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Predicting pesticide fate in small cultivated mountain watersheds using the DynAPlus model: Toward improved assessment of peak exposure

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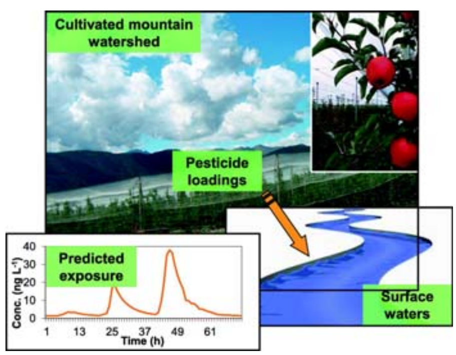
HIGHLIGHTS

- Pesticide concentrations in water typically exhibit short-term peaks.
- In small cultivated mountain basins, peaks can be shorter but much higher.
- Existing models are not suitable to predict exposure in mountain basins.
- DynAPlus model allows evaluating such situations.
- DynAPlus could potentially be used to improve ecological risk assessment.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of plant protection products (PPPs) in agricultural areas implies potential chemical loadings to surface waters, which can pose a risk to aquatic ecosystems and human health. Due to the spatio-temporal variability of PPP applications and of the processes regulating their transport to surface waters, aquatic organisms are typically exposed to pulses of contaminants. In small mountain watersheds, where runoff fluxes are more rapid due to the steep slopes, such exposure peaks are particularly likely to occur. In this work, a spatially explicit, dynamic model for predicting pesticide exposure in surface waters of cultivated mountain basins (DynAPlus) has been developed. The model has been applied to a small mountain watershed (133 km^2) located in the Italian Eastern Alps and characterized by intensive agriculture (apple orchards) around the main river and its tributaries. DynAPlus performance was evaluated for chlorpyrifos through experimental monitoring, using samples collected during the 2011 and 2012 productive seasons. The comparison between predictions and measurements resulted in a good agreement ($R^2 = 0.49$, efficiency factor 0.60), although a more accurate spatial information in the input scenario (e.g., field-specific applications, rainfall amount, soil properties) would dramatically improve model performance. A set of illustrative simulations performed for three PPPs highlighted the potential role of DynAPlus in improving exposure predictions for ecological risk assessment and pesticide management practices (e.g., for active ingredient and application rate selection), as well as for planning efficient monitoring campaigns and/or

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interpreting monitoring data. However, some model improvements (e.g., solid erosion and transport) and a more thorough model validation are desirable to enlarge the applicability domain.

