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Villamizar Velez, Martha Lucia orcid.org/0000-0002-6545-3807 and Brown, Colin David orcid.org/0000-0001-7291-0407 (2016) Modelling triazines in the valley of the River Cauca, Colombia, using the annualized agricultural non-point source pollution model. Agricultural water management. pp. 24-36. ISSN 0378-3774

https://doi.org/10.1016/j.agwat.2016.06.010

Modelling triazines in the valley of the River Cauca, Colombia, using the annualized agricultural non-point source pollution model

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Abstract

The annualized agricultural non-point source pollution model (AnnAGNPS) was applied to simulate losses of triazine herbicides to the River Cauca following application to sugarcane, maize and sorghum in the Cauca Valley of Colombia. Surface runoff was found to be the main driver of triazine losses to surface water in the catchment. Satisfactory simulation and validation of the hydrology was achieved after little calibration (Nash-Sutcliffe model efficiency = 0.70 and r^2 = 0.73). A fairly good simulation of pesticides was generally achieved, but some patterns in the measured data could not be simulated. Uncertainty analyses of sensitive input parameters were carried out which explained most of the concentrations that were not captured by the initial simulation; however, evidence of point source pollution was observed for some large concentrations measured upstream. Replacing triazine herbicides with mesotrione was predicted to result in an 87% reduction in pesticide losses expressed as a proportion of the total pesticide applied.

Keywords

AnnAGNPS; Atrazine; Simazine; Mesotrione; River Cauca; Uncertainty

Highlights

- AnnAGNPS was able to simulate a large catchment (three times the recommended area)
- AnnAGNPS can simulate runoff with reasonable accuracy under Colombian conditions

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- Methods are proposed for modelling a catchment with sparse data
- Uncertainty analysis could explain most of the discrepancies in the pesticide simulations

1 Introduction

The geographical valley of the River Cauca in the Valle del Cauca department, Colombia, is characterised by intensive agriculture where sugarcane is the main crop covering about 200,000 ha (approximately 50% of the arable land in the area) for the production of sugar and bioethanol. A monitoring study in 2010 and 2011 showed high levels of pesticides in the river (Sarria, 2015). In particular, the herbicides atrazine and simazine were found in most of the samples collected. Atrazine and simazine are used in Colombia for pre-emergence and early post-emergence weed control in sugarcane, maize and sorghum crops.

Despite the high potential risk for contamination of water by pesticides due to intensive agriculture in the proximity of the River Cauca and its tributaries, no catchment management or monitoring programmes are currently put in place by the government to investigate and reduce emissions. The main reasons for not tackling pesticide contamination in the area (and in general for the whole country) are that these programmes are especially expensive and require large investment from the government. An alternative to refine and reduce costs of water monitoring is to use mathematical modelling of pesticide fate as a tool to understand the dynamics of these substances in the catchment (Holvoet et al., 2007). The aim of this paper is to study the dynamics of the herbicides atrazine and simazine along with their routes of entry to the River Cauca by conducting catchment pesticide fate modelling for the first time for this area using a spatially distributed model of the geographical valley of the river.

The River Cauca is located between the west and the central Andean ranges in Colombia and is one of the two main rivers of the country. The river flows from its source in the Colombian Massif in the Cauca department for approximately 1,350 km, draining a watershed of 63,300 km^2 to its confluence with the River Magdalena in the Bolivar department and finally flowing out into the Caribbean Sea (Figure 1a). The river flows through 183 municipalities where about 16 million people live (about 38% of the population of Colombia). The watershed of the River Cauca in the Valle del Cauca department is particularly important to the economy of the country; most of the sugarcane industry and part of the coffee plantations are located in this area (CVC and Univalle, 2001). The River Cauca in the Valle del Cauca receives domestic and industrial discharges from 33 municipalities; the main ones are Cali, Jamundí, Yumbo, Palmira, Buga, Zarzal, Florida, Tuluá and Cartago.

1.1 AnnAGNPS model

The annualized agricultural non-point source pollution model (AnnAGNPS) (USDA ARS, 2006) is based upon the single event model, AGNPS (Young et al., 1989), which simulates non-point pollution from agricultural watersheds to surface water. A comprehensive description of all routines used in the model can be found in the AnnAGNPS manual (Bingner et al., 2011). The model was built as a series of interconnected modules by integrating different models that simulate hydrology, sediment, nutrient and pesticide transport along the watershed. The model operates on a daily time step using a cell approach by dividing the watershed into grid cells according to the specified degree of resolution. This cell approach enables analyses at any point in the watershed. Pollutants including pesticides are transported from cell to cell in a stepwise process. The cells and the stream network are generated from a digital elevation model of the watershed using TOPAGNPS, which has a set of modules from the topographic parameterization program (TOPAZ) that provides all the required topographic information (Garbrecht and Martz, 1995). The simulated hydrology in AnnAGNPS includes interception, evapotranspiration and surface runoff. Surface runoff is simulated using the Soil Conservation Service curve number (CN) method (USDA, 1986). The soil moisture balance is simulated for two composite soil layers, located above (up to 20 cm from the surface) and below plough depth (Bingner et al., 2011).

AnnAGNPS allows the simulation of any number of pesticides without accounting for any interactions between them. Information about management practices in the watershed can be provided for each cell in the model which allows the simulation of the spatial and temporal variation in the behaviour of contaminants. Pesticide transport is simulated using a modified version of GLEAMS (Leonard et al., 1987) where pesticide mass balance is calculated on a daily step for each cell. Chemical is divided between two phases, dissolved in the solution phase (C_w in mg/L) and adsorbed in the soil phase (C_s), using a simple linear adsorption isotherm. Pesticide transfer via runoff is calculated using Equation 1 where C_{av} is the runoff-available pesticide concentration in the surface soil layer (mg/kg) and B is the soil mass per unit of overland flow (kg/L) (Leonard et al., 1987).

$$C_w + C_s = C_{av} B \qquad (1)$$

Studies using the AnnAGNPS model for pesticide emissions are scarce; only a conference abstract (Lively et al., 2002) and two published papers (Heathman et al., 2008; Zuercher et al., 2011) were found in the literature; in all cases, atrazine was the pesticide simulated in agricultural watersheds in the USA. Lively et al. (2002) tested the modelling capacity of AnnAGNPS to simulate atrazine loads in a small watershed in Springfield, Illinois. The study showed great inconsistencies between the observed and simulated atrazine concentrations even after extensive calibration and validation; the authors concluded that the model might not be appropriate to accurately simulate atrazine losses. Heathman et al. (2008) applied the AnnAGNPS and SWAT models to simulate monthly and annual stream flow as well as atrazine emissions in the Cedar Creek watershed in north-east Indiana. Results from an uncalibrated simulation using AnnAGNPS showed poor simulations for all outputs, with model efficiency coefficients of 0.13, -2.06 and -0.64, respectively; atrazine concentrations were 100 times smaller than the observed data. SWAT achieved better simulations of the stream flow but also could not accurately simulate atrazine concentrations. Zuercher et al. (2011) also applied AnnAGNPS to the Cedar Creek watershed, as well as to a sub-catchment (Matson Ditch). The model evaluation was undertaken using more detailed monitoring data than Heathman et al. (2008). Runoff was satisfactorily simulated for both catchments after model calibration. The authors identified an error in the coding of the pesticide routine in AnnAGNPS model version 3.57, specifically a discrepancy in runoff units which was responsible for pesticide under-simulations in previous studies. After correction of the model code, atrazine simulations were successfully calibrated and validated. No sensitivity analysis was applied prior to calibration; pesticide concentrations were calibrated by adjusting the percentage of pesticide applied to soil and foliage as well as the percentage of wash off from foliage.

Modelling such large and complex catchments as the geographical valley of the River Cauca, requires a model able to simulate great variability in spatially-distributed information. The AnnAGNPS model provides this possibility for soil and land use data as well as the use of meteorological data from different stations along the catchment. The AnnAGNPS model has been tested for tropical conditions with satisfactory results for catchments up to 125 km^2 (Sarangi et al., 2007; Shamshad et al., 2008), but it has not been tested at the scale of the Valle del Cauca (8,638 km^2).

2 Methodology

2.1 Stream flow and triazine concentrations in the River Cauca

Measured daily stream flow along the River Cauca at the stations of La Balsa, Mediacanoa, Puente Guayabal and Anacaro were provided by the local environment agency (Corporación Autónoma Regional del Valle del Cauca, CVC). A study by Sarria (2015) measured atrazine and simazine concentrations at different monitoring stations along the River Cauca including Juanchito, Puerto Isaacs, Paso de la Torre, Mediacanoa, Puente Guayabal and Anacaro (Figure 1b). Water grab samples were collected in June and October 2010 and May 2011. Analyses were performed by solid-phase extraction (SPE) with C_{18} reversed-phase cartridges followed by high-performance liquid chromatography with UV/Visible detection (HPLC-

UV). Atrazine and simazine were always detected in each campaign in at least two stations. Detected concentration for atrazine varied between 0.052 and 0.481 μg/L; and for simazine between 0.050 and 0.344 μg/L.

2.2 Digital elevation model preparation and study area

A digital elevation model (DEM) for the south-west region of Colombia was obtained from the CGIAR-CSI SRTM 90m Database v4.1. The DEM was pre-processed using Arc Hydro 2.0 for ArcGIS 10 before its use in AnnAGNPS (Figure A–1). The general sequences of terrain pre-processing were followed, including stream enforcement by burn-in of the main river network using a river coverage DCW (Digital Chart of the World) map for Colombia. Afterwards, the watersheds for the Valle del Cauca were calculated and those sub-catchments draining to the River Cauca were selected as the study area (Figure A–2). The study area corresponds to a main river length of 303 km and a drainage area of 8,638 km^2 in the geographical valley between the CVC monitoring stations of Puente Hormiguero (W 76°28’36.5”, N 03°18’0.5”) and Anacaro (W 75°57’58.1”, N 04°47’0.6”); these points were defined as the catchment inlet and outlet in the model, respectively (Figure 1b).

The pre-processed DEM was used in the TOPAGNPS module of the AnnAGNPS model to generate grid data with topographic information to delineate the watersheds of the study area and to calculate the stream network. The values for critical source area (CSA) and minimum source channel length (MSCL) were set to 600 ha and 2000 m, respectively, which divided the watershed into 1410 cells. Then, the AGNPS GIS tool was used to fill the cell and reach databases generated by TOPAGNPS. The process comprised interception of the soils, land use and climate maps. The resulting cell and reach databases were then used together with all the other input parameters to execute the simulation. Outputs were selected to provide water and pesticide information for each monitoring station along the catchment; relevant information consisted of runoff flow and pesticide loads to each of these points and to the catchment outlet.

2.3 Model parameterisation

The AnnAGNPS model requires over 400 input parameters distributed across 34 modules (Bingner et al., 2011). The major difficulty for the parameterization of the River Cauca was the lack of some of the required input parameters in the model. A range of approaches was applied to fill gaps in the information, particularly on weather, crop, soil and pesticide parameters.

