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Linking phosphorus export and hydrologic modeling: a case study in Central Italy

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Abstract Soil erosion is an open topic, not only because soil fertility is lost, but also because nutrients are spilled into water bodies, thereby causing pollution. Research carried out in this field has amply described this process, but the interaction between these factors is complex and experimental research is needed to understand the production of loads of nutrients for different land uses. This paper describes a long-term monitoring case study using high-resolution rainfall data and runoff samples, carried out in the Lake Vico basin (Central Italy) to determine the phosphorus (P) export during erosive rainfall events. State of the art GIS-based basin characterization and advanced rainfall-runoff models are employed in order to describe the relationship between nutrient export and rainfall or runoff time distribution. Results show that the phosphorus export is strongly related to such time distributions, and less to the cumulative amount of rainfall or runoff.

Keywords Phosphorus export · Non-point source pollution · Soil Conservation Service-Curve Number · Green-Ampt infiltration model · Curve Number for Green-Ampt · Width Function based Instantaneous Unit Hydrograph

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Introduction

The formation and erosion of soil are natural processes, influenced by climate, morphology, and land use/land cover (LU/LC) changes. Communities influence land cover, especially through agricultural activity, thus accelerating processes of erosion. This not only reduces soil fertility but also represents a major problem for the environment, contributing to the silting of lakes and coastal areas, the clouding of freshwater, as well as the addition of nutrients to them, through eroded soil (Olem and Simpson 1994; Novotny 2005; Agnese et al. 2006; Pelorosso et al. 2009).

Regarding European water basins, point sources of water pollution have been noticeably reduced since the late 1960s due to their relative ease of identification and to the constant development of water purification. Unfortunately, the same cannot be said about pollution deriving from non-point sources (NPS) which, even today, pose a problem in maintaining the standard of water quality (Arheimer et al. 2004; Ripa et al. 2006). For this reason, agriculture is often cited as the sector of production with the greatest responsibility for the NPS pollution of freshwater and groundwater (Hoorman et al. 2008; Leone et al. 2008).

These topics are of great interest, especially as regards small basins characterized by a predominantly agricultural LU/LC. In fact, recent studies show that where small watersheds are concerned, it is not always possible to apply complex mathematical models to understand the mechanisms of nutrient transport to the river network (Sharpley et al. 2008; Garnier et al. 2010; Recanatesi et al. 2013).

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The present manuscript in particular is focused on the phosphorus export from soil caused by the surface water flowing; scientific literature shows that this phenomenon is dependent on the erosion of the soil and on the runoff volume, which in turn is linked with several factors such as rainfall intensity, temperature, and antecedent soil moisture content (Sharpley et al. 2001; Hoorman et al. 2008; Jin et al. 2009).

In recent years, a number of authors have tackled this topic: Ulen and Persson (1999) linked concentrations of particulate phosphorus to the discharge of five drainage classes; Lazzarotto et al. (2005) recognized that a proper monitoring technique requiring high temporal resolution is needed when linking dissolved reactive phosphorus with discharge; Gerten et al. (2004) modeled dynamic interactions between the terrestrial biosphere and the water cycle, employing a vegetation model; Kim et al. (2006) modeled specific discharge (discharge per unit area) and dependent nutrient concentration in total runoff, proposing a power function used to determine the regression relationship between runoff volume and dependent nutrient load in stormflow; Chen et al. (2013) applied a semi-distributed land use-based runoff process (SLURP) model for the load estimation and source apportionment of nitrogen and phosphorus. From the aforementioned literature, it is evident that direct measurement of the variables involved is highly recommendable in order to understand the relationship between nutrient export and hydrological variables. The major drawback of direct measurements is, obviously, the high cost of setting up and running a monitoring station and the length of time before data from a certain number of events becomes available. Hence, a simplified modeling technique would be extremely useful, allowing the disadvantages of direct measurements to be circumvented.

Results from the aforementioned literature also suggest that there is a need for an easy method of quantifying the relationships between the nutrient export and hydrologic variables involved in the phenomenon, such as rainfall and runoff. Empiric regressions linking nutrient export to cumulative values for rainfall and runoff may not provide adequate scientific support to planning choices in land management aimed at controlling water pollution from NPS. Indeed, in many case studies (e.g., Sharpley et al. 2008; Recanatesi et al. 2013), the relationship between nutrient export and cumulative rainfall has not provided satisfying results, but it would be preferable to refer to the instantaneous net runoff flowing above the terrain or to the net rainfall that can be transformed in runoff, i.e., the main factor responsible for nutrient export. This could be achieved using hydrological rainfall-runoff models able to determine effectively the time distribution of runoff or the rainfall excess, i.e., total storm precipitation minus losses (Serinaldi and Grimaldi 2011; Grimaldi and Petroselli 2014).

The aim of this paper is to describe the results of a real case study in Central Italy, where observations of nutrient export, i.e., the total load of phosphorus per unit area (kg/ha) removed from topsoil during rainfall events, and hydrological variables, such as gross rainfall intensity, are available. Combining observed data with advanced hydrological models able to characterize the basin runoff as controlled by the topography and by the infiltration processes will provide new insights into the nutrient export issue.

This paper is organized into the following main sections. The "Materials and methods" section describes the details of the case study area and of the techniques employed to estimate infiltration, rainfall excess, and runoff formation; in this section, information about the observed events used for the model evaluation is also provided. In the "Results and discussion" section, the proposed technique is applied to the case study catchment, providing data allowing the conclusions presented in the last section of the manuscript to be drawn.

