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

--Manuscript Draft--

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Abstract:	<p>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.</p> <p>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]).</p> <p>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</p>	

	<p>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 $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ 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.</p> <p>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.</p>
Response to Reviewers:	The response to Reviewers is performed in the attached "Revision_Notes" document.

1 1 URBAN SOILS AND SEDIMENTS

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6 3 **Dynamics of surface water quality driven by distinct urbanization patterns and**
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9 4 **storms in a Portuguese peri-urban catchment**

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1 19 **Abstract**

2 20 *Purpose:* Although influences of urban land-use on water quality have been widely investigated, the
3 21 impacts of different urbanization patterns, particularly in Mediterranean environments, are not well
4 22 understood. Focussing on a Portuguese peri-urban catchment with 40% urban cover, this paper
5 23 explores (i) the impact of areas with differing urban extent and storm drainage system on streamwater
6 24 quality, and (ii) temporal variations driven by season and storm events of differing magnitude,
7 25 intensity and antecedent weather.

8 26 *Materials and methods:* Water quality was assessed at the catchment outlet (E) and for three upstream
9 27 tributaries: (1) Porto Bordalo (PB), 39% urban with a new major road and piping of some overland
10 28 flow from impervious surfaces directly into the stream, (2) Espírito Santo (ES), 49% urban, mostly
11 29 comprising detached houses surrounded by gardens, and with overland flow infiltrating into
12 30 downslope pervious soils; and (iii) Quinta (Q), 22% urban with partial piping of overland flow from
13 31 a recent enterprise park area. Water samples were collected at different stages in storm hydrograph
14 32 responses to ten rainfall events in October 2011 to March 2013. Water quality variables analysed
15 33 included chemical oxygen demand (COD), nutrients (kjeldahl nitrogen [Nk-N], ammonium [NH₄-N],
16 34 nitrate [NO₃-N] and total dissolved phosphorus [TDP]) and heavy metals (zinc [Zn] and copper
17 35 [Cu]).

18 36 *Results and discussion:* Urban areas had great impact on COD, with highest median concentrations
19 37 in ES and lowest in Q. In ES, fertilizing lawns and gardens may have been responsible for its higher
20 38 median NO₃-N concentrations. High concentrations of heavy metals were recorded in PB and Q,
21 39 probably due to piping of road runoff directly into the stream. Generally, higher pollutant
22 40 concentrations were recorded in the first storm events after the summer drought, due to flushing of
23 41 accumulated solutes and a lower dilution effect, with Nk-N and NH₄-N exceeding water quality
24 42 standards. Over the wet season, increasing soil moisture favoured greater flow connectivity between
25 43 runoff processes from pollutant sources and the stream network, leading to a higher proportion of
26 44 samples exceeding pollution thresholds.

27 45 *Conclusions:* No direct relationship was identified between urban extent and water quality, possibly
28 46 due to the overriding impact of different storm drainage systems and flow connectivities of different
29 47 urban patterns. Hydrological regime, linked to seasonal changes, also exerted a major influence on
30 48 water quality dynamics. Information on the spatiotemporal dynamics of pollutants, linked to different
31 49 urban patterns and storm drainage systems, should help enable urban planners to minimize adverse
32 50 impacts of urbanization on aquatic ecosystems.

33 51
34 52 **Keywords** Flow connectivity • Heavy metals • Mediterranean climate • Storm events • Urban pattern
35 53 • 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~~Urbanization 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], copper [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, polychlorinated 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