Daily weather data from six meteorological stations along the watershed including Palmasola, Candelaria, Guacari, ICA, Univalle and Cabuyal stations (Figure A–3) as well as pan evaporation class A and maximum and minimum temperature data for Univalle station for 2010 and 2011 were provided by the Institute of Hydrology, Meteorology and Environmental Studies of Colombia, IDEAM. Thiessen polygons (Thiessen, 1911) were used to calculate the spatial distribution of the weather data from gauge stations in the catchment (Figure A–4).

Land use information for the valley of the River Cauca in 2011 showed that grassland, sugarcane, maize, sorghum and urban areas accounted for 88.7% of the area. These land uses were selected to be included in the simulation and the rest were treated as either grass in the case of other crops or urban areas in the case of any developed land. There is normally one crop of sugarcane per year whereas two full cropping cycles are possible for maize and sorghum. Sugarcane can be sown at any time during the year, so it is common to find sugarcane crops at different growth stages along the valley. Maize and sorghum are usually sown at the beginning of the two rainy seasons; the first sowing occurs in April/May, and the second in August/September (Campuzano and Navas, 2005). Crop growth parameters were derived from FAO information on length of crop development stages for various planting periods and for tropical climatic regions (Allen et al., 1998).

Pre-calculated actual evapotranspiration was supplied to the model as estimates from pan evaporation data for the meteorological station of Univalle due to the lack of other weather data to calculate this parameter directly within the model. Pan evaporation data (Ev_{pan} in mm) can be used to estimate actual evapotranspiration (Ev_{actual}) by using a multiplicative factor called the crop coefficient (K_c) of a reference crop (Equation 2) (Jensen et al., 1990).

$$Ev_{actual} = K_c \, Ev_{pan} \qquad (2)$$

The value of the crop coefficient depends on the crop type, crop growth stage, climate, and soil evaporation. The reference crop used was sugarcane since it is one of the main crops in the catchment with local data available from previous studies. Studies in the River Cauca have found that sugarcane has crop coefficients of 0.3 and 0.7 during its initial (2 to 4 months) and development (4 to 10 months) stages, respectively (Torres, 1995). Since there are no specific dates for sugarcane sowing and crops are present at different stages of development along the catchment, an annual average crop coefficient value of 0.57 was used to calculate the daily actual evapotranspiration.

Runoff curve numbers were supplied to the model for four cover types: cropped, bare soil, pasture and developed areas. Values proposed by the USDA (1986) for the cover types according to their practice or treatment and hydrological condition were initially assigned to each land use. Curve numbers for a straight row crop with good hydrological conditions were used for the crops, fallow information for bare soil, pasture with fair hydrological conditions for grassland and commercial/business curve numbers for the developed areas.

Soil property information and spatial data including soil and land use vector maps (1:50,000 scale) for the geographical valley (flat area of the catchment) were supplied by the CVC. Spatial information about soils in the valley showed presence of 18 soil orders, 42 soil suborders and more than 70 soil series. AnnAGNPS requires detailed information about soil properties, but the available information for the soil series in the Valle del Cauca only consists of a general description of the taxonomy, soil draining characteristics, soil structure, texture class, soil depth and pH (CVC, 2003). In order to simplify the parameterization, soil series were classified into 10 groups. The first step in this classification was to assign a potential level of risk for pesticide emissions to water bodies (from 1 to 5, with 1 the higher risk) to the soil orders based on the description of the hydrology behaviour in the soil taxonomy information from the USDA (1999). The highest level of risk was assigned to six soils including Argiustolls, Durustalfs, Endoaquepts, Epiaquepts, Ustifluvents and Ustorthents because of their proximity to surface water bodies, high groundwater tables or poorly draining soils that are generally artificially drained; these conditions favor surface runoff and the rapid loss of pesticides to surface water. The lowest risks were assigned to Dystrustepts, Haplustolls and Ustipsamments because of their free-draining character where overland flow is not expected. A final classification of the soil series into 10 soil groups was compiled by grouping soils with common characteristics such as soil depth, draining behaviour, and texture properties (Table A–1). There was roughly equal presence of all levels of risk of pesticide contamination in the catchment.

Non-available soil parameters were estimated with different models and assumptions: i) the percentages of clay, silt and sand were estimated as the midpoint value of the USDA soil textural class triangle using the texture class information for the soil group; ii) reported values of organic matter content for each municipality in the Valle del Cauca (Ramirez, 1983) were used to estimate this parameter for each soil group by identifying the main soil present in each area. Values of organic matter content for deeper horizons were estimated by applying multiplication factors to the value of top horizon of 0.25 (2nd horizon), 0.1 (3rd horizon), 0.05 (4th horizon) and 0.01 (5th and deeper horizons) to generate a decline in organic matter with depth as observed in most soils; whilst this is a crude assumption, it will be relatively insensitive in the model since most of the pesticide detected in the river was transported in surface runoff and thus interaction occurs with the topsoil only; iii) the bulk density for the top soil layer was estimated using a regression model from a study in the coffee region of Colombia (located to the north of the Valle del Cauca) which related the bulk density to the organic matter content with a coefficient of determination of 0.69 (Salamanca and Sadeghian, 2005). For deeper horizons, a fixed value of 1.3 g/cm^3 was used for the upper subsoil and then for the subsequent horizons the bulk density was increased by 0.1 g/cm^3 up to a maximum value of 1.6 g/cm^3; iv) the field capacity, wilting point and saturated hydraulic conductivity were estimated using pedotransfer functions from the SOILPAR2 model (Acutis and Donatelli, 2003). The British Soil Survey topsoil and subsoil LEACH functions (Hutson and Wagenet, 1992) were used to estimate the field capacity at -300 kPa and the wilting point at -1500 kPa, and the Jabro (1992) method was used for the saturated hydraulic conductivity. Tile drainage information in the model was supplied for the soils that were reported to be artificially drained in the valley (CVC, 2003).

Literature values of physicochemical information for atrazine and simazine were used in the model (Table 1). Degradation half-lives in soil determined under field conditions and reported by Lewis et al. (2015) were used for both triazines. Availability of pesticide residues in soil for transportation in surface runoff are determined not only by partitioning between soil and water which is provided as a user input, but also by the depth of the runoff interaction layer which is fixed within the model at a value of 1 cm and by a parameter describing efficiency for pesticide extraction (Pantone and Young, 1996) that takes a value between 0.05 and 0.2. Atrazine and simazine were simulated as pre-emergence applications to maize and sorghum on 1st May and 1st September. Lack of detailed information about pesticide usage in the catchment was a major limitation in the simulation, so data from pesticide labels in Colombia and other assumptions were needed to fill gaps in input requirements (Calister, 2011; Inveragro, 2013). The model was run assuming usage of each herbicide (atrazine and simazine) on 50% of target crops, but results were also analysed for total triazines to reduce uncertainties on the relative use of the two compounds.

Application rates in the model were adjusted to the central value of the annual recommended range of application rates on the product labels (1.20 kg of active ingredient (a.i.) ha^{-1} $year^{-1}$ in maize and sorghum and 3.84 kg a.i. ha^{-1} $year^{-1}$ in sugarcane) (Calister, 2011; Inveragro, 2013). For maize and sorghum an application rate of 0.30 kg a.i. ha^{-1} of each herbicide was assumed for each application date, assuming that each compound was used at full rate on 50% of the total crop area. Sugarcane sowing occurs at any time throughout the year, making it difficult to simulate when pesticide applications will take place. Assuming that new sugarcane crops can be planted in different areas along the catchment every month, this frequency of application was used in the model. Therefore, application rate of each pesticide used in the model was 0.32 kg a.i. ha^{-1} $month^{-1}$.

2.4 Calculation of the stream flow and baseflow in the study area

Since the study area did not include the source of the river, the model simulates less stream flow than is observed at the catchment outlet. In order to compare the simulated flow to the measured data, it was necessary to first calculate the observed stream flow generated only from the study area by subtracting the measured flow from upstream of the study area from the measured flow at the catchment outlet. Flow data used to calculated the observed flow in the study area included measured stream flow from a station upstream (La Balsa station W 76°35’36.8”, N 03°05’10.9” Figure 1b), near the simulated inlet (Puerto Hormiguero), and at the catchment outlet (Anacaro station). It was estimated that stream water from La Balsa would take three days to reach the catchment outlet in Anacaro based on an average velocity value of 1.30 m/s in this stream section and a river length of 400.5 km (CVC and Univalle, 2001). Therefore, the equation to calculate the observed stream flow from the study area ($Flow_{catchment,t}$) in m^3s^{-1} was:

$$Flow_{catchment,t} = Flow_{outlet,t} - Flow_{inlet,t-3} \quad (3)$$

where $Flow_{outlet,t}$ was the measured flow at the catchment outlet (Anacaro station) on day t and $Flow_{inlet,\ t-3}$, the inlet measured flow in m^3s^{-1} (La Balsa station) on day t-3.

The observed baseflow from the study area was estimated from the measured stream flow by hydrograph separation. Since the model does not simulate the baseflow, the observed baseflow had to be added to the simulated runoff in order to calculate the total stream flow. The web-based hydrograph analysis tool (WHAT) (Lim et al., 2005) was used to separate the hydrograph by applying the Eckhardt digital filtering method (Eckhardt, 2005). This is a widely-used method of hydrograph analysis which uses two parameters: the filtering parameter (α) and the maximum value of long-term ratio of baseflow to total stream flow (BFI_{max}) that can be modelled by the digital filter algorithm (Eckhardt, 2005):

$$Q_{b,t} = \frac{(1-BFI_{\max})\cdot\alpha\cdot Q_{b,t-1}+(1-\alpha)\cdot BFI_{max}\cdot Q_{s,t}}{1-\alpha\cdot BFI_{max}} \quad (4)$$

where, the baseflow at time t and $t-1$ are $Q_{b,t}$ *and* $Q_{b,t-1}$, respectively (both in m^3s^{-1}), and $Q_{s,t}$ (m^3s^{-1}) is the stream flow at time t (day) (Eckhardt, 2005). The parameter α can be determined with a recession analysis of the stream flow (Eckhardt, 2005). The recession curves between January 2010 and December 2011 for Anacaro station were used in the analysis. The parameter BFI_{max} is dependent on local hydrogeological conditions, but it is a non-measurable parameter. Eckhardt (2012) calculated mean values for both parameters by analysing data from 65 catchments in North America. The recommended α and BFI_{max} parameters for a perennial stream with a porous aquifer were 0.97 and 0.80, respectively. The BFI_{max} parameter for the studied area was obtained by calibration using the pre-calculated filtering value α. The best separation was obtained with a BFI_{max} of 0.80.

