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Dynamics of surface water quality driven by distinct urbanization patterns and storms in a Portuguese peri-urban catchment

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Corresponding Author:	Carla Sofia Santos Ferreira, Ph.D Instituto Politecnico de Coimbra PORTUGAL
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Instituto Politecnico de Coimbra
Corresponding Author's Secondary Institution:	
First Author:	Carla Sofia Santos Ferreira, Ph.D
First Author Secondary Information:	
Order of Authors:	Carla Sofia Santos Ferreira, Ph.D
	Rory Peter Dominic Walsh
	Maria de Lourdes Costa
	Celeste Oliveira Alves Coelho
	António José Dinis Ferreira
Order of Authors Secondary Information:	
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Abstract:	Purpose: Although influences of urban land-use on water quality have been widely investigated, the impacts of different urbanization patterns, particularly in Mediterranean environments, are not well understood. Focussing on a Portuguese peri-urban catchment with 40% urban cover, this paper explores (i) the impact of areas with differing urban extent and storm drainage system on streamwater quality, and (ii) temporal variations driven by season and storm events of differing magnitude, intensity and antecedent weather. Materials and methods: Water quality was assessed at the catchment outlet (E) and for upstream tributaries: (1) Porto Bordalo (PB), 39% urban with a new major road and piping of some overland flow from impervious surfaces directly into the stream, (2) Espírito Santo (ES), 49% urban, mostly comprising detached houses surrounded by gardens, and with overland flow infiltrating into downslope pervious soils; and (iii) Quinta (Q), 22% urban with partial piping of overland flow from a recent enterprise park area. Water samples were collected at different stages in storm hydrograph responses to ten rainfall events in October 2011 to March 2013. Water quality variables analysed included chemical oxygen demand (COD), nutrients (kjeldahl nitrogen [Nk-N], ammonium [NH4-N], nitrate [NO3-N] and total dissolved phosphorus [TDP]) and heavy metals (zinc [Zn] and copper [Cu]). Results and discussion: Urban areas had great impact on COD, with highest median concentrations in ES and lowest in Q. In ES, fertilizing lawns and gardens may have been responsible for its higher median NO3-N concentrations. High concentrations of heavy metals were recorded in PB and Q, probably due to piping of road runoff directly

	into the stream. Generally, higher pollutant concentrations were recorded in the first storm events after the summer, due to flushing of accumulated solutes and a lower dilution effect, with Nk-N and NH4-N exceeding water quality standards. Over the wet season, increasing soil moisture favoured greater flow connectivity between runoff processes from pollutant sources and the stream network, leading to a higher proportion of samples exceeding pollution thresholds. Conclusions: No direct relationship was identified between urban extent and water quality, possibly due to the overriding impact of different storm drainage systems and flow connectivities of urban patterns. Hydrological regime, linked to seasonal changes, also exerted a major influence on water quality dynamics. Information on the spatiotemporal dynamics of pollutants, linked to different urban patterns and storm drainage systems, should help enable urban planners to minimize adverse impacts of urbanization on aquatic ecosystems.
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URBAN SOILS AND SEDIMENTS

Dynamics of surface water quality driven by distinct urbanization patterns and storms in a Portuguese peri-urban catchment

Carla Sofia Santos Ferreira[1,2] • Rory Peter Dominic Walsh[3] • Maria de Lourdes Costa[1] • Celeste Oliveira Alves Coelho[2] • António José Dinis Ferreira[1]

[1] Research Centre for Natural Resources, Environment and Society (CERNAS), College of Agriculture, Polytechnic Institute of Coimbra, Coimbra, Portugal

[2] Centre for Environment and Marine Studies (CESAM), Department of Environment and Planning, University of Aveiro, Aveiro, Portugal

[3] Department of Geography, College of Science, Swansea University, Swansea, United Kingdom

✉ Carla Sofia Santos Ferreira

carla.ssf@gmail.com, cferreira@esac.pt

Phone.: +351239802940, Fax: +351239802

Abstract

Purpose: Although influences of urban land-use on water quality have been widely investigated, the impacts of different urbanization patterns, particularly in Mediterranean environments, are not well understood. Focussing on a Portuguese peri-urban catchment with 40% urban cover, this paper explores (i) the impact of areas with differing urban extent and storm drainage system on streamwater quality, and (ii) temporal variations driven by season and storm events of differing magnitude, intensity and antecedent weather.

Materials and methods: Water quality was assessed at the catchment outlet (E) and for three upstream tributaries: (1) Porto Bordalo (PB), 39% urban with a new major road and piping of some overland flow from impervious surfaces directly into the stream, (2) Espírito Santo (ES), 49% urban, mostly comprising detached houses surrounded by gardens, and with overland flow infiltrating into downslope pervious soils; and (iii) Quinta (Q), 22% urban with partial piping of overland flow from a recent enterprise park area. Water samples were collected at different stages in storm hydrograph responses to ten rainfall events in October 2011 to March 2013. Water quality variables analysed included chemical oxygen demand (COD), nutrients (kjeldahl nitrogen [Nk-N], ammonium [NH_4-N], nitrate [NO_3-N] and total dissolved phosphorus [TDP]) and heavy metals (zinc [Zn] and co~~u~~pper [Cu]).

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Conclusions: No direct relationship was identified between urban extent and water quality, possibly due to the overriding impact of different storm drainage systems and flow connectivities of different urban patterns. Hydrological regime, linked to seasonal changes, also exerted a major influence on water quality dynamics. Information on the spatiotemporal dynamics of pollutants, linked to different urban patterns and storm drainage systems, should help enable urban planners to minimize adverse impacts of urbanization on aquatic ecosystems.

Keywords Flow connectivity • Heavy metals • Mediterranean climate • Storm events • Urban pattern • Urban water quality

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1 Introduction

Population growth ~~has been recorded~~is a worldwide phenomenon and ~~, but particularly~~ in the Mediterranean region population is likely to have more than doubled by ~~in~~ 2020 compared with 1960 (Zdruli 2014). The increase of population is ~~inevitably linked with~~generally accompanied by the loss of ~~natural areas~~forest and agricultural land to urban expansion, and ~~with~~ the integration of fragmented rural areas surrounding growing cities into the urban system (e.g. Binns et al. 2003). The abandonment of the mountains and u~~U~~rbanization process influences landscape characteristics, such as its structure, function and dynamics (Çakir et al. 2008; Keestra et al. 2009), leading to major ~~with several~~ environmental and water resources impacts (e.g. Alphan 2003), ~~namely on water resources,~~ including both hydrological processes (e.g. Shuster et al. 2005; Fletcher et al. 2013) and water quality (e.g. Tu 2011; Barco 2008).~~Urbanization can have serious environmental impacts, including on water resources. The replacement of natural areas by urban structures affects both hydrological processes (e.g. Shuster et al. 2005; Fletcher et al. 2013), and water quality (e.g. Tu 2011; Barco 2008).~~

Urban areas are typically associated with many pollutants, including heavy metals (e.g. cadmium [Cd], co~~u~~pper [Cu], chromium [Cr], iron [Fe]~~,~~ and zinc [Zn]) (e.g. Yu et al. 2014), organic compounds (e.g. ~~BOD~~biochemical oxygen demand, ammonium, polycyclic aromatic hydrocarbons, polichlorinated byphenils, oil and grease) (Gilbert and Clausen 2006; Dias-Ferreira et al. *~~this issue~~in press*), nutrients (e.g. nitrates, phosphates) (Lin et al. 2014), and faecal coliforms (Mallin and Wheeler 2000). These pollutants are mainly provided by (i) industrial activities (Yu et al. 2014) and vehicular traffic (e.g. Carey et al. 2013); (ii) wastewater contamination, including from septic tanks and sewage system leaks (Le Pape et al. 2013), diffuse sources, and treated and untreated effluent from wastewater treatment plants and storm sewer overflows (Yu et al. 2014); and (iii) lawns and gardens maintenance, due to inappropriate fertilization and irrigation activities (Lin et al. 2014).

Although the type of urban development (e.g. industrial, commercial, residential, and recreational) determines the nature of pollutants released (e.g. Tu 2011), urban runoff generally has been considered a major non-point source of pollutants within catchments (e.g. Yu et al. 2016). Direct relationships have been reported between pollutant concentrations and percentage urban surface~~s~~ (e.g. Sliva and Williams 2001), with for example total impervious area being considered an indicator of aquatic ecosystem conservation status (e.g. Rautengarten 2006; Kuusisto-Hjort and Hjort 2013).

Other authors, however, suggest that the location of pollutant sources within the catchment, and the distance to the stream network, are better indicators of water quality (e.g. Yu et al. 2016). Urban areas located downslope may provide runoff flowing into the stream network, whereas runoff from upslope areas may be infiltrated and~~/or~~ retained in downslope pervious soils (e.g. Ferreira et al. 2015), preventing pollutants from reaching aquatic ecosystems. In catchments comprising mosaics of urban and non-urban land-uses, typical of peri-urban catchments, the connectivity between runoff/pollutant sources and water resources can vary greatly and have been little researched to date, particularly in Mediterranean environmental settings. Furthermore, there is a general lack of studies exploring the dynamics of pollutant concentrations and fluxes in peri-urban catchments (Rodríguez-Blanco 2013).

In order to ~~fulfil~~address ~~some of~~ these research gaps, this study investigates the spatial and temporal dynamics of ~~surface~~aspects of stream-water chemistry in a peri-urban catchment in Portugal, and explores in particular the influence of landscape pattern on flow and pollutant connectivity in storm events at different seasons and following differing antecedent weather associated with ~~contrasting climate settings, determined by~~ the Mediterranean climate.

~~This~~ The study aims to assess the impact of different urban patterns, in forms of different impervious cover and spatial arrangement of pervious and impervious surfaces, on surface water quality and discharge chemistry dynamics in a typical Portuguese peri-urban catchment. The specific objectives are to (i) assess water quality differences between three sub-catchments with distinct urbanization patterns and the catchment outlet, as regards to pH, ~~and dissolved fractions of~~ chemical oxygen demand (COD), nutrients (kjeldahl nitrogen [Nk-N], ammonium [NH_4-N], nitrate [NO_3-N] and total dissolved phosphorus [TDP]~~nitrogen and phosphorous~~), heavy metals (Cu and Zn) and major cations (calcium [Ca], magnesium [Mg] and sodium [Na]); (ii) explore temporal variations in~~of~~ water quality between and within ~~driven by distinct~~ storm events at different times~~-over the~~ of year; ~~(iii) examine chemical loops during storm events;~~ and (iii~~v~~) investigate whether~~if~~ pollutant threshold levels~~s~~ (according to Portuguese water quality standards)~~concentrations~~ were exceeded~~attained~~ and under which weather conditions~~settings, according with Portuguese water quality standards~~. A better understanding of the impact of urban patterns on ~~annual~~ water quality~~,~~ should enable~~guide~~ urban planners to minimize adverse impacts of urbanization on stream ecosystems.

2 Study site description

The study was carried out in the small (6.2 km^2), peri-urban Ribeira dos Covões~~, a small (620 ha) peri-urban~~ catchment on the outskirts of the city of Coimbra in central Portugal (Fig.1).

The catchment is characterized by sandstones with Fluvisols and Podsols in west and limestone with Leptic Cambisols in the east (WRB 2006).

The climate is humid Mediterranean. The mean annual temperature is 15°C, ~~linked~~ with monthly means varying from ~~a minimum in January (~~10°C in January to~~) and~~ a maximum of ~~in August (~~22°C in August~~)~~. The mean annual rainfall at Coimbra-Bencanta is 906mm, with wet winters and long dry summers (just 7% of ~~the~~ rainfall between June and August) (INMG, 1971-2000). This temporal pattern causes a strong seasonal variation ~~o~~in streamflow, although the perennial flow at the outlet is supplied by several springs (mainly on sandstone). Annual runoff averages 135mm, ranging from 76mm in the hydrological year (October to September) 2011/12 to 200mm in 2012/13, with baseflow accounting for 33-37% of streamflow (Ferreira et al. ~~*this issue*~~*in press* a).

Catchment land-use comprises urban areas (40%) dispersed within woodland (56%) and agricultural land~~fields~~ (4%). The woodland is dominated by eucalyptus, but with some pine plantations and a relict oak stand. Agricultural land-use consists of a few olive plantations, pasture areas for cattle along part of the main stream, and small family farms with vegetables. Urban land-use mainly comprises residential areas, some small supermarkets and shops, educational and health services, including a central hospital, and a few facilities (garage shops, sawmill and a pharmaceutic factory~~industry~~). An enterprise park, covering 5% of the catchment area, is under construction in the headwaters in the extreme southwest of the catchment (clearly visible in Fig.1). A network of roads extends across the catchment and includes a recent motorway. Residential areas differ greatly in urbanization style, comprising (i) areas of single-family houses, surrounded by gardens, and (ii) recent row-houses and apartment blocks. These distinct residential areas house approximately 26,700 inhabitants, with population densities ranging from <25 inhabitants km^{-2} to >9900 inhabitants km^{-2} (Pato et al. 2015).

In the newer urban areas, of high population density, part of the runoff from impervious surfaces is collected in culverts and gutters and routed or piped direct to the stream network. In contrast, in urban settlements surrounded by gardens, agricultural and woodland soils, stormwater tends to ~~just~~ dissipate in ~~these~~ adjacent areas of high permeability.

Domestic effluent, however, is piped to a large, ~~and~~ modern wastewater treatment plant (WWTP), located outside the catchment. However, a small WWTP, installed in around 1985,~~about 30 years ago~~ served an upslope urban core in Quinta sub-catchment until 2012, but was very inefficient and ~~although great treatment inefficiency. E~~effluent from it was released into a downslope woodland area and into a tributary. In 2012 the wastewater was linked to the larger sewerage network and the small WWTP was disabled.

3 Methodology

3.1 Research design

The research design comprised monitoring variations~~changes~~ in water quality at four sites in the Ribeira dos Covões catchment in~~during~~ 10 storms, covering a range of rainstorm sizes and antecedent weather (and season), over the period October 2011 to March 2013.

~~Streamflow was sampled at four sites within Ribeira dos Covões catchment (Fig. 1): the~~The sites comprised the catchment outlet at ESAC (E)~~,~~ and ~~at~~ three upstream sites in sub-catchments of distinct urban cover and pattern (Table 1). These were: (i) Espírito Santo (ES), the most urbanized (49% urban) sub-catchment containing areas of high impervious cover in upslope sites and lower impervious cover (detached houses surrounded by gardens), mainly in downslope locations; (ii) Porto Bordalo (PB), with 39% urban cover extending over the sub-catchment in ~~a~~ strip fashion~~shape~~, with row-house areas upslope and detached houses with greater impervious cover or only small gardens downslope) and part of the motorway; and (iii) Quinta (Q), 22% urban, mainly in upslope locations, comprising a small residential area (4%) and the enterprise park under construction (18%). Differences between urban patterns also include dissimilarities in the storm drainage system: (i) in ES, overland flow from impervious surfaces is dissipated in ~~surrounding~~adjacent downslope pervious soils; (ii) in PB, storm runoff from upslope urban areas is diverted into pervious soils, whereas from downslope impervious surfaces it is piped into the stream tributary or nearby abandoned fields; and (iii) in Q runoff from the residential area dissipates in downslope ~~surrounding~~ woodland~~ areas~~, whereas runoff from impervious surfaces within the new enterprise park is piped into a detention basin, which delays its flow into the stream network. Additional differences are ~~also~~ linked to~~with~~ physical properties of the sub-catchments. In terms of lithology, ES and Q are sandstone sub-catchments and PB a limestone sub-catchment, with the entire catchment at E being 56% sandstone, 41% limestone and 3% alluvial (Table 1).

~~Several w~~Water samples were collected at intervals manually at each site during each of 10 storm events. Th~~e~~is was facilitated by the small size of the catchment~~,~~ ~~and~~ the proximity ~~between~~of sampling sites, the use of a ~~allowed quick~~ car ~~trips during the storms to take the samples. Whenever possible, samples were collected by more than one~~and multiple personnel. Selection of storm events was aided by use of ~~The S~~sampl~~ed~~ing ~~storms were selected~~ using~~based on~~ weather forecasts~~,~~ and focus on the first rainstorms after the summer (storms 1, 2 and 7) and on storm events of different magnitudes over the wet season, including autumn (storms 3, 4 and 5), winter (storms 8, 9 and 10) and spring (storm 6), in order to cover seasonal differences in response over the year~~provide annual differences~~.

3.2 Water sampling

Three to fifteen samples covering the rising limb, peak and falling limb of storm responses at the four sites were collected during each of 10 storm events, monitored between October 2011 and March 2013. Whenever possible, the first sample of the event was collected immediately before rainfall started, if stream was flowing, to provide preceding baseflow water quality. Storm events were assumed to have stopped when no rainfall was recorded for 6h. In total 76 samples were collected at E, 75 at PB, 56 at ES and 58 at Q. Samples were collected in acid-washed 250 mL glassware and 2 L polyethylene bottles, placed in a dark chilled cooler (~4°C) and taken to the laboratory.

Hydrological data of 5-minute resolution were~~as~~ provided by an existing network of flow gauging stations at each site and five rainfall gauges distributed across the catchment (Figure 1). The Thiessen Polygon method was used to calculate the weighted mean rainfall, assumed to be constant over the catchment.

3.2 Laboratory analysis

Water samples were immediately analysed for pH by electrometry (Hach, Sension Portable case). Sample aliquots were filtered through 0.45 µm membranes (Millipore MF) and stored for later chemical analyses: (i) aliquots for dissolved nitrite (NO_2-N) and nitrate (NO_3-N);

(ii) aliquots for dissolved chemical oxygen demand (COD), kjeldahl nitrogen (Nk-N), ammonium (NH_4-N) and total dissolved phosphorus (TDP) were acidified with sulphuric acid (pH <2); (iii) aliquots for dissolved ions [sodium (Na), calcium (Ca) and magnesium (Mg)] and heavy metal analyses [zinc (Zn) and copper (Cu)] were acidified with nitric acid (pH 2-3). All aliquot samples were stored surrounded by ice and defrozen at room temperature before analysis.

Nitrite and nitrate concentrations were measured simultaneously with an automated segmented flow analyser (SAN^{++} system), using the cadmium reduction method (Skalar method 461-322; Skalar, 2004a). Given the normally very low nitrite concentration in rivers the analytical results are examined only as NO_3-N. Ammonium concentration was also determined by an automated segmented flow analyser, but using a modified Berthelot reaction (Skalar method 155-316; Skalar, 2004b). Kjeldahl nitrogen, including organic nitrogen, ammonia and ammonium, was measured after sulphuric acid digestion with a selenium catalyser, followed by distillation and titration with hydrochloric acid (Standard Method 4500-Norg B; APHA 1998).

COD and TDP were analysed using a multiparameter water quality instrument (Hach DR 2000). COD was determined colorimetrically after acid digestion and oxidation with dichromate, in accordance with ISO 15705:2002 standards (HI 93754A vials, Hanna Instruments). TDP was quantified, after persulfate acid digestion, colorimetrically by reacting with molybdate ascorbic acid and antimony potassium tartrate, adapted from 4500-P Standard Methods (HI 93758A vials, Hanna Instruments).

Cation and heavy metal analyses were made after digestion with nitric acid (Standard Method 3030-E; APHA 1998), by atomic absorption spectrophotometry (Perkin Elmer AA300), with direct air-acetylene flame and hollow cathode lamps (Standard Method 3111-B; APHA 1998). ~~The d~~Detection limits for Zn and Cu were~~as~~ 0.05 mg L^{-1} and 0.01 mg L^{-1}, respectively. Reagent blanks and duplicate samples were used for quality control purposes and mean concentration values (repeated analysis of each sample) were used for data analysis.

3.3 Data analysis

The hydrological regime of the ten sampled storms was characterized in terms of rainfall and stream discharge. For each storm event, the rainfall amount, duration and intensity were~~as~~ calculated. Rainfall intensity was described in terms of the event mean (Imed), and the maximum in 60- minutes (I_{60}). Seven-day and 14-day antecedent precipitation (API_7 and API_{14}) for each storm event were calculated using weighted mean rainfall data. Streamflow parameters used included instantaneous discharge (at the time of water sampling) and event peak and mean discharges. Stormflow and baseflow components were separated for individual events, using a mathematical digital filter (Nathan and McMahon 1990). The storm runoff coefficient for each event was calculated as the ratio of total storm runoff (discharge normalized by area) divided by event rainfall. The time to peak was defined as the time from the centroid of the rainfall to~~and~~ peak flow (Lana-Renault et al. 2011).

Water quality values for the ten rainfall events were compared with Portuguese standards of minimum surface water quality ~~ pH: 5.0-9.0, Nk: 2.0 mg L^{-1}, NH_4-N: 1.0 mg L^{-1}, TDP: 1.0 mg L^{-1}, Zn: 0.5 mg L^{-1} and Cu: 0.1 mg L^{-1}~~ (DL236/98) ~~, synthetized in~~ (Table 2). Portuguese~~These~~ standards do not exist~~include~~ for the monitored parameters COD, NO_3-N and major cations (Na, Ca and Mg).

The ~~S~~statistical significance of differences in parameters between the four sites were investigated using the non-parametric Kruskal-Wallis test. Whenever significant spatial and/or temporal water quality differences were identified ($p<0.05$), they~~sre~~ were further investigated~~ion~~ using the post-hoc Fisher's Least Significant Difference test, at the 0.05 significance level. For each site, relationships between different water quality parameters, and between these parameters and streamflow properties, were explored using Spearman's rank correlation coefficient (r), at 0.05 and 0.01 significance levels. Data analysis was performed ~~in~~using IBM SPSS Statistics 22 software.

4 Results ~~and analysis~~

4.1 Storm characteristics and streamflow response to storm events

Rainfall characteristics for the 10 storms sampled between October 2011 and March 2013 are shown in Table ~~2~~3. Storm totals ranged from 2.4 mm (storm 6) to 46.8 mm (storm 10), which had a return period of less ~~and were linked to return intervals lower~~ than 2 years, ~~except~~ but the return period of the maximum hourly intensity for storm 3 (15.6 mm h^{-1}) was~~hich reached~~ 3 years.

Streamflow responses at the four monitored sites are summarized in Table ~~3~~4 and Figure 2. Storm 1, recorded at the end of summer (23-24/10/2011) was not enough to trigger discharge in ES and Q. For the 10 storms, the mean storm runoff coefficient at PB (6.1%) was twice as high as~~than~~ at E (3.0%) and Q (2.7%), and also greater than at ES (4.4%). In the monitored storms, baseflow comprised~~encompassed~~ 46%-87% of ~~the~~ event flows at~~in~~ E, 51%-85% at~~in~~ Q and 58%-94% ~~in~~at ES, whereas at~~in~~ PB it was 16%-55%. The catchment and sub-catchments have a flashy behaviour, with response times ranging from 5-35 min at~~in~~ PB, 10-40 min at~~in~~ ES, 10-65 min ~~in~~at Q and 25-85 min at~~in~~ E.