1 78 al. 2013), diffuse sources, and treated and untreated effluent from wastewater treatment
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3 79 plants and storm sewer overflows (Yu et al. 2014); and (iii) lawns and gardens maintenance,
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5 80 due to inappropriate fertilization and irrigation activities (Lin et al. 2014).
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9 81 Although the type of urban development (e.g. industrial, commercial, residential, and
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11 82 recreational) determines the nature of pollutants released (e.g. Tu 2011), urban runoff
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13 83 generally has been considered a major non-point source of pollutants within catchments (e.g.
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16 84 Yu et al. 2016). Direct relationships have been reported between pollutant concentrations and
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18 85 percentage urban surfaces (e.g. Sliva and Williams 2001), with for example total impervious
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21 86 area being considered an indicator of aquatic ecosystem conservation status (e.g.
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24 87 Rautengarten 2006; Kuusisto-Hjort and Hjort 2013).
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27 88 Other authors, however, suggest that the location of pollutant sources within the catchment,
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29 89 and the distance to the stream network, are better indicators of water quality (e.g. Yu et al.
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32 90 2016). Urban areas located downslope may provide runoff flowing into the stream network,
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35 91 whereas runoff from upslope areas may be infiltrated and/or retained in downslope pervious
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37 92 soils (e.g. Ferreira et al. 2015), preventing pollutants from reaching aquatic ecosystems. In
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39 93 catchments comprising mosaics of urban and non-urban land-uses, typical of peri-urban
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42 94 catchments, the connectivity between runoff/pollutant sources and water resources can vary
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44 95 greatly and have been little researched to date, particularly in Mediterranean environmental
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46 96 settings. Furthermore, there is a general lack of studies exploring the dynamics of pollutant
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49 97 concentrations and fluxes in peri-urban catchments (Rodríguez-Blanco 2013).
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53 98 In order to fulfiladdress some of these research gaps, this study investigates the spatial and
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55 99 temporal dynamics of surfaceaspects of stream-water chemistry in a peri-urban catchment in
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58 100 Portugal, and explores in particular the influence of landscape pattern on flow and pollutant
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1 | 101 connectivity in storm events at different seasons and following differing antecedent weather
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3 | 102 associated with contrasting climate settings, determined by the Mediterranean climate.
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7 | 103 ~~This~~The study aims to assess the impact of different urban patterns, in forms of different
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9 | 104 impervious cover and spatial arrangement of pervious and impervious surfaces, on surface
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11 | 105 water quality and discharge chemistry dynamics in a typical Portuguese peri-urban
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13 | 106 catchment. The specific objectives are to (i) assess water quality differences between three
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15 | 107 sub-catchments with distinct urbanization patterns and the catchment outlet, as regards to pH,
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17 | 108 ~~and dissolved fractions of~~ chemical oxygen demand (COD), nutrients (Kjeldahl nitrogen [Nk-
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19 | 109 N], ammonium [NH₄-N], nitrate [NO₃-N] and total dissolved phosphorus [TDP]~~nitrogen and~~
20 |
21 | 110 phosphorous), heavy metals (Cu and Zn) and major cations (calcium [Ca], magnesium [Mg]
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23 | 111 and sodium [Na]); (ii) explore temporal variations ~~in~~of water quality between and within
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25 | 112 ~~driven by distinct~~ storm events at different times over the of year; (iii) ~~examine chemical~~
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27 | 113 ~~loops during storm events;~~ and (iiiiv) investigate whetherif pollutant threshold levels
28 |
29 | 114 (according to Portuguese water quality standards)~~concentrations~~ were exceededattained and
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31 | 115 under which weather conditionssettings, according with Portuguese water quality standards.
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33 | 116 A better understanding of the impact of urban patterns on ~~annual~~ water quality, should
34 |
35 | 117 enableguide urban planners to minimize adverse impacts of urbanization on stream
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37 | 118 ecosystems.

119 120 **2 Study site description**

121 The study was carried out in the small (6.2 km²), peri-urban Ribeira dos Covões, ~~a small (620~~
122 ~~ha) peri-urban~~ catchment on the outskirts of the city of Coimbra in central Portugal (Fig.1).

1 123 The catchment is characterized by sandstones with Fluvisols and Podsoles in west and
2
3 124 limestone with Leptic Cambisols in the east (WRB 2006).

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7 125 The climate is humid Mediterranean. The mean annual temperature is 15°C, ~~linked~~ with
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9 126 ~~monthly means varying from a minimum in January (10°C in January to) and~~ a maximum of
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11 ~~in August (22°C in August).~~ The mean annual rainfall at Coimbra-Bencanta is 906mm, with
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13 127
14 128 wet winters and long dry summers (~~just~~ 7% of ~~the~~ rainfall between June and August) (INMG,
15
16 129 1971-2000). This temporal pattern causes a strong seasonal variation ~~in~~ streamflow,
17
18 130 although the perennial flow at the outlet is supplied by several springs (mainly on sandstone).
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20 131 Annual runoff averages 135mm, ranging from 76mm in the hydrological year (October to
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22 132 September) 2011/12 to 200mm in 2012/13, with baseflow accounting for 33-37% of
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24 133 streamflow (Ferreira et al. *this issue in press* a).