2.5 Calculation of the simulated stream flow and pesticide concentrations

The simulated stream flow at the catchment outlet was calculated by adding the pre-calculated baseflow for the study area to the simulated runoff from AnnAGNPS. The simulated stream flow ($Flow_{x,t}$) at each monitoring station was calculated by adding the simulated runoff flow ($Runoff_{x,t}$) to the respective estimated baseflow ($Baseflow_{x,t}$) at each location (x) in m^3s^{-1} and day (t) and the inlet flow recorded at La Balsa station ($Flow_{inlet,t-n}$) with a lag time n based on the river length and average velocity to each monitoring station (Equation 5). The baseflow for each monitoring point was calculated by an analysis of the draining area contributing to the flow at each monitoring station.

$$Flow_{x,t} = Runoff_{x,t} + Baseflow_{x,t} + Flow_{inlet,t-n} \qquad (5)$$

AnnAGNPS simulates pesticide loss (in kg) at any point of the river network. Pesticide concentrations were calculated from the simulated pesticide loss and the simulated stream volume for each monitoring point. Pesticide simulations were carried out for individual pesticides (atrazine and simazine) and for both together in order to calculate the total emission of triazines. The simulation of total triazines reduces the uncertainty associated with the assumption of a 50% usage of the two herbicides on the target crops. Selection between the two triazines would depend on different factors that cannot be estimated, such as market price, availability and product rotation.

2.6 Model evaluation

Modelling results for stream flow and pesticide concentrations were evaluated against measured values in the River Cauca in order to assess the predictive capacity and the applicability of AnnAGNPS under Colombian conditions and constraints imposed by the data available for the geographical valley of the River Cauca. The evaluation of the simulated stream flow for the stations located at Mediacanoa, Puente Guayabal and Anacaro involved i) visual comparison of the observed and simulated hydrographs; ii) calculation of the coefficient of determination (r^2) to measure the strength of the linear relationship between observed and simulated data; iii) calculation of the percentage bias (PBIAS) that measures the average tendency of the simulated data to be under- or over-simulated compared to the observed data (Gupta et al., 1999); and iv) calculation of the Nash-Sutcliffe model efficiency coefficient (NS) which estimates the level of agreement between simulated and observed values and how well the plot of observed versus predicted values fits the one-to-one line (Nash and Sutcliffe, 1970).

The optimal value of PBIAS is 0.0, with negative values indicating model overestimation bias and positive values model underestimation bias. Moriasi et al. (2007) provided general guidelines for model evaluation based on PBIAS: very good between 0 and 10%, good between 10 and 15%, satisfactory between 15 and 25% and unsatisfactory for values above 25%. The NS can range from $-\infty$ to 1, with 1 being a perfect match between the model and the observed data and negative values indicating that the mean of the observed data is a better predictor than the model (Nash and Sutcliffe, 1970). Satisfactory and good results for stream flow simulations are considered to be between 0.36 and 0.75, and above 0.75, respectively (Van Liew et al., 2003).

Model calibration and validation were applied to the stream flow for two different periods of time. Calibration of the runoff curve numbers was carried out for crop and pasture land to increase the simulated runoff volume (Table 2). Curve numbers were first changed from good to poor hydrological conditions and then adjusted by increasing their values in increments of 2% while checking the Nash–Sutcliffe model efficiency coefficients and the coefficient of determination (r^2) of the line of observed vs. simulated flow data for the period 2010 – 2011. An increase of 10% in the curve numbers on top of changing from good to poor practice provided the best results for model calibration and validation. Validation of calibrated runoff curve numbers was carried out using weather and flow data for 2008 and 2009.

2.7 Uncertainty analysis

Uncertainty analysis was carried out to determine the impact of uncertain input parameters on the simulation of pesticide losses including the use of average pesticide degradation and sorption data, pesticide application date and average frequency of application to sugarcane.

Uncertainty in the use of average values for pesticide degradation and sorption as input to the model was assessed through a bounds analysis consisting of four simulations of total triazines run using the extreme values (maximum and/or minimum) of reported reference data for atrazine and simazine field studies (Table 1). Ranges in degradation half-life (DT_{50}) in soil (6 – 108 days) and soil-water partition coefficient normalised to organic carbon (K_{oc}) (89 – 513 mL g^{-1}) reported by Lewis et al. (2015) for atrazine were used in the simulation as these values span the range in data reported in the same source for simazine.

In addition, pesticide application date and the average frequency of application in sugarcane were other sources of uncertainty analysed. Two additional simulations were run for the pesticide application date; one simulation was run changing the application date to the 15th of the same months as in the original simulation and the other assuming an even distribution of the application rate across every single day within the period when triazines are likely to be applied. For the average frequency of application in sugarcane, an average application every two months of the central value of the annual recommended range of application rate was used (i.e. 0.64 kg a.i. ha^{-1} applied every two months) and compared to the original simulation (0.32 kg a.i. ha^{-1} every month). The rate of pesticide applied is a further source of uncertainty in the simulations. Separate simulations were not undertaken to assess this uncertainty because pesticide losses in surface runoff and concentrations in the River Cauca will vary proportionally to any change in the application rate used as model input.

2.8 Analysis of the areas of risk, practices and conditions for water contamination using AnnAGNPS

The modelling results were finally used to identify areas (or sub-watersheds) of risk for pesticide pollution that combine the effect on emissions from topography, soil type, land use and weather in the different watersheds. In addition, practices and conditions that are associated with increased pesticide contamination in the study area were analysed and some recommendations were formulated that can help reduce pesticide emissions. Two indicators of triazine emissions were calculated; the first was the pesticide usage per unit area for each sub-watershed and the second concerned the relative emission of pesticides to the River Cauca.

The area of maize, sorghum and sugarcane in each sub-watershed along with the application rates of atrazine and simazine for each crop were used to estimate the total amount of pesticide applied to each sub-watershed in kg (*PA*) and then divided by the sub-watershed area to estimate the total annual application of triazines in kg ha^{-1} of each watershed (*AA*):

$$AA = \frac{\left(\sum CA_j \times AAR_{atrazine,j}\right) + \left(\sum CA_j \times AAR_{simazine,j}\right)}{AW} = \frac{PA}{AW} \qquad (6)$$

where *CA* is the area of the crop *j* (ha), *AAR* is the annual application rate of atrazine or simazine (kg ha^{-1}) and *AW* is the area of each sub-watershed (ha). Note that this estimate is based solely on land use and pesticide usage data, not on modelling results.

The relative pesticide exported to the river (*RPE* in percentage) was calculated for each sub-watershed (Equation 7). The difference between the simulated pesticide load in each inlet and outlet of each sub-watershed was considered as the pesticide exported to surface water in kg (*PE*); then this amount was divided by the annual pesticide application in kg (*PA*) and multiplied by 100.

$$RPE = \frac{PE}{PA} \times 100 \qquad \textbf{(7)}$$

2.9 Alternative to triazine pesticides

A potential alternative to triazines, mesotrione, was simulated in order to compare pesticide losses between simulations. Mesotrione was simulated using the maximum annual recommended application rates: 0.27, 0.22 and 0.37 kg a.i./ha to maize, sorghum and sugarcane, respectively (Syngenta, 2012). Dyson et al. (2002) showed strong correlation of mesotrione adsorption and degradation with soil pH and organic carbon content. Paired half-life and K_{oc} values reported for a clay loam soil with pH 7.1 and 3.3% organic carbon were used in the simulation (Table 1). Mesotrione has similar sorption behaviour to atrazine and simazine but its degradation half-life is considerably shorter.

3 Results

3.1 Observed stream flow and baseflow separation

The observed stream flow accounting solely for flow in the study area is presented in Figure B–1 along with the upstream (La Balsa) and downstream (Anacaro) flow. All flow values obtained when applying Equation 3 to the measured flow data were positive, indicating that our estimate of three days for the flow to reach the outlet was precise enough for the study period. This is also confirmed by modelling results below. The flow at the catchment outlet over the whole period comprised 63% generated within the study catchment and 37% from upstream areas not simulated by the model. This flow was then used to calculate the baseflow in the catchment and to undertake model evaluation of the simulated stream flow. The filter parameter α was calculated to have a value of 0.998 which is equivalent to the recession constant calculated from the slope of the recession analysis for Anacaro station (Figure B–2). This value along with a BFI_{max} of 0.80 showed the best hydrograph separation (Figure B–3).

3.2 Simulated stream flow

An initial uncalibrated simulation using AnnAGNPS showed under-estimation in the flow at the catchment outlet (Figures 2 and 3a), consistently observed during periods of very high flow (more than 400 m^3/s). The calculated statistics showed a satisfactory NS (0.50), a good linear relation between the observed and the simulated flow (r^2 = 0.73), but with an unsatisfactory PBIAS value (30%).

Runoff curve numbers were calibrated in order to increase the runoff flow and better match peak flow. Best calibration in the current study based on NS was found when increasing the CN by 14% (NS = 0.71), however, a decrease in r^2 was observed for all adjustments larger than 8%. Therefore, the most suitable calibration was considered to result from an increase of 10% in the CN, in order to improve model performance without sacrificing linear correlation with the observed data (Figure 3b). The resulting PBIAS was good (10%) with some under-estimation. The calibrated flow at Mediacanoa and Puente Guayabal showed very good results (NS = 0.81, r^2 = 0.82, PBIAS = 11% and NS = 0.81, r^2 = 0.86, PBIAS = 6%, respectively; Figure B–4).

Four sets of CN increased from the baseline by between 8 and 14% were tested in model validation to confirm the decision of applying an increment of 10% in CN for model calibration. Model validation was carried out for the same watershed at the catchment outlet but for a different period of time (2008 – 2009). The best validation results were indeed obtained for an increase of the CN by 10% (NS = 0.63 and r^2 = 0.64) (Figures 3c and 4). This result showed the importance of using more than one statistical parameter to evaluate the calibration process. The validated runoff simulation was also classified as satisfactory according to the criterion of Van Liew et al. (2003). Less under-estimation was generally obtained for the validation period compared to the calibration period. The PBIAS statistic for model validation was very good (3%) and a satisfactory NS value was obtained (0.63). Periods of under-estimation (e.g. from February to April 2008 and from November to January 2008) and over-estimation (e.g. from April to August 2008) of the flow were observed causing a larger variance in data (Figure 3c) which resulted in a smaller linear correlation (r^2 = 0.64) than that obtained for the calibration period.

3.3 Pesticide concentrations

After calibration and validation of the simulated stream flow, AnnAGNPS was used to simulate atrazine, simazine and total triazine concentrations in the Valle del Cauca. The model achieved results in the same order of magnitude as the measured data and closely matched some of the observed concentrations for the stations along the catchment (Table 3). Measured concentrations of atrazine and simazine varied between not detectable and 0.481 μg/L while the simulated values ranged between not detectable and 0.259 μg/L. However, the model was not able to simulate the relatively large concentrations for atrazine in Mediacanoa in June 2010 and in Puerto Isaacs in May 2011, or for simazine in Juanchito and Paso de la Torre in October 2010 and in Puente Guayabal in May 2011. The model was not able to completely capture some patterns in the observed pesticide concentrations at different monitoring stations including some of the large concentrations observed upstream, the pattern of non-detections downstream and never detecting triazines at the catchment outlet.