Materials and methods

Description of the study area

The research area is within the basin of Vico Lake (40.15 km^2 total area: 27.9 km^2 land, 0.15 km^2 wetland, and 12.1 km^2 water body) located 55 km northwest of Rome and reported in Fig. 1. It is a volcanic lake, with a small emissary river and a marked water renewal time (17 years on average, as reported in Ripa et al. 2006). The lake's environment and LU/LC characteristics make it a paradigmatic case study to stress the impact of agricultural and forestry land use, since urbanized areas are negligible and there are no industrial areas affecting the watershed (Leone and Marini 1993). Indeed, settlements are reduced to dwellings in a small part of the basin, agriculture being the main human activity: 12.15 km^2 is wood covered and 14.40 km^2 is agricultural land, with 10.75 km^2 of intensive hazelnut cultivation. The Vico Lake basin offers an ideal study

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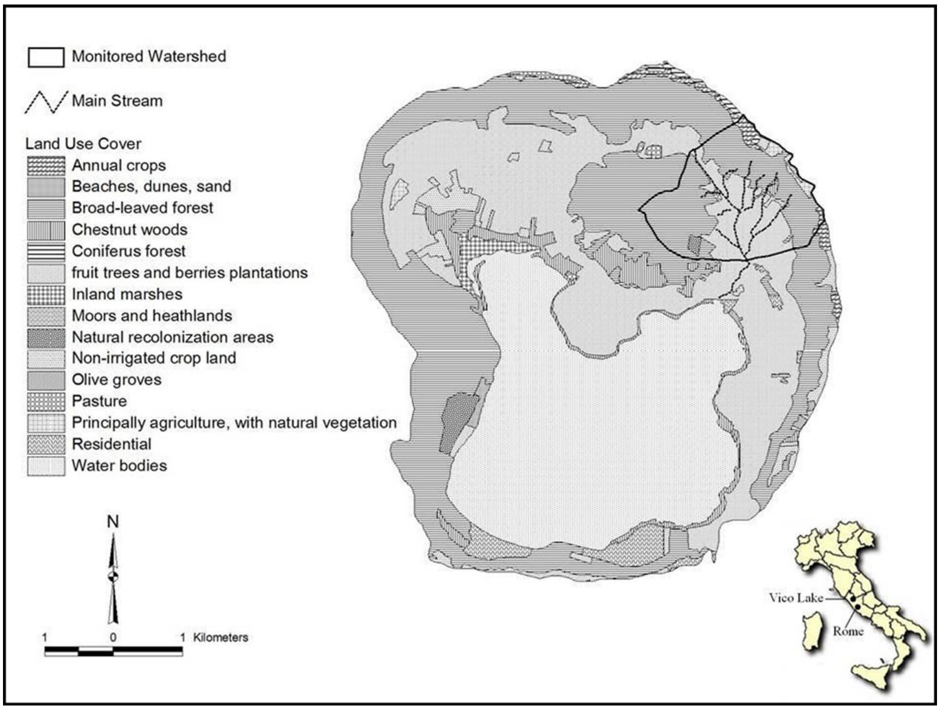

Fig. 1 Case study area localization

opportunity to highlight LU/LC impact on freshwater because the phosphorus cycle in this basin is influenced only by agriculture and forestry (Ripa et al. 2006).

From a pedological point of view, the main physical and chemical properties of the basin soils were evaluated, consulting a specific pedological study (Lulli et al. 1990). This study shows that the basin is mainly characterized by soils on leucitite lava and soils on pyroclastic deposits.

The monitored sub-basin is drained by its main stream, the Scardenato creek, shown in Fig. 1. At the monitoring point, the Scardenato basin has an area of 3.45 km^2 (8.3 % of the total basin area), a steep slope (10–30 % in the higher part of the basin and 3–10 % in the lower), and a difference in elevation above sea level of 308 m, from the highest to the lowest points in the basin.

This sub-basin is representative of the whole basin LU/LC: forestry in the upper part (30 % of the total surface area) and intensive hazelnut culture in the lower part (70 % of the total surface area).

Water sampling and analysis

The equipment used consisted of the following:

– An ARG 100 rain gauge for continuous rain monitoring. Readings were performed every second and recorded every 10 min. In this way, cumulated rainfall measurements were available at 10-min intervals. Rainfall registrations started in January 1998.
– An ISCO (ISCO Inc., Lincoln, NE, USA) 3700 compact sequential water sampler used to take water samples at 5-min intervals when a flood occurred within the Scardenato creek. Water samples were stored in bottles immerged in ice in an insulated container to keep the samples ready for water quality analysis. To measure dissolved P, 5 ml of filtered water sample was mixed with PhosVer powder reagent in a vial, allowing a few minutes for the color to develop. The absorption of the solution color was measured by a Hach DR-4000U spectrophotometer.

Infiltration and net rainfall estimation

The available gross rainfall time series was modeled, employing a recently proposed continuous framework named Continuous Modeling for Small and Ungauged Basins (COSMO4SUB) which allowed its division into single independent events characterized by an interval of no rainfall of at least 1 day between one event and the

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other (Grimaldi et al. 2012b). Basically, COSMO4SUB allows the fragmentation of the whole time series into many independent events, each one characterized by basic event properties such as duration, cumulative value of precipitation, and so on.

