Science of the Total Environment 616–617 (2018) 500–509

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Impact of rainfall patterns and frequency on the export of pesticides and heavy-metals from agricultural soils

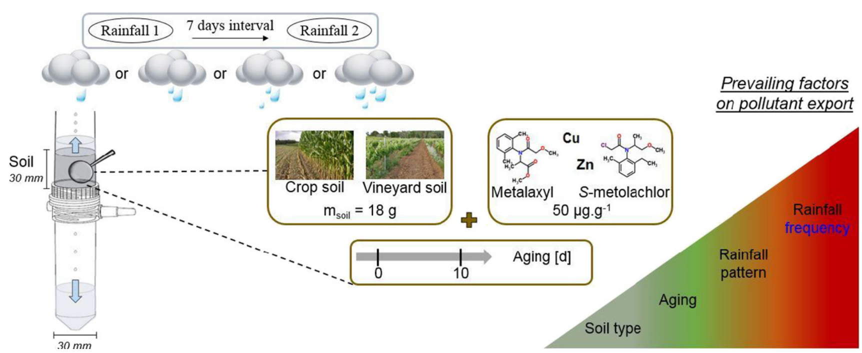
Fatima Meite, Pablo Alvarez-Zaldívar, Alexandre Crochet, Charline Wiegert, Sylvain Payraudeau, Gwenaël Imfeld *

*Laboratory of Hydrology and Geochemistry of Strasbourg (LHyGeS UMR 7517), University of Strasbourg, CNRS, ENGEES, 1 Rue Blessig, 67084 Strasbourg Cedex, France*

## HIGHLIGHTS

- Combining soil experiments and modeling to examine rainfall impact on pollutant export.
- Cu, Zn, metalaxyl and *S*-metolachlor leaching driven by rainfall duration and frequency
- Soil compaction reduced pollutant leaching after one rainfall and increased ponding.
- Soil characteristics and aging had less influence on pollutant leaching and ponding.
- Towards systematic evaluation of pollutant export in relation to rainfall patterns

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 1 September 2017
Received in revised form 26 October 2017
Accepted 29 October 2017
Available online xxxx

Editor: Jay Gan

*Keywords:*
Soil pollutant
Pollutant export
Pesticide mobilization
Rainfall patterns
Modeling
Atmosphere-topsoil interface

## ABSTRACT

The combined influence of soil characteristics, pollutant aging and rainfall patterns on the export of pollutants from topsoils is poorly understood. We used laboratory experiments and parsimonious modeling to evaluate the impact of rainfall characteristics on the ponding and the leaching of a pollutant mixture from topsoils. The mixture included the fungicide metalaxyl, the herbicide *S*-metolachlor, as well as copper (Cu) and zinc (Zn). Four rainfall patterns, which differed in their durations and intensities, were applied twice successively with a 7 days interval on each soil type. To evaluate the influence of soil type and aging, experiments included crop and vineyard soils and two stages of pollutant aging (0 and 10 days). The global export of pollutants was significantly controlled by the rainfall duration and frequency ($P < 0.01$). During the first rainfall event, the longest and most intense rainfall pattern yielded the largest export of metalaxyl ($44.5 \pm 21.5\%$ of the initial mass spiked in the soils), *S*-metolachlor ($8.1 \pm 3.1\%$) and Cu ($3.1 \pm 0.3\%$). Soil compaction caused by the first rainfall reduced in the second rainfall the leaching of remaining metalaxyl, *S*-metolachlor, Cu and Zn by 2.4-, 2.9-, 30- and 50-fold, respectively. In contrast, soil characteristics and aging had less influence on pollutant mass export. The soil type significantly influenced the leaching of Zn, while short-term aging impacted Cu leaching. Our results suggest that rainfall characteristics predominantly control export patterns of metalaxyl and *S*-metolachlor, in particular when the aging period is short. We anticipate our study to be a starting point for more systematic evaluation of the dissolved pollutant ponding/leaching partitioning and the export of pollutant mixtures from different soil types in relation to rainfall patterns.