1. Introduction

Agricultural activities can involve the use of insecticides, fungicides and other plant protection products (PPPs) and the use of these PPPs can be located near surface water bodies, thus creating a potential for adverse effects on aquatic ecosystems (e.g., McKnight et al., 2012; Schäfer et al., 2012). The problems related to multiple sources of pesticides and their effects on ecosystems have been among the most studied environmental issues in the last half century (White et al., 1967; Verro et al., 2009; Knäbel et al., 2012, 2016), and the need to reduce the risk for non-target terrestrial and aquatic organisms is acknowledged by the current European legislation (Directive 2000/60/EC; Regulation 1107/2009/EC; Directive 2009/128/EC; EC, 2000, 2009a, 2009b). In risk assessment for PPP in aquatic environments, one of the most important challenges concerns exposure characterization (Brock, 2010), since most of the PPP loadings to surface waters and the processes regulating their fate in the environment are heterogeneous in space and time (e.g., multiple sources with different application patterns, loadings to surface waters regulated by episodic events such as spray drift and rainfall). Due to such spatio-temporal heterogeneity, ecosystems are often exposed to sequential pulses of contaminants (e.g., Verro et al., 2009; Brock, 2010; O'Brien et al., 2016; Lorenz et al., 2017). In current procedures for effect and exposure assessment, a general lack of environmental realism and relevance was recently highlighted for both industrial chemicals and pesticides (EC, 2013; Vighi, 2013; Di Guardo and Hermens, 2013), and the need for more dynamic and realistic models and scenarios was pointed out (Di Guardo and Hermens, 2013; De Laender et al., 2015). Focusing on exposure modelling, the "steady-state attitude" (according to Di Guardo and Hermens, 2013), common to the regulatory models adopted for industrial chemicals (EC, 2004) is less pronounced in models adopted for pesticides (FOCUS, 2001), since dynamics in chemical emissions must be accounted for. However, the current description of environmental and ecosystem dynamics in these models is rather simple and based on a generally static picture of environmental compartments (Franco et al., 2017; Di Guardo et al., 2017). For PPP, simulation scenarios aim to represent a worst-case exposure (FOCUS, 2001), but the model and scenario ability in predicting worst-cases was questioned (Knäbel et al., 2012, 2014) and it may be disputed whether such exposure profiles also represent a realistic worst-case situation from an ecological perspective (Rico et al., 2016). To overcome the lack of realism in exposure models, for example, primary producer and organic carbon dynamics were incorporated into modelling tools for exposure predictions in lentic shallow-water environments, showing the potential magnitude of seasonal exposure variations related to the presence/abundance of such phases (Morselli et al., 2015; Di Guardo et al., 2017). Although several dynamic and/or spatially resolved models were developed in the last two decades to investigate PPP fate and exposure concentrations at different scales (e.g., Adriaanse, 1997; Renaud et al., 2008; Verro et al., 2009; Ghirardello et al., 2014), a fully dynamic modelling approach suitable for simulating chemical fate in small mountain watersheds, where high slopes can determine fast chemical movement with surface runoff and thus sudden chemical loadings to surface waters, is still missing. For example, the comprehensive, physically-based SWAT (Soil and Water Assessment Tool) model (Neitsch et al., 2005) was designed for slopes not >5% and should not be used for runoff simulations in small, steep basins also due to its daily time-step in calculations (Lee and Kim, 2009). In the present study, a new spatially explicit dynamic model (DynAPlus), integrating a new water-sediment model for river networks (DynANet) and the spatially-resolved air-soil model SoilPlus (Ghirardello et al., 2010, 2014), was developed and applied to investigate the fate of three pesticides (chlorpyrifos, pirimicarb and etofenprox) in a mountain stream (Novella River, Non Valley, Northern Italy), where apple orchards surround the river and its tributaries. DynAPlus requires, for example, time-varying input for meteorological parameters and suspended solids in water and spatially-resolved information concerning soil hydrological properties, organic carbon fraction and land use in the watershed. Water concentrations of chlorpyrifos, listed among priority substances according to Annex II of Directive 2008/105/EC (EC, 2008), were measured in the Novella River with high temporal resolution during the productive season in 2011 and 2012, and such data were used to assess the integrated model predictive ability, highlighting the valuable role of such a modelling tool in understanding the fate of non-point source, episodic-emission pollutants such as PPP in small steep watersheds.

2. Materials and methods

2.1. Case study description

The investigated water body is the Novella River, whose catchment (area = 133 km^2) is mostly located in the Trento province, Northern Italy (Fig. 1a). Like most of the valleys in the area, the Novella River basin is intensely cultivated and apple orchards occupy a relevant portion of the watershed (i.e., around 10%; ISPRA, 2017; GPTP, 2017). This kind of cultivation requires large external inputs to be maintained, and that includes a relevant amount of PPP, especially fungicides and insecticides (Brock, 2013). Since most of the area is characterized by high slopes, the risk for pesticide surface runoff cannot be considered as negligible. In addition, orchards are usually grown at lower altitudes (<1100 m a.m.s.l.), very close to the streambed, often without proper buffer strips, thus enhancing the risk for pesticide loadings to surface waters (Fig. 1b). Other main land uses in the valley are coniferous and mixed forest, pasture, bush and other uncultivated land (Fig. S1; ISPRA, 2017).

2.2. Water sampling

Water samples were collected in the Novella River during the productive seasons of the years 2011 and 2012. Chlorpyrifos (CHL) was selected as the target chemical, for model evaluation purposes. The sampling site was located at the border between the municipalities of Dambel and Cloz (Trento Province; Fig. 1b). During 2011, samples were grabbed manually at random dates and during an intense rain event occurred in July. Stream water was collected in aluminium containers. Samples were then labelled, immediately refrigerated and transported to the lab, where they were stored at −20 °C until analysis. In September 2011, an automatic sampler (ISCO 6712) was then installed at the sampling site and time-series of water samples were collected during several runoff events in 2011 and 2012. The sampler was equipped with a submerged probe (ISCO 720) to measure water level, which was recorded at intervals of 10 min. The sampler was programmed for starting sampling after a sudden increase in water level and for collecting other eleven 0.9-L samples every other hour, covering a period of 22 h. Water was collected in glass jars, which remained in the storage part of the automatic sampler (i.e., dark conditions, for typically 24 h to maximum 48 h) until manual transfer to labelled aluminium containers, which were then transported to the lab and stored at