Starting from the single independent gross rainfall events, the net rainfall distribution for each event was modeled according to two different schemes: the well-known Soil Conservation Service-Curve Number method (SCS-CN) and a recently proposed procedure named Curve Number for Green-Ampt (CN4GA) combining the SCS-CN method with the Green-Ampt infiltration scheme.

The Soil Conservation Service-Curve Number method (SCS 1972; NRCS 2008) is an empiric method (lumped in space and in time) that defines the total net runoff of a rainfall extreme event according to the following formula:

$$R_o = \frac{(R_f - I_a)^2}{R_f - I_a + S} \tag{1}$$

where R_o is the event runoff, R_f the gross rainfall, S the potential soil retention, and I_a the initial abstraction due to the interception, infiltration, and surface storage. S and I_a can be referred to the curve number (CN) parameter through

$$S = \frac{1,000}{\mathrm{CN}} - 10, \quad I_a = \lambda S \tag{2}$$

where S is measured in inches and the constant λ value is fixed at 0.2; CN is the only method parameter and is well classified with respect to soil properties and antecedent moisture conditions. Although the method is used worldwide, it has some limitations and drawbacks: in particular, Garen and Moore (2005), Eli and Lamont (2010), and Woodward et al. (2010) highlighted some incorrect uses, such as its application as an infiltration equation, so its use at a sub-daily timescale is not appropriate (Grimaldi et al. 2013a, b).

Conversely, the Green-Ampt (GA) infiltration equation (Green and Ampt 1911) is a physically based model to compute infiltration capacity; the GA model is based on the following:

$$\begin{cases} q_0 = r & \text{for } t < t_p \\ q_0(t) = K_s\left[1 + \dfrac{\Delta\theta \times \Delta h}{I(t)}\right] & \text{for } t \geq t_p \end{cases} \tag{3}$$

where r is the rainfall rate, q_0 is the infiltration rate, t is the time, t_p is the ponding time, $I(t)=(\theta_s-\theta_i)\times z_f=\Delta\theta\times z_f$ is the cumulative infiltration, $\Delta\theta=(\theta_s-\theta_i)$ is the soil moisture deficit (θ_i is the initial value of the soil-water content, assumed at the wilting point condition, and θ_s is the field saturated soil-water content), z_f is the saturated soil depth, K_s is the saturated hydraulic conductivity, and $\Delta h=(h_{surf}-h_f)$ is the driving matric pressure-head, containing both h_{surf} that is the pressure-head at the soil surface (i.e., the depth of water on the surface, often assumed equal to zero as in the case of ponding) and h_f that is a constant matric pressure-head at the moving wetting front. The GA model is an effective alternative as an excess rainfall method in the case of sub-daily rainfall-runoff continuous models, but its parameter values are difficult to estimate, although they can be linked to soil characteristics (Rawls et al. 1983; Brakensiek and Rawls 1983; Brakensiek et al. 1984). In particular, among the parameters featured in the GA equation, K_s is a key factor in the estimation of infiltration rates and requires great care in its measurement.

In order to combine the advantages of both the previously described methods, a mixed procedure named CN4GA that combines the simplicity of the SCS-CN method and the physical behavior of the Green-Ampt model has been proposed (Grimaldi et al. 2013a, b). The concept of CN4GA is that for a given storm, the computed SCS-CN initial abstraction and the total net rainfall amount are used to identify the ponding time and to calibrate the soil hydraulic conductivity parameter K_s of the Green-Ampt model, in doing so distributing within the storm event the net rainfall volume determined by the SCS-CN method according to the physically based Green-Ampt scheme. Applying the SCS-CN and CN4GA methods, two different net rainfall scenarios are available, characterized by the same total net rainfall amount but with different time distributions.

Terrain analysis and discharge estimation

In order to determine the hydrographs and the related peak discharges caused by the net rainfall distributions previously modeled using the SCS-CN and the CN4GA approaches, the Width Function based Instantaneous Unit Hydrograph (WFIUH) method is selected (Mesa and Mifflin 1986; Naden 1992). Basically, the WFIUH represents the residency time probability density function, i.e., it describes the total time that every rainfall drop takes to reach the outlet. In order to define the basin

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WFIUH, in the present work, a parsimonious hydrologic modeling algorithm (Grimaldi et al. 2010, 2012a) is applied, based on the following two steps: (A) implementation of advanced terrain analysis techniques for the digital elevation model (DEM) pre- and post-processing in order to estimate the watershed's main hydrogeomorphic features and (B) WFIUH convolution with the net rainfall scenario at the event scale for estimating the corresponding hydrograph. The WFIUH is calibrated using the river flow velocity parameter to match the observed time of concentration that is estimated from empiric formula (Grimaldi et al. 2012a). The two main steps and related sub-steps are described briefly as follows:

(A.1) Pits and flat areas are removed using the physically based erosion model for the pit and flat removal (PEM4PIT) method (Santini et al. 2009); flow direction and flow routing are defined using an optimized flow direction method (Nardi et al. 2008); the basin concentration time (T_c) is estimated using the empirical NRCS formula (NRCS 1997):

$$T_c = 0.0526[(1{,}000/\mathrm{CN}) - 9]L^{0.8}(\mathrm{WS})^{-0.5} \tag{4}$$

where T_c is the concentration time (min), L the maximum distance (ft) between the watershed divide and the outlet according to the determined flow paths, CN the basin average curve number, and WS the basin mean slope (%).

