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Pesticide load dynamics during stormwater flow events in Mediterranean coastal streams: Alexander stream case study

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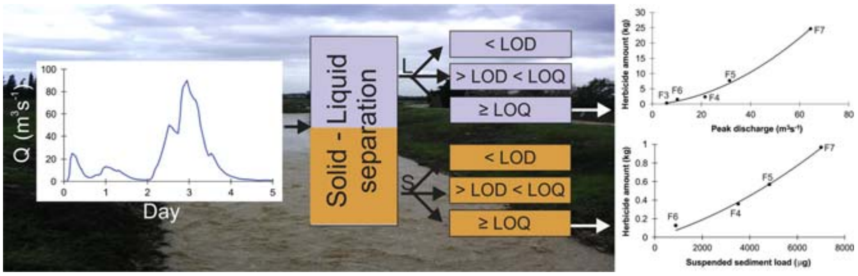
HIGHLIGHTS

- Pesticide-load dynamic is examined for both dissolved and adsorbed phases.
- Most pesticides are transported in the dissolved phase.
- Flood event magnitude and pesticide application method affect its concentration.
- Mix of pesticides is dominated by diuron (herbicide) and tebuconazole (fungicide).

GRAPHICAL ABSTRACT



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ABSTRACT

Cultivated land is a major source of pesticides, which are transported with the runoff water and eroded soil during rainfall events and pollute riverine and estuarine environments. Common ecotoxicological assessments of riverine systems are mainly based on water sampling and analysis of only the dissolved phase, and address a single pesticide's toxicological impact under laboratory conditions. A clear overview of mixtures of pesticides in the adsorbed and dissolved phases is missing, and therefore the full ecotoxicological impact is not fully addressed. The aim of this study was to characterize and quantify pesticide concentrations in both suspended sediment and dissolved phases, to provide a better understanding of pesticide-load dynamics during storm events in coastal streams in a Mediterranean climate. High-resolution sampling campaigns of seven flood events were conducted during two rainy seasons in Alexander stream, Israel. Samples of suspended sediments were separated from the solution and both media were analyzed separately for 250 pesticides. A total of 63 pesticides were detected; 18 and 16 pesticides were found solely in the suspended sediments and solution, respectively. Significant differences were observed among the pesticide groups: only 7% of herbicide, 20% of fungicide and 42% of insecticide load was transported with the suspended sediments. However, in both dissolved and adsorbed phases, a mix of pesticides was found which were graded from "mobile" to "non-mobile" with varied distribution coefficients. Diuron, and tebuconazole were frequently found in large quantities in both phases. Whereas insecticide and fungicide transport is likely governed by application time and method, the governing factor for herbicide load was the magnitude of the stream discharge. The results show a complex dynamic of pesticide load affected by excessive use of pesticides, which should be taken into consideration when designing projects to monitor riverine and estuarine water quality.

1. Introduction

Agricultural lands in Mediterranean climates are characterized by high soil-erosion rates, due to the coupling of high-intensity rainfall events (erosivity index) and bare soils (Garcia-Ruiz et al., 2015;

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Montgomery, 2007; Morin and Benyamini, 1977; Panagos et al., 2015a, 2015b). Whereas the former is related to the natural rainfall regime—rainfall amount, distribution, intensity, and raindrop kinetic energy, the latter is an outcome of agricultural practices—for example, intensive weed-control practices aimed at eliminating competition on water and nutrient resources with the desired crop (e.g., plantations, orchards, vineyards and other field crops) (Oerke, 2006). Soil erosion and transport by water initiates with particle detachment, due to the kinetic energy of the raindrop's impact on bare ground, and continues with inter-rill, rill and gully erosion. When soils are water-saturated, erosion intensifies, and full hydrological connectivity is reached between the fields on the hillslopes and the riverine system's drainage network (Covino, 2017; Sharma et al., 1991; Stieglitz et al., 2003; Valentin et al., 2005). In the riverine system, the eroded soil particles can potentially travel substantial distances in suspension, contributing significantly to global sediment fluxes to seas and oceans (Syvitski et al., 2005).

Surface-runoff water containing eroded soil particles from cultivated land often includes nutrients and applied pesticides released from the topsoil. This may result in direct and indirect physical, chemical and biological effects on water quality, thereby impacting the aquatic ecosystems (e.g., toxic algal blooms, poisoning and disturbances to food web structures), and posing a major global threat to human water security and river biodiversity (Beketov et al., 2013; Blann et al., 2009; Schwarzenbach et al., 2006; Vörösmarty et al., 2010). Pesticide fluxes are more difficult to quantify and trace (e.g., Bundschuh et al., 2014; Kronvang et al., 2003) than excessive fertilizer fluxes originating from cultivated land (e.g., Neal et al., 2012; Segal-Rozenhaimer et al., 2004). This is because fertilizer dynamics is easier to study by monitoring only a few key tracers in the surface water, such as phosphorus and nitrogen (e.g. Bennett et al., 2001; Minami and Fukushi, 1984). In addition, pesticide-load dynamics is affected by the partitioning of the chemical between dissolved and adsorbed phases. Some pesticides tend to bind with suspended sediments and are transported as particulate-bound pollutants, whereas others are more stable in their dissolved form in the surface runoff (Birch et al., 2015; Carpenter et al., 2016; Chapman et al., 2013; Ng et al., 2012). This dynamic can be highly influenced by field conditions (e.g., time of pesticide application and location; Pérez et al., 2017) and soil characteristics (e.g., clay and organic content; Larson et al., 1995).

