Field release modelling of pesticides and their transformation products during a first significant rainfall in a semi-arid region

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BACKGROUND

Introduction

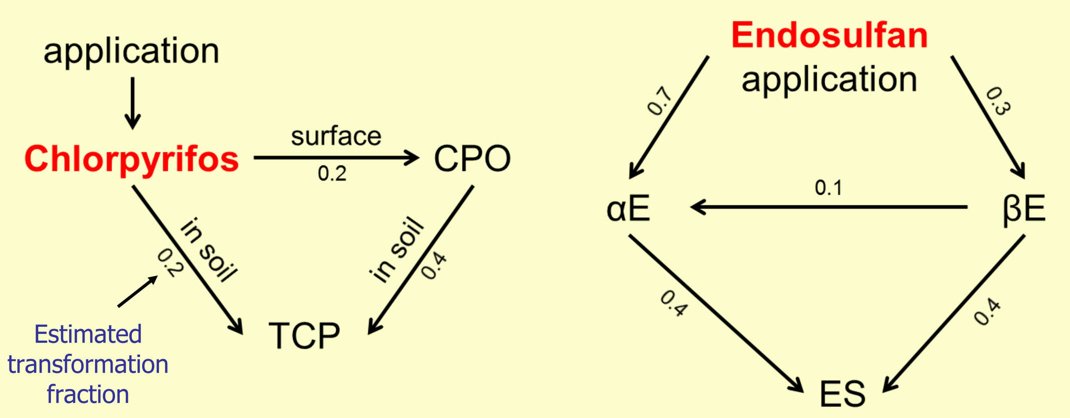
Background

- Mediterranean climate: wet winter, dry summer (April – September)
- Application of pesticides in the test basin: March – July, October
- Long intersection period of pesticide application and dry period
- Long time for transformation of pesticides

Aim of the study

- Dynamic modelling of pesticides and their transformation products during the dry time at catchment scale
- Modelling the release of those substances to the river during the first significant rain in 2009

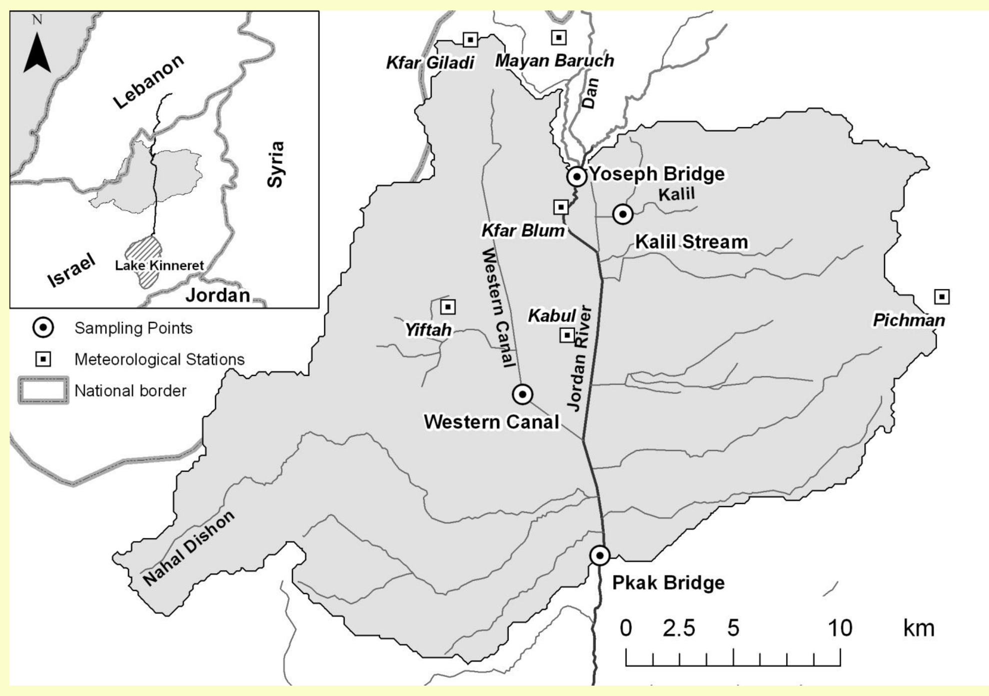
Substances



- Chlorpyrifos (CP)
- Chlorpyrifos Oxon (CPO)
- Trichloro-pyridinol (TCP)