(A.2) The WFIUH is estimated based on the following equation:

$$\mathrm{WFIUH}(t) = \frac{L_c(x)}{v_c(x)} + \frac{L_h(x)}{v_h(x)} \tag{5}$$

where L_c and L_h are the channel and hill slope flow path, respectively, for the generic cell x, with x=1 to n which is the number of basin cells, and v_c and v_h are channel and hill slope flow velocities; the hill slope velocity v_h is estimated as in Grimaldi et al. (2010) based on land cover and slope, while the channel flow velocity v_c is calibrated using the basin concentration time, so that the maximum WFIUH abscissa is equal to T_c (Petroselli 2012; Petroselli and Alvarez 2012).

(B) The WFIUH obtained as previously described is applied to the net rainfall event, both for SCS-CN and for CN4GA, in order to obtain the corresponding runoff scenario. Starting from the unit hydrograph definition, the discharge $Q(t)$ can be expressed using the following:

$$Q(t) = A_w \int_0^t \mathrm{WFIUH}(t-\tau)p(\tau)d\tau \tag{6}$$

where A_w is the watershed area, p is the net rainfall, and t is time.

In conclusion, the applied methodology allows for the estimation of both net rainfall intensities and discharges using either the SCS-CN approach or the CN4GA procedure. Correlations between these event characteristics and phosphorus export can then be evaluated as described in the next paragraph with regard to the case study.

Results and discussion

The basic soil properties of the case study, assumed from Rawls et al. (1983), are shown in Table 1; they are needed for CN4GA application and lead, event per event, to a different calibrated saturated hydraulic conductivity K_s so that the cumulative net rainfall is equal to the corresponding one obtained by applying SCS-CN.

The final and calibrated K_s values are shown in Table 2, together with the basic rainfall event properties. As explained, the single independent event was extracted from the rainfall time series using the COSMO4SUB

Table 1 Case study on basic soil properties assumed in CN4GA application: initial (θ_i) and field saturated (θ_s) soil-water content, initial value for saturated hydraulic conductivity (K_s), pressure-head at the soil surface (h_{surf}), and matric pressure-head at the moving wetting front (h_f)

Case study soil characteristics	
Soil type	Sandy loam
θ_s (−)	0.412
θ_i (−)	0.095
Initial K_s (mm/h)	25.9
h_{surf} (mm)	0
h_f (mm)	110

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Table 2 Rainfall event basic properties: event number and date, cumulative gross rainfall (R_f), duration, phosphorus export (P), SCS antecedent moisture condition (AMC), curve number (CN), potential retention (S), initial abstraction (I_a), event runoff (R_o), and calibrated CN4GA saturated hydraulic conductivity (K_s)

Event number	Date	R_f (mm)	Duration (h)	P (kg/ha)	AMC	CN	S (mm)	I_a (mm)	R_o (mm)	Calibrated K_s (mm/h)
1	1998 Dec 12	17.8	12.3	0.04	I	87.65	35.8	7.2	2.44	0.67
2	2001 Apr 8	18.8	12.7	0.10	I	86.14	40.9	8.2	2.19	1.50
3	2005 Nov 7	21.6	42.7	0.35	I	81.77	56.6	11.3	1.58	2.45
4	1999 Sept 10	17.8	1.5	0.55	I	87.65	35.8	7.2	2.44	3.08
5	1999 Oct 5	18.2	9.2	0.90	I	87.05	37.8	7.6	2.34	6.86
6	2008 Apr 9	20.4	9.8	1.11	I	83.67	49.6	9.9	1.83	2.28
7	2008 Nov 29	23.6	23.0	0.95	I	78.59	69.2	13.8	1.21	2.53
8	2008 Oct 29	16.0	9.3	1.20	I	90.27	27.4	5.5	2.92	1.91
9	2001 Sept 24	61.0	14.0	1.10	I	57.08	191.0	38.2	2.43	31.78
10	2008 Jan 17	82.0	28.2	2.10	I	57.08	191.0	38.2	8.17	5.62
11	2008 Feb 5	66.0	39.2	1.85	III	57.07	191.1	38.2	3.53	12.52
12	2008 Dec 13	162.2	70.3	2.11	I	57.08	191.0	38.2	48.81	1.74
13	1998 Oct 7	115.8	6.2	2.25	III	57.08	191.0	38.2	22.42	44.13

framework, its cumulative gross rainfall and event duration were determined, and the SCS-CN procedure was applied at the event scale in order to determine the event cumulative runoff. The SCS-CN antecedent moisture condition (AMC: "I" for dry soil, "II" for average wetted soil, and "III", for a wet soil) was determined based on the cumulative gross rainfall of the previous 5 days, while CN, and consequently S, I_a, and R_o, were estimated considering the land use cover (LUC) determined by means of the Corine Land Cover (CORINE 2000) project. For this purpose, in order to represent the surface conditions of the drainage basin and the degree of cover at rainfall time, a map of the European environmental landscape based on interpretation of satellite images and aerial photo interpretation was used. Furthermore, information regarding the ground cover level for different seasons, expressed in terms of square meters of leaf (half surface area) per square meter of ground (Law et al. 2008), was estimated through on site application of the leaf area index (LAI). The selected case study appears to be sufficiently representative because a large typology of storms is available, ranging from 16 to 162 mm total rainfall and from 1.5 to 70.3 h duration.

