Cod: 4.6005

MODELING HYDROLOGICAL AND BIOGEOCHEMICAL CONTROLS OF THE DISSIPATION OF P,P'-DDT FROM SOILS

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1. Introduction

Dichlorodiphenyltrichloroethane (DDT) and its metabolites are arguably among the most environmentally-relevant endocrine disruptors ever studied.[1] In Europe, DDT was the most used pesticide until the late 1970s (27,000 t y^{-1}). Since then, its use in Europe dropped to about 300 T y^{-1} in the early 1990s, following evidence of bioaccumulation. After 1995 no legal use has occurred in European countries.[2] The environmental pool of DDT in soils is estimated to represent 95% of the total environmental burden.[3] Changing environmental conditions and different types of disturbances can enhance remobilization from soils to the atmosphere or to aquatic ecosystems.Monitoring data from areas (such as Europe) where DDT underwent major restrictions or ban, generally display a steady decline in both biota and abiotic compartments. It is important to track such a decline and address the mechanisms of the underlying processes to enable meaningful prediction of the future environmental and human exposure to this harmful endocrine disruptor.
Large scale multimedia fate models have been successfully used to reproduce the long term trend of DDT environmental contamination.[3] Nevertheless these approaches miss the level of detail necessary to mechanistically assess hydrological and biogeochemical controls on its dissipation. We focused here on investigating the processes controlling the long-term trends of p,p'-DDT in soil in a region representative of central European conditions where DDT use was banned several decades ago.

2. Materials and methods

The area selected for this study is the Morava River catchment. The Morava is a tributary of the Danube River with a confluence located at the border between Austria and Slovakia, draining an area of 26658 km^2, mainly in the eastern part of the Czech Republic. The river is 354 km long, originating in the northeast of the Czech Republic at an elevation of 1371 m. DDT usage peaked in Czechoslovakia (recent Czech Republic and Slovakia, since 1993) during the early 1970s, and was banned in 1974. A large p,p'-DDT soil concentration dataset is available for the Morava catchment, spanning 2 decades (1995-2015). Time series of atmospheric concentrations of p,p'-DDT are also available for this region from 1996. Similarly, p,p'-DDT concentration data in river water and sediments are available from a study conducted in 2007 and 2008 in two central reaches of the Morava, covering a full year of continuous monitoring.[4, 5]
To quantitatively infer the processes controlling the long-term fate of p,p'-DDT in soil, a state-of-the-art high-resolution integrated hydrobiogeochemical-multimedia fate model – INCA-Contaminants – was employed.[6] INCA-Contaminants was recently developed by integrating a multimedia contaminant fate model, a hydrological model a biogeochemical model detailing organic carbon budgets in soil and river water, and a sediment dynamics model simulating soil erosion and in-stream transport, deposition and entrainment of sediments. The fate of DDT is calculated using compound-specific properties, atmospheric concentration data, atmospheric deposition data and meteorological data. INCA-Contaminants is therefore the state of the art tool capable of tracking, in a fully integrated way, the mass budget of DDT as a function of several hydrological and biogeochemical drivers under climate and land-use controls.

3. Results and discussion

Concentrations of p,p'-DDT in water and sediments were simulated with an acceptable level of accuracy (Figure 2). Considering the uncertainty of measurements there was no significant difference between mean dissolved phase concentrations predicted by the model and those measured in two central reaches of the Morava River. The magnitude of bed sediment concentrations was also successfully simulated