4.2 Water quality

4.2.1 Overview of water quality in the ten events at the four sites

Fig. 2 uses box plots to summarise water quality responses at each of the four sites to the ten rainstorms. The limestone PB sub-catchment showed significantly higher pH ($p<0.05$) than Q, ES and E, but median values over the 10 storms were 7.6, 7.4, 7.3 and 7.1, respectively, and thus~~all within the~~ slightly alkaline~~ range~~.

Significant differences in COD (dissolved phase) between sites were recorded ($p<0.05$), with lowest median concentration in the least urban Q (9.5 mg L^{-1}), intermediate values at PB (12.0 mg L^{-1}) and E (13.0 mg L^{-1}), and highest median COD in the most urbanized ES sub-catchment (17.8 mg L^{-1}) (Fig. 2). Ranges in values were substantial at all sites, with minima ~~at~~of 2.0 - 8.0 mg L^{-1} and maxima of 48.5 – 62.5 mg L^{-1} at E, PB and Q and 83.5 mg L^{-1} ~~in~~at ES.

Kjeldhal nitrogen in dissolved phase varied little between study sites, but was slightly higher at E (0.52 – 2.62 mg L^{-1}) and Q (0.50 – 2.83 mg L^{-1}), where cattle-rearing occurs in fields adjacent to the stream, than at ES (0.50 – 2.54 mg L^{-1}) and PB (0.47 – 2.54 mg L^{-1}) (Fig. 2). PB, however, ~~display~~experienced more than twice as many pollution occasions (12 values >2.0 mg L^{-1}, DL236/98) than the other sites (~~12 vs~~ 5 ~~in~~at E and Q and 4 ~~in~~at ES). Pollution thresholds ~~ant concentrations~~ were exceeded ~~reached~~ in storm 9 (winter) at all sites, in storms 7 (after summer) and 8 (winter) at E and PB, and storms 1 (after summer) and 5 (winter) at PB.

Similarly to Nk-N, slightly higher NH_4-N concentrations were recorded at E (0.04 - 1.63 mg L^{-1}) and Q (0.03 – 1.32 mg L^{-1}) than at PB (0.06 – 1.05 mg L^{-1}) and ES (0.02 – 0.91 mg L^{-1}) ($p>0.05$, Fig. 2). The water quality standard for NH_4-N (1.0 mg L^{-1}, DL236/98) was always complied with~~fulfilled~~ at ES, but exceeded~~surpassed~~ for 7, 3 and 1 samples collected at E, PB and Q, respectively. These pollution occasions were recorded during storms 7 (late summer) and 8 (winter) ~~in~~at E, and storm 1 (late summer, after a very dry period~~iest settings~~) ~~in~~at PB, as recorded for Nk-N, but in addition in storm 6 (spring) at PB and Q. ~~A r~~Relatively strong and statistically significant positive correlations were~~as~~ found between NH_4-N and Nk-N at E ($r=0.623$, $p<0.01$) and ES ($r=0.340$, $p<0.05$), but not at~~in~~ Q and PB ($p>0.05$).

Slightly lower NO_3–N concentrations were recorded at the least urbanized Q (0.04 – 3.47 mg L^{-1}) than at PB (0.04 – 7.90 mg L^{-1}), E (0.11 – 6.35 mg L^{-1}) and ES (0.29 – 5.24 mg L^{-1}) (Fig. 2). Correlations with COD, Nk-N and NO_3–N were weak albeit significant at all sites ($r<0.350$, $p<0.05$).

In contrast to nitrogen compounds, TDP varied significantly between sites ($p<0.05$), with median concentrations being greater at E and PB (0.07 mg L^{-1}) than at ES (0.06 mg L^{-1}) and Q (0.04 mg L^{-1}). Minimum~~a~~ concentrations were 0.01 mg L^{-1} at all sites, and maxima were ~~at~~ 0.39 mg L^{-1} at E, 0.25 mg L^{-1} at PB, 0.17 mg L^{-1} at ES and 0.14 mg L^{-1} at Q (Fig. 2). Phosphor~~o~~us was not a pollutant threat, ~~since~~as all values were far below the Portuguese water quality standard (1.0 mg L^{-1}). TDP was positively correlated with COD and Nk-N concentrations at~~in~~ PB ($r=0.459$ and 0.552, $p<0.05$). ~~In~~At ES and Q, TDP was only significantly correlated with Nk-N ($r=0.483$ and 0.467, $p<0.01$).

Water quality displayed differences in concentrations of major cations between monitoring sites ($p<0.05$)~~, distinct from previous chemical parameters~~ (Fig. 3). Sodium concentrations were significantly lower at PB (median ~~values of~~ 5.7 mg L^{-1}, ~~although~~ range~~ing from~~ 0.7 – 23.1 mg L^{-1}) than at ES (18.6 mg L^{-1}, 2.0 – 34.7 mg L^{-1}), E (14.7 mg L^{-1}, 1.3 – 29.3 mg L^{-1}) and Q (11.9 mg L^{-1}, 1.1 – 28.1 mg L^{-1}). Calcium concentrations were significantly higher at E (median 34.4 mg L^{-1}, 11.0 – 89.9 mg L^{-1}) and ES (30.9 mg L^{-1}, 18.4 – 49.9 mg L^{-1}) than at Q (22.6 mg L^{-1}, 10.0 – 36.4 mg L^{-1}) and PB (19.8 mg L^{-1}, 8.3 – 81.4 mg L^{-1}). Mg concentrations were higher ($p<0.05$) at ES (median 10.4 mg L^{-1}, 3.6 – 19.3 mg L^{-1}), than at E (6.9 mg L^{-1}, 0.8 – 18.6 mg L^{-1}), Q (3.3 mg L^{-1}, 1.3 – 7.0 mg L^{-1}) and PB (2.3 mg L^{-1}, 0.6 – 27.8 mg L^{-1}).

Sodium increased with increasing Mg, but with a stronger correlation~~s~~ at~~in~~ E (r=0.709, $p<0.01$) than at PB, ES and Q (r=0.569, 0.391 and 0.358, $p<0.01$). Sodium displayed significant positive correlations with Ca only at E and PB (r=0.464 and 0.423). Calcium and magnesium~~Mg~~ were strongly correlated with each other at all sites (r= 0.633 - 0.735, $p<0.01$)~~,~~ except ~~at~~ Q.

As regards ~~to~~ heavy metals, median dissolved Zn concentrations in~~over~~ the study storm events~~period~~ were slightly higher at PB (0.140 mg L^{-1}) ~~t~~than at Q, E and ES~~ (0.140 mg L^{-1},~~ (0.114 mg L^{-1}, 0.113 mg L^{-1} and 0.088 mg L^{-1}, respectively) (Fig. 3). ~~Highest c~~Concentrations exceeded Zn water quality standards (0.5 mg L^{-1}) in 7 samples at E (0.53 - 0.91 mg L^{-1}), 2 samples at PB (0.56 – 0.59 mg L^{-1}) and 2 samples at~~in~~ Q (0.52 - 0.60 mg L^{-1}), but none at ES (maximum only 0.40 mg L^{-1}). Pollutant levels~~concentrations~~ of Zn were attained after summer ~~in~~at E and PB (storm 7), but also during winter at~~in~~ PB (storm 8), E and Q (storm 9). A strong positive correlation was recorded between Zn and Nk-N concentrations at E (r=0.682, $p<0.01$), whereas at PB and Q, Zn correlated significantly with TDP (r=0.524 and 0.564, $p<0.01$). At ES and Q, Zn was significantly~~tatistically~~ correlated with both Nk-N and TDP (r=0.544 and 0.638, $p<0.01$).

Median copper~~Cu~~ concentrations for ~~over~~ the study storm events~~period~~ were slightly higher at Q than at PB, E and ES (0.033 mg L^{-1}, 0.030 mg L^{-1}, 0.029 mg L^{-1} and 0.028 mg L^{-1}) ($p>0.05$) (Fig. 3). Highest Cu concentrations were 0.200 mg L^{-1} at ES, 0.174 mg L^{-1} at E, 0.102 mg L^{-1} at PB and 0.094 mg L^{-1} at Q. Pollutant levels of Cu (>0.10 mg L^{-1}, DL236/98) were recorded~~ached~~ only for one sample at E and one sample at ES, during storms 9 and 10, respectively.

Copper~~u~~ and ~~Zinc~~ zinc were positively correlated with each other at~~in~~ all monitored sites (r ranged from 0.365 to 0.532, $p<0.05$). ~~In~~At ES and PB, Cu was significantly correlated with Nk-N ($r=0.481$ and 0.579, $p<0.01$) and NH_4-N ($r=0.481$ and 0.501, $p<0.01$). ~~In~~At Q, Cu only correlated significantly with Nk-N ($r=0.536$, $p<0.01$).

4.2.2 Between-storm variation over the study period

Between-storm differences in water quality response~~s~~ are apparent at the monitoring sites in Figures 2 and 3. Generally, COD and nutrients displayed higher concentrations in storms recorded in late summer (1, 2 and 7) ~~and~~with decreasing values over the wet season, achieving lowest concentrations in late winter (storms 5 and 10) (Fig. 2). Seasonal differences in COD were greater for PB than for Q, ES and E.

Nk-N concentration varied less with season, with median concentrations for late summer storms being less than twice as high than for late winter storms. Greater seasonal differences were recorded for NH_4-N concentrations, with storm medians being 3-4 times greater for late summer than late winter storms at ES, E and PB, but only 1.4 times as high at the least urbanized Q sub-catchment~~s~~.

As regards nitrates~~to~~ (NO_3–N), PB, Q and E displayed higher storm median concentrations in storms recorded after summer than in late winter (0.86 mg L^{-1} vs 0.42 mg L^{-1}; 0.50 mg L^{-1} vs 0.36 mg L^{-1} and 1.35 mg L^{-1} vs 1.01 mg L^{-1}, respectively), whereas ES displayed 3 times higher storm median concentrations in late winter than late summer storms (1.63 mg L^{-1} vs 0.86 mg L^{-1}).

TDP concentrations were twice higher in PB and E in late summer than late winter storms, but differences were much smaller at Q and ES. Lowest TDP concentrations were ~~measur~~recorded in storm 3, with the greatest rainfall intensity, and storm 4, with the wettest antecedent conditions (Table ~~2~~3).

In ~~C~~contrast~~ry to previous water quality parameters~~, major cations exhibited higher concentrations in wetter than drier settings (Fig. 3). Median Na concentrations measured during storms 6 and 10, with greatest antecedent rainfall in previous 7 days (42.5 mm and 47.3 mm) were 2.5-, 1.8-, 1.5- and 1.3- fold~~s~~ higher than during storms after the summer (storms 1, 2 and 7)~~,~~ for ES (26.3 mg L^{-1} vs 10.4 mg L^{-1}), Q (16.8 mg L^{-1} vs 9.2 mg L^{-1}), PB (9.5 mg L^{-1} vs 6.3 mg L^{-1}) and E (19.4 mg L^{-1} vs 14.4 mg L^{-1}), respectively. Similar patterns were found for Ca and ES, but no specific temporal pattern was recorded at E and Q.

The heavy metals Zn and Cu tended to show higher concentrations in late summer than late winter storms. Thus, median Zn concentrations were 2.5- in E (0.140 mg L^{-1} vs 0.055 mg L^{-1}), 2.2- in PB (0.222 mg L^{-1} vs 0.102 mg L^{-1}), 1.9- in Q (0.143 mg L^{-1} vs 0.074 mg L^{-1}) and 1.4-times higher (0.084 mg L^{-1} vs 0.058 mg L^{-1}) in ES during late summer (storms 1, 2 and 7) than late winter storms (5 and 10). Similar patterns were recorded for Cu. Some pollutant-level values of Zn and Cu were also recorded (see section 4.2.1).

4.2.3 Hydrochemistry dynamics during storms

Changes in water quality during a storm event showed distinct patterns during storms recorded after summer (storms 1, 2 and 7) than in~~remaining~~ storms later in the wet season. Given the extent of the dataset, this section focuses on intra-storm variation of three chemical parameters included in the Portuguese water quality standards: NH_4-N (which is strongly correlated with Nk-N at E and ES), Zn (which is strongly correlated with Cu) and TDP, for the late summer storm 7 and winter storm 9. Storm 7 was a multiple storm event with two peaks in rainfall five hours apart (Fig. 4). It also includes the first runoff recorded in ES and Q after the 2012 summer dry season. Storm 9 is a typical winter season event (Fig. 5).

NH_4-N storm dynamics

During storm 7 (Fig. 4), highest NH_4-N concentrations were recorded at baseflow (prior to rainfall) in E, and with the initial storm runoff in PB and Q, with concentrations then decreasing as discharge increased~~with increasing peak flow~~. After the first discharge peak, NH_4-N rose as discharge f~~a~~ell ~~in~~at E, whereas ~~in~~at PB it remained low. In Q, samples in storm 7 are too few to deduce the pattern, but in storm 2 (not shown) rose as discharge fall, as at E. Changes in NH_4-N concentration at ES were small, though the number of samples were few.

After an initial flush of higher concentrations in the rising limb of the hydrograph, NH_4-N concentrations~~ recorded~~ in the winter storm 9 ~~show~~varied ~~an~~ inversely~~ pattern to~~ with streamflow (Fig. 5). ~~, with an initial flush of higher concentrations in the rising limb of the hydrograph, before decreasing with peak discharge and increasing again over the falling limb of the hydrograph. Nevertheless, p~~ Whereas peak concentrations ~~in~~at E and PB were reached during the initial storm runoff, ~~whereas in~~at ES and Q they were attained in the falling limb.

~~In~~At E, however, a clear difference between both storms was noticed at pre-storm baseflow, with high and low concentrations ~~in~~prior to the late summer and winter storms, respectively. Similar patterns to NH_4-N were in general recorded for Nk-N (not shown), in storms 7 and 9.

TDP storm dynamics

TDP concentrations, albeit never exceeding Portuguese national guidelines, changed within storms differently from NH_4-N and Nk-N concentrations. In storm 7 (Fig. 4), TDP was low at baseflow in E and increased progressively over the first storm peak, attaining highest concentrations on the falling limb, before a sharp fall. Nevertheless, with rainfall restart during storm 7, TDP concentration tended to follow discharge, with a peak at peakflow, followed by a progressive decline to pre-event level on the falling limb of the hydrograph. In ES, however, TDP concentration increased on the rising limb to a peak at peak flow~~.~~, before declining ~~After the peak, TDP concentration first decreased~~ as discharge f~~a~~ell. There were too few samples to define patterns during the second peak. ~~On the other hand~~In contrast, at PB and Q, peak TDP concentrations were recorded on the initial rising limb, with lowest concentrations at peak flow. After rainfall restart during storm 7, TDP concentrations at PB followed discharge variation, with values in late falling limb lower than those recorded in the second rising limb and peak flow.

In winter storm 9 (Fig. 5), ~~at~~ E and PB experienced a marked peak in TDP in the rising limb before falling to low values at peak flow and in the falling limb. At ES, however, peak TDP was recorded after peak discharge and TDP values throughout the storm hydrograph were higher ~~at post~~ than at pre-storm baseflow. At PB, high TDP concentration was also recorded by the end of the falling limb.

Dissolved Zn storm dynamics

~~Regarding to Zn, h~~High-magnitude and distinct temporal changes in dissolved zinc were recorded in the late summer storm (Fig. 4). Generally, Zn concentrations were low at pre-storm baseflow and reached multiple peaks at peak flow and during the falling limb. Only at Q were Zn concentrations higher during the rising limb. In the wet season storm (Fig. 5), Zn displayed massive peaks at E and Q, both in the rising and again in the falling limb of the hydrograph, but only in the rising limb at PB. Changes were more muted at ES, with peak concentration recorded at peak discharge.

Although Cu concentrations followed similar intra-storm variation as Zn, pollutant levels were only recorded in winter storms (Fig. 3), also after peak discharge.

5 Discussion

5.1 Differences in hydrological responses between sites

Before discussing the water quality results, differences in hydrological response between the sub-catchments are explained. Urbanization and the associated increase in impervious surfaces have been widely reported to enhance runoff (e.g. Zhang and Shuster 2014; Yao et al. 2015). Nevertheless, for the 10 storms studied, the storm runoff coefficient in the 40% urbanized Ribeira dos Covões catchment ranged only between 1.6% and 5.5%. In part this reflects the high permeability of the catchment provided by the sandstone and limestone bedrock (Ferreira et al. *this issue* a).

Within the study catchment, PB (39% urban area and 15% impervious) displayed both the greatest storm runoff coefficients (2.5% - 11.8%) and quickest response times (5-35 minutes). In contrast, the more highly urbanized ES sub-catchment (49% urban, 27% impervious) experienced lower storm runoff coefficients (2.4% to 6.7%) and slightly higher response times (10-40 minutes). This is thought to be a consequence of distinct drainage systems. In PB, part of the runoff from downslope impervious surfaces is directly piped into the stream, leading to enhanced connectivity between overland flow sources and the stream network. In ES, however, runoff from paved surfaces is mostly diverted into pervious soils, and/or piped into downslope woodland areas, favouring water retention and infiltration, hence reducing the storm runoff response of the stream.

Such an explanation would conform to findings of previous studies highlighting the significance of storm drainage systems (not simply % of impervious area) enhancing flashiness of storm runoff (e.g. Yang et al. 2011, Miller et al. 2014) and much reduced effects of impervious surfaces when not connecting to a storm sewer system (e.g. Hammer 1972).

In Q sub-catchment, containing the largest woodland area (73%) and the smallest impervious ~~are~~ cover (5%), storm runoff coefficients were the lowest (0.8% - 4.9%). ~~This findings are in accord~~s~~ance with previous studies reporting lower runoff in forested than agriculture and urban catchments, due to higher transpiration and interception losses (e.g. Wang et al. 2013).~~ Storm runoff coefficients in Q, however, were only a little lower than in ES, possibly because overland flow from paved surfaces in the enterprise park, located within Q, is piped into a detention basin and then released direct into the stream network, rather than being directed~~ly~~

into pervious soils as within ES. Contrary to the typical flashy hydrographs with greater peak flows found in highly urbanized areas (e.g. Vidon et al. 2009), ES displayed longer-duration hydrographs, sometimes without a clear peak flow (Figs. 4 and 5), in contrast to the quicker response times of Q, even in small events (Table ~~3~~4).

That higher storm runoff coefficients for Q were found in storms following driest antecedent weather conditions may indicate that normally pervious soil is also providing overland flow, because of the low infiltration capacity induced by water repellency, particularly given the 73% extent of woodland~~ areas~~ in the catchment (e.g. Ferreira et al. 2016).

Differences in hydrological response between monitoring sites in Ribeira dos Covões may also reflect differences~~similarities~~ in lithology. In PB, underlain by~~overlaying~~ limestone, baseflow represented~~s less than~~ 16-55% of event runoff, whereas in ES and Q, the sandstone sub-catchments, it is ~~greater than 55~~58-~~-~~94% and 49-85% respectively (Table ~~3~~4).

5.2 Influence of urban pattern on water quality

The Ribeira dos Covões results suggest that areas with different urbanization pattern have distinct impacts on surface water quality, particularly in terms of COD, TDP, major cations and pH ($p<0.05$). Nitrogen (Nk-N, NH_4-N and NO_3-N) and heavy metals (Zn and Cu), however, did not show significant differences between sites over the study period ($p>0.05$), but nevertheless at least~~achieved~~ occasionally exceeded water quality standards ~~pollutant concentrations in~~at the four monitoring sites.

5.2.1 Chemical oxygen demand and nitrates

The ES sub-catchment, with largest urban land-use (49%) and imperviousness, displayed higher concentrations of COD and NO_3-N (median values of 18.0 mg L^{-1} and 1.46 mg L^{-1}) than E, PB and Q (Fig. 2), with ~~displaying decreased~~ concentrations increasing with percentage~~according with the extent of~~ impervious surface~~s~~ (Table 1). Enhanced COD and NO_3-N values elsewhere are usually attributed to wastewater contamination (e.g. Wilbers et al. 2014). However, given the separate sewage and storm runoff drainage systems in Ribeira dos Covões, as well as the location of the WWTP outside the catchment, treated~~ment plant~~ effluent would not seem to be a major pollutant source. COD and NO_3-N can be provided by diffuse sewage sources and ~~have also been found in~~ road runoff, which can be an important pollutant source due to the high runoff volumes that can be involved (e.g. Crabtree et al. 2006; Pereira et al. 2015). Both these sources may be significant in the Ribeira dos Covões catchment.

NO_3-N is the dominant nitrogen form in ES (median values of ~~1.22 mg L^{-1} and~~ 1.46 mg L^{-1}~~, respectively~~), and may be linked with use of fertilizer in the mainly detached houses with gardens and lawns, covering 15% of the urban pattern of ES (Table 1), as found in such detached house areas elsewhere (e.g. Lin et al. 2014; Carey et al. 2013). Some of the NO_3-N in ES may also have derived from the small agricultural area~~ of agricultural fields~~ adjacent to the stream channel. Fertilizer application in both urban and agricultural areas is usually carried out during spring and summer, which may in part explain the high concentrations of NO_3-N recorded during storms in late summer (Fig. 2).

5.2.2 Kjeldhal nitrogen and ammonium

Higher concentrations of Nk-N and NH_4-N were recorded at the catchment outlet at E and at Q, which has ~~i~~the lowest urban land-use (22%), than at ES and PB. ~~In~~At both E and Q sites, organic compounds were the dominant form of nitrogen, given the relatively low NO_3-N concentrations (median values of 1.01 mg L^{-1} and 0.35 mg L^{-1}) and the small percentage of NH_4-N in relation to Nk-N (34% and 25%, respectively). Extensive cattle rearing in ~~the~~ agricultural fields in~~located~~ upslope and channel-margin locations in E and Q ~~sampling sites, and surrounding water channel~~, is thought to be a major source of Nk-N and NH_4-N, and may explain why~~ the~~ ~~pollutant~~ concentrations~~ measured~~ often exceeded pollution guidelines (maxima~~um concentrations~~ of 1.87 mg L^{-1} ~~of~~ Nk-N and 1.32 mg L^{-1} ~~of~~ NH_4-N, Fig. 2)~~ often exceeded pollution guidelines~~.

