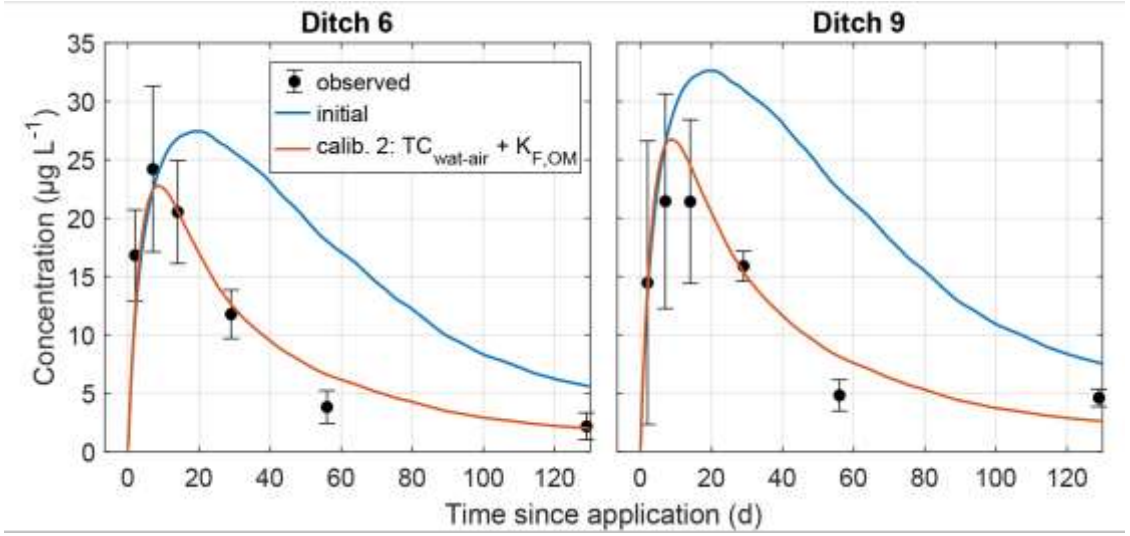


5. Optimization procedure and results (calibration 2)

Concentration in 0-6 cm sediment layer

Lower c_{wat} leads to increased fit: lower concentrations in sediment

$K_{F,om}$ increase of initial 2072 to 6150 and 5160 L/kg (ditch 6 and 9)

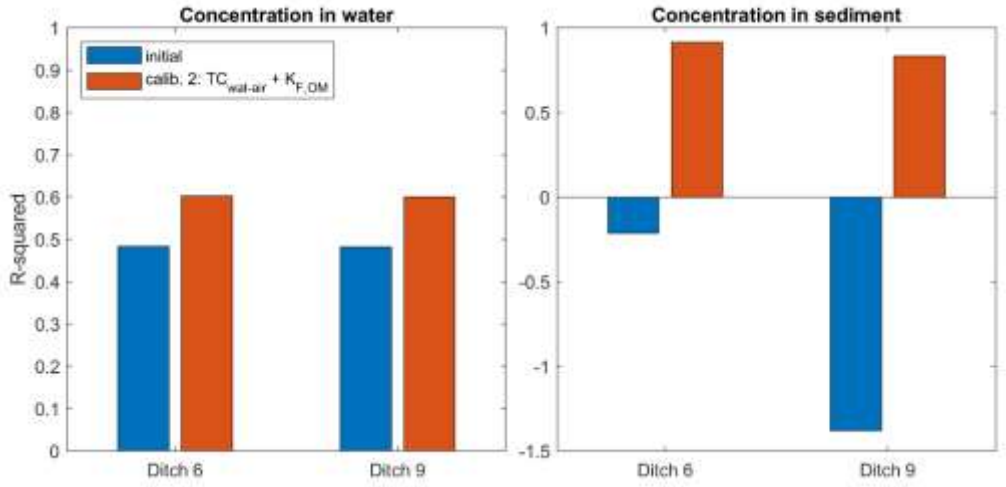


5. Optimization procedure and results (calibration 2)

R^2, quantifying goodness of fit
(1:perfect, negative: worse than average concentration in time)

Increased fit in water
(mismatch at t=0 persists)

Substantial improvement in sediment, R^2>0



6. Discussion and conclusions

Discussion

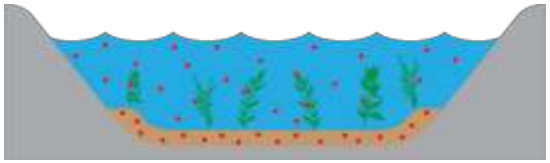
Microlayer chlorpyrifos

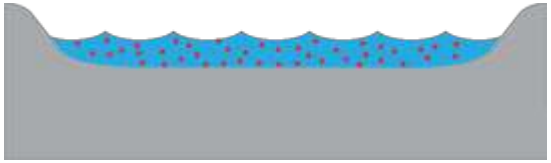
Volatilization underestimated by

(i) instantaneous mixing over water depth

(simulation h = 1 cm: 12%

and for h = 55 cm: <1% in first h post-appl)





(ii) average value of resistance to transport in gas phase by Liss & Slater (1974), instead of aerodynamic resistance, depending on wind speed

6. Discussion and conclusions

Conclusions

Volatilisation concept of TOXSWA to improve, especially in gas phase

Site-specific $K_{F,om}$ values important for $PEC_{sediment}$

Wider testing in the field
(i) may lead to improvement of model concepts, and
(ii) warranted to underpin use TOXSWA in regulatory risk assessments

Thanks and questions welcome

Thanks to my co-authors ☺

Field test of the TOXSWA pesticide fate model: Comparison of simulated and observed chlorpyrifos in water, sediment and macrophytes in four stagnant ditches

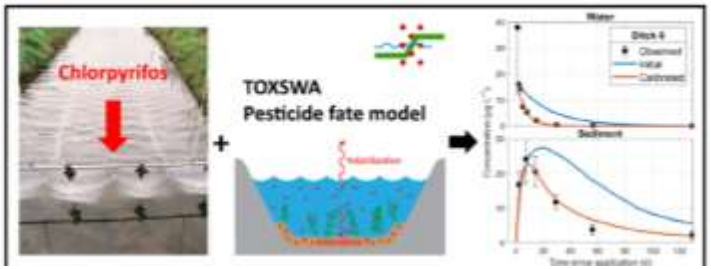
Pauline I. Adriaanse *, Maarten C. Braakhekke, Wim H.J. Beltman, Steven J.H. Crum

Wageningen Environmental Research, Wageningen UR, Wageningen, the Netherlands

HIGHLIGHTS

- TOXSWA was evaluated based on a field experiment with chlorpyrifos in 4 ditches.
- Maximally 3–8% applied chlorpyrifos was found in sediment, 18–60% in macrophytes.
- Parametrization based on lab-experiments and literature resulted in a poor fit.
- Optimization of volatilization and sorption coefficients gave strong improvement.
- TOXSWA can reproduce observations if good parameter estimates are available.

GRAPHICAL ABSTRACT



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