in the same two sub-catchments. The model typically captured the order of magnitude of bed sediment concentrations. The bulk of p,p'-DDT (over 90%) in the water column was predicted to be associated to suspended particles and DOC.
The concentration of p,p'-DDT in background soils of the Czech Republic displayed a highly significant ($p<0.001$by the Mann-Kendall test) decline. The same trends was successfully reproduced by the calibrated model (Figure 1). The dissipation trend was primarily sensitive to degradation half-life in soil. The best agreement between predicted and observed dissipation trends was obtained by using a degradation half-life in soil (τ) in the range $3000 < \tau < 3800$ days. There is a large uncertainty around p,p'-DDT reaction half-life in soil. The τ obtained from INCA-Contaminant calibration was 3x longer than the upper τ range reported in literature et al.[7] but within the range of 187 to 4331 days as reported by Hornsby et al.[8]
Degradation of p,p'-DDT is expected to be the controlling process for the dissipation of p,p'DDT from soils. (Figure 3). Degradation represented 88% of the total p,p'-DDT loss (on a yearly base) from the soil, while the remaining loss was due to diffuse and superficial run-off (Figures 3a and 3d). During periods of high precipitation and high river discharge the runoff flux could temporarily exceed total degradation in soil as a main dissipation process (Figure 3a). Total atmospheric inputs had a very small influence on the overall budget of p,p'-DDT in the Morava catchment, being 1.5 orders of magnitude lower than the total p,p'-DDT losses from degradation, runoff, erosion and volatilization) (Fig. 3c).
For the first time this assessment was obtained from an integrative model framework linking hydrological, biogeochemical and physical processes with a very high level of detail in scenario description.

Acknowledgments
The research leading to these results has acquired a financial grant from the People Program (Marie Curie action) of the Seventh Framework Program of EU according to the REA Grant Agreement No. 291782. The research is further co-financed by the South-Moravian Region. This paper reflects solely the authors' views and the European Union is not liable for any use that may be made of the information contained therein.

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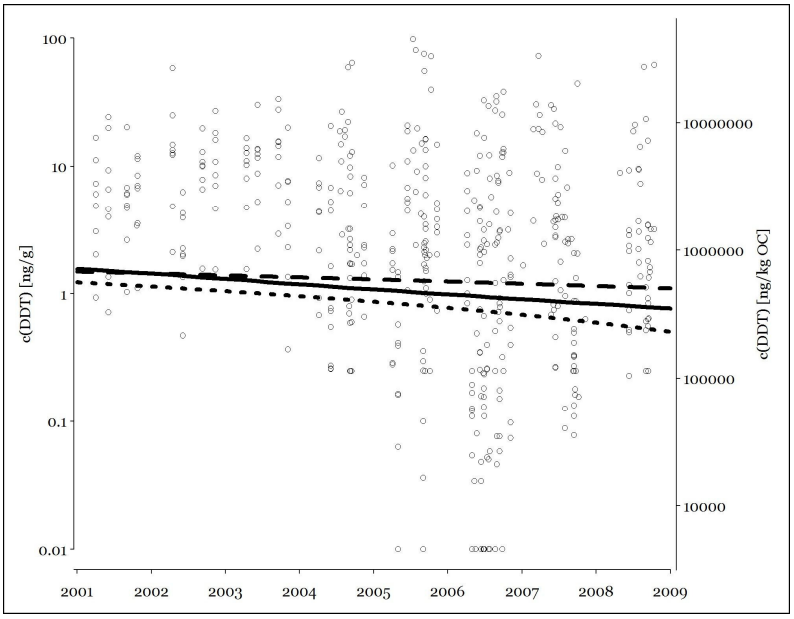

Figure 1: Historical p,p'DDT soil concentration data in the Morava River Catchment (points). Dashed and dotted lines represent statistical regression based on two different methods: Solid line, temporal trends calculated using the calibrated INCA-Contaminants model.