An ~~A~~additional Nk-N and NH_4-N source~~s~~ may ~~arise~~ occasionally be~~from~~ untreated domestic wastewater. Contamination by leaks in the sewage drainage system~~,~~ was observed occasionally~~,~~ through the colour and smell of surface water. Sewage leaks, however, are prone to influence water quality in all the study sites. In Q sub-catchment, past soil contamination from the abandoned WWTP, which received domestic wastewater from upslope urban cores and spread it downstream without treatment until ~~few years ago~~2012, may also be a potential source of Nk-N and NH_4-N~~ concentrations~~. These soil contamination sources may explain why~~ the~~ pollution~~ant~~ levels~~concentrations~~ were exceeded~~ reached~~ only in late winter storms (Fig. 2), because of greater connectivity with stream network, favoured by ~~increasing~~the higher soil moisture content at that time. Great concentrations of NH_4-N can be toxic to aquatic organisms (e.g. Lin et al. 2014).

5.2.3 Total dissolved phosphorus

Highest~~r~~ concentrations of TDP were found at~~in~~ E and PB (median values of 0.07 mg L^{-1} at~~in~~ both sites, $p<0.05$). Phosphorus in urban areas is usually associated with household sources, such as laundry and dishwasher detergents, as well as organic matter biodegradation in domestic wastewater (e.g. Carey et al. 2013), but it can also derive from garden fertilizers. Apart from sewage leaks already discussed, pavement and car washes were often~~usually~~ observed within PB, which forms an~~located~~ upstream part of E. In PB, high concentrations of TDP could possibly~~may~~ also be ~~also~~ associated with ~~soil properties, given~~ the clay content ~~nature~~ of the limestone soils. ~~I~~Tus, in Xujiawan catchment, Southwest China, phosphorus enters the runoff and open water bodies mainly through transport in the~~with~~ clay and fine silt fractions (Yang et al. 2009).

Although TDP concentrations never exceeded~~were always below~~ the Portuguese water quality standard (1 mg L^{-1}), all ~~the~~ sites recorded~~attained~~ concentrations above the 0.1 mg L^{-1} established as the critical phosphorus level in runoff for eutrophication (US EPA 1986). This critical level was surpassed in 32% of the samples collected in PB, 21% in E, 7% in ES but only 3% in the least urbanized Q sub-catchment which is 73% woodland (maximum concentrations of 0.25 mg L^{-1}, 0.39 mg L^{-1}, 0.17 mg L^{-1} and 0.14 mg L^{-1}, respectively).

5.2.4 Heavy metals

Although draining the smallest urban cover, Q displayed higher median concentrations of Cu and Zn (0.03 mg L^{-1} and 0.11 mg L^{-1}), similar to PB covered by 39% urban area (0.03 mg L^{-1} and 0.14 mg L^{-1}, respectively). Heavy metals are typically associated with vehicular traffic and road runoff in urban situations (e.g. Crabtree et al. 2006; Herrera 2007). ~~, Ferreira et al. *this issuein press* b).~~ In Ribeira dos Covões catchment, a complementary study ~~also~~

~~investigated~~of heavy metals~~ concentrations~~ in runoff collected~~ in~~ from four ~~distinct~~ roads provided direct evidence of the capacity of road runoff to generate heavy metal pollution in the catchment (Ferreira et al. *in press* b). Although heavy metal concentrations varied through~~were variable over the~~ time, ~~-~~they~~and~~ displayed a direct relationship with vehicular traffic intensity, with dissolved ~~concentrations of~~ Cu and Zn recording maxima~~attained~~ of 0.2 mg L^{-1} and 0.5 mg L^{-1}~~.~~, respectively. Nevertheless, heavy metals in road runoff were mostly in particulate form,~~ since~~ as total concentrations of Cu and Zn reached 0.7 mg L^{-1} and 5.0 mg L^{-1}, respectively. ~~These results highlight the capacity of road runoff to threat surface water quality within the study site.~~

The ~~H~~higher concentrations recorded at~~in~~ Q probably result from road runoff from the enterprise park area being piped directly to the detention basin and diverted into the stream network, i.e. high connectivity between source and stream network. In PB, road runoff, particularly from the major national road. is in part~~ially~~ piped to fields adjacent to~~nearby~~ the stream, ~~particularly from the major national road. Increasing~~ Higher moisture content in soils receiving road runoff (as in prolonged wet weather) may favour ~~the~~ connectivity with the stream network, and been responsible for ~~led toto~~ the occasional pollutant concentrations that were recorded (maximum Zn of 0.59 mg L^{-1} and Cu of 0.10 mg L^{-1}) (Fig. 3).

ES, despite draining the largest impervious cover (27%), recorded lower Zn and Cu concentrations (Fig. 3), possibly because road runoff is diverted into pervious soils, located at a greater distance ~~o~~from the stream network than at PB. These contrasts highlight the importance of variations in~~the~~ stormwater drainage system characteristics ~~and those variations~~ in controlling urban runoff quantity and quality, rather than~~not~~ simply % urbanization, as found also to be the case in Tucson, Arizona (Gallo et al. 2013).

5.2.5 Major cations and pH

~~Despite~~Although not included in Portuguese water quality standards, major cation~~s~~ concentrations (Na, Ca and Mg), do not constitute~~seem to represent~~ a ~~major~~ water quality problem. These solutes are usually associated with rock composition, explaining the significant positive correlations with baseflow ($p<0.05$). In Ribeira dos Covões, Ca and Mg concentrations (Fig. 3) were in accordance with those found in streamwater of forest catchments at Colorado, overlaying sedimentary rocks including, among others, sandstone and limestone. In these Colorado catchments, Miller (2002) reported Ca, Mg and Na concentrations ranging from 41 mg L^{-1} to 101 mg L^{-1}, 3 mg L^{-1} to 25 mg L^{-1} and 1 mg L^{-1} to 5 mg L^{-1}, respectively. The ~~L~~lower concentrations of Na, Ca and Mg recorded~~measured~~ in PB, despite its~~overlaying~~ limestone lithology, ~~however,~~ may be associated with its lower baseflow fraction~~s~~ (Table ~~3~~4). Higher Na concentrations than those reported by Miller (2002) may be linked to~~with~~ higher evapotranspiration. The limestone lithology of PB~~Bedrock differences~~ may ~~also~~ explain its highest pH ~~in PB~~ (median of 7.6, $p<0.05$).

5.3 Temporal dynamics in water quality parameters

Streamwater quality varied considerably seasonally and within storm events. Several factors of the hydrological regime can affect temporal dynamics including storm and antecedent rainfall characteristics, stream discharge, the proportions of baseflow and storm runoff, and flow connectivity between source areas and the stream (e.g. Yang et al. 2009; Zhao et al. 2015).

COD, nutrients (Nk-N, NH_4-N, NO_3-N and TDP) and heavy metals (Zn and Cu) displayed higher median concentrations in storms recorded in late summer than in the wet season~~s~~ (Figures 2 and 3), possibly due to two mechanisms: (i) pollutant accumulation ~~during dry periods~~ and subsequent flushing during the first rainfall events after long dry periods~~settings~~, although no statistically significant correlations with antecedent rainfall were identified ($p>0.05$); and (ii) decreased dilution effect provided by (a) lower summer baseflow component, which is typically associated with~~to~~ better water quality than surface water (e.g. Carey et al. 2013); and (b) lower storm runoff volume.

During dry conditions ~~S~~solutes precipitate~~deposited during dry conditions~~ and accumulate~~d~~ within ~~the~~ catchment and sub-catchment soils due to water table drawdown and reduced soil water content, leading to restrictions on biogeochemical activity. Accumulated solutes are than available for mobilization during rainfall and subsequent runoff (Vidon et al. 2009; Gallo et al. 2013). The flushing process recorded in late summer led to higher NH_4-N and Nk-N during the rising limb of the hydrograph in E, PB and Q (Fig. 4), exceeding on a~~in~~ few occasions the water quality standards. Higher NO_3-N concentrations in late summer than wet season storms may be also a consequence of their greater availability ~~associated~~ with crop and garden fertilizer application in spring and early summer, in association with ~~-~~Portuguese Mediterranean climatic setting. The first flush effect ~~on higher concentrations~~ after extended dry periods have been also reported in urban settings by previous authors (e.g. Barco et al. 2008).

Phosphorus and heavy metals (Zn and Cu), however, seem to be less easily mobilized than NH_4-N and Nk-N, as~~since~~ peak concentrations were reached after peak flows (Fig. 4). Peak concentrations of Zn, in a few cases exceeded water quality standards in PB and E (maxima~~um~~ of 0.59 mg L^{-1} and 0.55 mg L^{-1}, respectively). The later timing of peak concentrations of TDP, Zn and Cu can be possibly associated with soil absorption capacity and the difficulty to be detached/dissolved and transported by overland flow, as noted by Yang et al. (2009). The delayed peak in Zn and and Cu also suggests that soil sources adjacent to roads and development of connectivity between roads, soil and the stream network are of greater significance than simply quick runoff from the roads.

In PB, overland flow from paved surfaces seems to be the major runoff and pollutant source, explaining quicker runoff and solute responses than at the other monitoring sites (Fig. 4). Although in Q there is also ~~a~~ partial piping of overland flow from paved surfaces, solute transport may have been delayed by the detention basin.

The overall higher COD and nutrient concentrations in late summer storms are also thought to be a consequence of lower dilution by reduced summer baseflows (Table ~~3~~4),~~. Lower baseflow provide minor dilution of solutes washed-off by stormflow,~~ as recorded elsewhere by Wilbers et al. (2014). This is supported~~corroborated~~ by the negative correlations found between all nutrient concentrations and baseflow ($p<0.05$), at most of the sites. In E, however, peak concentrations of NH_4-N and Nk-N were measured under baseflow conditions, before rainfall start, and recession limb, with few samples exceeding water quality standards. This highlights a combination of possible contamination from baseflow and ~~, thus, a~~ potential dilution by cleaner~~from~~ stormflow. This ~~D~~dilution effect provided by stormflow is also noticeable~~d~~ in NH_4-N and Nk-N responses~~loops~~, that show~~linked with~~ decreasing concentrations with increasing runoff volume (Fig. 4).

In ES, however, increasing runoff volume during storms observed in late summer does not seem to have an important diluting influence~~role~~ on nutrient~~s~~ concentrations~~.~~, as ~~In turn,~~ NH_4-N, Nk-N and TDP concentrations increased with discharge ~~followed discharge tendency~~ and attained highest values~~concentrations~~ at~~with~~ peak flow. These distinct solute responses~~loops~~ compared with those at~~from~~ other monitored sites may be linked to the greatest storm runoff coefficients of ES (Table ~~3~~4). Stormflow, however, only showed a statistically significant positive correlation with NH_4-N concentration~~s~~ ($p<0.05$).

~~In~~At E and ES, higher concentrations of Nk-N and NH_4-N were recorded on the recession limb than at the beginning of late summer storms. In E and PB in the summer storms (Fig. 4) and in E and Q in the winter storm (Fig. 5) Zn concentration showed marked peaks both on the rising limb and the recession limb. This may indicate that lateral movement of Zn (and Cu, which behaved similarly), Nk-N and NH_4-N in soil by slower throughflow may be providing the delayed second peak, whereas~~to add to~~ the smaller initial peak derives from flushing by overland flow and road runoff.~~, as reported elsewhere by Yang et al. (2009).~~

Over the course of the wet season, repeated storm events appear to have led to progressive exhaustion of COD, nutrient and heavy metal sources, evidenced by much lower concentrations in late winter than in summer storms (Figures 2 and 3), as reported in other catchments with a Mediterranean climate (e.g. Bowes et al. 2009; Siwek et al. 2012).

During winter storms, Nk-N, NH_4-N and TDP exhibited similar responses~~loops~~ to those experienced in late-summer storms, namely increased concentrations during the rising limb, lower values at peak flow and increasing concentrations over the falling limb of the hydrograph. In PB, concentrations of NH_4-N, Nk-N, Zn and Cu during the falling limb were usually lower than at the beginning of storm runoff.

High concentrations of nutrients (Nk-N, NH_4-N, NO_3-N and TDP) and heavy metals (Zn and Cu) during winter storms may be a result of greater flow connectivity between solute sources and the stream network (rather than just the arrival of slower throughflow, as suggested earlier). Thus, ~~I~~in E~~,~~ ~~a larger number of samples displayed~~ Zn exceeded pollution levels~~ant concentrations~~ more frequently in ~~during~~ winter than in late-~~–~~summer storms. In Q, Zn concentrations only exceeded water quality standards in winter storms (Fig. 3). The increased flow connectivity resulted from increasing soil moisture over the wet season in the catchment leading to decreasing infiltration and surface water retention capacity (Ferreira et al. 2015), thus favouring runoff and solute transfer into downslope areas.

In ES, highest NH_4-N, Nk-N and Cu concentrations measured during the falling limb of winter storms (sometimes exceeding water quality standards) (Fig. 5), may be provided by upslope urban areas lacking a storm drainage system. In E and Q, higher NH_4-N and Nk-N also reached pollutant concentrations in the falling limbs of a few winter storms (Fig. 2) and pollutant concentrations of Zn were reached in Q only during winter storms (Fig. 3). The increased concentrations of these nitrogen forms and heavy metals in Q over the wet season, may partly result from possible leaching of soils polluted by the abandoned WWTP.

6 Conclusions

The results of this study of the small, peri-urban Ribeira dos Covões catchment in central Portugal, suggest that (i) storm rainfall, antecedent rainfall and seasonal Mediterranean rainfall regime and (ii) urbanization pattern, notably the extent, location and degree of continuity of impervious surfaces and type of storm drainage system, together largely determine ~~runoff response and~~ temporal dynamics of pollutant and solutes ~~dynamics~~~~transport~~ during storm events via their influences on runoff responses, thereby, influencing catchment water quality and aquatic ecosystem sustainability.

Significant increases in COD and TDP with increasing urban area of the monitored catchment and sub-catchments were recorded. The Quinta (Q) sub-catchment, with lowest urban cover (22%) and largest woodland (73%), displayed lowest COD concentrations than the other more urbanized (39-49%) catchments. Together with Espírito Santo (ES), this sub-catchment also showed lower TDP concentrations than recorded~~measured in~~ at the catchment outlet (E) and at Porto Bordalo (PB). ES, however, drains the largest urban area (49%) and impervious cover (27%), but the upslope location of most impervious surfaces and the dispersion of overland flow in downslope pervious soils (in woodland and agricultural fields) minimize~~s~~ the potential impacts on streamflow. Nevertheless, the ES urban pattern, characterized mainly by detached houses surrounded by green spaces, may have led to higher NO_3-N concentrations than in the other sites, due to high applications of fertilizer to lawns and gardens.

The sub-catchments (PB and Q) with ~~U~~urban areas characterized by storm drainage systems connecting road runoff directly to the stream network~~ (PB and Q)~~, displayed higher concentrations of heavy metals (Zn and Cu), typically associated with vehicular traffic. Hence ~~High~~greater connectivity between the stream network and surrounding land-use may be also an important parameter affecting water quality. Thus, in E and Q, higher Nk-N and

NH_4-N concentrations are thought to result from ~~be a consequence of extensive~~ cattle-rearing in agricultural fields adjacent to their stream networks.

Generally, median concentrations of COD, nutrient parameters and heavy metals were greater in late summer than winter storms. This pattern was attributed to (i) the accumulation of pollutant sources~~lutes~~ ~~on and~~ in surface soil and on roads ~~in the surface~~ during prolonged dry periods and ~~the~~ subsequent flushing during the first rainfall and runoff events, and (ii) the lower dilution effect provided by low summer baseflow~~streamflow~~. These mechanisms led to concentrations of Nk-N and NH_4-N exceeding pollution thresholds in some~~a few~~ samples at all the monitored sites, mostly in the rising limb of the hydrograph in late summer storm events.

Storm events over the wet season, however, led to increasing soil moisture ~~contents~~ that enhanced the connectivity between pollutant sources, runoff processes and the stream network. Greater wet-season connectivity may explain pollutant levels~~concentrations~~ of Zn attained in PB and Q, mostly during the falling limb of the hydrograph, as well as pollutant concentrations of Cu in ES and E.

Intra- and inter-storm variations over the study period demonstrate that solute (including pollutant) transport in an urban Mediterranean environment may not be effectively predicted using simple relationships with hydrological conditions or rainfall. This study has demonstrated that a~~A~~ larger storm event dataset, covering all seasons and a range of storm sizes and antecedent weather, is needed to understand the impact of different urban patterns, and complex land-use mosaics in peri-urban areas, on hydrochemical response of the catchment and its sub-catchments to storm events. This study, however, covered only selected pollutant and solute parameters; in particular, additional monitoring of dissolved oxygen and microbial contamination parameters should be added to give a fuller picture of the impact of urban activities.

Understanding the impact of urbanization pattern and storm drainage systems on hydrochemical dynamics is both relevant and crucial to help~~guide~~ policymakers~~decision-makers and policy actors~~ design and~~to~~ implement the most appropriate~~suitable~~ solutions to achieve good water quality and preserve aquatic ecosystems. Pollution control policies should include urban planning and be adjusted to fit changes over space and time, focusing on (1) pollutant flushing in late-summer storms and (2) increasing flow connectivity through the wet season. Upslope urban cores and dispersed urban patterns should favour runoff dispersion in downslope pervious soils. This will favour not only overland flow retention and infiltration but also prevent~~ing~~ pollutants from reaching the stream channel.

Acknowledgements This research was carried out as part of (1) research fellowship SFRH/BD/64493/2009, funded by FCT, under QREN – POPH and co-funded by ESF and MEC national funds, and (2) research project PTDC/AUR-URB/123089/2010, funded by FCT, COMPETE and European Regional Development Fund. The authors would like to acknowledge Daniel Soares and Célia Bento for water sampling assistance, and Alécia Branco, María Fernandez and Romina Baston for their support on laboratorial work.

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Tables

Table 1 – Catchment and sub-catchment characteristics: land-use/cover, mean slope and lithology. Within urban areas, impervious surfaces comprise roads and buildings;~~,~~ semi-pervious surfaces include ~~involves~~ construction sites, parking zones, courtyards and ~~sidewalks~~pavements;~~,~~ and pervious surfaces ~~encompasses~~ comprise gardens.

	ESAC (outlet) - E	Porto Bordalo - PB	Espírito Santo - ES	Quinta - Q
Area (ha)	620	113	56	150
Mean slope (°)	10	12	8	4
Land-use / Land cover (%)				
Urban	40	39	49	22
Impervious	*17*	*15*	*27*	*5*
Semi-pervious	*11*	*9*	*7*	*10*
Pervious	*12*	*15*	*15*	*7*
Woodland	56	57	46	73
Agriculture	4	4	5	5
Lithology (%)				
Sandstone	56	2	98	100
Limestone	41	98	0	0
Alluvial	3	0	2	0

Table 2 – Portuguese standards for minimum surface water quality (DL236/98), re~~garding~~lating to chemical parameters measured in the current study.

pH	N_K-N	NH_4-N	TDP	Zn	Cu
	($mg\ L^{-1}$)				
5.0-9.0	2.0	1.0	1.0	0.5	0.1

Table ~~2~~ 3 – Rainfall characteristics for the 10 storm events monitored (Imean: mean intensity, I_{60}: maximum hourly rainfall intensity, API_7: 7-day antecedent rainfall, and AP_{14}: 14-day antecedent rainfall).

Storm	Date	Rainfall (mm)	Duration (h)	I_{mean} (mm h^{-1})	I_{60} (mm h^{-1})	API_7 (mm)	API_{14} (mm)
1*	23-24 Oct 2011	7.9	13.0	0.6	3.1	0.0	0.1
2*	26 Oct 2011	3.8	3.5	1.1	8.4	28.1	28.1
3	02 Nov 2011	24	2.3	10.7	15.9	22.7	50.8
4	14 Nov 2011	8.9	7.8	1.1	3.6	32.9	98.5
5	16 Dec 2011	3.6	4.5	0.8	1.6	33.6	43.2
6	04 May 2012	2.4	7.4	0.3	1.3	42.5	82.6
7*	25-26 Sept 2012	14.3	16.7	0.9	4.1	14.3	14.3
8	08-10 Jan 2013	9.9	28.9	0.3	2.3	0.0	17.0
9	15-17 Jan 2013	20.2	21.4	0.9	5.4	25.4	25.4
10	25-29 March 2013	46.8	93.25	0.5	5.3	47.3	70.8

* Storms recorded after summer

Table ~~3~~ 4 – Streamflow responses to the 10 rainstorms at the catchment outlet (E: ESAC) and the three sub-cat

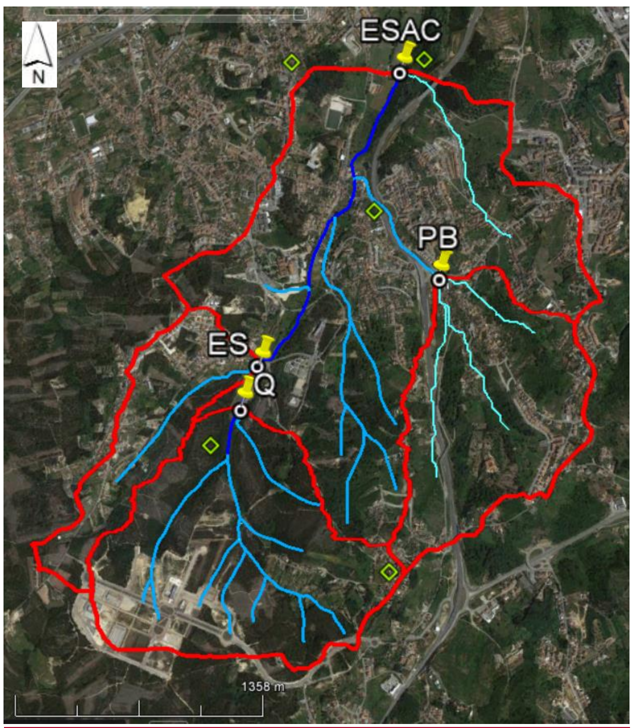
ES: Espírito Santo and Q: Quinta).