Results from the net rainfall and the terrain analysis/discharge estimation procedures are summarized in Table 3: for each event, gross and net rainfall peak intensities are given, together with the peak discharge values, i.e., the maximum of the $Q(t)$ occurring during the runoff phase. Confirming results in the literature (Grimaldi et al. 2013a, b), the application of the CN4GA procedure furnished a peak discharge greater than that obtained with the SCS-CN method in every case except one.

Table 3 Event rainfall intensities and discharge values: observed gross rainfall peak intensity (gross I_{max}), net rainfall peak intensity modeled with SCS-CN (SCS-CN I_{max}) and with CN4GA (CN4GA I_{max}), and peak discharge modeled with SCS-CN (SCS-CN Q_p) and with CN4GA (CN4GA Q_p)

Event number	Gross I_{max} (mm/10 min)	SCS-CN I_{max} (mm/10 min)	CN4GA I_{max} (mm/10 min)	SCS-CN Q_p (m^3/s)	CN4GA Q_p (m^3/s)
1	1.20	0.28	0.53	1.06	1.77
2	2.20	0.36	0.73	1.23	1.84
3	2.40	0.28	0.75	0.97	2.76
4	3.80	0.77	1.35	3.61	4.33
5	10.00	1.43	1.40	4.28	4.57
6	3.60	0.24	1.83	1.22	4.03
7	2.20	0.29	0.43	1.29	1.27
8	5.20	0.54	2.76	2.63	6.36
9	11.40	1.25	1.47	3.95	4.76
10	4.20	0.63	2.60	2.25	7.07
11	5.40	0.61	2.34	2.52	7.04
12	2.60	1.04	1.56	4.33	7.71
13	34.60	4.17	17.91	13.75	39.44

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Although the number of considered rainfall events is very limited from a statistical point of view (only 13 events) and could affect the results of the following regressions, a general behavior between phosphorus export and hydrological variables can be investigated. As a first attempt to link hydrologic variables and the nutrient export, in Fig. 2, the relationship between phosphorus export and gross rainfall peak intensity is shown. A simple logarithmic relationship is proposed, linking phosphorus export and observed gross rainfall peak intensity; as can be noted, a low regression coefficient (0.31) is obtained, showing a very low correlation between the measured values, which is also evident looking at the scattered points in the figure. The analysis seems to suggest that there is not a strong correlation between phosphorus export and the gross rainfall peak intensity considered as a key variable among the hydrologic variables. Indeed, the dispersion of the points is high, and no particular trend is evident, a sign that the complexity of the phenomenon cannot be explained considering only the gross rainfall peak intensity. Such results are confirmed by previous literature: for instance, Gao et al. (2008) showed that the phosphorus export increased with rainfall intensity and increasing gradient.

An improvement of the correlation is achieved linking the phosphorus export with the net rainfall peak intensities, as shown in Fig. 3, where simple logarithmic relationships are proposed again; looking at Fig. 3, the phosphorus export seems to be more correlated with the net rainfall peak intensities: indeed, there is a low increase in the correlation coefficient considering the SCS-CN approach (from 0.31 to 0.35) and a moderate increase considering the CN4GA approach (from 0.31 to 0.55). Moreover, the dispersion of the points is reduced with respect to Fig. 2, and this circumstance seems to suggest that the CN4GA approach could be more effective in modeling the phosphorus export at basin scale. Indeed, in recent literature, it has been shown that phosphorus export is more dependent on net rainfall intensity compared with gross rainfall intensity (i.e., Recanatesi et al. 2013).

Figure 4 shows, finally, the relationship between phosphorus export and the modeled peak discharges; again, simple logarithmic equations are proposed, and from Fig. 4, it can be noted how the dispersion of the points tends to slightly diminish with respect to Fig. 3. Regarding the correlation coefficients, for the SCS-CN approach, a 0.42 value is obtained, while for CN4GA, a 0.63 value is obtained. This is not surprising because rainfall-runoff modeling is not based only on a linear filter considering the net rainfall intensities, according to Eq. 6, but also on the topography convergence and the consequent terrain analysis-based flow routing. Indeed, it is well established that phosphorus export is strictly dependent on erosion processes, which in turn are strongly affected by surface runoff (i.e., Rodríguez-Blanco et al. 2013).

Such results are confirmed by previous literature; for instance, when linking phosphorus export with stream flow data, Krishna Prasad et al. (2005) obtained a