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30 134 Catchment land-use comprises urban areas (40%) dispersed within woodland (56%) and
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32 135 agricultural landfields (4%). The woodland is dominated by eucalyptus, but with some pine
33
34 136 plantations and a relict oak stand. Agricultural land-use consists of a few olive plantations,
35
36 137 pasture areas for cattle along part of the main stream, and small family farms with vegetables.
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38 138 Urban land-use mainly comprises residential areas, some small supermarkets and shops,
39
40 139 educational and health services, including a central hospital, and a few facilities (garage
41
42 140 shops, sawmill and a pharmaceutical factory industry). An enterprise park, covering 5% of the
43
44 141 catchment area, is under construction in the headwaters in the extreme southwest of the
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46 142 catchment (clearly visible in Fig.1). A network of roads extends across the catchment and
47
48 143 includes a recent motorway. Residential areas differ greatly in urbanization style, comprising
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50 144 (i) areas of single-family houses, surrounded by gardens, and (ii) recent row-houses and
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52 145 apartment blocks. These distinct residential areas house approximately 26,700 inhabitants,
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1 146 with population densities ranging from <25 inhabitants km⁻² to >9900 inhabitants km⁻² (Pato
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3 147 et al. 2015).

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7 148 In the newer urban areas, of high population density, part of the runoff from impervious
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9 149 surfaces is collected in culverts and gutters and routed or piped direct to the stream network.

10
11 150 In contrast, in urban settlements surrounded by gardens, agricultural and woodland soils,
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13
14 151 stormwater tends to ~~just~~ dissipate in ~~these~~ adjacent areas of high permeability.

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18 152 Domestic effluent, however, is piped to a large, ~~and~~ modern wastewater treatment plant
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20 153 (WWTP), located outside the catchment. However, a small WWTP, installed in around
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22 154 1985, about 30 years ago served an upslope urban core in Quinta sub-catchment until 2012,
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24
25 155 but was very inefficient and although great treatment inefficiency. Effluent from it was
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27 156 released into a downslope woodland area and into a tributary. In 2012 the wastewater was
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29
30 157 linked to the larger sewerage network and the small WWTP was disabled.
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37 159 **3 Methodology**

40 160 **3.1 Research design**

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44 161 The research design comprised monitoring ~~variationsechanges~~ in water quality at four sites in
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46 162 the Ribeira dos Covões catchment induring 10 storms, covering a range of rainstorm sizes
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49 163 and antecedent weather (and season), over the period October 2011 to March 2013.

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52 164 ~~Streamflow was sampled at four sites within Ribeira dos Covões catchment (Fig. 1): the~~
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55 165 sites comprised the catchment outlet at ESAC (E); and ~~at~~ three upstream sites in sub-
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57 166 catchments of distinct urban cover and pattern (Table 1). These were: (i) Espírito Santo (ES),
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1 167 the most urbanized (49% urban) sub-catchment containing areas of high impervious cover in
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3 168 upslope sites and lower impervious cover (detached houses surrounded by gardens), mainly
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5 169 in downslope locations; (ii) Porto Bordalo (PB), with 39% urban cover extending over the
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8 170 sub-catchment in a strip fashionshape, with row-house areas upslope and detached houses
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10 171 with greater impervious cover or only small gardens downslope) and part of the motorway;
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13 172 and (iii) Quinta (Q), 22% urban, mainly in upslope locations, comprising a small residential
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15 173 area (4%) and the enterprise park under construction (18%). Differences between urban
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18 174 patterns also include dissimilarities in the storm drainage system: (i) in ES, overland flow
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20 175 from impervious surfaces is dissipated in surrounding adjacent downslope pervious soils; (ii)
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23 176 in PB, storm runoff from upslope urban areas is diverted into pervious soils, whereas from
24
25 177 downslope impervious surfaces it is piped into the stream tributary or nearby abandoned
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28 178 fields; and (iii) in Q runoff from the residential area dissipates in downslope surrounding
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30 179 woodland ~~areas~~, whereas runoff from impervious surfaces within the new enterprise park is
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33 180 piped into a detention basin, which delays its flow into the stream network. Additional
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35 181 differences are ~~also~~ linked to physical properties of the sub-catchments. In terms of
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38 182 lithology, ES and Q are sandstone sub-catchments and PB a limestone sub-catchment, with
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40 183 the entire catchment at E being 56% sandstone, 41% limestone and 3% alluvial (Table 1).