	Peak discharge ($L\ s^{-1}$)				Mean discharge ($L\ s^{-1}$)				Baseflow fraction (%)				Storm runoff coefficient (%)			
Storm	E	PB	ES	Q	E	PB	ES	Q	E	PB	ES	Q	E	PB	ES	Q
1	241	82	0	0	26	8	0	0	46	16	-	-	1.8	4.6	-	-
2	149	83	29	54	37	7	12	9	61	16	64	51	2.0	4.2	6.0	2.7
3	1448	643	94	348	385	88	34	104	56	23	58	54	4.5	7.3	3.6	4.2
4	386	140	46	102	140	27	25	34	65	22	81	81	3.6	7.2	4.7	1.9
5	122	43	15	17	56	6	8	13	74	18	72	49	1.6	2.5	2.4	0.8
6	127	63	11	16	77	5	5	13	87	27	94	85	2.2	4.8	2.7	1.8
7	550	260	50	73	107	30	29	24	56	18	79	65	4.1	9.8	5.6	2.9
8	191	76	46	55	27	4	7	10	77	31	65	73	1.8	3.3	6.7	2.7
9	733	258	50	94	95	12	18	28	74	31	86	85	3.2	5.9	3.5	2.1
10	1789	588	72	269	313	41	24	48	87	55	86	79	5.5	11.8	4.1	4.9

Figures

Legend

Sampling sites
Drainage area
Stream network
Perennial
Intermittent
Ephemeral



Legend

Legend	Hydrological network	Stream network
Sampling sites	Flow measurements	Perennial
Drainage area	Rainfall gauges	Intermittent
		Ephemeral

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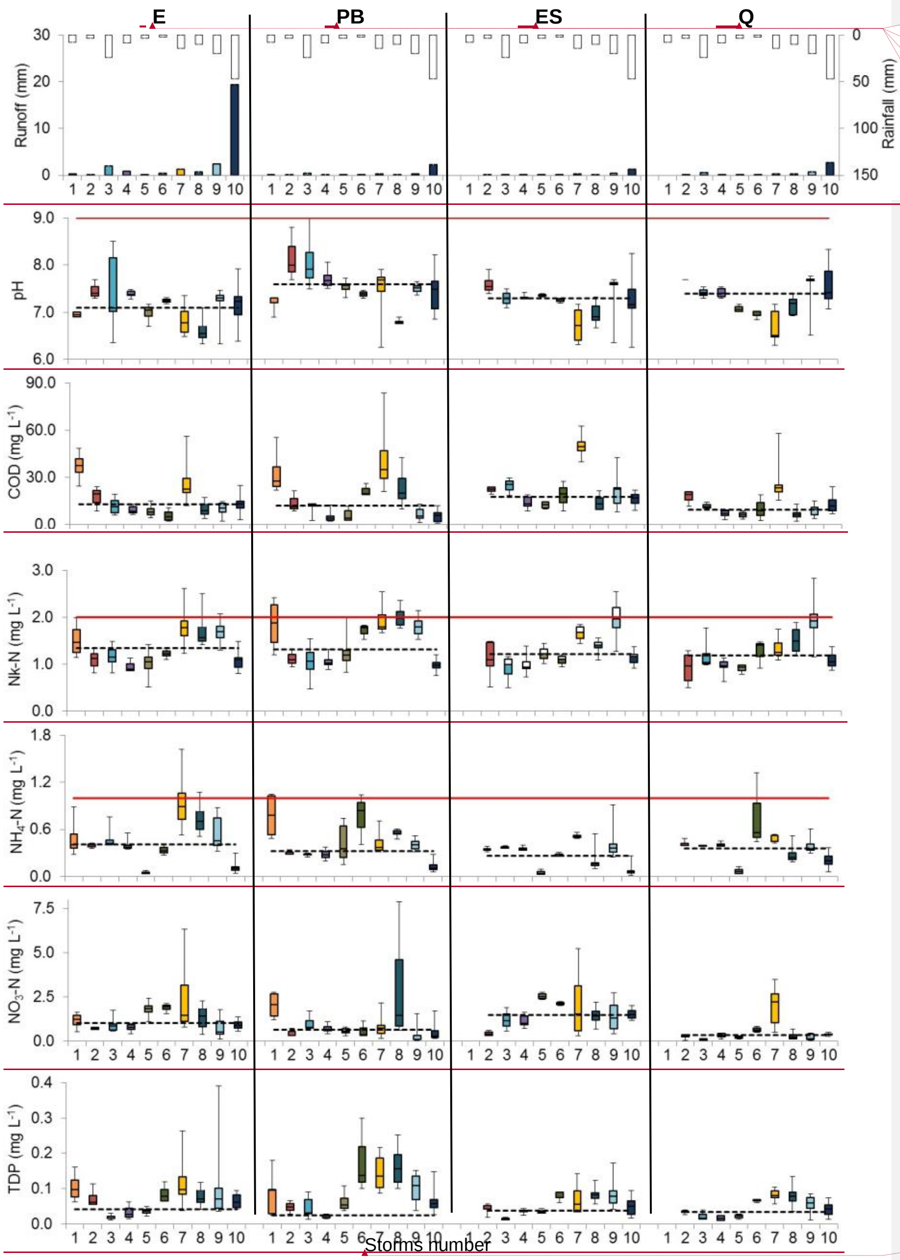
Figure 1 - Ribeira dos Covões catchment and location of the sampling sites – E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and Q: Quinta (adapted from Google Earth, 2014).



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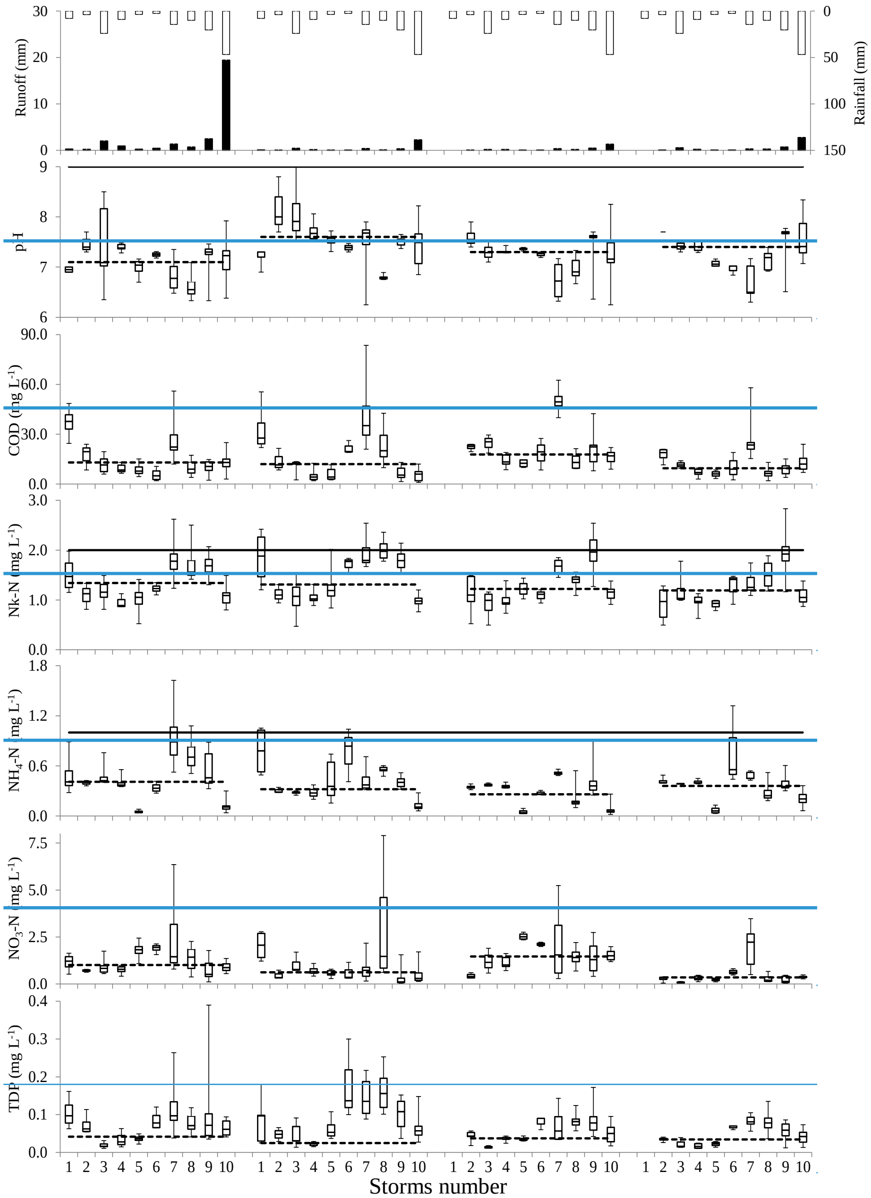
E	PB	ES	Q



Runoff (mm)
Rainfall (mm)
pH
COD (mg L-1)
Nk-N (mg L-1)
NH4-N (mg L-1)
NO3-N (mg L-1)
TDP (mg L-1)
1 2 3 4 5 6 7 8 9 10
Storms number

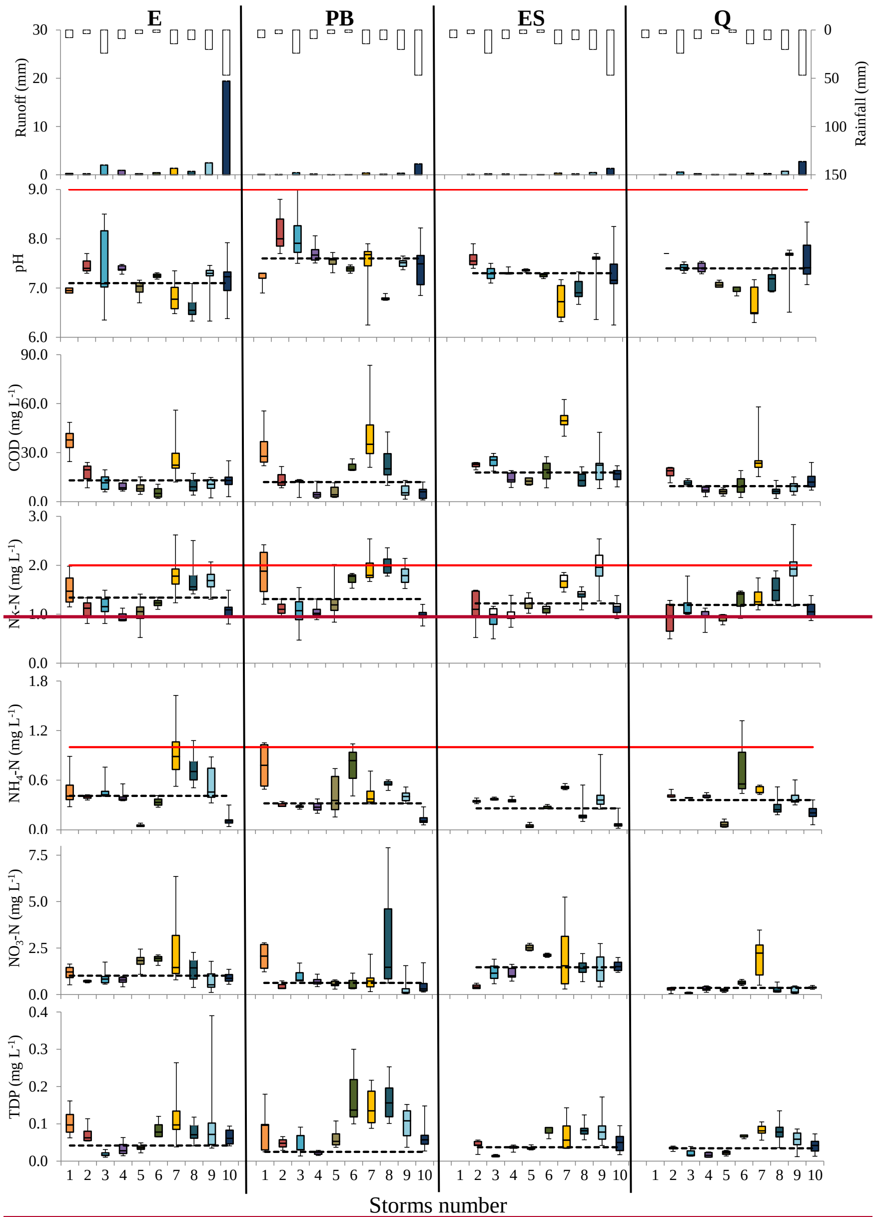
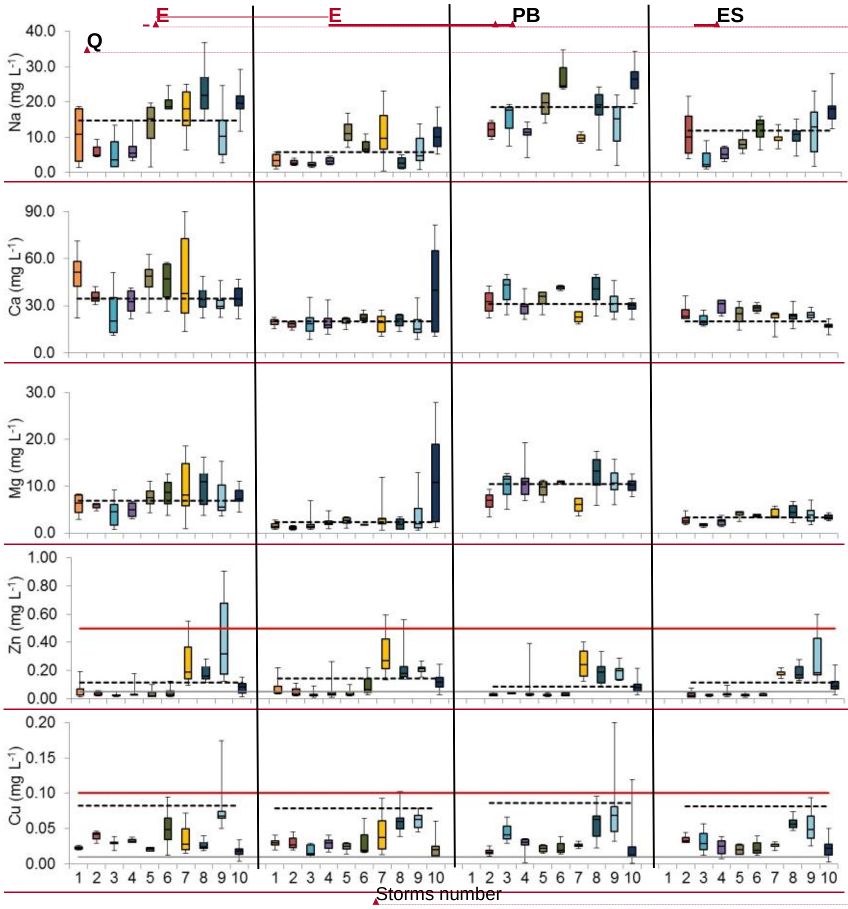


Figure 2 - Rainfall and runoff~~, as well as~~and box plots (median, upper (75) and lower (25) quartiles, maximum and minimum) showing pH, COD, N_K~~k~~, NH_4-N, NO_3-N and TDP concentrations ~~in~~ at ESAC (E), Porto Bordalo (PB), Espírito Santo (ES) and Quinta (Q) for the ten storms monitored between October 2011 and March 2013. Black d~~D~~ashed lines represent median ~~concentration~~ values at each~~per~~ study site and ~~full~~ red lines represent Portuguese minimum water quality standards (DL236/98). ~~–~~The standard for

TDP is 1.0 mg L^{-1} and is not shown as it is above the scale of the graphs~~represented because it is out of range~~.



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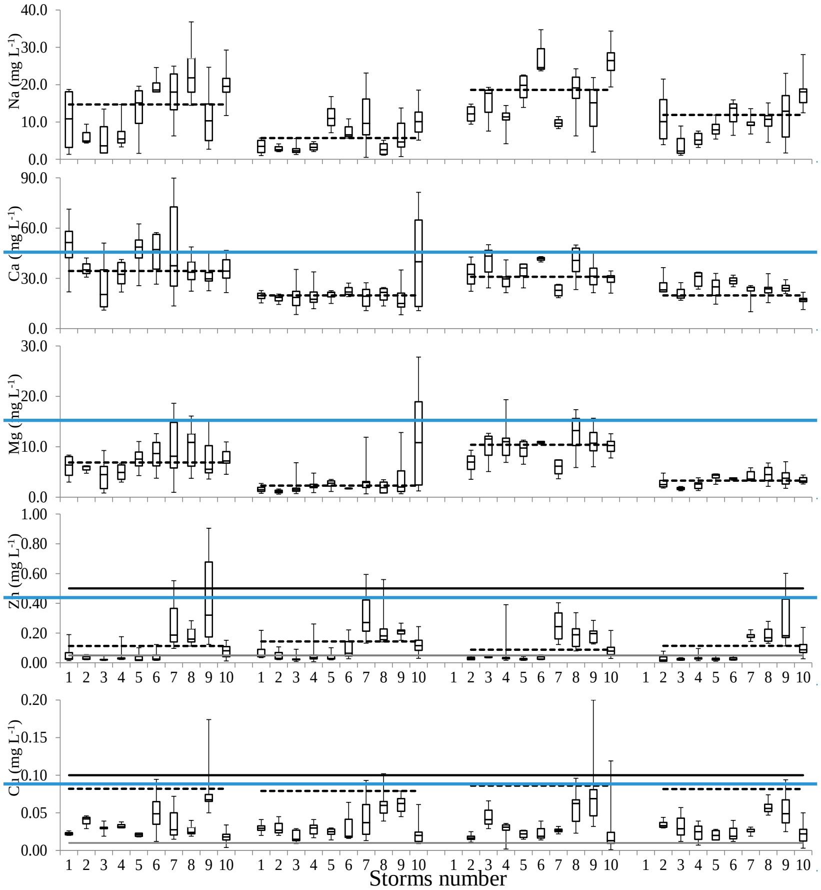
E	PB	ES	Q


Na (mg L-1)
Ca (mg L-1)
Mg (mg L-1)
Zn (mg L-1)
Cu (mg L-1)
Storms number

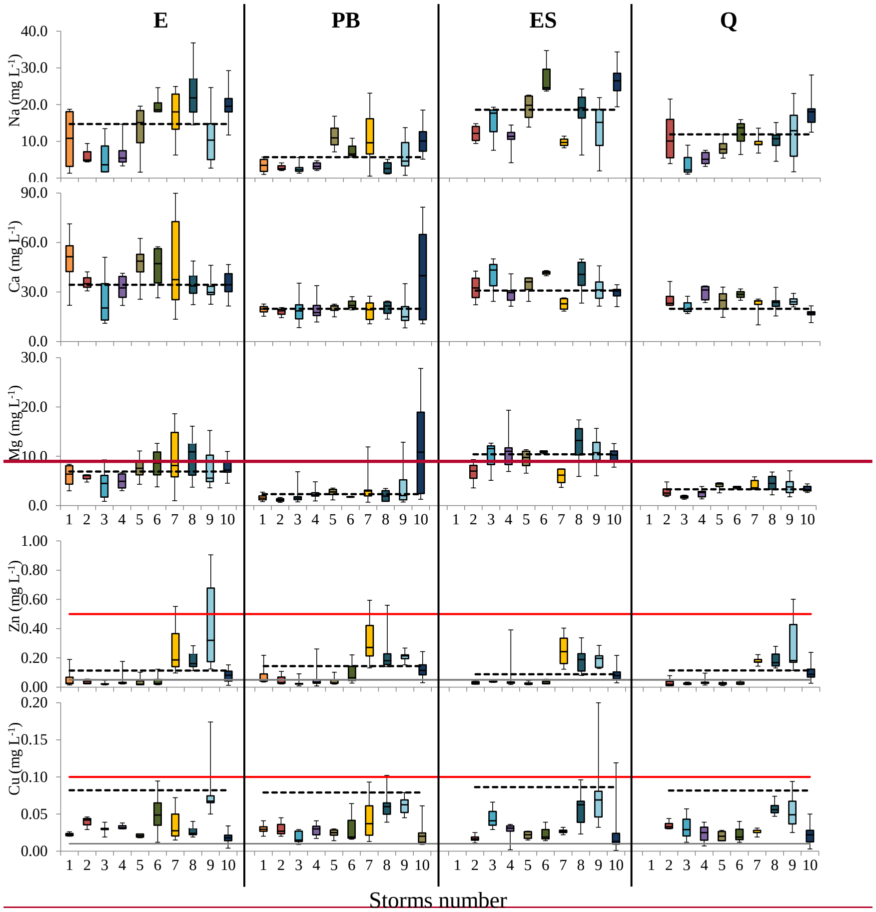
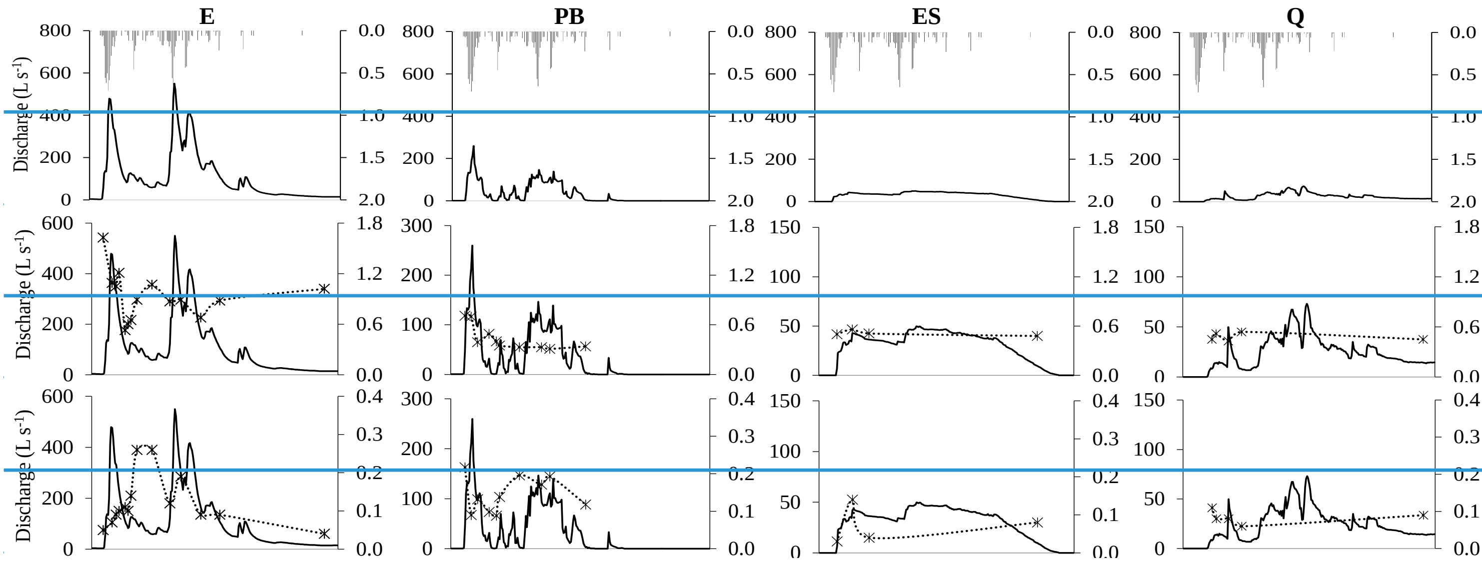
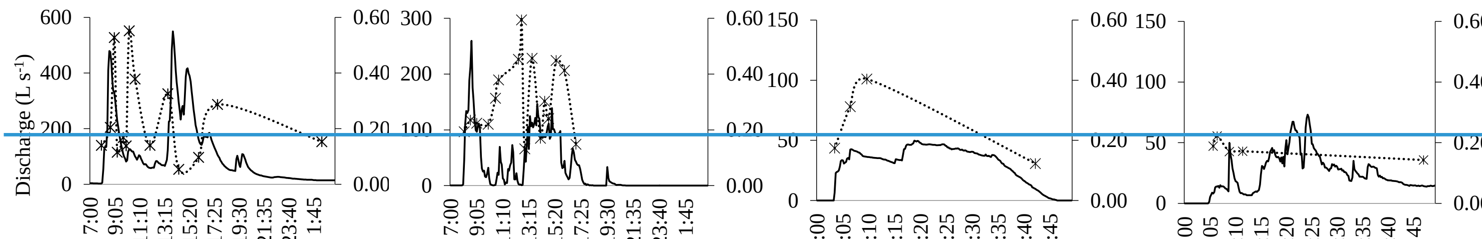


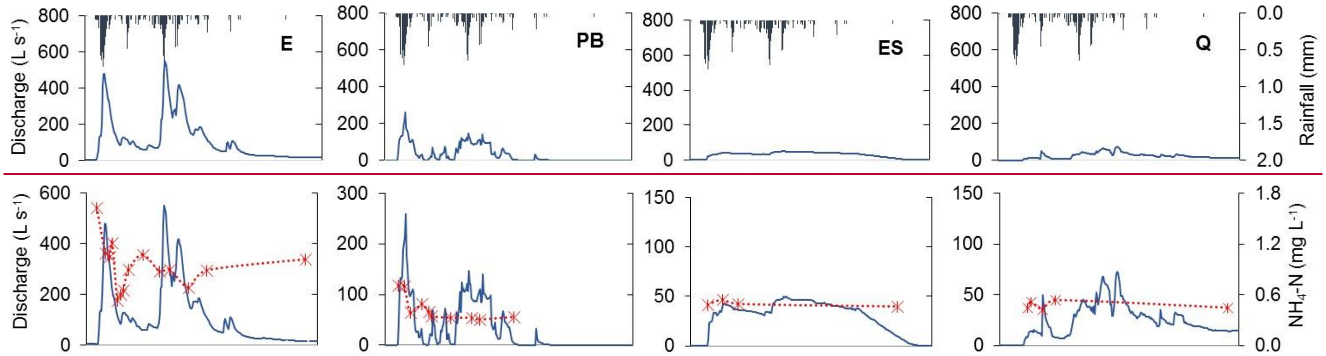
Figure 3 - ~~—~~Box plots (median, upper (75) and lower (25) quartiles, maximum and minimum) showing major cations (Na, Ca and Mg) and heavy metals (Zn and Cu) concentrations ~~in~~ at ESAC (E), Porto Bordalo (PB), Espírito Santo (ES) and Quinta (Q) for the ten storms monitored between October 2011 and March 2013. Black d~~D~~ashed lines represent median ~~concentration~~ values at each~~per~~ study site and ~~full black~~red lines represent Portuguese minimum water quality standards (DL236/98). Grey lines in Zn and Cu represent detection limits.