3.4 Uncertainty analysis

Results of the uncertainty analysis are summarised and compared to both the original simulation obtained using average parameters and the observed concentrations in Table 4. The range of concentrations obtained from each analysis did not always cover the observed data, particularly the observed large concentrations at Mediacanoa in June 2010, Juanchito and Paso de la Torre in October 2010 and Puerto Isaacs in May 2011. However, the analysis provided possible explanations for the patterns of non-detections that were not captured by the original simulation. Sorption and degradation parameters had contrasting effects between sampling periods (Table 4) depending on the interval between the day of pesticide application and monitoring date. Uncertainty in pesticide application date had a big effect on pesticide fate and yielded most of the largest ranges in simulated concentrations.

3.5 Analysis of the areas of risk for water contamination using AnnAGNPS

A map of the total annual triazine application per sub-basin area is shown in Figure 5a. The maximum usage corresponded to areas with a high cropping density (Table B–1). Watersheds with over 1.5 kg/ha of triazine application such as 2, 3, 4, 5 and 9, have more than 40% of their area planted with the target crops with the majority being sugarcane. These areas with intensive triazine usage are mostly located in the top and middle part of the catchment. A map of pesticide export to the River Cauca as a proportion of that applied shows that export values ranged from 0.01 to 0.27% (Figure 5b). The highest relative pesticide export was for the sub-watershed located in the middle of the catchment and the total percentage loss at the catchment outlet during the simulation period was 0.04% of applied.

3.6 Alternative for triazine pesticides

Simulations using mesotrione evaluated the effect on river contamination of replacing triazine herbicides with this pesticide. Simulated mesotrione losses at the monitoring stations were up to two orders of magnitude smaller than for triazines (Table B–2). Table 5 compares the calculated usage and simulated emission figures for triazines and mesotrione and shows the potential reduction of these figures from the replacement of triazines with mesotrione. There was 84% reduction in the mass of pesticide applied and 87% reduction in relative pesticide exported, yielding a total reduction of pesticide mass exported to the River Cauca of 96%.

4 Discussion

4.1 Simulation of stream flow and pesticide losses

The initial simulation of the stream flow was partially satisfactory according to the Van Liew et al. (2003) criterion (NS = 0.50 and r^2 = 0.73), but the simulation showed under-estimation of runoff during periods of high flow by up to a factor of two. The Valle del Cauca Department, located in the Pacific region of the country, is one of the most vulnerable areas to el Niño and la Niña phenomena in Colombia. The cold ENSO episodes (la Niña) are manifested with an increase in rainfall, resulting in a higher occurrence of floods, landslides and windstorms, whereas el Niño is characterised by a decrease in rainfall, increasing the occurrence of droughts and forest fires (IDEAM, 2001). El Niño began to manifest the year before our study period in May 2009, reaching its highest stage of development between late December 2009 and early January 2010 (IDEAM, 2010), and causing very low observed flows at the beginning of the simulation period. Then, a period of neutralization by the gradual cooling of the waters of the Pacific Ocean was observed until the middle of 2011 when low ocean temperatures gave way to La Niña, reaching its maximum intensity at the end of the year; during this period La Niña caused extreme flow events that were greatly under-estimated by the simulation using AnnAGNPS.

Other studies using the AnnAGNPS model found under-estimation of runoff (Mohammed et al., 2004; Sarangi et al., 2007; Shamshad et al., 2008; Suttles et al., 2003; Yuan et al., 2001). Runoff under-estimation in a 333-km^2 watershed in Georgia was due to inadequate representation of the land cover according to Suttles et al. (2003). Chahor et al. (2014) conducted a simulation with AnnAGNPS for a 207-ha agricultural watershed located in Navarre, Spain, observing seasonal over- (summer and autumn) and under-estimation (winter and spring) in the runoff. Yuan et al. (2001) found for a 82-ha watershed in the Mississippi delta that AnnAGNPS under-estimated runoff for periods of extreme rainfall events (rainfall over 80 mm per day); the authors attributed this behaviour to the use of a small culvert opening at the monitoring station which could have impounded the water increasing the apparent water depth and therefore causing over-estimation of the measured flow. However, since a similar behaviour was observed when La Niña phenomena took place in the Valle del

Cauca, low response by the model in the simulation of runoff from extreme rainfall events is another likely explanation for this behaviour.

Most of the previous studies using AnnAGNPS and AGNPS have successfully calibrated runoff by modifying the curve numbers (e.g. Chahor et al. (2014); Shamshad et al. (2008); Sarangi et al. (2007); Baginska et al. (2003)). Curve numbers are generally adjusted equally for all cover types in most of the studies. Chahor et al. (2014) found over-estimation of the runoff during summer and autumn seasons and under-estimation throughout winter and spring, so CN were calibrated by adjusting their values by seasons; this approach noticeably improved the runoff simulation (from NS = -1.52 to NS = 0.75). For the River Cauca, calibration of the CN was only carried out for crops and pasture cover types since these areas account for approximately 83% of the catchment. Shamshad et al. (2008) used a similar methodology to calibrate the CN for a 125-km^2 watershed in Malaysia, applying adjustments of 2% each time and using the observed versus simulated flow plot and statistical parameters that included r^2 and NS to evaluate the best results.

Similar modelling performance (NS = 0.70 and r^2 = 0.73) has been observed in other studies after calibration. For instance, Mohammed et al. (2004) observed under-estimation of flow by 14% after calibration (NS = 0.73 and r^2 = 0.87). Parajuli et al. (2009) compared simulations using AnnANGPS and SWAT for watersheds in Kansas; model efficiency for the simulation of runoff after calibration was better for AnnAGNPS than SWAT (0.69 and 0.56, respectively) while results for model validation were similar for both models (0.47 for AnnAGNPS and 0.48 for SWAT).

The developers of AnnAGNPS suggest the use of the model in agricultural watersheds with size up to 3,000 km^2 (Bosch et al., 2001). The studied catchment exceeds this limit by three times (8,638 km^2). Simulation of large catchments can imply an increased number of grid cells which cannot be easily handled by the system capacity or can require the use of computer clusters. Thus, the maximum catchment size in a grid-based model is determined by the maximum number of cells that can be simulated with the available computer specifications. The stream flow results with a 2.5-km grid resolution suggest that the model was suitably representative of the study area and that AnnAGNPS can simulate runoff with reasonable accuracy under Colombian conditions. Sensitivity analyses for AnnAGNPS and AGNPS carried out in other studies (e.g. Leon et al. (2004) and Haregeweyn and Yohannes (2003)) show that grid size generally exhibits little or no sensitivity for runoff simulations. For example, Haregeweyn and Yohannes (2003) found no significant improvement in the runoff simulation using AGNPS when increasing the resolution from 100 to 200 m grid size. A slightly better performance using AGNPS in the simulation of peak flow was observed by Leon et al. (2004) with a 2-km grid size than with a more detailed 1-km grid but differences were not significant. More detailed grids require a more comprehensive description of the catchment but do not always imply an improvement in the simulation.

In this study, a bug was found regarding pesticide output from the AnnAGNPS model. The model simulates pesticides mass dissolved in water and attached to soil particles in the runoff water. The expected behaviour of atrazine is to be mostly dissolved in water (Helling, 1970) but the opposite was observed in the model output. This issue was discussed with the developers of the model. Only the dissolved fraction is reported here as this matches the analytical methodology that measured concentrations dissolved in water following filtering through a 0.45-µm mesh.

4.2 Uncertainty analysis

Uncertainty analyses showed that pesticide application date was the most critical input parameter. These results agree with the findings of other studies (Boithias et al., 2014; Boulange et al., 2012; Holvoet et al., 2005). Holvoet et al. (2005) suggested that application date had greater impact than application rate and rainfall errors to simulate atrazine emissions based on a sensitivity analysis for SWAT. In the present study, the simulation of triazine herbicides was affected by pesticide availability in the runoff interaction layer which was mainly influenced by the application date, pesticide sorption, degradation rate, and timing of rainfall event. This finding is in agreement with a study by Boithias et al. (2014) who carried out a sensitivity study for SWAT using plausible ranges of application dates for two contrasting pre-emergence herbicides; the authors showed that the effect of the application date was a pesticide-specific factor influenced by their bioavailability.

Uncertainty regarding the use of average pesticide sorption and degradation properties as input data was tested by a bounds analysis using extreme values for these parameters reported in pesticide databases. The simulations showed the large impact that both parameters have on the simulation of pesticide emissions; particularly the pesticide half-life showed slightly higher sensitivity for pesticide concentrations than the K_{oc}. The pesticide module in AnnAGNPS considers two fixed parameters that affect pesticide transport (Bingner et al., 2011): i) the runoff interaction layer which corresponds to the top 1 cm of the soil where pesticides are available for surface runoff; and ii) the efficiency for pesticide extraction (Pantone and Young, 1996), described by the extraction ratio whose value ranges between 0.05 and 0.2 depending on the conditions for runoff and erosion and the tendency for pesticides to be transported in solution or attached to the soil (Leonard and Wauchope, 1980). Both parameters determine the availability of pesticide for surface runoff and have fixed values in the model which cannot be modified by the user. Larger pesticide sorption and degradation values would increase the pesticide residence time in the interaction layer which results in availability of residues for surface runoff over a longer period of time.

Results from all the uncertainty analyses showed that the simulated ranges of pesticide concentrations did cover most of the pesticide concentrations observed in the measured data but these uncertainties did not explain all discrepancies in the simulation. The simulation did not include point sources of pesticides since they are very difficult to predict because they can occur randomly at any time/location in the catchment. The large concentrations that were not covered by the model or the uncertainty analyses are potentially caused by point-source pollution from handling pesticides or cleaning spraying equipment since they occurred during recession flow without association to any runoff event or change in the flow.

Most model evaluations assume absolute quality of the measured data; nevertheless monitoring data are prone to error due to different sources of uncertainty in sample collection, handling and analysis (Baginska et al., 2003). Single samples from each sampling location were collected which constitute an important source of uncertainty due to temporal variability in the concentrations during the day and between sampling dates; integrated sampling techniques would provide more reliable data than grab samples (Holvoet et al., 2007). The restricted amount of monitoring data was a limiting factor for the assessment of pesticide simulations. There could be differences in the magnitude of pesticide emissions for specific days but it is also important to assess the model performance in the simulation of the overall pattern of pesticides throughout the year. Other studies with a limited amount of catchment information have opted to carry out further monitoring studies to set up more reliable databases (e.g. Shamshad et al. (2008)). However, the model as it stands can be used for a comparative assessment of the areas of risk, practices and conditions that can contribute to surface water contamination in the Valle del Cauca.