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43 184 ~~Several w~~Water samples were collected at intervals manually at each site during each of 10
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45 185 storm events. This was facilitated by the small size of the catchment, and the proximity
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48 186 between of sampling sites, the use of a allowed quick car trips during the storms to take the
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51 187 samples. Whenever possible, samples were collected by more than one and multiple
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53 188 personnel. Selection of storm events was aided by use of The S sampled storms were
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56 189 ~~selected using based on~~ weather forecasts; and focus on the first rainstorms after the summer
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58 190 (storms 1, 2 and 7) and on storm events of different magnitudes over the wet season, including
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1 191 autumn (storms 3, 4 and 5), winter (storms 8, 9 and 10) and spring (storm 6), in order to cover
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3 192 seasonal differences in response over the year~~provide annual differences.~~
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10 194 **3.2 Water sampling**

14 195 Three to fifteen samples covering the rising limb, peak and falling limb of storm responses
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16 196 at the four sites were collected during each of 10 storm events, monitored between October
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18 197 2011 and March 2013. Whenever possible, the first sample of the event was collected
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20 198 immediately before rainfall started, if stream was flowing, to provide preceding baseflow
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22 199 water quality. Storm events were assumed to have stopped when no rainfall was recorded for
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24 200 6h. In total 76 samples were collected at E, 75 at PB, 56 at ES and 58 at Q. Samples were
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26 201 collected in acid-washed 250 mL glassware and 2 L polyethylene bottles, placed in a dark
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28 202 chilled cooler (~4°C) and taken to the laboratory.
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34 203 Hydrological data of 5-minute resolution were provided by an existing network of flow
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36 204 gauging stations at each site and five rainfall gauges distributed across the catchment (Figure
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38 205 1). The Thiessen Polygon method was used to calculate the weighted mean rainfall, assumed
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40 206 to be constant over the catchment.
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48 208 **3.2 Laboratory analysis**

52 209 Water samples were immediately analysed for pH by electrometry (Hach, Sension Portable
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54 210 case). Sample aliquots were filtered through 0.45 µm membranes (Millipore MF) and stored
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56 211 for later chemical analyses: (i) aliquots for dissolved nitrite (NO₂-N) and nitrate (NO₃-N);
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1 | 212 (ii) aliquots for dissolved chemical oxygen demand (COD), kjeldahl nitrogen (Nk-N),
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3 | 213 ammonium (NH₄-N) and total dissolved phosphorus (TDP) were acidified with sulphuric
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5 | 214 acid (pH <2); (iii) aliquots for dissolved ions [sodium (Na), calcium (Ca) and magnesium
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7 |
8 | 215 (Mg)] and heavy metal analyses [zinc (Zn) and copper (Cu)] were acidified with nitric acid
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10 | 216 (pH 2-3). All aliquot samples were stored surrounded by ice and defrozen at room
11 |
12 |
13 | 217 temperature before analysis.

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16 | 218 Nitrite and nitrate concentrations were measured simultaneously with an automated
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18 | 219 segmented flow analyser (SAN⁺⁺ system), using the cadmium reduction method (Skalar
19 |
20 | 220 method 461-322; Skalar, 2004a). Given the normally very low nitrite concentration in rivers
21 |
22 | 221 the analytical results are examined only as NO₃-N. Ammonium concentration was also
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24 | 222 determined by an automated segmented flow analyser, but using a modified Berthelot
25 |
26 | 223 reaction (Skalar method 155-316; Skalar, 2004b). Kjeldahl nitrogen, including organic
27 |
28 | 224 nitrogen, ammonia and ammonium, was measured after sulphuric acid digestion with a
29 |
30 | 225 selenium catalyser, followed by distillation and titration with hydrochloric acid (Standard
31 |
32 | 226 Method 4500-Norg B; APHA 1998).

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35 | 227 COD and TDP were analysed using a multiparameter water quality instrument (Hach DR
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37 | 228 2000). COD was determined colorimetrically after acid digestion and oxidation with
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39 | 229 dichromate, in accordance with ISO 15705:2002 standards (HI 93754A vials, Hanna
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41 | 230 Instruments). TDP was quantified after persulfate acid digestion, colorimetrically by
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43 | 231 reacting with molybdate ascorbic acid and antimony potassium tartrate, adapted from 4500-
44 |
45 | 232 P Standard Methods (HI 93758A vials, Hanna Instruments).