E
PB
ES
Q
Discharge (L s-1)
Discharge (L s-1)
Discharge (L s-1)



Discharge (L s-1)
600
400
200
0
0.60
0.40
0.20
0.00
300
100
150
50
7:00
9:05
11:10
13:15
15:20
17:25
19:30
21:35
23:40
1:45



E
PB
ES
Q
Discharge (L s-1)
Rainfall (mm)
NH4-N (mg L-1)
800
600
400
200
0
0.0
0.5
1.0
1.5
2.0
300
150
100
50
1.8
1.2
0.6

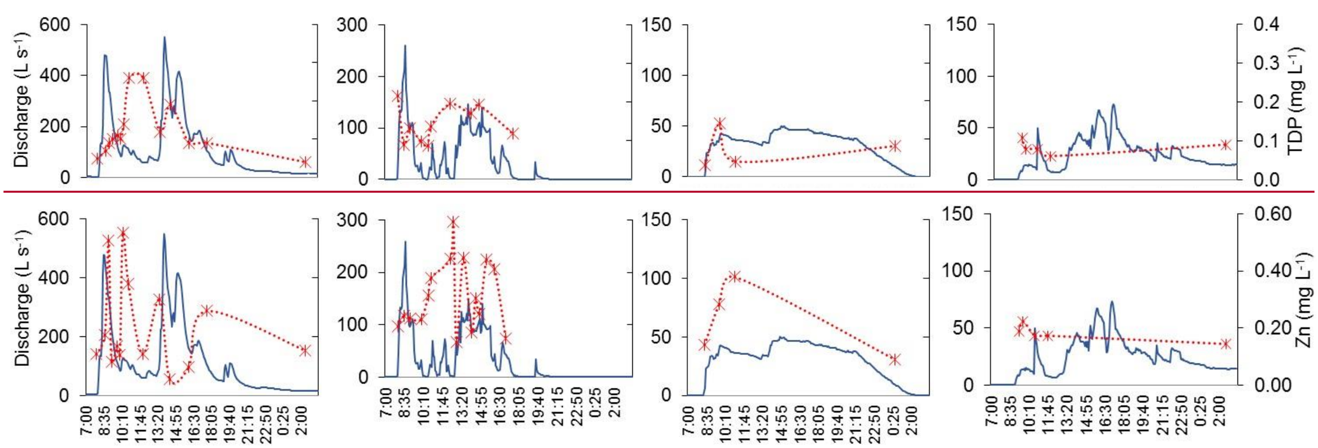
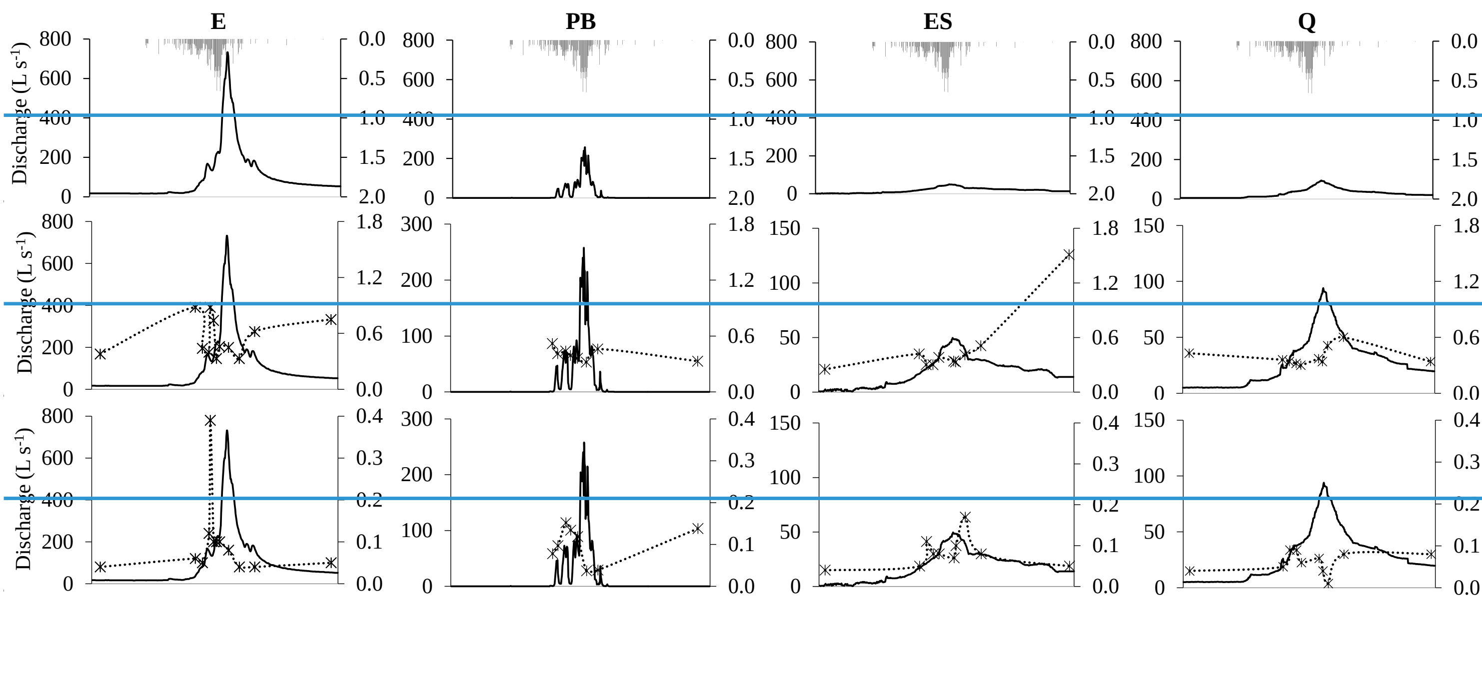
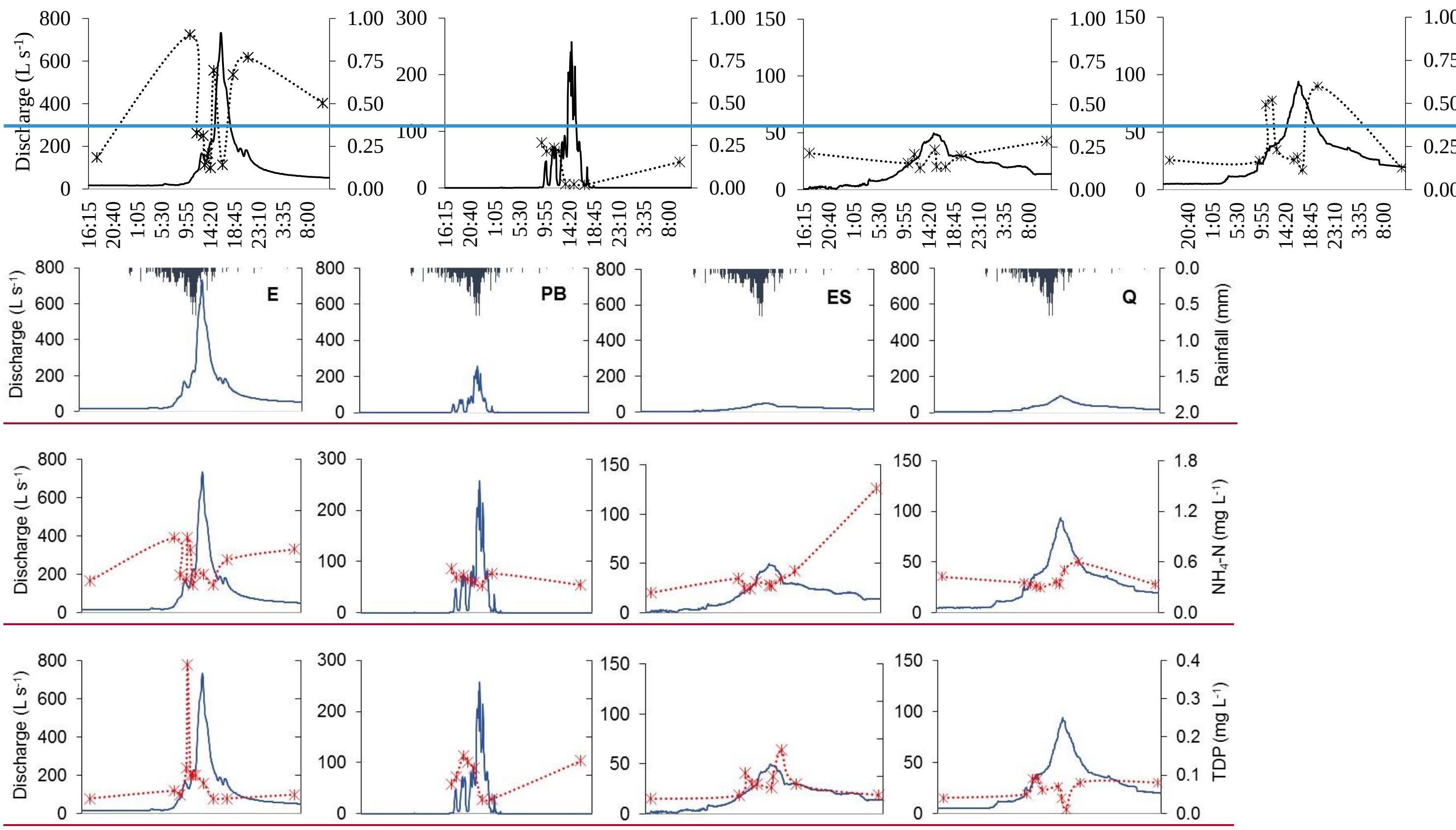


Figure 4 – Ammonium nitrogen (NH_4-N), total dissolved phosphor~~o~~us (TDP) and zinc (Zn) responses (~~dotted~~ ~~green~~red lines) to~~in~~ the late-summer 25-26 Sept 2012 rainstorm event (storm 7) at the four catchment sites (E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and Q: Quinta in relation to rainfall and discharge.



E
PB
ES
Q
Discharge (L s-1)
Discharge (L s-1)
Discharge (L s-1)


Discharge (L s-1)
E
PB
ES
Q
Rainfall (mm)
NH4-N (mg L-1)
TDP (mg L-1)

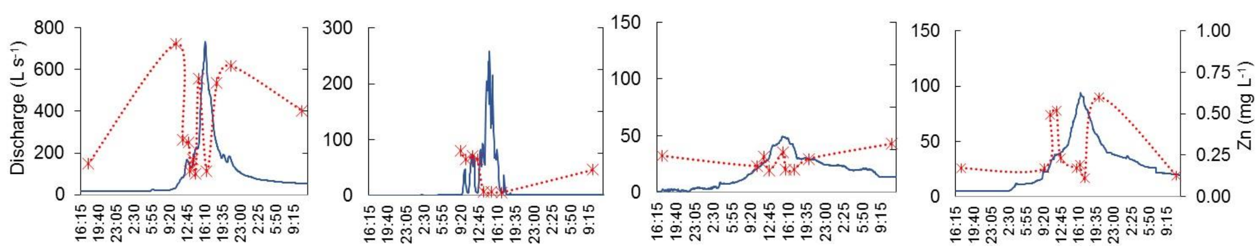


Figure 5 - Ammonium nitrogen (NH_4-N), total dissolved phosphor~~o~~us (TDP) and zinc (Zn) responses (~~dotted~~ ~~green~~red lines) ~~in~~ to the late~~-~~wi
15-17 Jan 2013 rainstorm event (storm 9) at the four catchment sites (E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and Q: Quinta) in relati
to rainfall and discharge.

URBAN SOILS AND SEDIMENTS

Dynamics of surface water quality driven by distinct urbanization patterns and storms in a Portuguese peri-urban catchment

Carla Sofia Santos Ferreira[1,2] • Rory Peter Dominic Walsh[3] • Maria de Lourdes Costa[1] • Celeste Oliveira Alves Coelho[2] • António José Dinis Ferreira[1]

[1] Research Centre for Natural Resources, Environment and Society (CERNAS), College of Agriculture, Polytechnic Institute of Coimbra, Coimbra, Portugal

[2] Centre for Environment and Marine Studies (CESAM), Department of Environment and Planning, University of Aveiro, Aveiro, Portugal

[3] Department of Geography, College of Science, Swansea University, Swansea, United Kingdom

✉ Carla Sofia Santos Ferreira

carla.ssf@gmail.com, cferreira@esac.pt

Phone.: +351239802940, Fax: +351239802

Abstract

Purpose: Although influences of urban land-use on water quality have been widely investigated, the impacts of different urbanization patterns, particularly in Mediterranean environments, are not well understood. Focussing on a Portuguese peri-urban catchment with 40% urban cover, this paper explores (i) the impact of areas with differing urban extent and storm drainage system on streamwater quality, and (ii) temporal variations driven by season and storm events of differing magnitude, intensity and antecedent weather.

Materials and methods: Water quality was assessed at the catchment outlet (E) and for three upstream tributaries: (1) Porto Bordalo (PB), 39% urban with a new major road and piping of some overland flow from impervious surfaces directly into the stream, (2) Espírito Santo (ES), 49% urban, mostly comprising detached houses surrounded by gardens, and with overland flow infiltrating into downslope pervious soils; and (iii) Quinta (Q), 22% urban with partial piping of overland flow from a recent enterprise park area. Water samples were collected at different stages in storm hydrograph responses to ten rainfall events in October 2011 to March 2013. Water quality variables analysed included chemical oxygen demand (COD), nutrients (kjeldahl nitrogen [Nk-N], ammonium [NH_4-N], nitrate [NO_3-N] and total dissolved phosphorus [TDP]) and heavy metals (zinc [Zn] and copper [Cu]).

Results and discussion: Urban areas had great impact on COD, with highest median concentrations in ES and lowest in Q. In ES, fertilizing lawns and gardens may have been responsible for its higher median NO_3-N concentrations. High concentrations of heavy metals were recorded in PB and Q, probably due to piping of road runoff directly into the stream. Generally, higher pollutant concentrations were recorded in the first storm events after the summer drought, due to flushing of accumulated solutes and a lower dilution effect, with Nk-N and NH_4-N exceeding water quality standards. Over the wet season, increasing soil moisture favoured greater flow connectivity between runoff processes from pollutant sources and the stream network, leading to a higher proportion of samples exceeding pollution thresholds.

Conclusions: No direct relationship was identified between urban extent and water quality, possibly due to the overriding impact of different storm drainage systems and flow connectivities of different urban patterns. Hydrological regime, linked to seasonal changes, also exerted a major influence on water quality dynamics. Information on the spatiotemporal dynamics of pollutants, linked to different urban patterns and storm drainage systems, should help enable urban planners to minimize adverse impacts of urbanization on aquatic ecosystems.

Keywords Flow connectivity • Heavy metals • Mediterranean climate • Storm events • Urban pattern • Urban water quality

1 Introduction

Population growth is a worldwide phenomenon and in the Mediterranean region population is likely to have more than doubled by 2020 compared with 1960 (Zdruli 2014). The increase of population is generally accompanied by the loss of forest and agricultural land to urban expansion, and the integration of fragmented rural areas surrounding growing cities into the urban system (e.g. Binns et al. 2003). The abandonment of the mountains and urbanization process influences landscape characteristics, such as its structure, function and dynamics (Çakir et al. 2008; Keestra et al. 2009), leading to major environmental and water resources impacts (e.g. Alphan 2003), including both hydrological processes (e.g. Shuster et al. 2005; Fletcher et al. 2013) and water quality (e.g. Tu 2011; Barco 2008).

Urban areas are typically associated with many pollutants, including heavy metals (e.g. cadmium [Cd], copper [Cu], chromium [Cr], iron [Fe] and zinc [Zn]) (e.g. Yu et al. 2014), organic compounds (e.g. biochemical oxygen demand, ammonium, polycyclic aromatic hydrocarbons, polichlorinated byphenils, oil and grease) (Gilbert and Clausen 2006; Dias-Ferreira et al. *in press*), nutrients (e.g. nitrates, phosphates) (Lin et al. 2014), and faecal coliforms (Mallin and Wheeler 2000). These pollutants are mainly provided by (i) industrial activities (Yu et al. 2014) and vehicular traffic (e.g. Carey et al. 2013); (ii) wastewater contamination, including from septic tanks and sewage system leaks (Le Pape et al. 2013), diffuse sources, and treated and untreated effluent from wastewater treatment plants and storm sewer overflows (Yu et al. 2014); and (iii) lawns and gardens maintenance, due to inappropriate fertilization and irrigation activities (Lin et al. 2014).

Although the type of urban development (e.g. industrial, commercial, residential, and recreational) determines the nature of pollutants released (e.g. Tu 2011), urban runoff generally has been considered a major non-point source of pollutants within catchments (e.g. Yu et al. 2016). Direct relationships have been reported between pollutant concentrations and percentage urban surface (e.g. Sliva and Williams 2001), with for example total impervious area being considered an indicator of aquatic ecosystem conservation status (e.g. Rautengarten 2006; Kuusisto-Hjort and Hjort 2013).

Other authors, however, suggest that the location of pollutant sources within the catchment, and the distance to the stream network, are better indicators of water quality (e.g. Yu et al. 2016). Urban areas located downslope may provide runoff flowing into the stream network, whereas runoff from upslope areas may be infiltrated and retained in downslope pervious soils (e.g. Ferreira et al. 2015), preventing pollutants from reaching aquatic ecosystems. In catchments comprising mosaics of urban and non-urban land-uses, typical of peri-urban catchments, the connectivity between runoff/pollutant sources and water resources can vary greatly and have been little researched to date, particularly in Mediterranean environmental settings. Furthermore, there is a general lack of studies exploring the dynamics of pollutant concentrations and fluxes in peri-urban catchments (Rodríguez-Blanco 2013).

In order to address these research gaps, this study investigates the spatial and temporal dynamics of aspects of streamwater chemistry in a peri-urban catchment in Portugal, and explores in particular the influence of landscape pattern on flow and pollutant connectivity in storm events at different seasons and following differing antecedent weather associated with the Mediterranean climate. The study aims to assess the impact of different urban patterns, in forms of different impervious cover and spatial arrangement of pervious and impervious surfaces, on surface water quality and discharge chemistry dynamics in a typical Portuguese peri-urban catchment. The specific objectives are to (i) assess water quality differences between three sub-catchments with distinct urbanization patterns and the catchment outlet, as regards to pH, chemical oxygen demand (COD), nutrients (kjeldahl nitrogen [Nk-N], ammonium [NH_4-N], nitrate [NO_3-N] and total dissolved phosphorus [TDP]), heavy metals (Cu and Zn) and major cations (calcium [Ca], magnesium [Mg] and sodium [Na]); (ii) explore temporal variations in water quality between and within storm events at different times of year; and (iii) investigate whether pollutant threshold levels (according to Portuguese water quality standards) were exceeded and under which weather conditions. A better understanding of the impact of urban patterns on water quality should enable urban planners to minimize adverse impacts of urbanization on stream ecosystems.

2 Study site description

The study was carried out in the small (6.2 km^2), peri-urban Ribeira dos Covões catchment on the outskirts of the city of Coimbra in central Portugal (Fig.1). The catchment is characterized by sandstones with Fluvisols and Podsols in west and limestone with Leptic Cambisols in the east (WRB 2006).