- β-Endosulfan (bE)
- α-Endosulfan (aE)
- Endosulfan Sulfate (ES)

Catchment and Sampling campaign



Characteristics of the test catchment

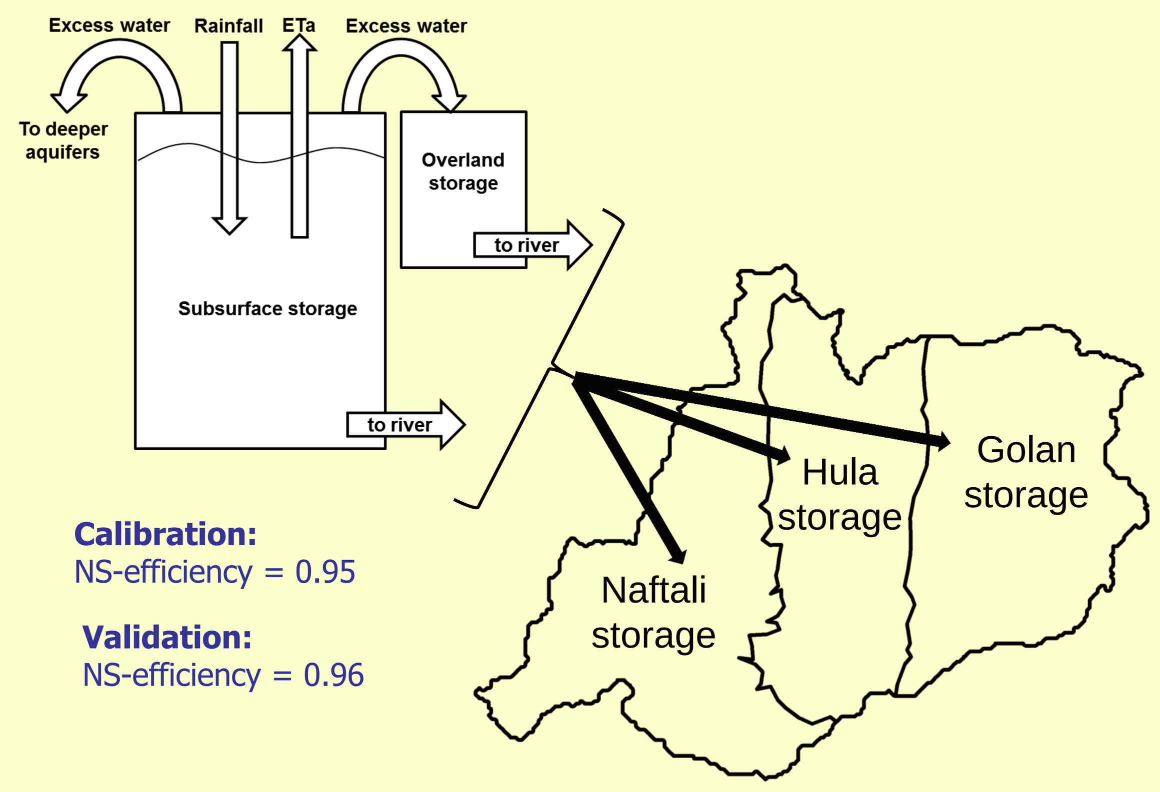
- Area: 613 km², average catchment elevation: 444 m.a.s.l.
- Flow length from inlet to outlet: ~ 17 km
- Average discharge: 13 m³/s
- Discharge regime: Parde coefficient 0.5 (summer) and 2 (winter)
- Most discharge is provided by karstic springs from outside of the test catchment

HYDROLOGY AND METEOROLOGY

Characteristics of the first rain event in autumn 2009

- Date: 20.09.2009
- Dry period before: ~ 5 month
- Peak rainfall intensity: 19 mm/h, rainfall amount: 24.5 mm
- Discharge increase at outlet: 4.99 m³/s → 5.92 m³/s (14%)