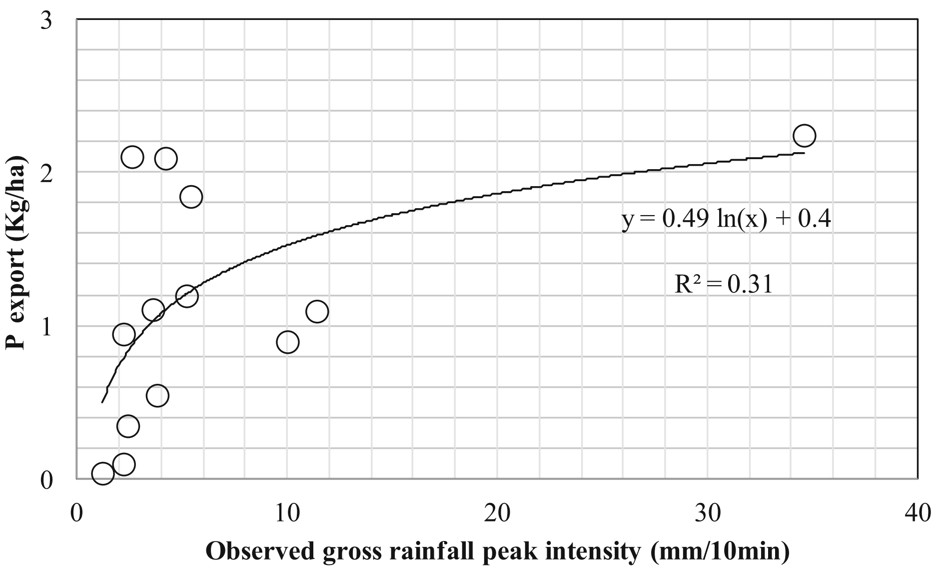

Fig. 2 Relationship between phosphorus export and gross rainfall peak intensity

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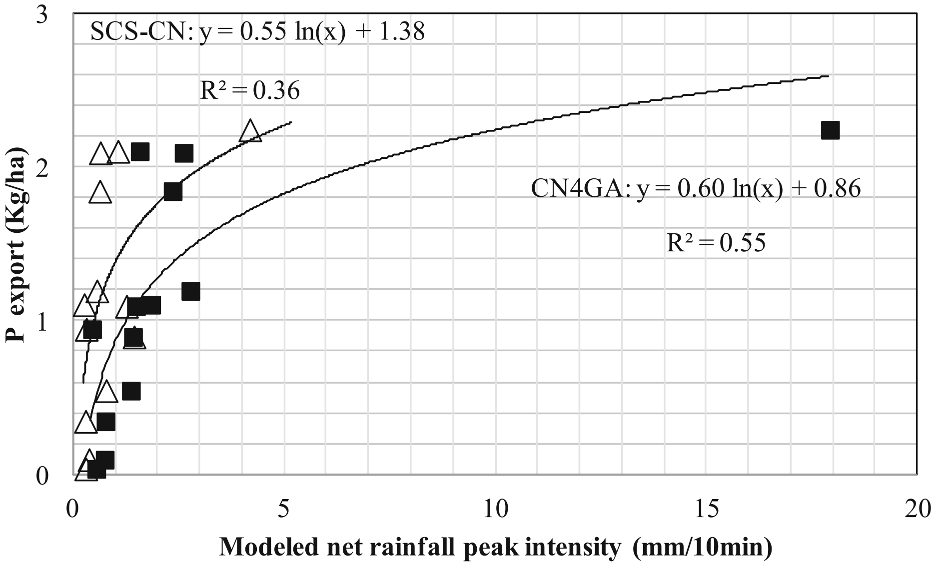

Fig. 3 Relationship between phosphorus export and net rainfall peak intensity: *white triangles* SCS-CN, *black squares* CN4GA

correlation coefficient of 0.45, while Vidon and Cuadra (2011) obtained a correlation coefficient of 0.69; Haygarth and Jarvis (1997) also monitored storms at 3-h intervals, and the pattern for phosphorus export was closely related to discharge.

The increasing correlation between the phosphorus export and the basic characteristics of a given rainfall-runoff event, starting from the gross rainfall intensity up to the modeled peak discharge, suggests a direct relationship with the hydrologic characterization of a given storm, in particular regarding the runoff formation and its parameterization. From the literature, it is well known that phosphorus export is caused mainly by the initial rise of the storm (Sharpley et al. 1999), in particular for events occurring after a long period without rainfall, according to what is called the "environmental memory" principle. In order to confirm such results and to determine in particular how the rainfall intensity distribution affects the phosphorus export, the storms described in Table 2 were classified according to an objective criterion in three classes. A "class-I" event is defined as one in which 33 % or more of the cumulative precipitation (gross, net SCS-CN, or net CN4GA) occurred in the first 33 % of the storm's total duration, defined as in the following: regarding the gross

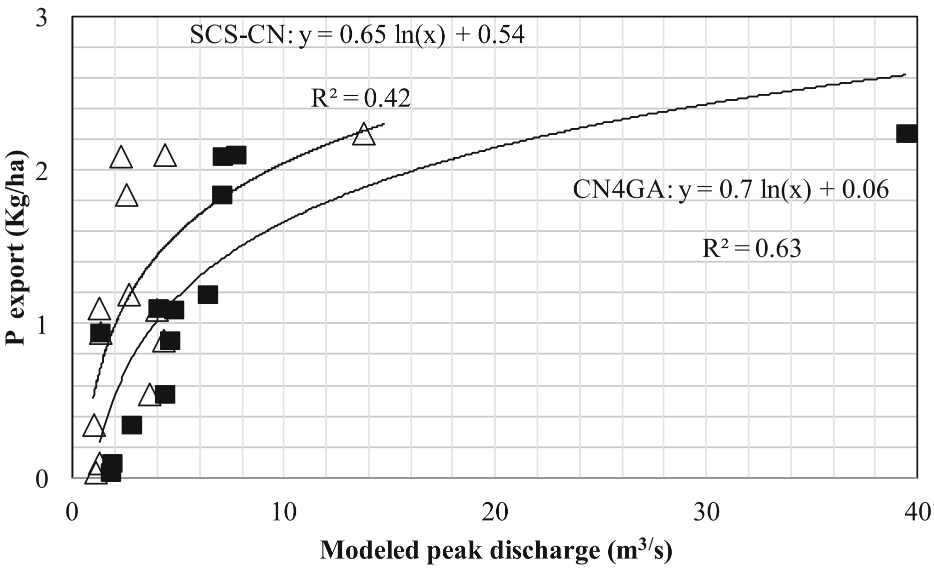

Fig. 4 Relationship between phosphorus export and peak discharges: *white triangles* SCS-CN, *black squares* CN4GA