The climate is humid Mediterranean. The mean annual temperature is 15°C, with monthly means varying from 10°C in January to a maximum of 22°C in August. The mean annual rainfall at Coimbra-Bencanta is 906mm, with wet winters and long dry summers (just 7% of rainfall between June and August) (INMG, 1971-2000). This temporal pattern causes a strong seasonal variation in streamflow, although the perennial flow at the outlet is supplied by several springs (mainly on sandstone). Annual runoff averages 135mm, ranging from 76mm in the hydrological year (October to September) 2011/12 to 200mm in 2012/13, with baseflow accounting for 33-37% of streamflow (Ferreira et al. *in press* a).

Catchment land-use comprises urban areas (40%) dispersed within woodland (56%) and agricultural land (4%). The woodland is dominated by eucalyptus, but with some pine plantations and a relict oak stand. Agricultural land-use consists of a few olive plantations, pasture areas for cattle along part of the main stream, and small family farms with vegetables. Urban land-use mainly comprises residential areas, some small supermarkets and shops, educational and health services, including a central hospital, and a few facilities (garage shops, sawmill and a pharmaceutic factory). An enterprise park, covering 5% of the catchment area, is under construction in the headwaters in the extreme southwest of the catchment (clearly visible in Fig.1). A network of roads extends across the catchment and includes a recent motorway. Residential areas differ greatly in urbanization style, comprising (i) areas of single-family houses, surrounded by gardens, and (ii) recent row-houses and apartment blocks. These distinct residential areas house approximately 26,700 inhabitants, with population densities ranging from <25 inhabitants km^{-2} to >9900 inhabitants km^{-2} (Pato et al. 2015).

In the newer urban areas, of high population density, part of the runoff from impervious surfaces is collected in culverts and gutters and routed or piped direct to the stream network. In contrast, in urban settlements surrounded by gardens, agricultural and woodland soils, stormwater tends to dissipate in adjacent areas of high permeability.

Domestic effluent, however, is piped to a large, modern wastewater treatment plant (WWTP), located outside the catchment. However, a small WWTP, installed in around 1985, served an upslope urban core in Quinta sub-catchment until 2012, but was very inefficient and effluent from it was released into a downslope woodland area and into a tributary. In 2012 the wastewater was linked to the larger sewerage network and the small WWTP was disabled.

3 Methodology

3.1 Research design

The research design comprised monitoring variations in water quality at four sites in the Ribeira dos Covões catchment in 10 storms, covering a range of rainstorm sizes and antecedent weather (and season), over the period October 2011 to March 2013.

T sites comprised the catchment outlet at ESAC (E) and three upstream sites in sub-catchments of distinct urban cover and pattern (Table 1). These were: (i) Espírito Santo (ES), the most urbanized (49% urban) sub-catchment containing areas of high impervious cover in upslope sites and lower impervious cover (detached houses surrounded by gardens), mainly in downslope locations; (ii) Porto Bordalo (PB), with 39% urban cover extending over the sub-catchment in strip fashion, with row-house areas upslope and detached houses with greater impervious cover or only small gardens downslope) and part of the motorway; and (iii) Quinta (Q), 22% urban, mainly in upslope locations, comprising a small residential area (4%) and the enterprise park under construction (18%). Differences between urban patterns also include dissimilarities in the storm drainage system: (i) in ES, overland flow from impervious surfaces is dissipated in adjacent downslope pervious soils; (ii) in PB, storm runoff from upslope urban areas is diverted into pervious soils, whereas from downslope impervious surfaces it is piped into the stream tributary or nearby abandoned fields; and (iii) in Q runoff from the residential area dissipates in downslope woodland, whereas runoff from impervious surfaces within the new enterprise park is piped into a detention basin, which delays its flow into the stream network. Additional differences are linked to physical properties of the sub-catchments. In terms of lithology, ES and Q are sandstone sub-catchments and PB a limestone sub-catchment, with the entire catchment at E being 56% sandstone, 41% limestone and 3% alluvial (Table 1).

Water samples were collected at intervals manually at each site during each of 10 storm events. This was facilitated by the small size of the catchment, the proximity of sampling sites, the use of a car and multiple personnel. Selection of storm events was aided by use of weather forecasts and focus on the first rainstorms after the summer (storms 1, 2 and 7) and on storm events of different magnitudes over the wet season, including autumn (storms 3, 4 and 5), winter (storms 8, 9 and 10) and spring (storm 6), in order to cover seasonal differences in response over the year.

3.2 Water sampling

Three to fifteen samples covering the rising limb, peak and falling limb of storm responses at the four sites were collected during each of 10 storm events, monitored between October 2011 and March 2013. Whenever possible, the first sample of the event was collected immediately before rainfall started, if stream was flowing, to provide preceding baseflow water quality. Storm events were assumed to have stopped when no rainfall was recorded for 6h. In total 76 samples were collected at E, 75 at PB, 56 at ES and 58 at Q. Samples were collected in acid-washed 250 mL glassware and 2 L polyethylene bottles, placed in a dark chilled cooler (~4°C) and taken to the laboratory.

Hydrological data of 5-minute resolution were provided by an existing network of flow gauging stations at each site and five rainfall gauges distributed across the catchment (Figure

1). The Thiessen Polygon method was used to calculate the weighted mean rainfall, assumed to be constant over the catchment.

3.2 Laboratory analysis

Water samples were immediately analysed for pH by electrometry (Hach, Sension Portable case). Sample aliquots were filtered through 0.45 μm membranes (Millipore MF) and stored for later chemical analyses: (i) aliquots for dissolved nitrite (NO_2-N) and nitrate (NO_3-N); (ii) aliquots for dissolved chemical oxygen demand (COD), kjeldahl nitrogen (Nk-N), ammonium (NH_4-N) and total dissolved phosphorus (TDP) were acidified with sulphuric acid (pH <2); (iii) aliquots for dissolved ions [sodium (Na), calcium (Ca) and magnesium (Mg)] and heavy metal analyses [zinc (Zn) and copper (Cu)] were acidified with nitric acid (pH 2-3). All aliquot samples were stored surrounded by ice and defrozen at room temperature before analysis.

Nitrite and nitrate concentrations were measured simultaneously with an automated segmented flow analyser (SAN^{++} system), using the cadmium reduction method (Skalar method 461-322; Skalar, 2004a). Given the normally very low nitrite concentration in rivers the analytical results are examined only as NO_3-N. Ammonium concentration was also determined by an automated segmented flow analyser, but using a modified Berthelot reaction (Skalar method 155-316; Skalar, 2004b). Kjeldahl nitrogen, including organic nitrogen, ammonia and ammonium, was measured after sulphuric acid digestion with a selenium catalyser, followed by distillation and titration with hydrochloric acid (Standard Method 4500-Norg B; APHA 1998).

COD and TDP were analysed using a multiparameter water quality instrument (Hach DR 2000). COD was determined colorimetrically after acid digestion and oxidation with dichromate, in accordance with ISO 15705:2002 standards (HI 93754A vials, Hanna Instruments). TDP was quantified, after persulfate acid digestion, colorimetrically by reacting with molybdate ascorbic acid and antimony potassium tartrate, adapted from 4500-P Standard Methods (HI 93758A vials, Hanna Instruments).

Cation and heavy metal analyses were made after digestion with nitric acid (Standard Method 3030-E; APHA 1998), by atomic absorption spectrophotometry (Perkin Elmer AA300), with direct air-acetylene flame and hollow cathode lamps (Standard Method 3111-B; APHA 1998). Detection limits for Zn and Cu were 0.05 mg L^{-1} and 0.01 mg L^{-1}, respectively.

Reagent blanks and duplicate samples were used for quality control purposes and mean concentration values (repeated analysis of each sample) were used for data analysis.

3.3 Data analysis

The hydrological regime of the ten sampled storms was characterized in terms of rainfall and stream discharge. For each storm event, the rainfall amount, duration and intensity were calculated. Rainfall intensity was described in terms of the event mean (Imed), and the maximum in 60- minutes (I_{60}). Seven-day and 14-day antecedent precipitation (API_7 and API_{14}) for each storm event were calculated using weighted mean rainfall data. Streamflow parameters used included instantaneous discharge (at the time of water sampling) and event peak and mean discharges. Stormflow and baseflow components were separated for individual events, using a mathematical digital filter (Nathan and McMahon 1990). The storm runoff coefficient for each event was calculated as the ratio of total storm runoff (discharge normalized by area) divided by event rainfall. The time to peak was defined as the time from the centroid of the rainfall to peak flow (Lana-Renault et al. 2011).

Water quality values for the ten rainfall events were compared with Portuguese standards of minimum surface water quality (DL236/98) (Table 2). Portuguese standards do not exist for the monitored parameters COD, NO_3-N and major cations (Na, Ca and Mg).

The statistical significance of differences in parameters between the four sites were investigated using the non-parametric Kruskal-Wallis test. Whenever significant spatial and/or temporal water quality differences were identified ($p<0.05$), they were further investigated using the post-hoc Fisher's Least Significant Difference test, at the 0.05 significance level. For each site, relationships between different water quality parameters, and between these parameters and streamflow properties, were explored using Spearman's rank correlation coefficient (r), at 0.05 and 0.01 significance levels. Data analysis was performed using IBM SPSS Statistics 22 software.

4 Results

4.1 Storm characteristics and streamflow response to storm events

Rainfall characteristics for the 10 storms sampled between October 2011 and March 2013 are shown in Table 3. Storm totals ranged from 2.4 mm (storm 6) to 46.8 mm (storm 10), which had a return period of less than 2 years, but the return period of the maximum hourly intensity for storm 3 (15.6 mm h^{-1}) was 3 years.

Streamflow responses at the four monitored sites are summarized in Table 4 and Figure 2. Storm 1, recorded at the end of summer (23-24/10/2011) was not enough to trigger discharge in ES and Q. For the 10 storms, the mean storm runoff coefficient at PB (6.1%) was twice as high as at E (3.0%) and Q (2.7%), and also greater than at ES (4.4%). In the monitored storms, baseflow comprised 46%-87% of event flows at E, 51%-85% at Q and 58%-94% at ES, whereas at PB it was 16%-55%. The catchment and sub-catchments have a flashy behaviour, with response times ranging from 5-35 min at PB, 10-40 min at ES, 10-65 min at Q and 25-85 min at E.

4.2 Water quality

4.2.1 Overview of water quality in the ten events at the four sites

Fig. 2 uses box plots to summarise water quality responses at each of the four sites to the ten rainstorms. The limestone PB sub-catchment showed significantly higher pH ($p<0.05$) than Q, ES and E, but median values over the 10 storms were 7.6, 7.4, 7.3 and 7.1, respectively, and thus slightly alkaline.

Significant differences in COD (dissolved phase) between sites were recorded ($p<0.05$), with lowest median concentration in the least urban Q (9.5 mg L^{-1}), intermediate values at PB (12.0 mg L^{-1}) and E (13.0 mg L^{-1}), and highest median COD in the most urbanized ES sub-catchment (17.8 mg L^{-1}) (Fig. 2). Ranges in values were substantial at all sites, with minima of 2.0 - 8.0 mg L^{-1} and maxima of 48.5 – 62.5 mg L^{-1} at E, PB and Q and 83.5 mg L^{-1} at ES. Kjeldhal nitrogen in dissolved phase varied little between study sites, but was slightly higher at E (0.52 – 2.62 mg L^{-1}) and Q (0.50 – 2.83 mg L^{-1}), where cattle-rearing occurs in fields adjacent to the stream, than at ES (0.50 – 2.54 mg L^{-1}) and PB (0.47 – 2.54 mg L^{-1}) (Fig. 2).

PB, however, experienced more than twice as many pollution occasions (12 values >2.0 mg L^{-1}, DL236/98) than the other sites (5 at E and Q and 4 at ES). Pollution thresholds were exceeded in storm 9 (winter) at all sites, in storms 7 (after summer) and 8 (winter) at E and PB, and storms 1 (after summer) and 5 (winter) at PB.

Similarly to Nk-N, slightly higher NH_4-N concentrations were recorded at E (0.04 - 1.63 mg L^{-1}) and Q (0.03 – 1.32 mg L^{-1}) than at PB (0.06 – 1.05 mg L^{-1}) and ES (0.02 – 0.91 mg L^{-1}) ($p>0.05$, Fig. 2). The water quality standard for NH_4-N (1.0 mg L^{-1}, DL236/98) was always complied with at ES, but exceeded for 7, 3 and 1 samples collected at E, PB and Q, respectively. These pollution occasions were recorded during storms 7 (late summer) and 8 (winter) at E, and storm 1 (late summer, after a very dry period) at PB, as recorded for Nk-N, but in addition in storm 6 (spring) at PB and Q. Relatively strong and statistically significant positive correlations were found between NH_4-N and Nk-N at E ($r=0.623$, $p<0.01$) and ES ($r=0.340$, $p<0.05$), but not at Q and PB ($p>0.05$).

Slightly lower NO_3–N concentrations were recorded at the least urbanized Q (0.04 – 3.47 mg L^{-1}) than at PB (0.04 – 7.90 mg L^{-1}), E (0.11 – 6.35 mg L^{-1}) and ES (0.29 – 5.24 mg L^{-1}) (Fig. 2). Correlations with COD, Nk-N and NO_3–N were weak albeit significant at all sites ($r<0.350$, $p<0.05$).

In contrast to nitrogen compounds, TDP varied significantly between sites ($p<0.05$), with median concentrations being greater at E and PB (0.07 mg L^{-1}) than at ES (0.06 mg L^{-1}) and Q (0.04 mg L^{-1}). Minimum concentrations were 0.01 mg L^{-1} at all sites, and maxima were 0.39 mg L^{-1} at E, 0.25 mg L^{-1} at PB, 0.17 mg L^{-1} at ES and 0.14 mg L^{-1} at Q (Fig. 2). Phosphorus was not a pollutant threat, as all values were far below the Portuguese water quality standard (1.0 mg L^{-1}). TDP was positively correlated with COD and Nk-N concentrations at PB (r=0.459 and 0.552, $p<0.05$). At ES and Q, TDP was only significantly correlated with Nk-N (r=0.483 and 0.467, $p<0.01$).

Water quality displayed differences in concentrations of major cations between monitoring sites ($p<0.05$) (Fig. 3). Sodium concentrations were significantly lower at PB (median 5.7 mg L^{-1}, range 0.7 – 23.1 mg L^{-1}) than at ES (18.6 mg L^{-1}, 2.0 – 34.7 mg L^{-1}), E (14.7 mg L^{-1}, 1.3 – 29.3 mg L^{-1}) and Q (11.9 mg L^{-1}, 1.1 – 28.1 mg L^{-1}). Calcium concentrations were significantly higher at E (median 34.4 mg L^{-1}, 11.0 – 89.9 mg L^{-1}) and ES (30.9 mg L^{-1}, 18.4 – 49.9 mg L^{-1}) than at Q (22.6 mg L^{-1}, 10.0 – 36.4 mg L^{-1}) and PB (19.8 mg L^{-1}, 8.3 – 81.4 mg L^{-1}). Mg concentrations were higher ($p<0.05$) at ES (median 10.4 mg L^{-1}, 3.6 – 19.3 mg L^{-1}), than at E (6.9 mg L^{-1}, 0.8 – 18.6 mg L^{-1}), Q (3.3 mg L^{-1}, 1.3 – 7.0 mg L^{-1}) and PB (2.3 mg L^{-1}, 0.6 – 27.8 mg L^{-1}).

Sodium increased with increasing Mg, but with a stronger correlation at E (r=0.709, $p<0.01$) than at PB, ES and Q (r=0.569, 0.391 and 0.358, $p<0.01$). Sodium displayed significant positive correlations with Ca only at E and PB (r=0.464 and 0.423). Calcium and magnesium were strongly correlated with each other at all sites (r= 0.633 - 0.735, $p<0.01$) except Q.

As regards heavy metals, median dissolved Zn concentrations in the study storm events were slightly higher at PB (0.140 mg L^{-1}) than at Q, E and ES(0.114 mg L^{-1}, 0.113 mg L^{-1} and 0.088 mg L^{-1}, respectively) (Fig. 3). Concentrations exceeded Zn water quality standards (0.5 mg L^{-1}) in 7 samples at E (0.53 - 0.91 mg L^{-1}), 2 samples at PB (0.56 – 0.59 mg L^{-1}) and 2 samples at Q (0.52 - 0.60 mg L^{-1}), but none at ES (maximum only 0.40 mg L^{-1}). Pollutant levels of Zn were attained after summer at E and PB (storm 7), but also during winter at PB (storm 8), E and Q (storm 9). A strong positive correlation was recorded between Zn and Nk-N concentrations at E (r=0.682, $p<0.01$), whereas at PB and Q, Zn correlated significantly with TDP (r=0.524 and 0.564, p<0.01). At ES and Q, Zn was significantly correlated with both Nk-N and TDP (r=0.544 and 0.638, p<0.01).

Median copper concentrations for the study storm events were slightly higher at Q than at PB, E and ES (0.033 mg L^{-1}, 0.030 mg L^{-1}, 0.029 mg L^{-1} and 0.028 mg L^{-1}) (p>0.05) (Fig. 3). Highest Cu concentrations were 0.200 mg L^{-1} at ES, 0.174 mg L^{-1} at E, 0.102 mg L^{-1} at PB and 0.094 mg L^{-1} at Q. Pollutant levels of Cu (>0.10 mg L^{-1}, DL236/98) were recorded only for one sample at E and one sample at ES, during storms 9 and 10, respectively.

Copper and zinc were positively correlated with each other at all monitored sites (r ranged from 0.365 to 0.532, p<0.05). At ES and PB, Cu was significantly correlated with Nk-N (r=0.481 and 0.579, p<0.01) and NH_4-N (r=0.481 and 0.501, p<0.01). At Q, Cu only correlated significantly with Nk-N (r=0.536, p<0.01).

4.2.2 Between-storm variation over the study period

Between-storm differences in water quality response are apparent at the monitoring sites in Figures 2 and 3. Generally, COD and nutrients displayed higher concentrations in storms recorded in late summer (1, 2 and 7) with decreasing values over the wet season, achieving lowest concentrations in late winter (storms 5 and 10) (Fig. 2). Seasonal differences in COD were greater for PB than for Q, ES and E.

Nk-N concentration varied less with season, with median concentrations for late summer storms being less than twice as high than for late winter storms. Greater seasonal differences were recorded for NH_4-N concentrations, with storm medians being 3-4 times greater for late summer than late winter storms at ES, E and PB, but only 1.4 times as high at the least urbanized Q sub-catchment.

As regards nitrates (NO_3–N), PB, Q and E displayed higher storm median concentrations in storms recorded after summer than in late winter (0.86 mg L^{-1} vs 0.42 mg L^{-1}; 0.50 mg L^{-1} vs 0.36 mg L^{-1} and 1.35 mg L^{-1} vs 1.01 mg L^{-1}, respectively), whereas ES displayed 3 times higher storm median concentrations in late winter than late summer storms (1.63 mg L^{-1} vs 0.86 mg L^{-1}).

TDP concentrations were twice higher in PB and E in late summer than late winter storms, but differences were much smaller at Q and ES. Lowest TDP concentrations were recorded in storm 3, with the greatest rainfall intensity, and storm 4, with the wettest antecedent conditions (Table 3).

In contrast, major cations exhibited higher concentrations in wetter than drier settings (Fig. 3). Median Na concentrations measured during storms 6 and 10, with greatest antecedent rainfall in previous 7 days (42.5 mm and 47.3 mm) were 2.5-, 1.8-, 1.5- and 1.3- fold higher than during storms after the summer (storms 1, 2 and 7) for ES (26.3 mg L^{-1} vs 10.4 mg L^{-1}), Q (16.8 mg L^{-1} vs 9.2 mg L^{-1}), PB (9.5 mg L^{-1} vs 6.3 mg L^{-1}) and E (19.4 mg L^{-1} vs 14.4 mg L^{-1}), respectively. Similar patterns were found for Ca and ES, but no specific temporal pattern was recorded at E and Q.

The heavy metals Zn and Cu tended to show higher concentrations in late summer than late winter storms. Thus, median Zn concentrations were 2.5- in E (0.140 mg L^{-1} vs 0.055 mg L^{-1}), 2.2- in PB (0.222 mg L^{-1} vs 0.102 mg L^{-1}), 1.9- in Q (0.143 mg L^{-1} vs 0.074 mg L^{-1}) and 1.4-times higher (0.084 mg L^{-1} vs 0.058 mg L^{-1}) in ES during late summer (storms 1, 2 and 7) than late winter storms (5 and 10). Similar patterns were recorded for Cu. Some pollutant-level values of Zn and Cu were also recorded (see section 4.2.1).

4.2.3 Hydrochemistry dynamics during storms

Changes in water quality during a storm event showed distinct patterns during storms recorded after summer (storms 1, 2 and 7) than in storms later in the wet season. Given the extent of the dataset, this section focuses on intra-storm variation of three chemical parameters included in the Portuguese water quality standards: NH_4-N (which is strongly correlated with Nk-N at E and ES), Zn (which is strongly correlated with Cu) and TDP, for the late summer storm 7 and winter storm 9. Storm 7 was a multiple storm event with two peaks in rainfall five hours apart (Fig. 4). It also includes the first runoff recorded in ES and Q after the 2012 summer dry season. Storm 9 is a typical winter season event (Fig. 5).

NH_4-N storm dynamics

During storm 7 (Fig. 4), highest NH_4-N concentrations were recorded at baseflow (prior to rainfall) in E, and with the initial storm runoff in PB and Q, with concentrations then decreasing as discharge increased. After the first discharge peak, NH_4-N rose as discharge fell at E, whereas at PB it remained low. In Q, samples in storm 7 are too few to deduce the pattern, but in storm 2 (not shown) rose as discharge fall, as at E. Changes in NH_4-N concentration at ES were small, though the number of samples were few.

After an initial flush of higher concentrations in the rising limb of the hydrograph, NH_4-N concentrations in the winter storm 9 varied inversely with streamflow (Fig. 5). Whereas peak concentrations at E and PB were reached during the initial storm runoff, at ES and Q they were attained in the falling limb. At E, however, a clear difference between both storms was noticed at pre-storm baseflow, with high and low concentrations prior to the late summer and winter storms, respectively.

Similar patterns to NH_4-N were in general recorded for Nk-N (not shown), in storms 7 and 9.

TDP storm dynamics

TDP concentrations, albeit never exceeding Portuguese national guidelines, changed within storms differently from NH_4-N and Nk-N concentrations. In storm 7 (Fig. 4), TDP was low at baseflow in E and increased progressively over the first storm peak, attaining highest concentrations on the falling limb, before a sharp fall. Nevertheless, with rainfall restart during storm 7, TDP concentration tended to follow discharge, with a peak at peakflow, followed by a progressive decline to pre-event level on the falling limb of the hydrograph. In ES, however, TDP concentration increased on the rising limb to a peak at peak flow, before declining as discharge fell. There were too few samples to define patterns during the second peak. In contrast, at PB and Q, peak TDP concentrations were recorded on the initial rising limb, with lowest concentrations at peak flow. After rainfall restart during storm 7, TDP concentrations at PB followed discharge variation, with values in late falling limb lower than those recorded in the second rising limb and peak flow.