5 Conclusions

This modelling study was useful to determine the minimum site-specific data requirements to simulate triazine emissions from maize, sorghum and sugarcane in the Valle del Cauca. One of the major difficulties in the application of the model was the lack of information about the catchment. A combination of field data, modelling and assumptions were used to estimate some of the input parameters. This approach resulted in a good hydrological simulation of the

River Cauca. Triazine concentrations were not always well simulated compared to the measured data though good results were observed for some stations and monitoring days. Uncertainty analysis of some of the input parameters could not explain all discrepancies in the simulation and showed that an important uncertainty in the simulation was the lack of site-specific information for pesticide application dates to crops, mainly sugarcane. There is evidence for point-source pollution events in the catchment which should be investigated further. Catchment management approaches should include a pesticide monitoring programme combined with pesticide modelling as the most viable and efficient approach to further investigate the nature of pesticide concentration in the area.

Acknowledgements

The authors are grateful to the Administrative Department of Science, Technology and Innovation in Colombia (Colciencias) for the funding of this work. We are also grateful to the research group GICAMP at the Universidad del Valle in Colombia, especially to Professor Martha I. Páez, Dr. William Ocampo and Rodrigo Sarria for providing us with pesticide monitoring data; and to the Corporación Autónoma Regional del Valle del Cauca (CVC) for the soil and land use data. In addition, the authors wish to thank Dr. Ronald Bingner from the USDA-ARS for his technical assistance with the model.

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Table 1 Physicochemical properties for pesticides simulated by the model.

Physicochemical property	**Atrazine**[a]	**Simazine**[a]	**Mesotrione**
Solubility (mg L^{-1})	35	5	160[a]
K_{oc} (simulated value) (mL g^{-1})	100	130	33[b]
K_{oc} (reported range) (mL g^{-1})	89 – 513	129 – 138	
DT_{50} in field soil (simulated value) (days)	29	27	4.5[b]
DT_{50} in field soil (reported range) (days)	6 – 108	27 – 102	
DT_{50} in water (days)	86	96	5.3[a]

[a]Lewis et al. (2015); [b]Dyson et al. (2002).

Table 2 Initial and calibrated runoff curve numbers.

Hydrologic group	**Uncalibrated CN**		**Calibrated CN**	
	Crop[a]	**Pasture**[a]	**Crop**	**Pasture**
A	67	49	79	76
B	78	69	89	87
C	85	79	97	95
D	89	84	100	98

[a]USDA (1986)

Table 3 Measured and simulated concentrations of atrazine, simazine and total triazines (all in μg/L) for the six sampling locations and three sampling periods. Measured concentrations are from Sarria (2015).

Sampling Month-Year/ location	**Day**	**Atrazine concentration**[1]		**Simazine concentration**[2]		**Triazine concentration**	
		Observed	**Simulated**	**Observed**	**Simulated**	**Observed**	**Simulated**
June 2010							
Juanchito	9	<0.005	<0.005	<0.010	<0.010	<0.010	<0.010
P. Isaacs	10	<0.005	<0.005	<0.010	<0.010	<0.010	<0.010
P. Torre	10	<0.005	<0.005	<0.010	<0.010	<0.010	<0.010
Mediacanoa	10	0.481	0.018	<0.010	0.013	0.481	0.031
P. Guayabal	11	0.052	0.039	0.050	0.029	0.102	0.068
Anacaro	11	<0.005	0.039	<0.010	0.028	<0.010	0.067
October 2010							
Juanchito	26	<0.005	<0.005	0.112	<0.010	0.112	<0.010
P. Isaacs	11	<0.005	<0.005	<0.010	<0.010	<0.010	<0.010
P. Torre	11	<0.005	0.012	0.104	0.011	0.104	0.023
Mediacanoa	25	0.052	0.043	0.010 – 0.034	0.051	0.052	0.094
P. Guayabal	25	0.058	0.070	<0.010	0.082	0.058	0.152
Anacaro	25	<0.005	0.131	<0.010	0.129	<0.010	0.259
May 2011							
Juanchito	10	<0.005	<0.005	<0.010	<0.010	<0.010	<0.010
P. Isaacs	11	0.224	<0.005	<0.010	<0.010	0.224	<0.010
P. Torre	11	<0.005	0.015	<0.010	<0.010	<0.010	0.025
Mediacanoa	12	<0.005	0.042	0.010 – 0.034	0.030	<0.010	0.072
P. Guayabal	12	0.088	0.044	0.344	0.032	0.432	0.076
Anacaro	12	<0.005	0.034	<0.010	0.024	<0.010	0.058

[1] LOD = 0.005 μg/L and LOQ = 0.015 μg/L; [2] LOD = 0.010 μg/L and LOQ = 0.034 μg/L

Table 4 Effect of key uncertainty of input parameters on total triazine concentrations together with the measured and calibrated simulation data

Sampling Month-Year/ location	**Measured (μg/L)**	**Simulated (μg/L)**	**Uncertainty evaluated / Range of triazine conc. (μg/L)**		
			DT_{50} and K_{oc}	**Application date**	**Avg. application frequency to sugarcane**
June-2010					
Juanchito	<0.010	<0.010	<0.010	<0.010 – 0.244	<0.010
P. Isaacs	<0.010	<0.010	<0.010	<0.010 – 0.148	<0.010
P. Torre	<0.010	<0.010	<0.010	<0.010 – 0.028	<0.010
Mediacanoa	0.481	0.031	<0.010 – 0.048	<0.010 – 0.048	<0.010 – 0.031
P. Guayabal	0.102	0.068	<0.010 – 0.105	<0.010 – 0.068	<0.010 – 0.068
Anacaro	<0.010	0.067	<0.010 – 0.098	<0.010 – 0.067	<0.010 – 0.067
October-2010					
Juanchito	0.112	<0.010	<0.010	<0.010	<0.010
P. Isaacs	<0.010	<0.010	<0.010	<0.010	<0.010
P. Torre	0.104	0.023	<0.010 – 0.034	<0.010	<0.010 – 0.023
Mediacanoa	0.052	0.094	<0.010 – 0.123	0.051 – 0.486	<0.010 – 0.094
P. Guayabal	0.058	0.152	<0.010 – 0.199	0.049 – 0.665	0.014 – 0.152
Anacaro	<0.010	0.259	0.017 – 0.391	<0.010 – 1.03	0.028 – 0.259
May-2011					
Juanchito	<0.010	<0.010	<0.010	<0.010 – 0.150	<0.010
P. Isaacs	0.224	<0.010	<0.010	<0.010	<0.010
P. Torre	<0.010	0.025	<0.010 – 0.042	<0.010 – 0.025	0.025 – 0.050
Mediacanoa	<0.010	0.072	<0.010 – 0.114	<0.010 – 0.510	0.072 – 0.141
P. Guayabal	0.432	0.076	<0.010 – 0.119	<0.010 – 0.591	0.076 – 0.149
Anacaro	<0.010	0.058	<0.010 – 0.092	<0.010 – 1.11	0.058 – 0.112

LOD = 0.010 μg/L and LOQ = 0.034 μg/L

Table 5 Pesticide usage, export to the catchment outlet and percentage loss for mesotrione and triazines along the potential reduction of these figures from the hypothetical replacement of triazine herbicides with mesotrione.

	Mesotrione	**Triazines**	**Potential reduction (%)**
Average pesticide application per year over the whole catchment (kg a.i. ha^{-1})	0.13	0.78	84
Pesticide exported at the catchment outlet (kg a.i. $year^{-1}$)	119	2,889	96
Pesticide loss (% of applied)	0.11	0.85	87

Dyson, J.S., Beulke, S., Brown, C.D., Lane, M.C.G., 2002. Adsorption and degradation of the weak acid mesotrione in soil and environmental fate implications. Journal of Environmental Quality 31(2) 613-618.

Lewis, K.A., Green, A., Tzilivakis, J., Warner, D., 2015. The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire, 2006-2015.

Sarria, R., 2015. Desarrollo de una herramienta para la gestión de la calidad del agua del Río Cauca en su paso por el Departamento del Valle basado en sistemas inteligentes, Chemistry Department. Universidad del Valle: Cali, Colombia.

USDA, 1986. Technical Release 55: Urban Hydrology for Small Watershed, NRCS-USDA.

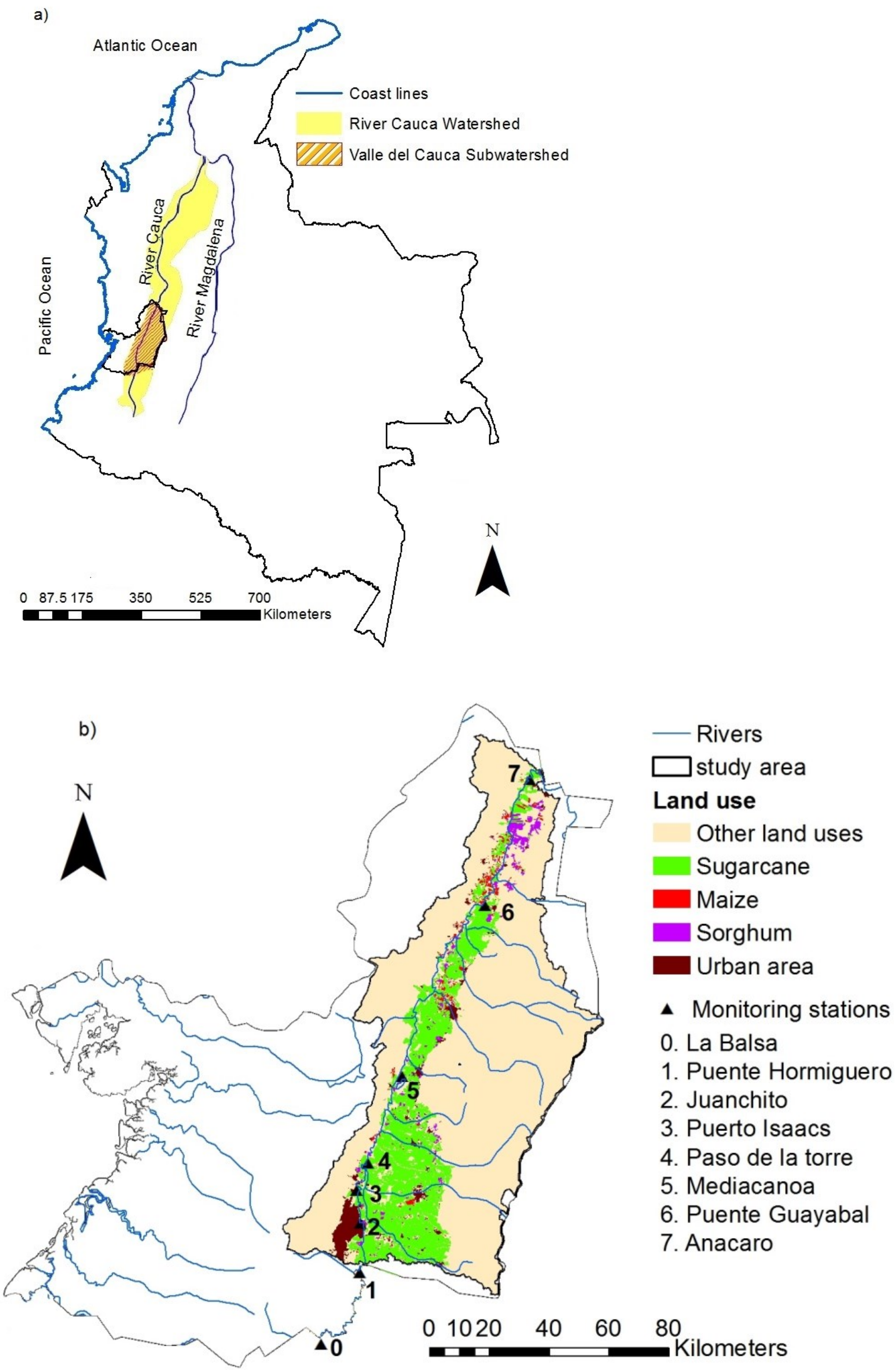


Figure 1 a) Location of the River Cauca catchment in Colombia and its watershed in the Valle del Cauca (Adapted from CVC and Univalle (2001)) and b) Map of the studied watershed of the River Cauca in the Valle del Cauca (study area), crops where triazines could have been used and the CVC monitoring stations. The administrative boundary area of the Valle del Cauca department is included.