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storm, its duration was determined applying COSMO4SUB considering an interval of no rain between one event and the other of at least 24 consecutive hours (Grimaldi et al. 2012b); regarding the net storm durations, for the SCS-CN and CN4GA approaches, they were determined as the time interval between the beginning and the end of the surface runoff as provided by the methods: obviously, the duration of the considered rainfall event can vary depending on whether the gross rainfall or the net rainfall is taken into account.

Similarly, a “class-II” (or “class-III”) event is defined as one in which 33 % or more of the cumulative precipitation (gross, net SCS-CN, or net CN4GA) occurred in the second (or third) 33 % of the storm’s duration. In Table 4, the event classification according to the specified criterion is shown, and in Fig. 5, an example of rainfall event classification is shown (event no. 13). Looking at the rainfall hydrographs, it can be noted that the gross rainfall (starting at 0.3 h and ending at 6.5 h) can be classified as a “class-III” event, since a percentage greater than 40 % fell in the last third of the rainfall duration. Concerning the SCS-CN net hydrograph (starting at 3.6 h and ending at 6.5 h), the same “class-III” classification can be assumed, since the majority of the net rainfall fell at the end of the rainfall event. Conversely, concerning the CN4GA net hyetograph (starting at 3.6 h and ending at 5.5 h), it can be noted that the same event can be classified as a “class-I,” since the majority of the net rainfall is represented by the spike at 3.6 h.

Table 4 Rainfall event classification: type I (II or III): 33 % or more of the cumulative precipitation have occurred in the first (second or third) 33 % of the storm duration, respectively, for observed gross rainfall and net rainfall modeled with SCS-CN and with CN4GA

Event number	Gross rainfall	SCS-CN	CN4GA
1	I	I	I
2	I	I	I
3	II	I	I
4	III	II	II
5	II	I	II
6	III	II	I
7	I	III	III
8	II	I	II
9	II	I	II
10	II	III	I
11	III	III	II
12	I	II	II
13	III	III	I

Considering the previously described classification of the rainfall events and repeating the elaboration for the three classes independently, the results appear as in Table 5, where for brevity only the correlation coefficients R^2 are reported: as can be seen from Table 5, when linking phosphorus export to gross rainfall intensity, the R^2 passes from a value of 0.31 if all the events are considered together, to 0.47 for the “class-I” events (4 events out of 13), 0.01 for the “class-II” events (5 events out of 13), and 0.64 for the “class-III” events (4 events out of 13). This behavior seems to suggest that “class-II” events are not correlated with phosphorus export.

When considering the relationship between phosphorus export and net rainfall peak intensities, the R^2 passes from values of 0.36 (for the SCS-CN approach) and from 0.55 (for the CN4GA approach) if all the events are considered together to values of 0.59 (SCS-CN) and 0.81 (CN4GA) for “class-I” events (6 events out of 13 for both SCS-CN and CN4GA), to 0.12 (SCS-CN) and 0.14 (CN4GA) for the “class-II” events (3 events out of 13 for SCS-CN and 6 for CN4GA), and to 0.58 for SCS-CN “class-III” events (4 events out of 13), while for “class-III” events for CN4GA, there is only one rainfall event, so it is not possible to evaluate any correlation.

The results reported in Table 5 suggest that the correlation between phosphorus export and hydrologic modeling is improved when in the presence of a “class-I” event, in particular for the CN4GA approach, that again offers a better correlation between the involved measured values.

Finally, when considering the relationship between the phosphorus export and the peak discharges, the R^2 passes from values of 0.42 (for the SCS-CN approach) and 0.63 (for the CN4GA approach) if all the events are considered together, to values of 0.75 (SCS-CN) and 0.80 (CN4GA) for “class-I” events (again 6 events out of 13 for both SCS-CN and CN4GA), to 0.08 (SCS-CN) and 0.87 (CN4GA) for “class-II” events (again 3 events out of 13 for SCS-CN and 6 for CN4GA), and to 0.53 for SCS-CN “class-III” events (again 4 events out of 13), while for “class-III” events for CN4GA, there is only one rainfall event, so again no correlation has been possible. The last results confirm what was previously discussed for net rainfall peak intensities, i.e., an increase in the correlation coefficients when considering “class-I” events with respect to all the events considered