In winter storm 9 (Fig. 5), E and PB experienced a marked peak in TDP in the rising limb before falling to low values at peak flow and in the falling limb. At ES, however, peak TDP was recorded after peak discharge and TDP values throughout the storm hydrograph were higher than at pre-storm baseflow. At PB, high TDP concentration was also recorded by the end of the falling limb.

Dissolved Zn storm dynamics

High-magnitude and distinct temporal changes in dissolved zinc were recorded in the late summer storm (Fig. 4). Generally, Zn concentrations were low at pre-storm baseflow and reached multiple peaks at peak flow and during the falling limb. Only at Q were Zn concentrations higher during the rising limb. In the wet season storm (Fig. 5), Zn displayed massive peaks at E and Q, both in the rising and again in the falling limb of the hydrograph, but only in the rising limb at PB. Changes were more muted at ES, with peak concentration recorded at peak discharge.

Although Cu concentrations followed similar intra-storm variation as Zn, pollutant levels were only recorded in winter storms (Fig. 3), also after peak discharge.

5 Discussion

5.1 Differences in hydrological responses between sites

Before discussing the water quality results, differences in hydrological response between the sub-catchments are explained. Urbanization and the associated increase in impervious surfaces have been widely reported to enhance runoff (e.g. Zhang and Shuster 2014; Yao et al. 2015). Nevertheless, for the 10 storms studied, the storm runoff coefficient in the 40% urbanized Ribeira dos Covões catchment ranged only between 1.6% and 5.5%. In part this reflects the high permeability of the catchment provided by the sandstone and limestone bedrock (Ferreira et al. *this issue* a).

Within the study catchment, PB (39% urban area and 15% impervious) displayed both the greatest storm runoff coefficients (2.5% - 11.8%) and quickest response times (5-35 minutes). In contrast, the more highly urbanized ES sub-catchment (49% urban, 27% impervious) experienced lower storm runoff coefficients (2.4% to 6.7%) and slightly higher response times (10-40 minutes). This is thought to be a consequence of distinct drainage systems. In PB, part of the runoff from downslope impervious surfaces is directly piped into the stream, leading to enhanced connectivity between overland flow sources and the stream network. In ES, however, runoff from paved surfaces is mostly diverted into pervious soils, and/or piped into downslope woodland areas, favouring water retention and infiltration, hence reducing the storm runoff response of the stream.

Such an explanation would conform to findings of previous studies highlighting the significance of storm drainage systems (not simply % of impervious area) enhancing flashiness of storm runoff (e.g. Yang et al. 2011, Miller et al. 2014) and much reduced effects of impervious surfaces when not connecting to a storm sewer system (e.g. Hammer 1972).

In Q sub-catchment, containing the largest woodland area (73%) and the smallest impervious cover (5%), storm runoff coefficients were the lowest (0.8% - 4.9%). Storm runoff coefficients in Q, however, were only a little lower than in ES, possibly because overland flow from paved surfaces in the enterprise park, located within Q, is piped into a detention basin and then released direct into the stream network, rather than being directed into pervious soils as within ES. Contrary to the typical flashy hydrographs with greater peak flows found in highly urbanized areas (e.g. Vidon et al. 2009), ES displayed longer-duration hydrographs, sometimes without a clear peak flow (Figs. 4 and 5), in contrast to the quicker response times of Q, even in small events (Table 4).

That higher storm runoff coefficients for Q were found in storms following driest antecedent weather conditions may indicate that normally pervious soil is also providing overland flow, because of the low infiltration capacity induced by water repellency, particularly given the 73% extent of woodland in the catchment (e.g. Ferreira et al. 2016).

Differences in hydrological response between monitoring sites in Ribeira dos Covões may also reflect differences in lithology. In PB, underlain by limestone, baseflow represented16-55% of event runoff, whereas in ES and Q, the sandstone sub-catchments, it is 58-94% and 49-85% respectively (Table 4).

5.2 Influence of urban pattern on water quality

The Ribeira dos Covões results suggest that areas with different urbanization pattern have distinct impacts on surface water quality, particularly in terms of COD, TDP, major cations and pH ($p<0.05$). Nitrogen (Nk-N, NH_4-N and NO_3-N) and heavy metals (Zn and Cu), however, did not show significant differences between sites over the study period ($p>0.05$), but nevertheless at least occasionally exceeded water quality standards at the four monitoring sites.

5.2.1 Chemical oxygen demand and nitrates

The ES sub-catchment, with largest urban land-use (49%) and imperviousness, displayed higher concentrations of COD and NO_3-N (median values of 18.0 mg L^{-1} and 1.46 mg L^{-1}) than E, PB and Q (Fig. 2), with concentrations increasing with percentage impervious surface (Table 1). Enhanced COD and NO_3-N values elsewhere are usually attributed to wastewater contamination (e.g. Wilbers et al. 2014). However, given the separate sewage and storm runoff drainage systems in Ribeira dos Covões, as well as the location of the WWTP outside the catchment, treated effluent would not seem to be a major pollutant source. COD and NO_3-N can be provided by diffuse sewage sources and road runoff, which can be an important pollutant source due to the high runoff volumes that can be involved (e.g. Crabtree et al. 2006; Pereira et al. 2015). Both these sources may be significant in the Ribeira dos Covões catchment.

NO_3-N is the dominant nitrogen form in ES (median values of 1.46 mg L^{-1}), and may be linked with use of fertilizer in the mainly detached houses with gardens and lawns, covering 15% of the urban pattern of ES (Table 1), as found in such detached house areas elsewhere (e.g. Lin et al. 2014; Carey et al. 2013). Some of the NO_3-N in ES may also have derived from the small agricultural area adjacent to the stream channel. Fertilizer application in both urban and agricultural areas is usually carried out during spring and summer, which may in part explain the high concentrations of NO_3-N recorded during storms in late summer (Fig. 2).

5.2.2 Kjeldhal nitrogen and ammonium

Higher concentrations of Nk-N and NH_4-N were recorded at the catchment outlet at E and at Q, which has the lowest urban land-use (22%), than at ES and PB. At both E and Q sites, organic compounds were the dominant form of nitrogen, given the relatively low NO_3-N concentrations (median values of 1.01 mg L^{-1} and 0.35 mg L^{-1}) and the small percentage of NH_4-N in relation to Nk-N (34% and 25%, respectively). Extensive cattle rearing in agricultural fields in upslope and channel-margin locations in E and Q, is thought to be a major source of Nk-N and NH_4-N, and may explain why concentrations often exceeded pollution guidelines (maxima of 1.87 mg L^{-1} Nk-N and 1.32 mg L^{-1} NH_4-N, Fig. 2).

An additional Nk-N and NH_4-N source may occasionally be untreated domestic wastewater. Contamination by leaks in the sewage drainage system was observed occasionally through the colour and smell of surface water. Sewage leaks, however, are prone to influence water quality in all the study sites. In Q sub-catchment, past soil contamination from the abandoned WWTP, which received domestic wastewater from upslope urban cores and spread it downstream without treatment until 2012, may also be a potential source of Nk-N and NH_4-N. These soil contamination sources may explain why pollution levels were exceeded only in late winter storms (Fig. 2), because of greater connectivity with stream network, favoured by the higher soil moisture content at that time. Great concentrations of NH_4-N can be toxic to aquatic organisms (e.g. Lin et al. 2014).

5.2.3 Total dissolved phosphorus

Highest concentrations of TDP were found at E and PB (median values of 0.07 mg L^{-1} at both sites, $p<0.05$). Phosphorus in urban areas is usually associated with household sources, such as laundry and dishwasher detergents, as well as organic matter biodegradation in domestic wastewater (e.g. Carey et al. 2013), but it can also derive from garden fertilizers. Apart from sewage leaks already discussed, pavement and car washes were often observed within PB, which forms an upstream part of E. In PB, high concentrations of TDP could possibly also be associated with the clay content of the limestone soils. Tus, in Xujiawan catchment, Southwest China, phosphorus enters the runoff and open water bodies mainly through transport in the clay and fine silt fractions (Yang et al. 2009).

Although TDP concentrations never exceeded the Portuguese water quality standard (1 mg L^{-1}), all sites recorded concentrations above the 0.1 mg L^{-1} established as the critical phosphorus level in runoff for eutrophication (US EPA 1986). This critical level was surpassed in 32% of the samples collected in PB, 21% in E, 7% in ES but only 3% in the least urbanized Q sub-catchment which is 73% woodland (maximum concentrations of 0.25 mg L^{-1}, 0.39 mg L^{-1}, 0.17 mg L^{-1} and 0.14 mg L^{-1}, respectively).

5.2.4 Heavy metals

Although draining the smallest urban cover, Q displayed higher median concentrations of Cu and Zn (0.03 mg L^{-1} and 0.11 mg L^{-1}), similar to PB covered by 39% urban area (0.03 mg L^{-1} and 0.14 mg L^{-1}, respectively). Heavy metals are typically associated with vehicular traffic and road runoff in urban situations (e.g. Crabtree et al. 2006; Herrera 2007). In Ribeira dos Covões catchment, a complementary study of heavy metals in runoff collected from four roads provided direct evidence of the capacity of road runoff to generate heavy metal pollution in the catchment (Ferreira et al. *in press* b). Although heavy metal concentrations varied through time, they displayed a direct relationship with vehicular traffic intensity, with dissolved Cu and Zn recording maxima of 0.2 mg L^{-1} and 0.5 mg L^{-1}, respectively. Nevertheless, heavy metals in road runoff were mostly in particulate form, as total concentrations of Cu and Zn reached 0.7 mg L^{-1} and 5.0 mg L^{-1}, respectively.

The higher concentrations recorded at Q probably result from road runoff from the enterprise park area being piped directly to the detention basin and diverted into the stream network, i.e. high connectivity between source and stream network. In PB, road runoff, particularly from the major national road, is in part piped to fields adjacent to the stream. Higher moisture content in soils receiving road runoff (as in prolonged wet weather) may favour connectivity with the stream network, and been responsible for the occasional pollutant concentrations that were recorded (maximum Zn of 0.59 mg L^{-1} and Cu of 0.10 mg L^{-1}) (Fig. 3).

ES, despite draining the largest impervious cover (27%), recorded lower Zn and Cu concentrations (Fig. 3), possibly because road runoff is diverted into pervious soils, located at a greater distance from the stream network than at PB. These contrasts highlight the importance of variations in stormwater drainage system characteristics in controlling urban runoff quantity and quality, rather than simply % urbanization, as found also to be the case in Tucson, Arizona (Gallo et al. 2013).

5.2.5 Major cations and pH

Although not included in Portuguese water quality standards, major cation concentrations (Na, Ca and Mg), do not constitute a water quality problem. These solutes are usually associated with rock composition, explaining the significant positive correlations with baseflow ($p<0.05$). In Ribeira dos Covões, Ca and Mg concentrations (Fig. 3) were in accordance with those found in streamwater of forest catchments at Colorado, overlaying sedimentary rocks including, among others, sandstone and limestone. In these Colorado catchments, Miller (2002) reported Ca, Mg and Na concentrations ranging from 41 mg L^{-1} to 101 mg L^{-1}, 3 mg L^{-1} to 25 mg L^{-1} and 1 mg L^{-1} to 5 mg L^{-1}, respectively. The lower concentrations of Na, Ca and Mg recorded in PB, despite its limestone lithology, may be associated with its lower baseflow fraction (Table 4). Higher Na concentrations than those reported by Miller (2002) may be linked to higher evapotranspiration. The limestone lithology of PB may explain its highest pH (median of 7.6, $p<0.05$).

5.3 Temporal dynamics in water quality parameters

Streamwater quality varied considerably seasonally and within storm events. Several factors of the hydrological regime can affect temporal dynamics including storm and antecedent rainfall characteristics, stream discharge, the proportions of baseflow and storm runoff, and flow connectivity between source areas and the stream (e.g. Yang et al. 2009; Zhao et al. 2015).

COD, nutrients (Nk-N, NH_4-N, NO_3-N and TDP) and heavy metals (Zn and Cu) displayed higher median concentrations in storms recorded in late summer than in the wet season (Figures 2 and 3), possibly due to two mechanisms: (i) pollutant accumulation and subsequent flushing during the first rainfall events after long dry periods, although no statistically significant correlations with antecedent rainfall were identified ($p>0.05$); and (ii) decreased dilution effect provided by (a) lower summer baseflow component, which is typically associated with better water quality than surface water (e.g. Carey et al. 2013); and (b) lower storm runoff volume.

During dry conditions solutes precipitate and accumulate within catchment and sub-catchment soils due to water table drawdown and reduced soil water content, leading to restrictions on biogeochemical activity. Accumulated solutes are than available for mobilization during rainfall and subsequent runoff (Vidon et al. 2009; Gallo et al. 2013). The flushing process recorded in late summer led to higher NH_4-N and Nk-N during the rising limb of the hydrograph in E, PB and Q (Fig. 4), exceeding on a few occasions the water quality standards. Higher NO_3-N concentrations in late summer than wet season storms may be also a consequence of their greater availability with crop and garden fertilizer application in spring and early summer, in association with Portuguese Mediterranean climatic setting. The first flush effect after extended dry periods have been also reported in urban settings by previous authors (e.g. Barco et al. 2008).

Phosphorus and heavy metals (Zn and Cu), however, seem to be less easily mobilized than NH_4-N and Nk-N, as peak concentrations were reached after peak flows (Fig. 4). Peak concentrations of Zn, in a few cases exceeded water quality standards in PB and E (maxima of 0.59 mg L^{-1} and 0.55 mg L^{-1}, respectively). The later timing of peak concentrations of TDP, Zn and Cu can be possibly associated with soil absorption capacity and the difficulty to be detached/dissolved and transported by overland flow, as noted by Yang et al. (2009). The delayed peak in Zn and and Cu also suggests that soil sources adjacent to roads and development of connectivity between roads, soil and the stream network are of greater significance than simply quick runoff from the roads.

In PB, overland flow from paved surfaces seems to be the major runoff and pollutant source, explaining quicker runoff and solute responses than at the other monitoring sites (Fig. 4). Although in Q there is also partial piping of overland flow from paved surfaces, solute transport may have been delayed by the detention basin.

The overall higher COD and nutrient concentrations in late summer storms are also thought to be a consequence of lower dilution by reduced summer baseflows (Table 4), as recorded elsewhere by Wilbers et al. (2014). This is supported by the negative correlations found between all nutrient concentrations and baseflow ($p<0.05$), at most of the sites. In E, however, peak concentrations of NH_4-N and Nk-N were measured under baseflow conditions, before rainfall start, and recession limb, with few samples exceeding water quality standards. This highlights a combination of possible contamination from baseflow and potential dilution by cleaner stormflow. This dilution effect provided by stormflow is also noticeable in NH_4-N and Nk-N responses, that show decreasing concentrations with increasing runoff volume (Fig. 4).

In ES, however, increasing runoff volume during storms observed in late summer does not seem to have an important diluting influence on nutrient concentrations, as NH_4-N, Nk-N and TDP concentrations increased with discharge and attained highest values at peak flow. These distinct solute responses compared with those at other monitored sites may be linked to the greatest storm runoff coefficients of ES (Table 4). Stormflow, however, only showed a statistically significant positive correlation with NH_4-N concentration ($p<0.05$).

At E and ES, higher concentrations of Nk-N and NH_4-N were recorded on the recession limb than at the beginning of late summer storms. In E and PB in the summer storms (Fig. 4) and in E and Q in the winter storm (Fig. 5) Zn concentration showed marked peaks both on the rising limb and the recession limb. This may indicate that lateral movement of Zn (and Cu, which behaved similarly), Nk-N and NH_4-N in soil by slower throughflow may be providing the delayed second peak, whereas the smaller initial peak derives from flushing by overland flow and road runoff.

Over the course of the wet season, repeated storm events appear to have led to progressive exhaustion of COD, nutrient and heavy metal sources, evidenced by much lower concentrations in late winter than in summer storms (Figures 2 and 3), as reported in other catchments with a Mediterranean climate (e.g. Bowes et al. 2009; Siwek et al. 2012).

During winter storms, Nk-N, NH_4-N and TDP exhibited similar responses to those experienced in late-summer storms, namely increased concentrations during the rising limb, lower values at peak flow and increasing concentrations over the falling limb of the hydrograph. In PB, concentrations of NH_4-N, Nk-N, Zn and Cu during the falling limb were usually lower than at the beginning of storm runoff.

High concentrations of nutrients (Nk-N, NH_4-N, NO_3-N and TDP) and heavy metals (Zn and Cu) during winter storms may be a result of greater flow connectivity between solute sources and the stream network (rather than just the arrival of slower throughflow, as suggested earlier). Thus, in E Zn exceeded pollution levels more frequently in winter than in late-summer storms. In Q, Zn concentrations only exceeded water quality standards in winter storms (Fig. 3). The increased flow connectivity resulted from increasing soil moisture over the wet season in the catchment leading to decreasing infiltration and surface water retention capacity (Ferreira et al. 2015), thus favouring runoff and solute transfer into downslope areas.

In ES, highest NH_4-N, Nk-N and Cu concentrations measured during the falling limb of winter storms (sometimes exceeding water quality standards) (Fig. 5), may be provided by upslope urban areas lacking a storm drainage system. In E and Q, higher NH_4-N and Nk-N also reached pollutant concentrations in the falling limbs of a few winter storms (Fig. 2) and pollutant concentrations of Zn were reached in Q only during winter storms (Fig. 3). The increased concentrations of these nitrogen forms and heavy metals in Q over the wet season, may partly result from possible leaching of soils polluted by the abandoned WWTP.

6 Conclusions

The results of this study of the small, peri-urban Ribeira dos Covões catchment in central Portugal, suggest that (i) storm rainfall, antecedent rainfall and seasonal Mediterranean rainfall regime and (ii) urbanization pattern, notably the extent, location and degree of continuity of impervious surfaces and type of storm drainage system, together largely determine temporal dynamics of pollutant and solutes during storm events via their influences on runoff responses, thereby, influencing catchment water quality and aquatic ecosystem sustainability.

Significant increases in COD and TDP with increasing urban area of the monitored catchment and sub-catchments were recorded. The Quinta (Q) sub-catchment, with lowest urban cover (22%) and largest woodland (73%), displayed lowest COD concentrations than the other more urbanized (39-49%) catchments. Together with Espírito Santo (ES), this sub-catchment also showed lower TDP concentrations than recorded at the catchment outlet (E) and at Porto Bordalo (PB). ES, however, drains the largest urban area (49%) and impervious cover (27%), but the upslope location of most impervious surfaces and the dispersion of overland flow in downslope pervious soils (in woodland and agricultural fields) minimize the potential impacts on streamflow. Nevertheless, the ES urban pattern, characterized mainly by detached houses surrounded by green spaces, may have led to higher NO_3-N concentrations than in the other sites, due to high applications of fertilizer to lawns and gardens.

The sub-catchments (PB and Q) with urban areas characterized by storm drainage systems connecting road runoff directly to the stream network, displayed higher concentrations of heavy metals (Zn and Cu), typically associated with vehicular traffic. Hence greater connectivity between the stream network and surrounding land-use may be also an important parameter affecting water quality. Thus, in E and Q, higher Nk-N and NH_4-N concentrations are thought to result from cattle-rearing in agricultural fields adjacent to their stream networks.

Generally, median concentrations of COD, nutrient parameters and heavy metals were greater in late summer than winter storms. This pattern was attributed to (i) the accumulation of pollutant sources in surface soil and on roads during prolonged dry periods and subsequent flushing during the first rainfall and runoff events, and (ii) the lower dilution effect provided by low summer baseflow. These mechanisms led to concentrations of Nk-N and NH_4-N exceeding pollution thresholds in some samples at all the monitored sites, mostly in the rising limb of the hydrograph in late summer storm events.

Storm events over the wet season, however, led to increasing soil moisture that enhanced the connectivity between pollutant sources, runoff processes and the stream network. Greater wet-season connectivity may explain pollutant levels of Zn attained in PB and Q, mostly during the falling limb of the hydrograph, as well as pollutant concentrations of Cu in ES and E.

Intra- and inter-storm variations over the study period demonstrate that solute (including pollutant) transport in an urban Mediterranean environment may not be effectively predicted using simple relationships with hydrological conditions or rainfall. This study has demonstrated that a larger storm event dataset, covering all seasons and a range of storm sizes and antecedent weather, is needed to understand the impact of different urban patterns, and complex land-use mosaics in peri-urban areas, on hydrochemical response of the catchment and its sub-catchments to storm events. This study, however, covered only selected pollutant and solute parameters; in particular, additional monitoring of dissolved oxygen and microbial contamination parameters should be added to give a fuller picture of the impact of urban activities.

Understanding the impact of urbanization pattern and storm drainage systems on hydrochemical dynamics is both relevant and crucial to help policymakers design and implement the most appropriate solutions to achieve good water quality and preserve aquatic ecosystems. Pollution control policies should include urban planning and be adjusted to fit changes over space and time, focusing on (1) pollutant flushing in late-summer storms and (2) increasing flow connectivity through the wet season. Upslope urban cores and dispersed urban patterns should favour runoff dispersion in downslope pervious soils. This will favour not only overland flow retention and infiltration but also prevent pollutants from reaching the stream channel.

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Tables

Table 1 – Catchment and sub-catchment characteristics: land-use/cover, mean slope and lithology. Within urban areas, impervious surfaces comprise roads and buildings; semi-pervious surfaces include construction sites, parking zones, courtyards and pavements; and pervious surfaces comprise gardens.

	ESAC (outlet) - E	Porto Bordalo - PB	Espírito Santo - ES	Quinta - Q
Area (ha)	620	113	56	150
Mean slope (°)	10	12	8	4
Land-use / Land cover (%)				
Urban	40	39	49	22
Impervious	*17*	*15*	*27*	*5*
Semi-pervious	*11*	*9*	*7*	*10*
Pervious	*12*	*15*	*15*	*7*
Woodland	56	57	46	73
Agriculture	4	4	5	5
Lithology (%)				
Sandstone	56	2	98	100
Limestone	41	98	0	0
Alluvial	3	0	2	0

Table 2 – Portuguese standards for minimum surface water quality (DL236/98), relating to chemical parameters measured in the current study.

pH	N_K-N	NH_4-N	TDP	Zn	Cu
	(mg L^{-1})				
5.0-9.0	2.0	1.0	1.0	0.5	0.1

Table 3 – Rainfall characteristics for the 10 storm events monitored (Imean: mean intensity, I_{60}: maximum hourly rainfall intensity, API_7: 7-day antecedent rainfall, and AP_{14}: 14-day antecedent rainfall).