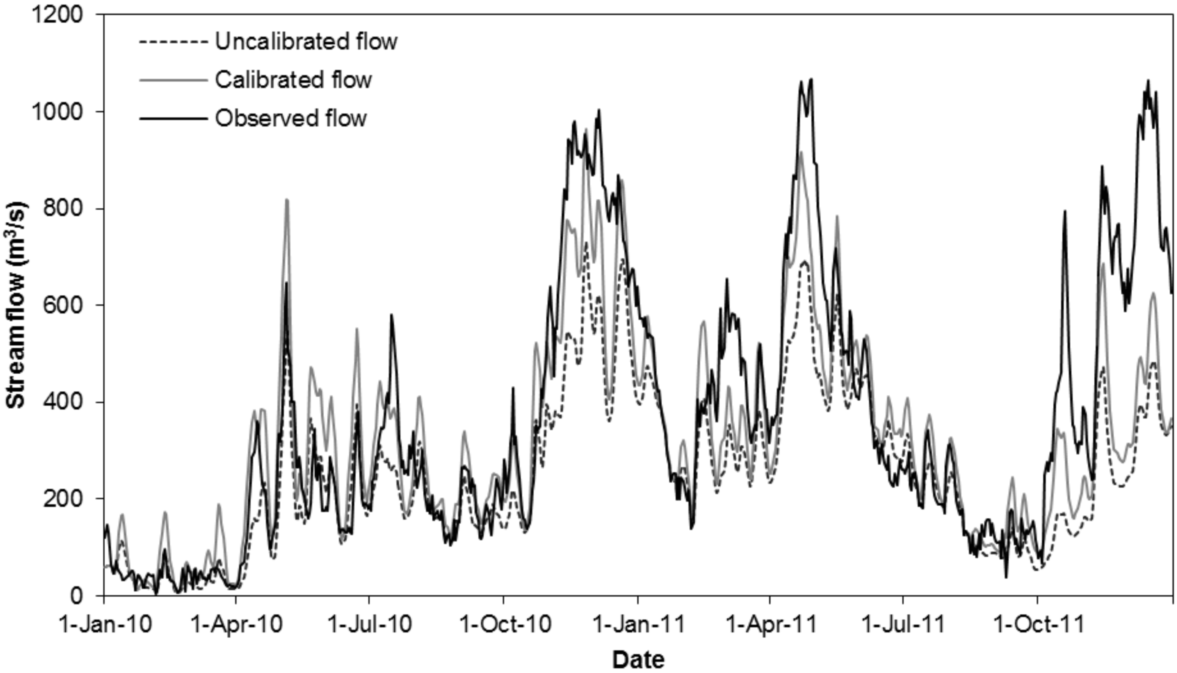


Figure 2 Effect of model calibration on the simulated flow (calibrated against uncalibrated flow) compared to the observed flow at Anacaro station for the period 2010 – 2011.

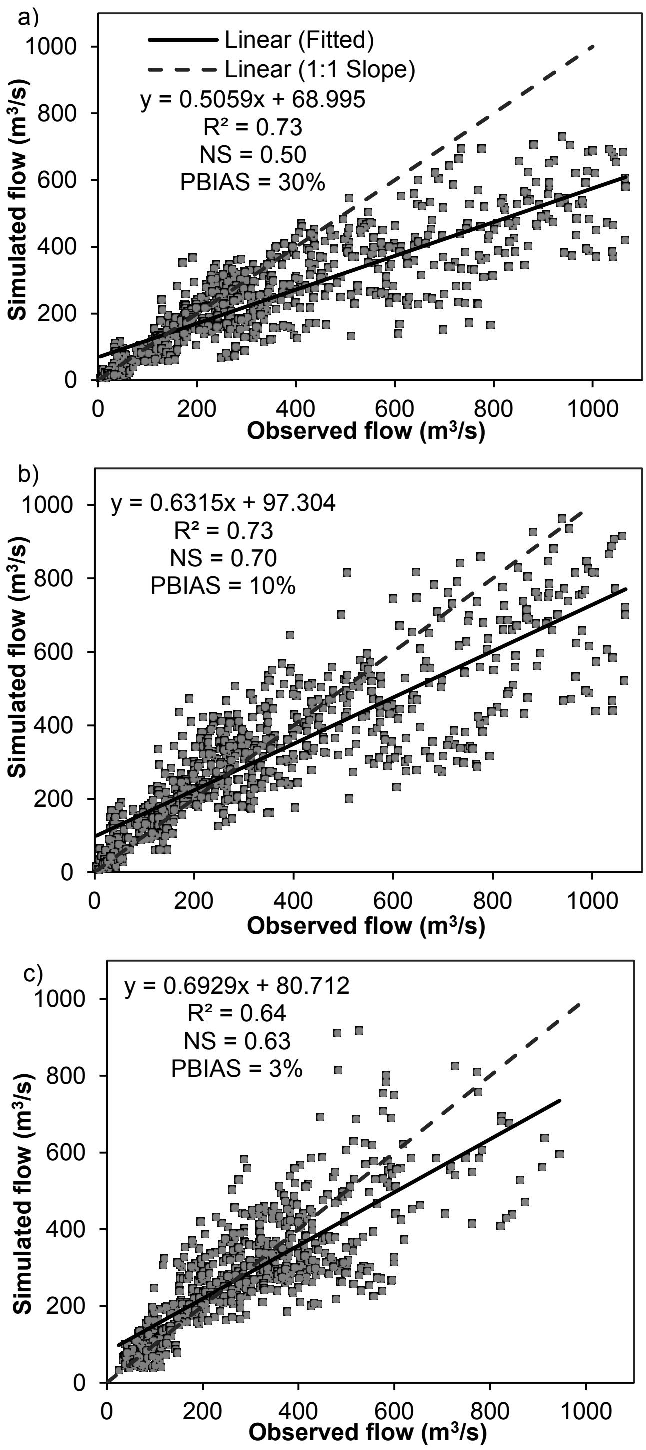


Figure 3 Plot of simulated versus observed flow together with the linear fit (solid line) and the one-to-one line (dashed line) for the a) uncalibrated simulation (2010 – 2011), b) calibrated simulation (2010 – 2011), and c) validation period (2008 – 2009) at Anacaro station. The plot also shows the equation fitted to the linear model, the coefficient of determination, the Nash–Sutcliffe model efficiency coefficient and the PBIAS.

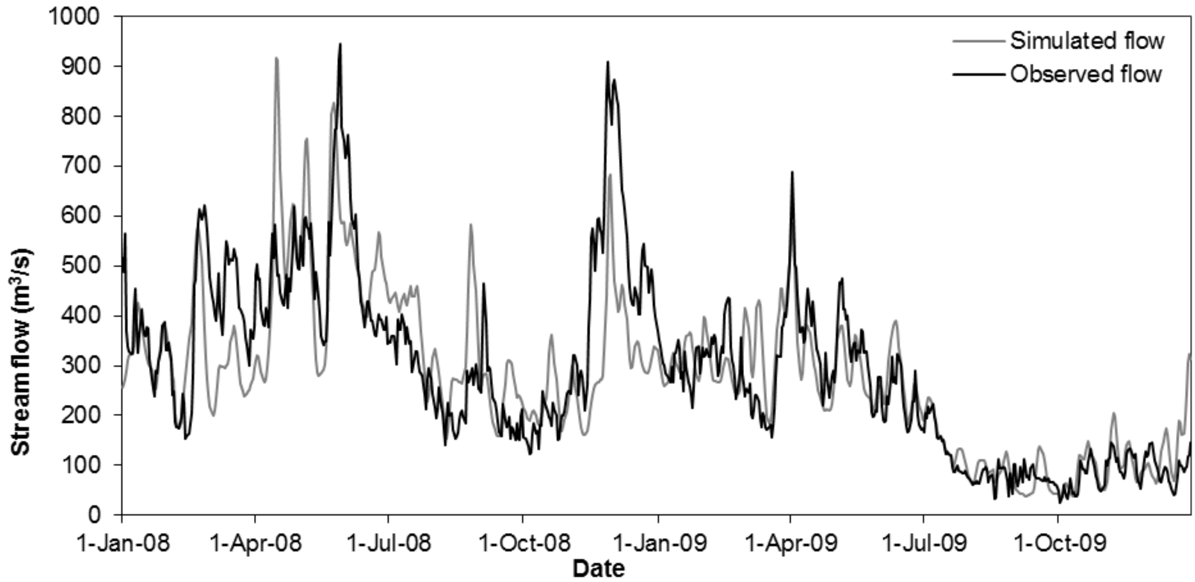


Figure 4 Comparison of the observed and simulated stream flow in the study area for validation period (2008 – 2009).