While awareness of sediment-bound pesticide toxicity has risen in the last few decades (Bundschuh et al., 2014; Kronvang et al., 2003), efforts to establish benchmarks have only recently been initiated (e.g., Nowell et al., 2016; Rodrigues et al., 2017), along with studies that continually monitor pesticide concentrations (e.g., Pérez et al., 2017). Significant knowledge gaps still exist regarding pesticide-load dynamics during flood events, in particular with respect to differentiating the pesticide distribution between (i) baseflows and flood events, and (ii) dissolved and particulate-bound phases. This basic information may contribute to a more realistic environmental risk assessment of non-point contamination sources, and knowledge of the mitigation requirements (e.g., Bereswill et al., 2013) required to reduce the potential threat to biological functioning of different aquatic species, ranging from diatoms and bacteria to fish, vertebrates, and birds (e.g., Ayas et al., 1997; Beketov et al., 2013; DeLorenzo et al., 2001; Fasola et al., 1998; Köhler and Triebskorn, 2013; Liess and Von Der Ohe, 2005; Mora, 1997).

This potential risk is a profound threat, especially in Mediterranean streams, which are ecosystems that are under continuous water stress. These streams are characterized by seasonal rain periods, with dry summers and wet winters, during which the dominant riverine flows are stormwater flow events (hereafter flood events), while low baseflows or dry riverbeds are often maintained between storm events (Gasith and Resh, 1999; Hershkovitz and Gasith, 2013). Deposition of suspended sediments with bound (or attached) pesticides may occur in streambeds and estuary banks and floodplains, where they may remain during the dry season or until the next flood event (Gasith and Resh, 1999). Once the pesticides that are bound to soil colloids are resuspended in the aquatic environment, they may undergo geochemical changes and become available to biota (Chapman et al., 2013; Turner, 2003). Therefore, the aim of this study was to characterize and quantify pesticide concentrations in both the suspended sediments and dissolved phases, while following the flood events in Alexander stream. We hypothesized that flood events are the dominant contributor of pesticides to this stream, and that significant amounts of pesticides are transported adsorbed to suspended sediments as well as in the dissolved phase.

2. Material and methods

2.1. Study site

Alexander stream lies within a typical coastal watershed located at the eastern part of the Mediterranean Sea. The watershed spans a total area of 553 km^2 with mean annual rainfall of 570 mm. The main stream channel runs over 45 km in a general east–west direction, with three main tributaries (Bahan, Shchem and Teenim) that all start from the Samaria mountains, and continue through the lowlands of Hefer valley, where they converge at different locations (Fig. 1). Alexander stream flows into a well-defined micro-estuary before entering the Mediterranean Sea. The watershed drainage area can be roughly divided into four parts: (i) the upper part consists of mountain slopes, composed mainly of limestone and dolomite rocks and characterized by Cambisols (Terra Rossa and Rendzina soils; ~40% clay, 0.3–2% soil organic carbon (SOC)); (ii) the middle part consists of rolling hills, made of limestone and chalk lithology covered with Chromic Luvisols (Brown Hamra; ~7% clay, 0.3–1% SOC); (iii) the lowland part is a typical mixture of Chromic Vertisols (Grumusol; ~65% clay, 0.3–2% SOC) and sandy Luvisols (Hamra; 4% clay, 0.3–0.6% SOC); (iv) a narrow section consisting of sand dunes along the estuary. The western part of the watershed is a highly fertile valley, characterized by intensive agricultural activity covering 45% of its watershed area (Fig. 1). The eastern watershed is characterized by steep terrain, with agricultural land use dominated mainly by citrus and olives trees, as well as vineyards. A total of 66% of the entire watershed is used for agriculture, mainly orchards, plantations and field crops (Tal et al., 2007).

2.2. Data acquisition and field sampling

Discharge records were retrieved from the Eliashiv hydrometric station which has been operated by the Israel Hydrological Services since 1967. Flood events were defined as times with stream flow having a peak discharge above 2 m^3 s^{-1}, providing a clear distinction between floods and baseflows. This flow limit was defined to differentiate occasional releases of treated wastewater and fishponds into the stream, reaching up to ~1.5 m^3 s^{-1}, from baseflow discharge, which fluctuates around a daily mean value of 0.14 m^3 s^{-1}. Data on land use and soil type were obtained from the Israel National Geographic Information Database and analyzed using ArcGIS (v10.1 by ESRI).

Data pertaining to potential pollutant sources, agricultural activities and potential pesticide usage were obtained via interviews conducted with local farmers and professionals representing different stakeholders, such as Yad-Hanna wastewater-treatment plant, Ministry of Environmental Protection, Ministry of Agriculture and Rural Development, Nature & Parks Authority, local municipal authority, Sharon Drainage Basin Authority. This source of information will be referred to herein as ‘personal communication’.

Runoff water samples were collected during flood events automatically using an automated sampler (Sigma 900, Hach Company, Loveland, CO) equipped with twenty-four 350-mL glass bottles, and manually as grab samples using 2- and 4-L glass bottles. Baseflow water was sampled four times during the 2014 dry season and analyzed for dissolved pesticides to determine typical baseflow pesticide load.