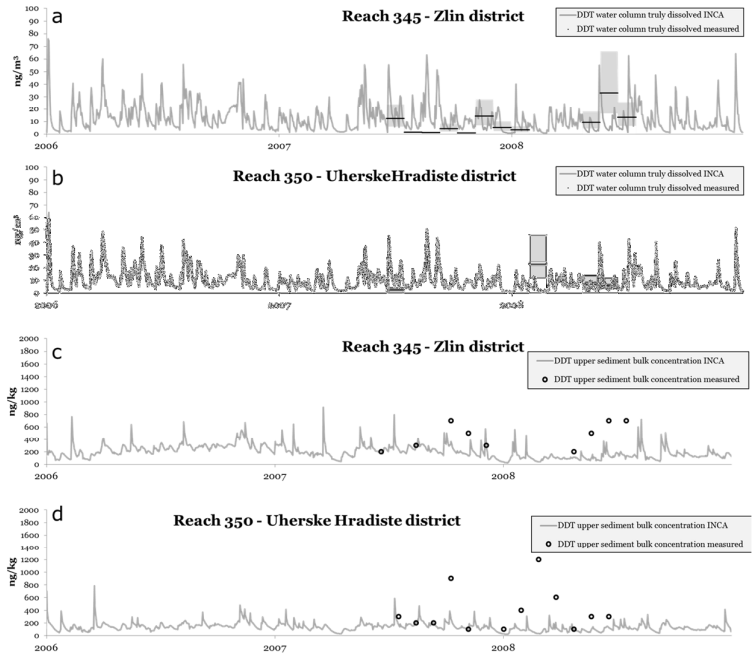

Figure 2: p,p'-DDT concentration calibration results of INCA-Contaminants for selected sub-catchments: a) truly dissolved concentrations in Zlin district, b) truly dissolved concentrations in Uherske Hradiste district, c) upper sediment bulk concentrations in Zlin district, d) upper sediment bulk concentrations in Uherske Hradiste district.

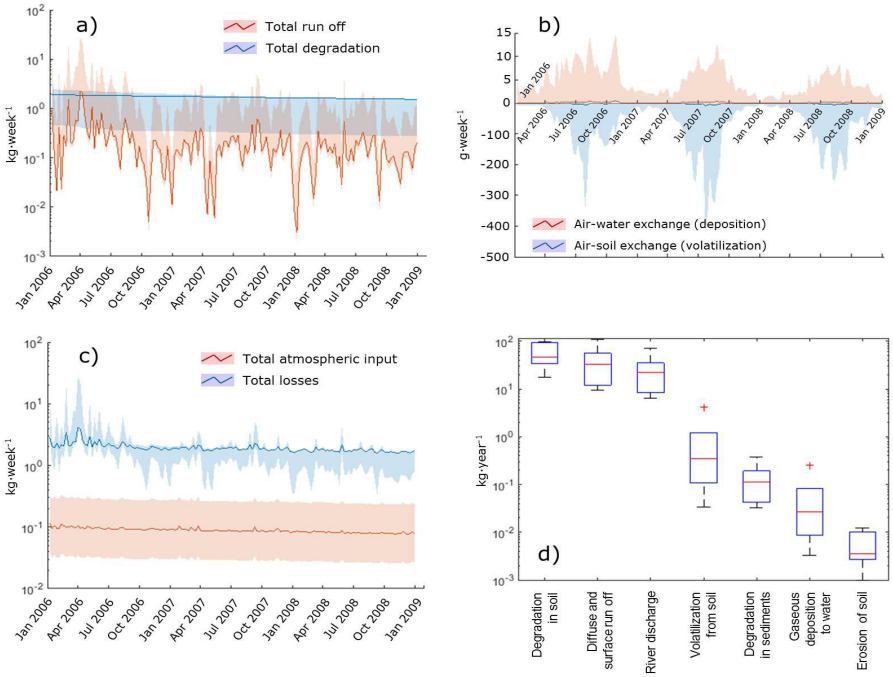

Figure 3: Multimedia exchange and transformation fluxes of p,p'-DDT calculated by INCA-Contaminants (data are presented with a weekly resolution): a) Comparison between the two most important dissipation processes. b) air-water and air-soil exchange. c) total atmospheric input compared to total losses from soil. d) Comparison among calculated yearly integrated fluxes of principal fate processes (average of 2006-2008). Shaded areas and boxplot represents the range of the parameters obtained by varying Kow, τ and SOC mineralization rate by one order of magnitude around their "best-fit" values