Hydrological model



Calibration:
NS-efficiency = 0.95

Validation:
NS-efficiency = 0.96

CHEMICAL MODEL

Field mass balance

Recursive formulation of pesticide pools (e.g. TCP)

$$m_{TCP,field,t+1} = \left(m_{TCP,t} + k_{CP} \cdot m_{CP,t} \cdot ff_{CP-TCP} + k_{CPO} \cdot m_{CPO,t} \cdot ff_{CPO-TCP}\right) \cdot \left(1 - k_{TCP}\right)$$

Available mass of TCP; Transformed mass of CP; Transformed mass of CPO; Transformation of TCP

$m =$ Substance mass

$t =$ timestep

$k =$ Decay constant

$ff =$ Formation fraction

Release to river

Modified pesticide runoff formula (OECD)

$$M_{runoff} = \frac{Q}{P} \cdot corr \cdot m_{field} \cdot \frac{100}{1 + K_{OC} \cdot f_{OC}}$$

Mass of pesticide in runoff; Runoff coefficient; Mass of pesticide on field; Sorption

Empirical correction for slope, interception and width of buffer zone

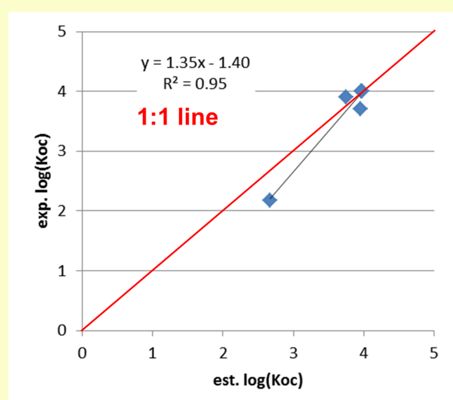
PARAMETRIZATION

Scenarios

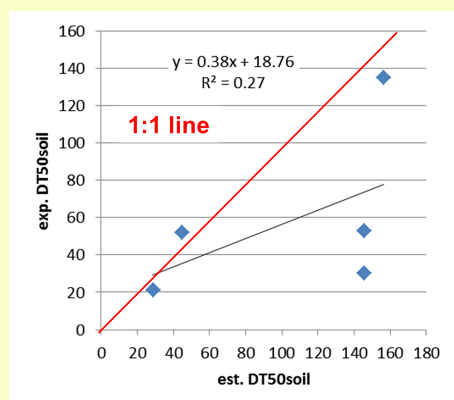
1. Scenario (S1): Pesticide applications from March to July
2. Scenario (S2): Pesticide applications from April to July and Sept. to Oct.
3. Soil transformation scenario
   - Soil half-lives, classical approach
4. Surface transformation scenario
   - Overlapping of dry period and pesticide application
   - → Photolysis half-lives and volatilization (Mediterranean climate)

Central question: How can a consistent parameter set (same environmental conditions) be found?

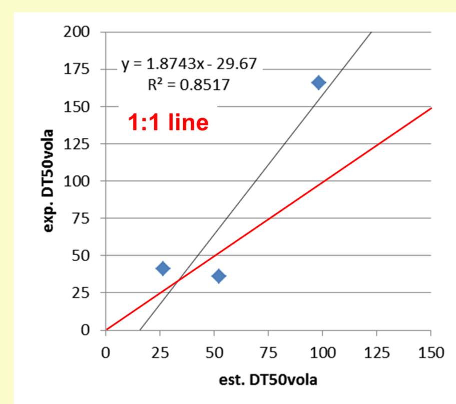
K_{OC} derived from solubility after Gerstl (1990)



$DT50_{soil}$ estimated using BIOWIN



$DT50_{vola}$ estimated using Voutsas et al. (2005) (model 2)



Estimated formation fractions using Fenner et al. (2009).

	ff_{est}	ff_{exp}
CP→TCP	0.2	0.25[1]-0.38[2]
CP→CPO	0.2	-
CPO→TCP	0.4	-
βE →ES	0.4	0.343
αE →ES	0.4	0.343
βE →αE	0.1	-

Estimated (ff_{est}) and experimental (ff_{exp}) formation fractions; [1]Chai et al. (2008), [2]PPDB (2009), [3]calculated after Fenner et al. (2009) and Ghadiri and Rose (2001)