Storm	Date	Rainfall (mm)	Duration (h)	I_{mean} (mm h^{-1})	I_{60} (mm h^{-1})	API_7 (mm)	API_{14} (mm)
1*	23-24 Oct 2011	7.9	13.0	0.6	3.1	0.0	0.1
2*	26 Oct 2011	3.8	3.5	1.1	8.4	28.1	28.1
3	02 Nov 2011	24	2.3	10.7	15.9	22.7	50.8
4	14 Nov 2011	8.9	7.8	1.1	3.6	32.9	98.5
5	16 Dec 2011	3.6	4.5	0.8	1.6	33.6	43.2
6	04 May 2012	2.4	7.4	0.3	1.3	42.5	82.6
7*	25-26 Sept 2012	14.3	16.7	0.9	4.1	14.3	14.3
8	08-10 Jan 2013	9.9	28.9	0.3	2.3	0.0	17.0
9	15-17 Jan 2013	20.2	21.4	0.9	5.4	25.4	25.4
10	25-29 March 2013	46.8	93.25	0.5	5.3	47.3	70.8

* Storms recorded after summer

Table 4 – Streamflow responses to the 10 rainstorms at the catchment outlet (E: ESAC) and the three sub-catchm

Espírito Santo and Q: Quinta).

	Peak discharge ($L s^{-1}$)				Mean discharge ($L s^{-1}$)				Baseflow fraction (%)				Storm runoff coefficient (%)			
Storm	E	PB	ES	Q	E	PB	ES	Q	E	PB	ES	Q	E	PB	ES	Q
1	241	82	0	0	26	8	0	0	46	16	-	-	1.8	4.6	-	-
2	149	83	29	54	37	7	12	9	61	16	64	51	2.0	4.2	6.0	2.7
3	1448	643	94	348	385	88	34	104	56	23	58	54	4.5	7.3	3.6	4.2
4	386	140	46	102	140	27	25	34	65	22	81	81	3.6	7.2	4.7	1.9
5	122	43	15	17	56	6	8	13	74	18	72	49	1.6	2.5	2.4	0.8
6	127	63	11	16	77	5	5	13	87	27	94	85	2.2	4.8	2.7	1.8
7	550	260	50	73	107	30	29	24	56	18	79	65	4.1	9.8	5.6	2.9
8	191	76	46	55	27	4	7	10	77	31	65	73	1.8	3.3	6.7	2.7
9	733	258	50	94	95	12	18	28	74	31	86	85	3.2	5.9	3.5	2.1
10	1789	588	72	269	313	41	24	48	87	55	86	79	5.5	11.8	4.1	4.9

Figures

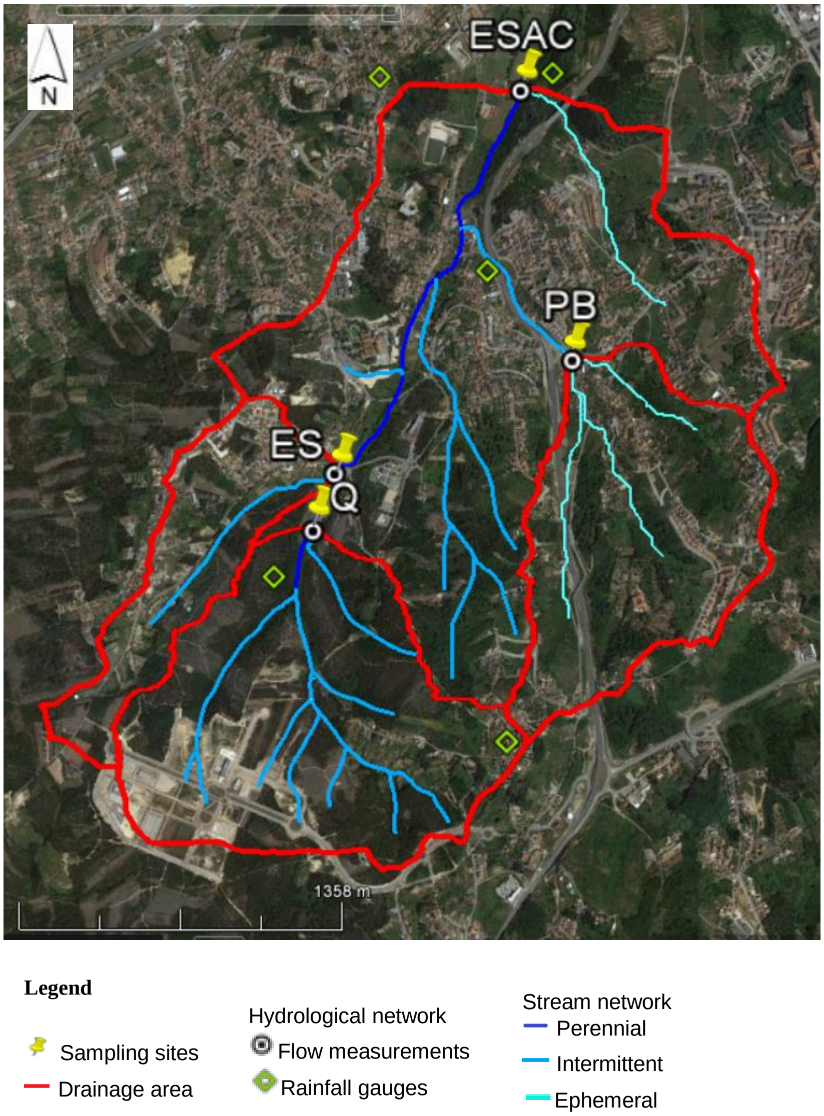


Figure 1 - Ribeira dos Covões catchment and location of the sampling sites – E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and Q: Quinta (adapted from Google Earth, 2014).

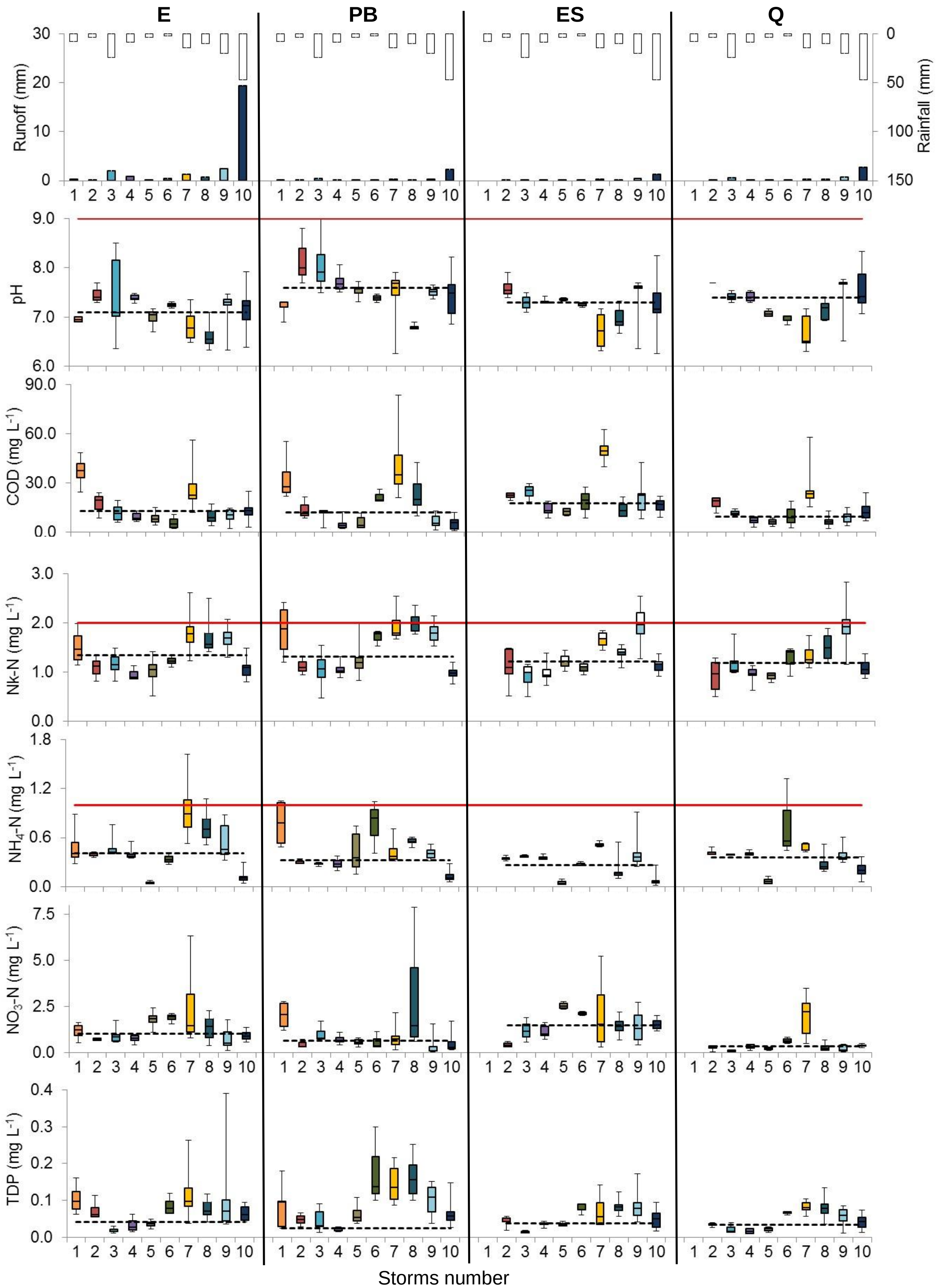


Figure 2 - Rainfall and runoff and box plots (median, upper (75) and lower (25) quartiles, maximum and minimum) showing pH, COD, N_K, NH_4-N, NO_3-N and TDP concentrations at ESAC (E), Porto Bordalo (PB), Espírito Santo (ES) and Quinta (Q) for the ten storms monitored between October 2011 and March 2013. Black dashed lines

represent median values at each study site and red lines represent Portuguese minimum water quality standards (DL236/98). The standard for TDP is 1.0 mg L^{-1} and is not shown as it is above the scale of the graphs.

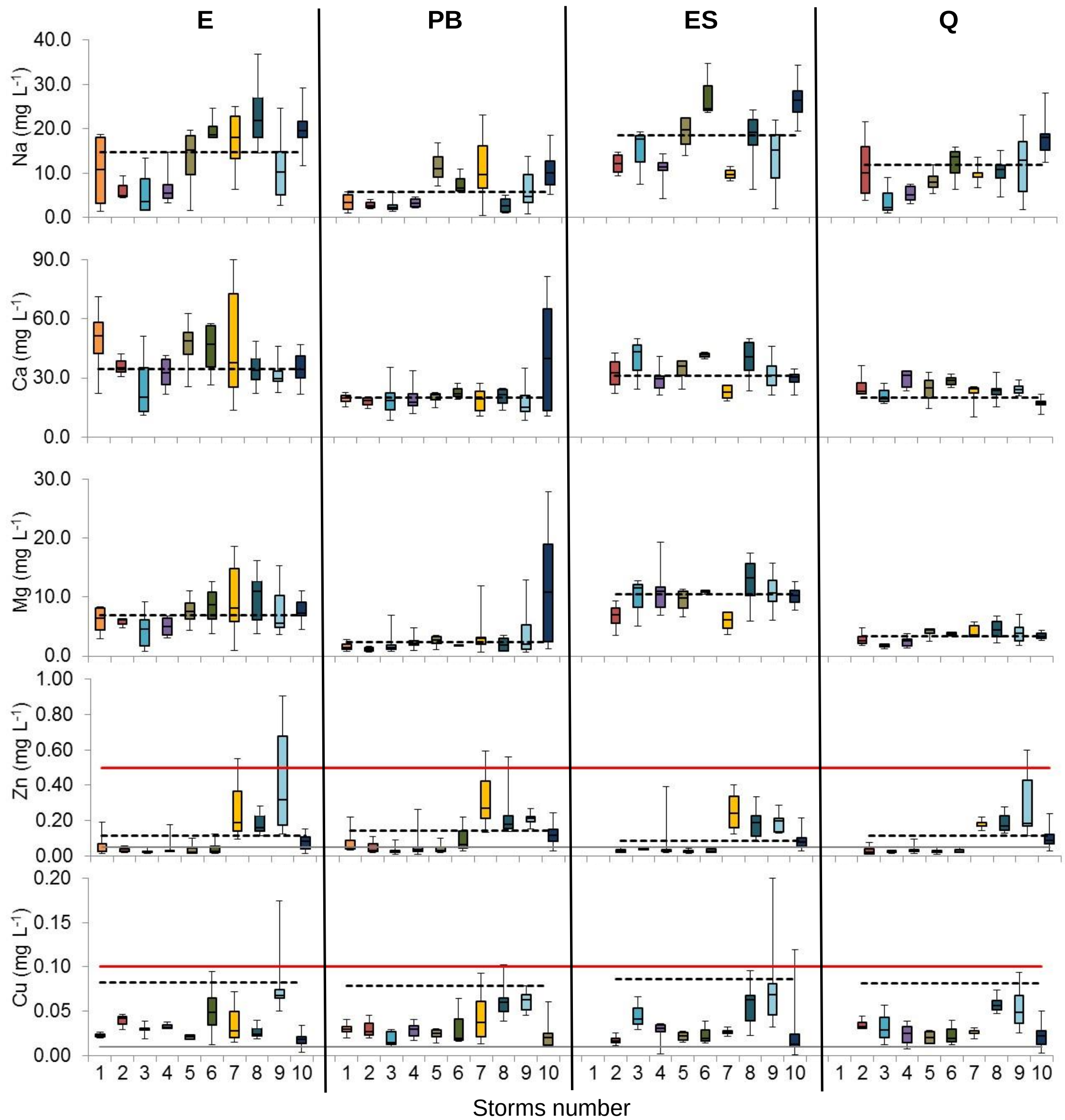


Figure 3 - Box plots (median, upper (75) and lower (25) quartiles, maximum and minimum) showing major cations (Na, Ca and Mg) and heavy metals (Zn and Cu) concentrations at ESAC (E), Porto Bordalo (PB), Espírito Santo (ES) and Quinta (Q) for the ten storms monitored between October 2011 and March 2013. Black dashed lines represent median values at each study site and red lines represent Portuguese minimum water quality standards (DL236/98). Grey lines in Zn and Cu represent detection limits.

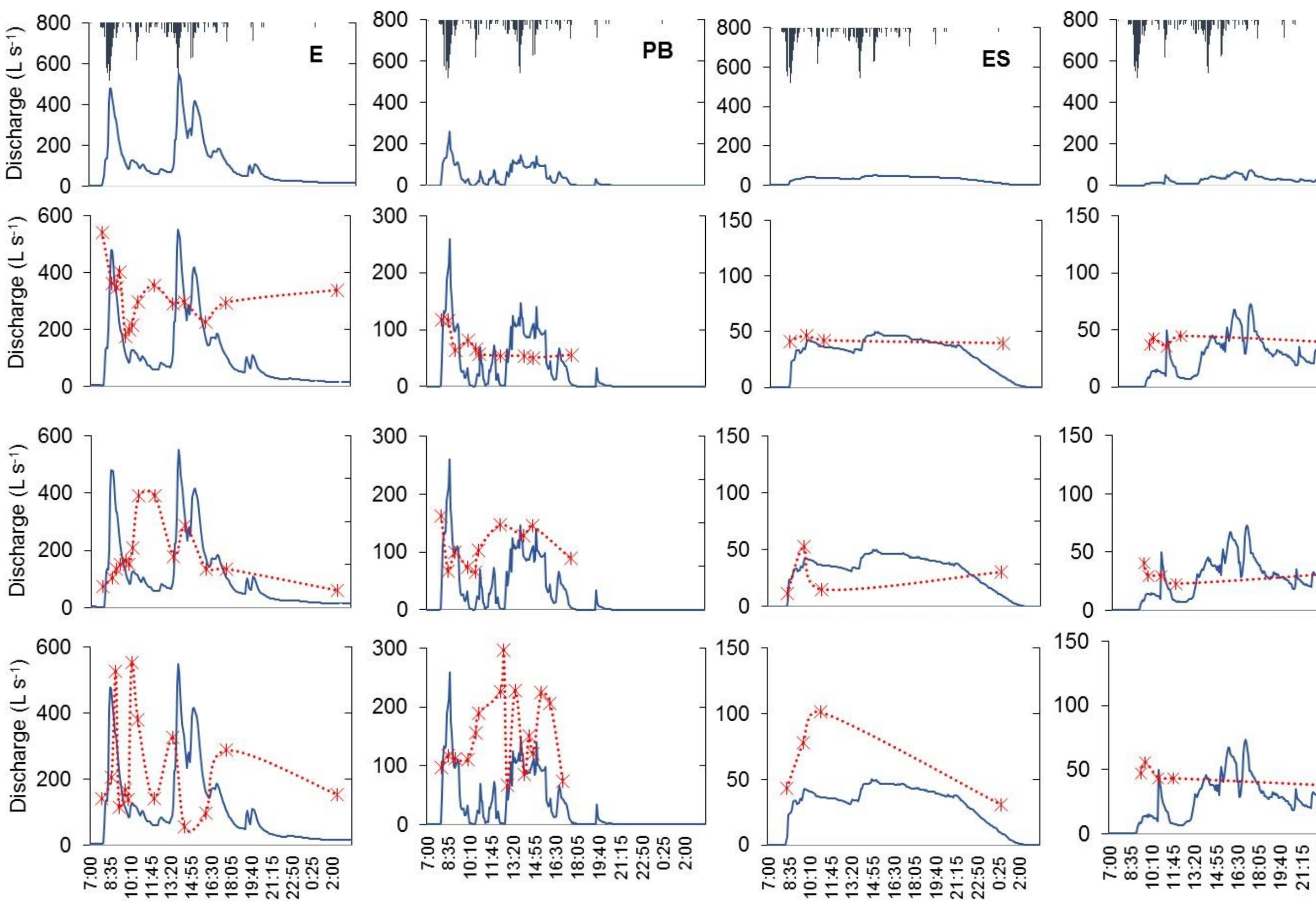
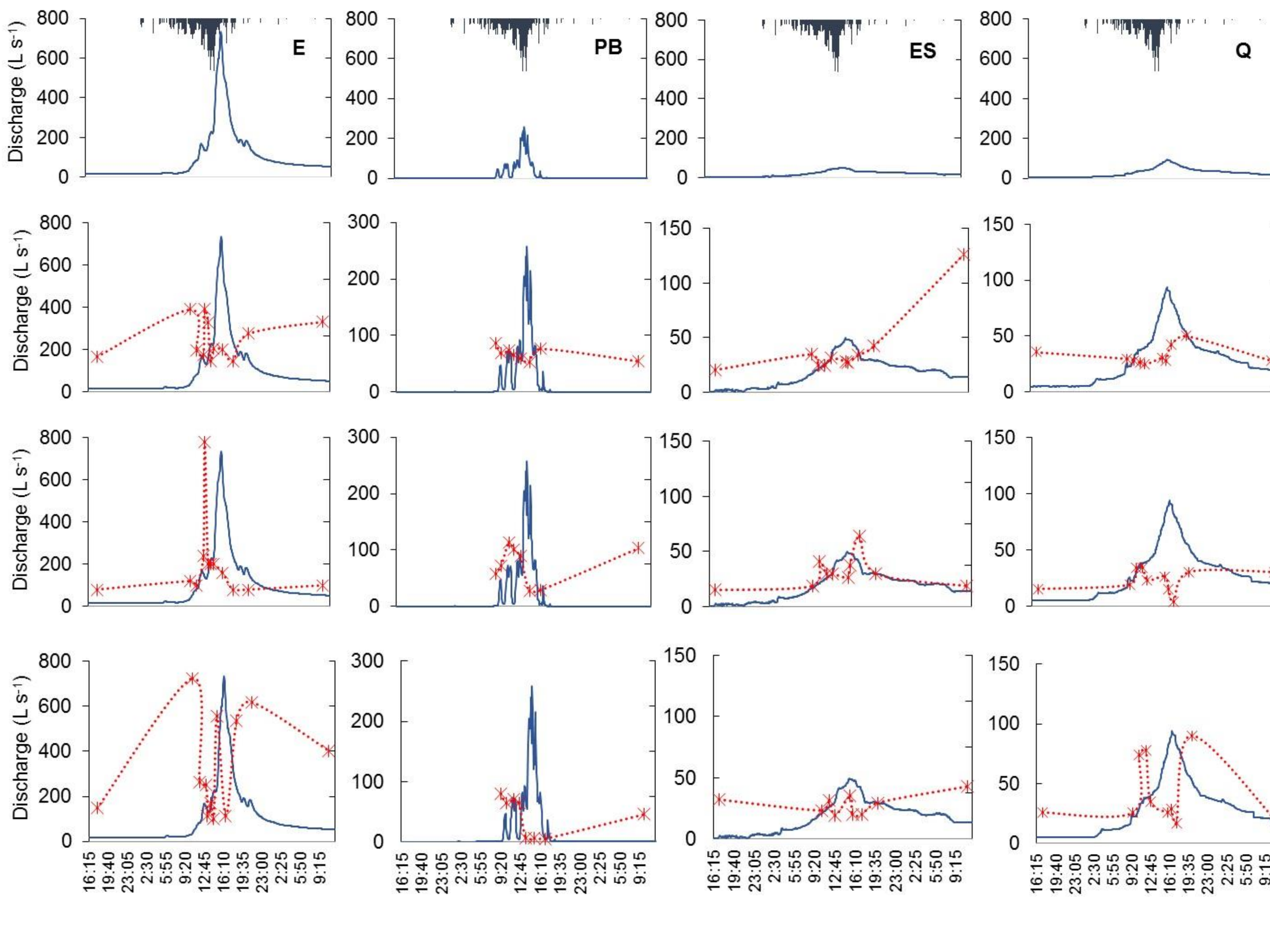


Figure 4 – Ammonium nitrogen (NH_4-N), total dissolved phosphorus (TDP) and zinc (Zn) responses (red lines
2012 rainstorm event (storm 7) at the four catchment sites (E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and
and discharge.



E
PB
ES
Q
Discharge (L s-1)
16:15
19:40
23:05
2:30
5:55
9:20
12:45
16:10
19:35
23:00
2:25
5:50
9:15

Figure 5 - Ammonium nitrogen (NH_4-N), total dissolved phosphorus (TDP) and zinc (Zn) responses (red lines) t
rainstorm event (storm 9) at the four catchment sites (E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and Q: C
discharge.