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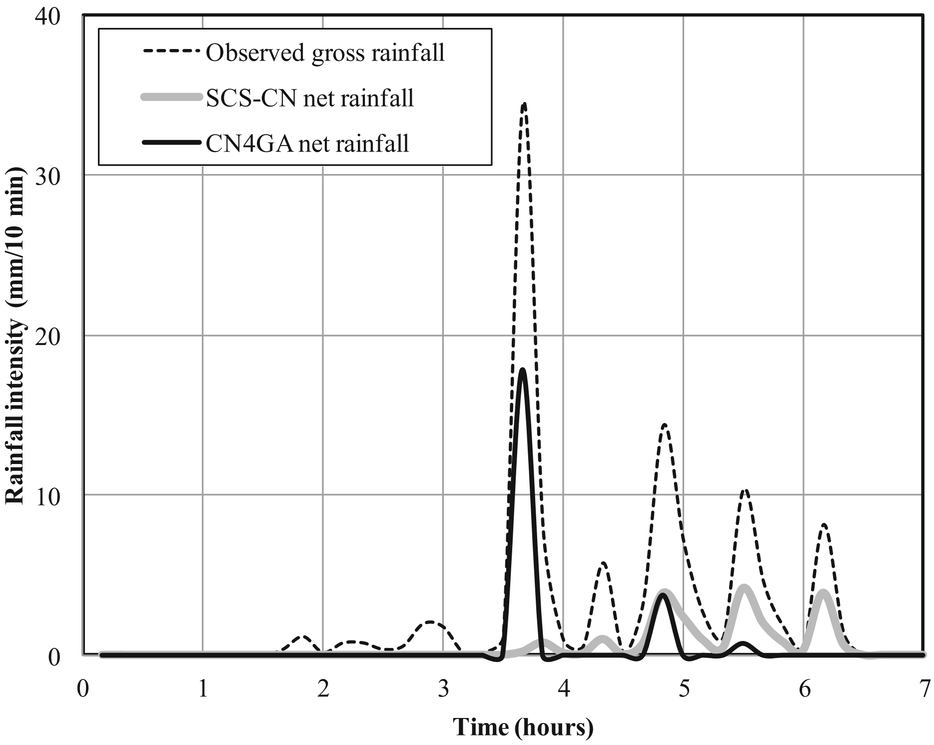

Fig. 5 Event no. 13: observed gross rainfall, SCS-CN and CN4GA modeled net rainfall

together. The high R^2 values obtained in the CN4GA application could be explained since CN4GA is able to reconstruct the main characteristics of the rainfall distribution (with particular regard to rainfall peaks) since it is essentially an infiltration model, a circumstance that the SCS-CN approach is not able to furnish because it is an empiric model not valid at sub-daily scale.

It is also noteworthy that R^2 strongly increases in the CN4GA modeled "class-II" events when passing from the correlation between phosphorus export and net rainfall to the corresponding one considering peak discharge (from 0.14 to 0.87). This result highlights the importance of a detailed modeling of the surface runoff movement, as in the case of the WFIUH formulation, able to consider channel and hill slope dynamics and to keep into account different velocities from cell to cell based on land cover and topography. A similar behavior is not found when applying the WFIUH framework to the net rainfall distribution modeled with the SCS-CN method: here, for "class-II" events, we observe a R^2 value of 0.12 when considering the modeled net rainfall peak intensity but only 0.08 when considering the modeled peak discharge. This unexpected result could be explained considering the limited number of available rainfall events, which is three for the SCS-CN approach and six for CN4GA. The described results highlight the importance of modeling phosphorus export considering physically based infiltration and runoff formation schemes, such as in the case of the Green-Ampt and the WFIUH formulations.

Table 5 Correlation coefficients (R^2) for the rainfall events, not classified and classified according Table 4: observed gross rainfall peak intensity (gross I_{max}), net rainfall peak intensity modeled with SCS-CN (SCS-CN I_{max}) and with CN4GA (CN4GA I_{max}), and peak discharge modeled with SCS-CN (SCS-CN Q_p) and with CN4GA (CN4GA Q_p)

R^2	Gross I_{max}	SCS-CN I_{max}	CN4GA I_{max}	SCS-CN Q_p	CN4GA Q_p
Not classified	0.31	0.36	0.55	0.42	0.63
Class-I	0.47	0.59	0.81	0.75	0.80
Class-II	0.01	0.12	0.14	0.08	0.87
Class-III	0.64	0.58	NA	0.53	NA

Conclusions

In the present manuscript, results from a long-term monitoring study in a small and agricultural basin in

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Central Italy are presented with the aim of linking phosphorus export and hydrological modeling. Phosphorus is one of the major non-point sources of water pollution resulting mainly from agricultural practices (also in consequence of land use/land cover changes), and the need for an easy method of quantifying the relationship between such pollution and hydrological variables is well known in literature. In the present work, two different methods (SCS-CN and CN4GA) for estimating net rainfall have been employed, the surface runoff was modeled according the WFIUH framework, and the discharge scenarios have been correlated to the phosphorus samplings from observed events. The results show that the correlation between phosphorus export and hydrological variables increases when passing from a consideration of gross precipitation to net precipitation and finally to discharge. The latter, topography-governed, variable seems to be the key variable in estimating phosphorous export, and hence, there is a need to model basin response to a given rainfall event accurately when dealing with land planning and water pollution estimation. This is confirmed by the fact that better correlations were found when employing the CN4GA method compared with the SCS-CN method, for all the investigated hydrological variables. It is well known, indeed, that the SCS-CN method is not applicable at sub-daily scale and that an infiltration model should be preferred, such as in the case of CN4GA, which is based on the Green-Ampt equation and is designed to be easily employed in particular for small and ungauged basins, where the modeler is often forced to apply empirical or semi-empirical models in order to avoid complex mathematical models requiring a great quantity of input data. Anyway, further research is needed and already ongoing, in particular considering a greater number of observed rainfall events, comparing different case studies, and considering also simple erosion models that could be integrated in the runoff formation mechanisms.

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