Parameters used in the chemical modelling

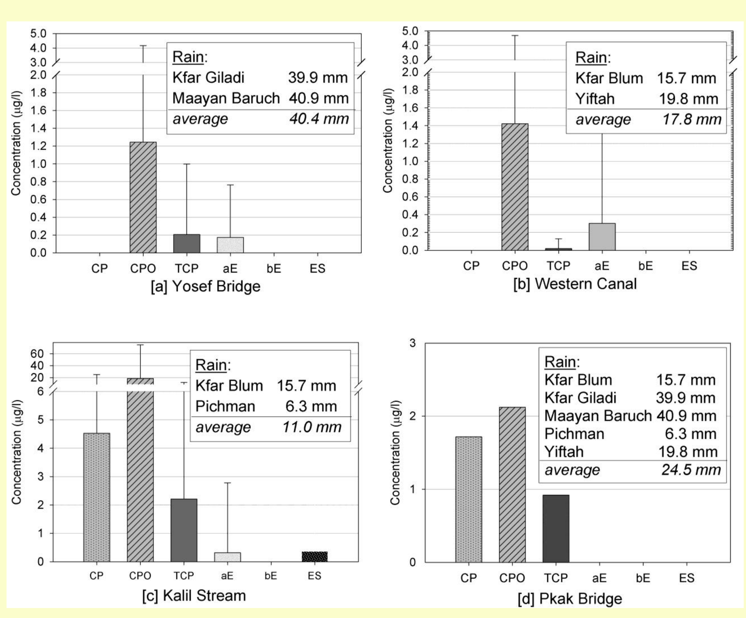
Ws – Water solubility, DT50 – half-life, vp - vapor pressure, est. – estimated, exp. - experimental

	$DT50_{soil}$ est. (d)[1]	$DT50_{vola}$ est.(d)[11]	$DT50_{photo}$ exp./est (d)	Ws (mg/l)	v_p (mmHg)	$Log(K_{oc})$ est. [4]
CP	29	27	17[7]	1.05[2]	2.03E-05[12]	3.75
CPO	28	79	33[7]	25.97[3]	6.65E-06[9]	3.03
TCP	45	11	1[8]	80.85[3]	1.03E-03[9]	2.67
αE	146	52	>200[6]	0.51[12]	3.00E-06[12]	3.97
βE	146	98	>200[6]	0.45[12]	6.00E-07[12]	3.98
ES	157	137	250[10]	0.48[12]	2.80E-07[12]	3.97

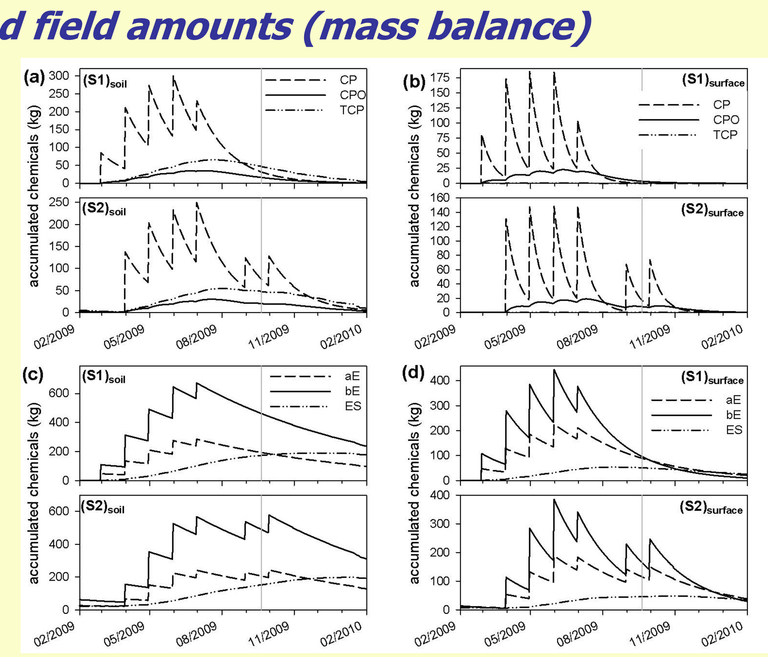
[1]estimated by Biowin Primary survey model (Howard et al., 1992), [2]experimental values from PPDB (2009), [3]estimated values by WSKOW 1.41 (Meylan et al., 1996), [4]estimated from solubility after Gerstl (1990), [6]GFEA (2004), [7]calculated by values of Walia et al. (1988), [9]estimated by MPBPWIN (USEPA, 2000), [10]estimated as more stable than parent compounds, [11]Voutsas et al. (2005), [12]EpiWin experimental database