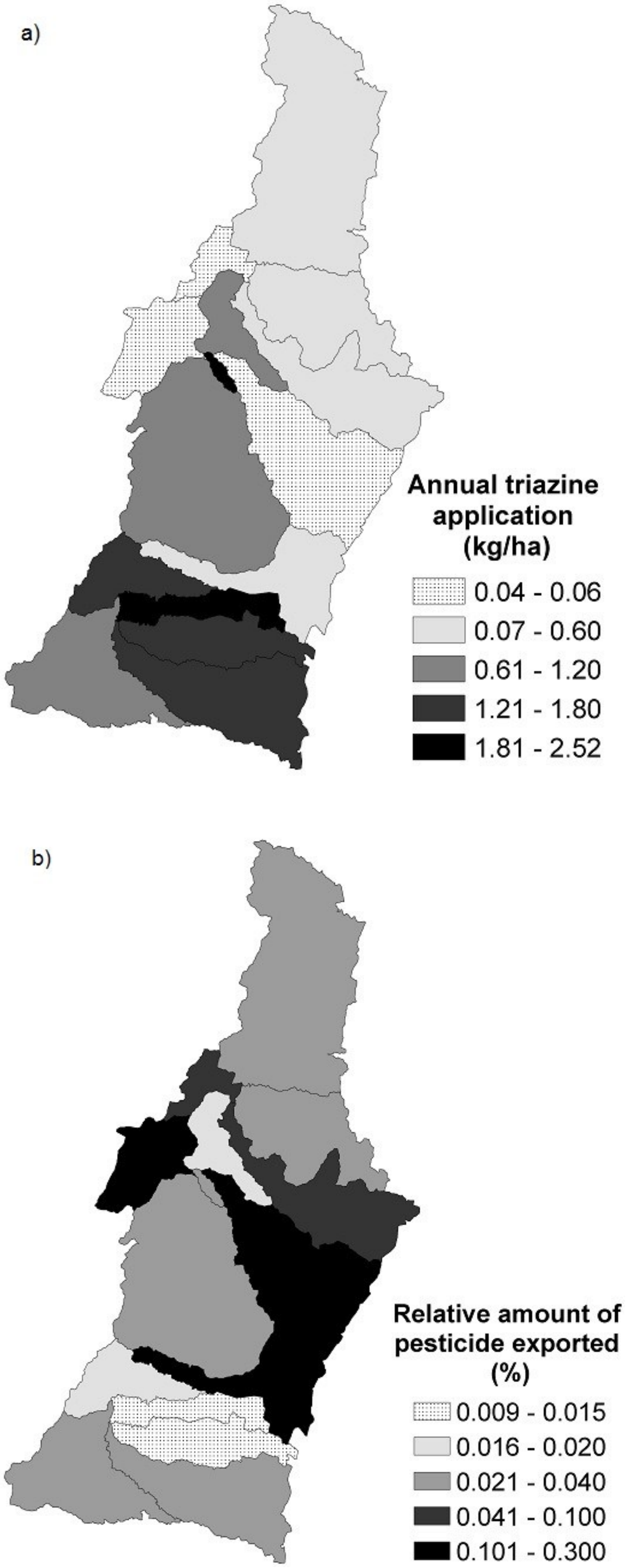


Figure 5 Maps of a) pesticide application per unit area and b) relative pesticide export to the river Cauca predicted using AnnAGNPS.

Supplementary information

Appendix A

Appendix for the methodology section

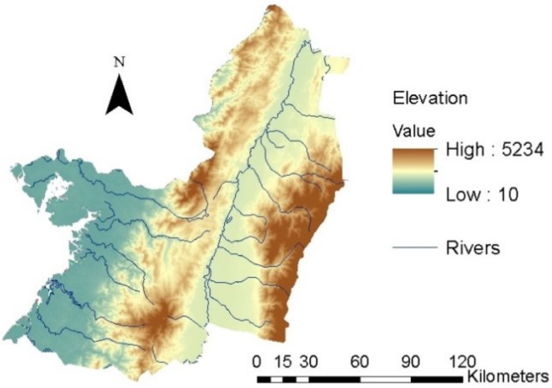


Figure A–1 Map of the pre-processed digital elevation model and burn-in of rivers.

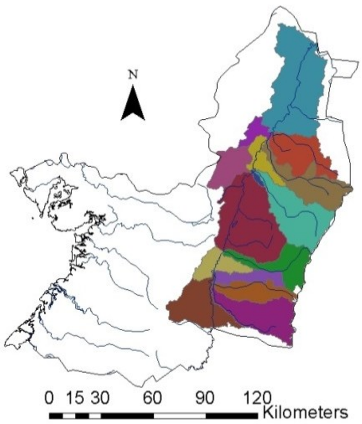


Figure A–2 Calculation of the watersheds that comprise the River Cauca in the Valle del Cauca department using Arc Hydro. The administrative area and rivers of the Valle del Cauca department are also shown.

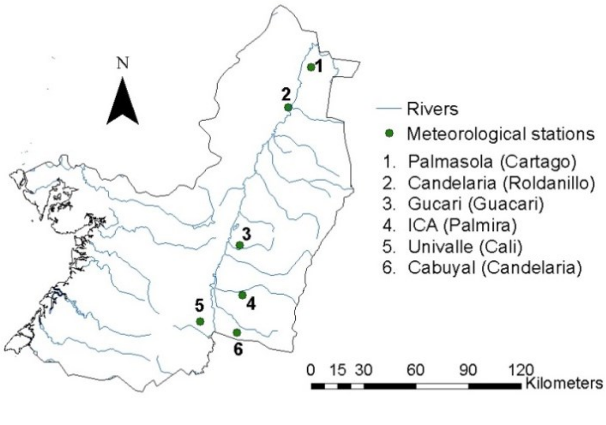


Figure A–3 Location of the meteorological stations.

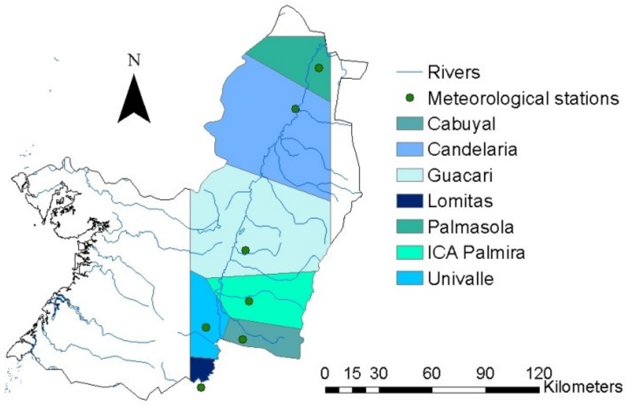


Figure A–4 Location of the calculated Thiessen polygons (Thiessen, 1911) for the meteorological stations. The administrative area and rivers of the Valle del Cauca department are also included.

Table A–1 Soil classification, area and hydrologic soil group used in AnnAGNPS model.

Soil group	Risk	Hydrologic soil group[1]	Draining behaviour	Soil series	Area (%)
1	1	B	Free-draining	ES4	3.6
2	1	C	Moderate draining	C41, VA9, C63	4.6
3	2	D	Artificially drained	V26, VA4, V13, VS49, V55, V25, C13	15.2
4	2	C	Moderate draining	V23, V62, V110, V166, V127	6.4
5	3	D	Artificially drained Poor-draining	V10, V29, VS41A, VS36A, S24, V136, VA12, CAI, R07, PO-36, V45	14.5
6	4	C	Moderate draining	VA10, V67, V153, V149, V4, V111, V5, V85, V2, C108, 148A	13.7
7	4	C	Moderate draining	V91, V119, V106, V170, V115	3.5
8	5	B	Free-draining	V32, ES9, V101, V18, V51, V155, V31	17.9
9	5	B	Free-draining	V65, V122, V22, VA2, V56, VA16, V68, V3, V114, V17, V124, S23, V15	19.4
10	5	A	Excessive-draining	V89, R29	1.3

[1]Hydrologic soil group based on the USDA (1986).

Appendix B

Appendix for the results section

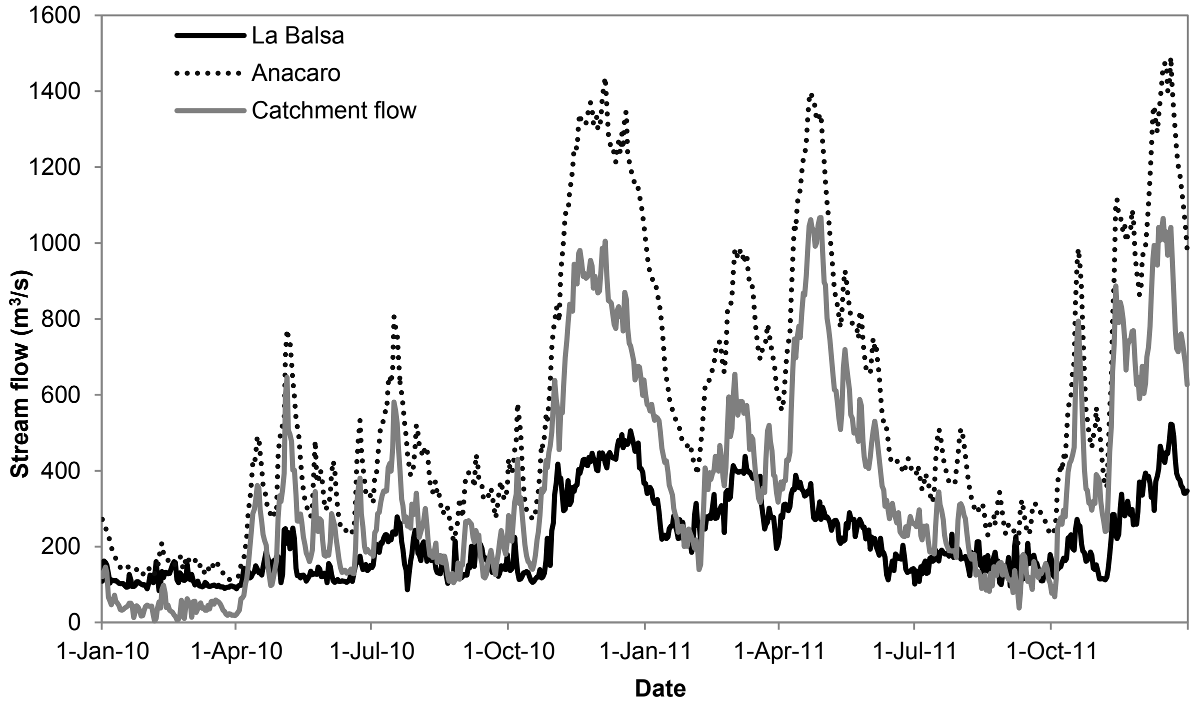


Figure B–1 Observed stream flow in the study area for 2010 and 2011

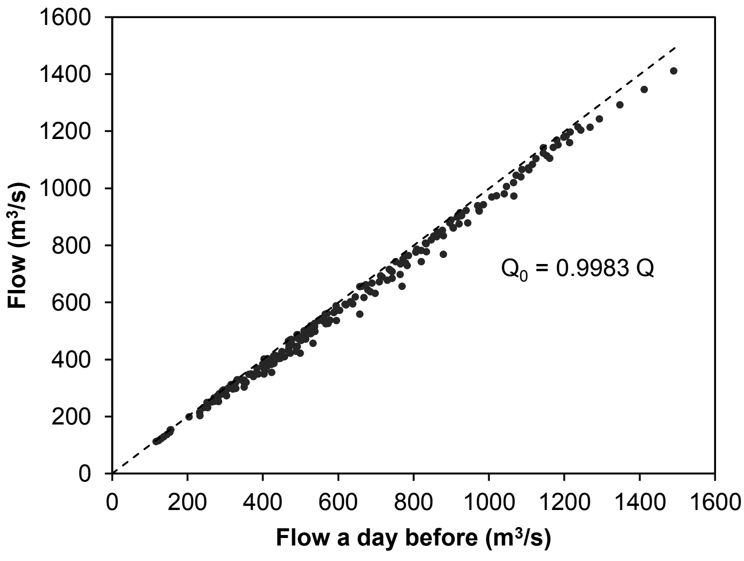


Figure B–2 Plot of flow (Q_0) against the flow on the day before (Q) at Anacaro station together with the line fitted from the origin through the upper envelope and the regression equation. The slope corresponds to the recession constant.