## 1. Introduction

Pesticides are widely used to control pests while sludge from wastewater treatment plants (WWTP) containing heavy metals is often spread

* Corresponding author.
*E-mail address:* imfeld@unistra.fr (G. Imfeld).

https://doi.org/10.1016/j.scitotenv.2017.10.297

as fertilizers (McLaren et al., 2004). Heavy metals, such as Cu or Zn, are also widely used in perennial cultures, such as vineyards. Pesticides and heavy-metals may accumulate in agricultural soils and, following rainfall-runoff events, eventually reach surface water and groundwater. Predicting the mobilization and the export of pollutants from soils into aquatic ecosystems is thus essential to limit transport risks and evaluate toxicological exposure (Arias-Estévez et al., 2008; Schäfer et al., 2012). In this context, the topsoil layer (0–5 cm) plays a critical role to control water and pollutant fluxes, in particular in the case of pre-emergent pesticide applications on bare soils, or of perennial cultures, which are often characterized by unvegetated interrows and heavy-metal accumulation in topsoil. Understanding the role of both extrinsic factors, in particular the rainfall characteristics, and intrinsic factors, including characteristics of soil or pollutants, is required to estimate export pathways of pollutants from topsoil.

Pesticides and metals can be exported from the soil to surface water by runoff, i.e., ponding and overland flow (Lefrancq et al., 2014; Schwarzenbach and Westall, 1981; Shi et al., 2011). Ponding occurs when the rainfall intensity overcomes the topsoil infiltration capacity. Depending of slope and upstream-downstream hydrological connectivity, ponded water can generate runoff reaching aquatic ecosystems. Pollutants are also exported into sub-surface water by leaching when rainwater carries dissolved pollutants through the soil profile. While the rhizosphere have been shown to play a critical role to control pollutant leaching (Crowley et al., 2001; Diez et al., 2015), only little is known about the role of topsoil on pollutant mobilization in relation to rainfall. In agricultural catchments prone to Hortonian runoff, ponding/leaching water partitioning is mainly controlled by topsoil hydraulic properties, i.e. bulk density and saturated hydraulic conductivity (Armand, 2009; Chahinian et al., 2006). This latter can decrease by two orders of magnitudes between crop sowing and harvest because rainfall event frequencies modify the ponding/leaching threshold (Armand, 2009; Lefrancq et al., 2017).

Export of pollutants by ponding and runoff or leaching is also controlled by intrinsic factors, such as the physico-chemical properties of the pollutant (Gevao et al., 2000) and the soil hydrodynamics and characteristics (Buekers, 2007; Green and Ampt, 1911). In particular, the availability and mobility of pollutants in soils tend to decrease over time due to pollutant diffusion and sorption into mineral and organic fractions, a process termed "aging" (Komárek et al., 2010; Ma et al., 2006a). Aging can control the fraction of pollutant mobilized and transported from the soil either in the freely-dissolved phase or associated with soil particles and colloids (Gevao et al., 2000; Huang et al., 2015; Jalali and Khanlari, 2008; Sauvé et al., 2000; Tang et al., 2006). Together with aging, pollutant transformation, including speciation of metals and degradation of organic pollutants, can influence the extent of pollutant export from topsoil. Pollutant aging and transformation are themselves controlled by soil-extrinsic factors, such as the time between an application and a rainfall event (Huang et al., 2015; Nolan et al., 2008).

While pollutant aging in soils may decrease pollutant export, successive rainfalls may increase it (Goldreich et al., 2011; Huang et al., 2015). In addition, rainfall intensity and duration may primarily affect pollutant mobilization and export from the soil. Larger rainfall intensities have been shown to increase leaching of isoproturon from soil columns (Beulke et al., 2002), while successive rainfall events doubled leaching of metolachlor from topsoil at the second event (Goldreich et al., 2011). However, the contribution of intrinsic and extrinsic factors to the export of both organic and inorganic pollutants from soils has been, to date, rarely quantified (Beulke et al., 2002; Nolan et al., 2008; Sauvé et al., 2000). In this context, laboratory experiments can help to constrain and hierarchize factors controlling pollutant export to drive modeling approaches potentially used in the field (Banzhaf and Hebig, 2016).