RESULTS

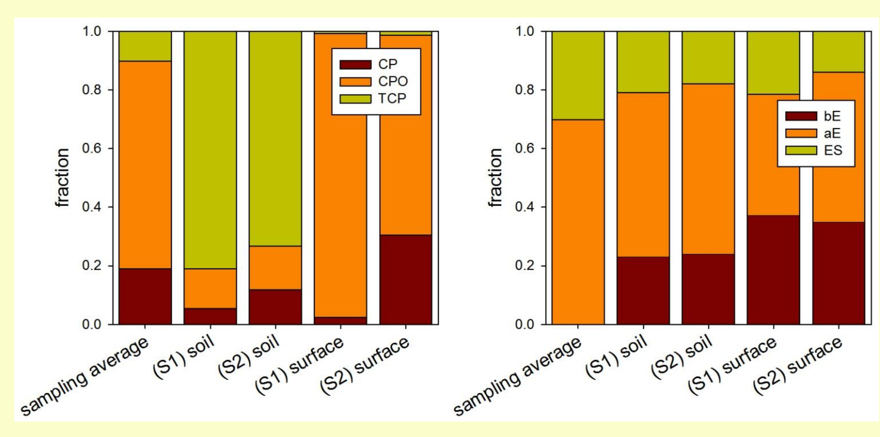
River sampling



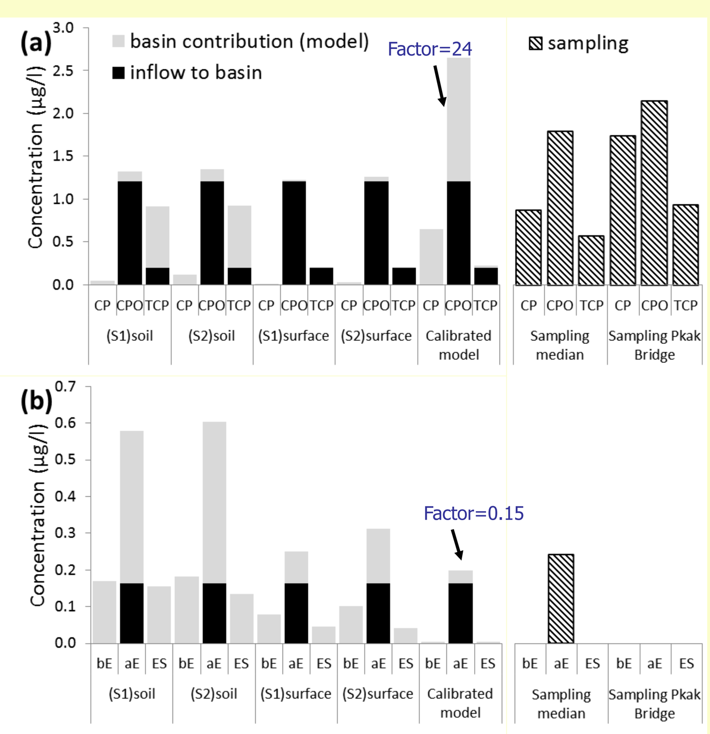
Modelled field amounts (mass balance)



Modelled relative concentrations



Modelled river concentrations



Calibration:
Multiplication of best substance group scenario by a factor.

CP group:
R²:0.44 → 0.73
RMSE: 1.2→0.8

Endosulfan group:
R² = 1→ 1
RMSE = 0.24 → 0.02

CONCLUSIONS

- The Hula valley was an important source of pesticides and transformation products (TPs) during the first significant rainfall in autumn 2009 in the Upper Jordan River basin. TPs were found in large concentrations in the stream water.
- A conceptual model was introduced for a dynamic modelling of the fate of pesticides and TPs. This model is a new contribution to simulation studies on organic chemicals and their transformation products as it works on catchment scale.
- Modelling and sampling results suggest surface transformation to be a major process in this region, at least for the CP group. Best model results showed a good correlation to samples.
- Further experimental work is suggested for transformation processes during the dry time in semi-arid regions in order to get an improved model parameterisation

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