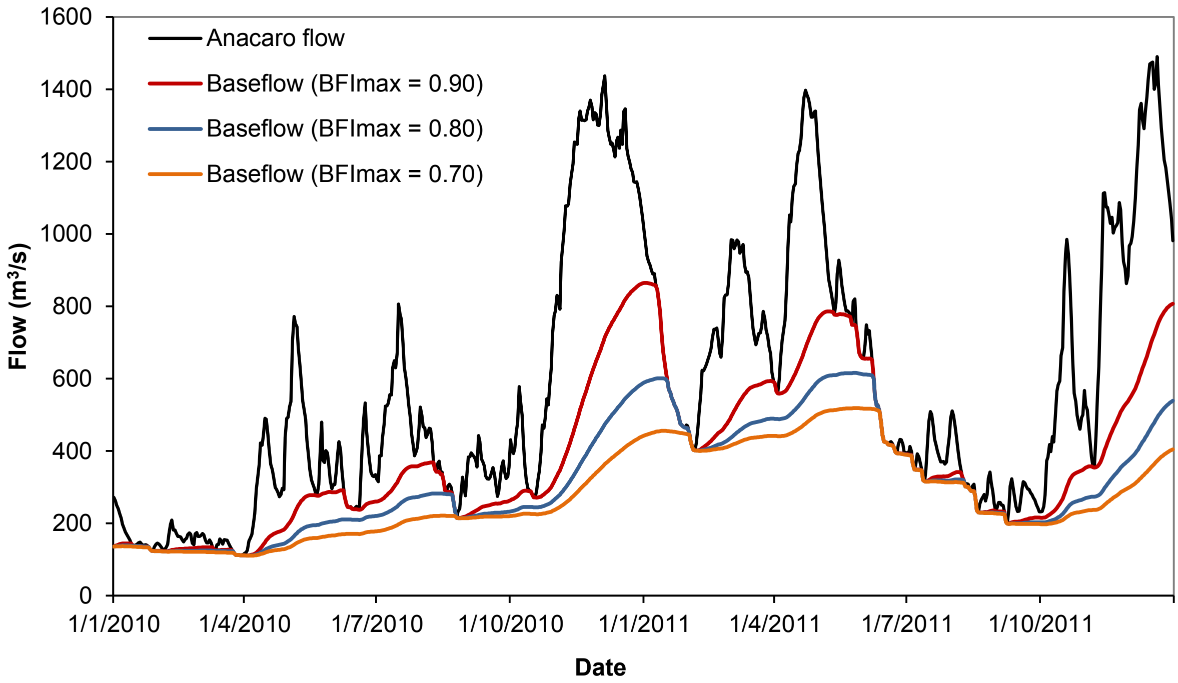
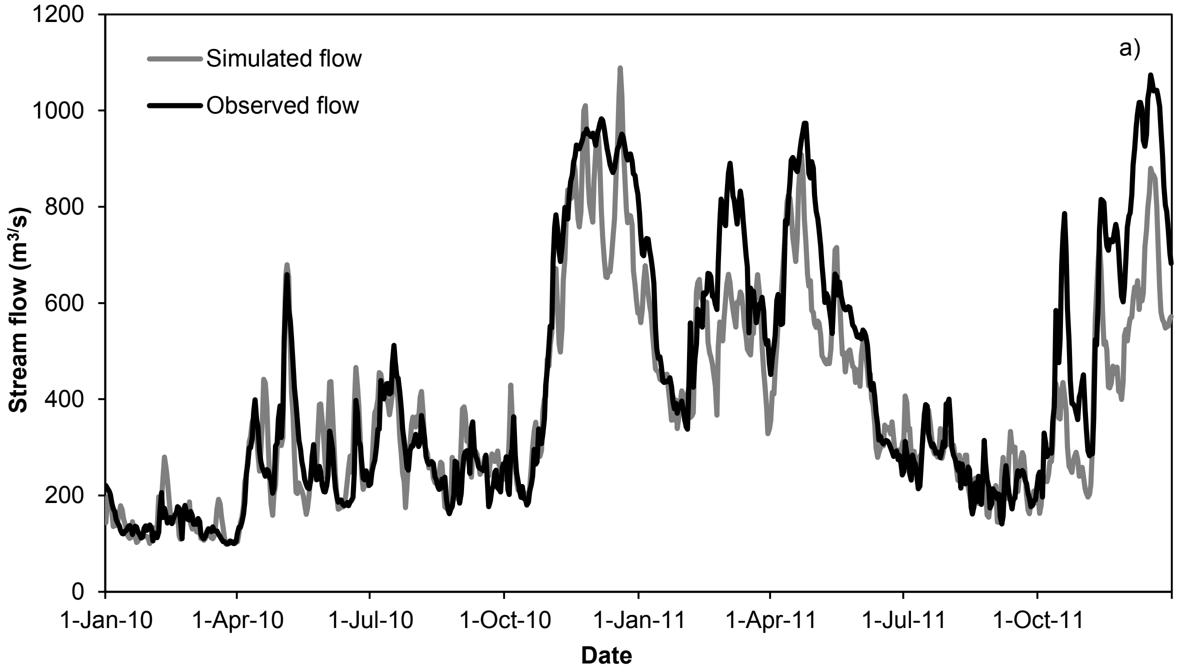


Figure B–3 Flow at Anacaro and baseflow curves calculated by hydrograph separation using BFI_{max} values of 0.90, 0.80 and 0.70 and a filter parameter α of 0.998.



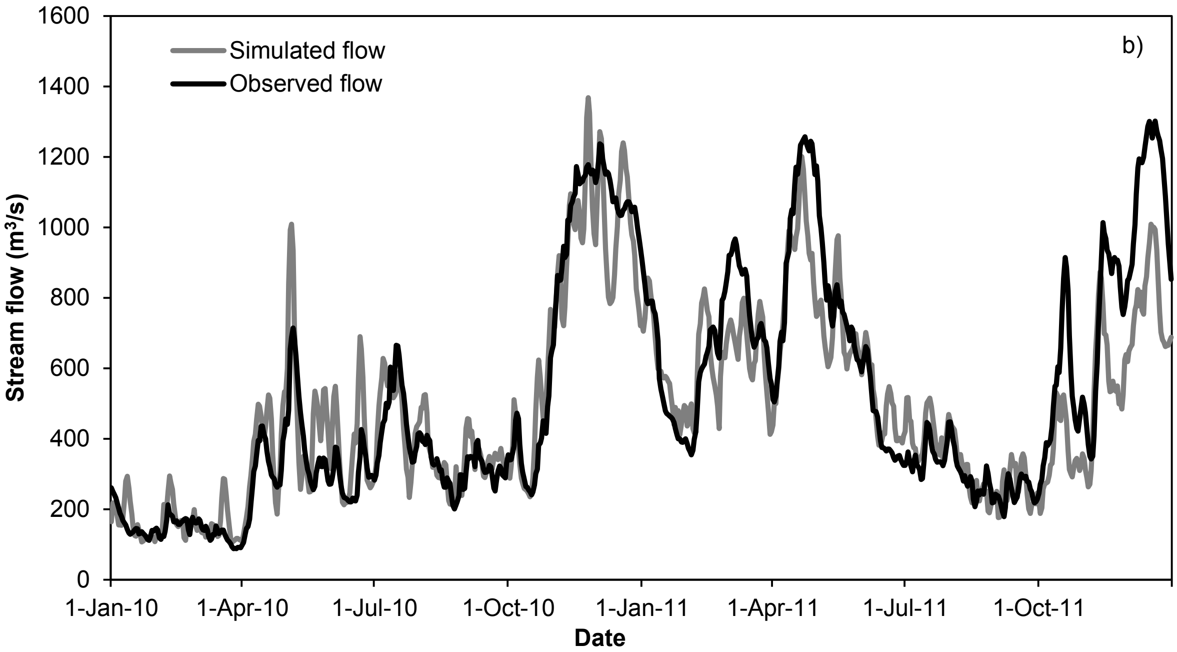


Figure B–4 Observed and simulated flow after calibration for a) Mediacanoa and b) Puente Guayabal stations.

Table B–1 Annual application of pesticide calculated for each sub-basin along with the percentage areas of target crops (sugarcane, maize and sorghum) and sub-basin areas in hectares.

Sub-watershed	Sugarcane (%)	Maize (%)	Sorghum (%)	Total crops (%)	Sub-basin area (ha)	Annual pesticide application (kg/ha)
1	22.8	0.3	1.0	24.0	67,640	0.89
2	39.4	0.3	0.6	40.3	74,215	1.52
3	38.9	1.1	1.3	41.4	41,028	1.52
4	55.3	0.1	0.8	56.1	25,146	2.13
5	39.5	1.3	1.1	41.9	32,224	1.55
6	14.6	0.1	0.6	15.2	51,308	0.57
7	1.3	0.1	0.0	1.4	37,510	0.05
8	27.1	0.4	1.7	29.2	141,946	1.07
9	58.3	12.6	10.5	81.4	2,867	2.52
10	1.4	0.7	0.1	2.2	90,456	0.06
11	22.5	3.8	2.1	28.4	24,383	0.94
12	4.0	0.5	0.7	5.1	66,071	0.17
13	0.3	2.2	0.1	2.6	15,216	0.04
14	13.7	0.0	0.0	13.7	63,475	0.53
15	11.7	4.0	6.0	21.7	130,315	0.57
Whole catchment	19.5	1.1	1.6	22.3	863,800	0.78

Table B–2 Comparison of simulated mesotrione and triazine concentrations for each sampling location.

Sampling Location	Day	Triazine (μg/L)	Mesotrione (μg/L)
June 2010			
Juanchito	9	<0.010	0.000
P. Isaacs	10	<0.010	0.000
P. Torre	10	<0.010	0.000
Mediacanoa	10	0.031	0.001
P. Guayabal	11	0.068	0.002
Anacaro	11	0.067	0.003
October 2010			
Juanchito	26	<0.010	0.000
P. Isaacs	11	<0.010	0.000
P. Torre	11	0.023	0.001
Mediacanoa	25	0.094	0.001
P. Guayabal	25	0.152	0.001
Anacaro	25	0.259	0.003
May 2011			
Juanchito	10	<0.010	0.000
P. Isaacs	11	<0.010	0.000
P. Torre	11	0.025	0.001
Mediacanoa	12	0.072	0.002
P. Guayabal	12	0.076	0.002
Anacaro	12	0.058	0.002

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Thiessen, A.H., 1911. Precipitation averages for large areas. Monthly Weather Review 39 1082-1084.

USDA, 1986. Technical Release 55: Urban Hydrology for Small Watershed, NRCS-USDA.

Wischmeier, W.H., Smith, D.D., 1978. Predicting rainfall erosion losses: a guide to conservation planning, Agriculture Handbook 282. USDA-ARS, USA.