The purpose of this study was to evaluate how rainfall patterns (i.e., intensity-duration-volume) influence the export of synthetic pesticides and heavy metals from agricultural topsoils in relation to i) soil characteristics, ii) rainfall frequency, and iii) short-term pollutant aging (ten days). We used laboratory experiments with topsoil from experimental vineyard (Duplay et al., 2014) or crop catchments (Lefrancq et al., 2017), which cover relevant agricultural land uses where pesticides and heavy metals can reach bare soil. Widely used anilide pesticides, i.e., the fungicide metalaxyl and the pre-emergence herbicide *S*-metolachlor, as well as Cu and Zn were used as model pollutants in a mixture because they may accumulate in topsoil (Duplay et al., 2014; Lefrancq et al., 2017). To evaluate sensitive parameters controlling pollutant ponding and leaching, a parsimonious physically-based model was developed to derive key parameters (i.e, the saturated hydraulic conductivity $K_{sat}$ and the organic carbon partition coefficient $K_{oc}$) that regulate pollutant export.

## 2. Material and methods

### 2.1. Chemicals and artificial rainwater

Metalaxyl ($C_{15}H_{21}NO_4$, methyl N-(methoxyacetyl)-N-(2,6-xylyl)-DL-alaninate) and *S*-metolachlor ($C_{15}H_{22}ClNO_2$, (*S*)-2-Chloro-N-(2-ethyl-6-methyl-phenyl)-N-(1-methoxypropan-2-yl)acetamide) were purchased from Sigma-Aldrich (St. Louis, MO, USA), with purity of 99.8 and 98.2% respectively. Copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$) and salts used for the preparation of the artificial rainwater were purchased from Sigma-Aldrich (St. Louis, MO, USA) with purity ≥97%. The water solubility, octanol-water partition coefficient $K_{ow}$ (log) and organic carbon partition coefficient $K_{oc}$ are 7100 $mg \cdot L^{-1}$, 1.7 and 163 $L \cdot mg^{-1}$ for metalaxyl, and 480 $mg \cdot L^{-1}$, 3.0 and 185 $L \cdot mg^{-1}$ for *S*-metolachlor, respectively (Kegley et al., 2016; PPDB Pesticide Properties DataBase, 2009). The soil/water partition coefficient (log $K_d$) of Cu and Zn used in this study were 2.7 and 3.1 $L \cdot mg^{-1}$, respectively (Allison and Allison, 2005). The artificial rainwater was prepared according to the ERM-CA408 reference material (ERM certification report, 2010) with ultra-pure water and targeted pH of 6.3 $\pm$ 0.6.

### 2.2. Soil collection

A calcareous clay-loamy surface soil (0 to 5 cm) (Rouffach, Haut-Rhin, Alsace, France) (Duplay et al., 2014) and a silty-clay soil (0 to 5 cm) from a crop catchment (Alteckendorf, Bas-Rhin, Alsace, France) (Lefrancq et al., 2017) were collected on August 6 and 7 2015. About 50 kg of soil were collected in a conventional vineyard plot of 12.5 $\times$ 70 m with weeded rows every two rows (along seven ungrassed rows). In parallel, about 50 kg of soil from a 47 ha crop catchment (corn and wheat) were sampled diagonally in between crop rows every two rows and over 25 rows. Soils were thoroughly homogenized and sieved to 2 mm to increase reproducibility between experiments. As a result, this study focuses on soil matrix flow and excludes preferential flow through macropores (Banzhaf and Hebig, 2016). Methods used for physical characterization of soils, including granulometry analysis, are provided in Table S1. The detailed physico-chemical characteristics of the soils and initial pollutant concentrations in the crop and vineyard soils used for the experiments are provided in Table S2. The vineyard soil contains more clays (68.5%) and carbonates (27.1%), while the crop soil was characterized by more organic matter (5.52%), sand (10.3%) and silt (61.5%). The crop soil is neutral (pH 7.0) while the vineyard soil is more alkaline (pH 8.1).

### 2.3. Rainfall patterns

To retrieve the four rainfall patterns, the Alsatian foothills region (France) was selected as a major cultural areas in temperate climate where orographic effect intensifies extreme rainfalls (i.e., the 99$^{th}$ percentile of precipitation during wet days or maximum amount of precipitation in five consecutive days) (Dankers and Hiederer, 2008). The selected rainfall station (47°57′9 N, 07°17′3 E, Rouffach, Haut-Rhin, France) is located in the experimental vineyard catchment from which