46 |
47 | 233 Cation and heavy metal analyses were made after digestion with nitric acid (Standard Method
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49 | 234 3030-E; APHA 1998), by atomic absorption spectrophotometry (Perkin Elmer AA300), with
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1 235 direct air-acetylene flame and hollow cathode lamps (Standard Method 3111-B; APHA
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3 236 1998). ~~The d~~Detection limits for Zn and Cu ~~were~~as 0.05 mg L⁻¹ and 0.01 mg L⁻¹, respectively.
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7 237 Reagent blanks and duplicate samples were used for quality control purposes and mean
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9 238 concentration values (repeated analysis of each sample) were used for data analysis.
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16 240 **3.3 Data analysis**

20 241 The hydrological regime of the ten sampled storms was characterized in terms of rainfall and
21
22 242 stream discharge. For each storm event, the rainfall amount, duration and intensity ~~were~~as
23
24 243 calculated. Rainfall intensity was described in terms of the event mean (I_{med}), and the
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26
27 244 maximum in 60- minutes (I₆₀). Seven-day and 14-day antecedent precipitation (API₇ and
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29 245 API₁₄) for each storm event were calculated using weighted mean rainfall data. Streamflow
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32 246 parameters used included instantaneous discharge (at the time of water sampling) and event
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34 247 peak and mean discharges. Stormflow and baseflow components were separated for
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37 248 individual events, using a mathematical digital filter (Nathan and McMahon 1990). The
38
39 249 storm runoff coefficient for each event was calculated as the ratio of total storm runoff
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42 250 (discharge normalized by area) divided by event rainfall. The time to peak was defined as the
43
44 251 time from the centroid of the rainfall ~~to~~and peak flow (Lana-Renault et al. 2011).
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48 252 Water quality values for the ten rainfall events were compared with Portuguese standards of
49
50 253 minimum surface water quality ~~pH: 5.0-9.0, Nk: 2.0 mg L⁻¹, NH₄-N: 1.0 mg L⁻¹, TDP: 1.0~~
51
52 254 ~~mg L⁻¹, Zn: 0.5 mg L⁻¹ and Cu: 0.1 mg L⁻¹-(DL236/98), ~~synthesized in~~-(Table 2).
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54
55 255 Portuguese~~These standards do not exist~~include for the monitored parameters COD, NO₃-N
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57 256 and major cations (Na, Ca and Mg).
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1 257 ~~The~~ Statistical significance of differences in parameters between the four sites were
2
3 258 investigated using the non-parametric Kruskal-Wallis test. Whenever significant spatial
4
5
6 259 and/or temporal water quality differences were identified (p<0.05), the ~~ysre~~ were further
7
8 260 investigated ~~edion~~ using the post-hoc Fisher's Least Significant Difference test, at the 0.05
9
10 261 significance level. For each site, relationships between different water quality parameters,
11
12 262 and between these parameters and streamflow properties, were explored using Spearman's
13
14 263 rank correlation coefficient (r), at 0.05 and 0.01 significance levels. Data analysis was
15
16 264 performed using IBM SPSS Statistics 22 software.
17
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25 266 **4 Results and analysis**

28 267 **4.1 Storm characteristics and streamflow response to storm events**

31
32 268 Rainfall characteristics for the 10 storms sampled between October 2011 and March 2013
33
34 269 are shown in Table 23. Storm totals ranged from 2.4 mm (storm 6) to 46.8 mm (storm 10),
35
36 270 which had a return period of less and were linked to return intervals lower than 2 years, except
37
38 271 but the return period of the maximum hourly intensity for storm 3 (15.6 mm h⁻¹) was high
39
40 272 reached 3 years.
41
42
43
44

45 273 Streamflow responses at the four monitored sites are summarized in Table 34 and Figure 2.

46
47 274 Storm 1, recorded at the end of summer (23-24/10/2011) was not enough to trigger discharge
48
49
50 275 in ES and Q. For the 10 storms, the mean storm runoff coefficient at PB (6.1%) was twice as
51
52 276 high asthan at E (3.0%) and Q (2.7%), and also greater than at ES (4.4%). In the monitored
53
54 277 storms, baseflow comprised encompassed 46%-87% of the event flows at E, 51%-85% at
55
56 278 Q and 58%-94% inat ES, whereas at PB it was 16%-55%. The catchment and sub-
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1 279 catchments have a flashy behaviour, with response times ranging from 5-35 min ~~at~~ PB, 10-
2
3 280 40 min ~~at~~ ES, 10-65 min ~~in~~ Q and 25-85 min ~~at~~ E.
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10 282 **4.2 Water quality**

13 283 *4.2.1 Overview of water quality in the ten events at the four sites*

16 284 Fig. 2 uses box plots to summarise water quality responses at each of the four sites to the ten
17
18 285 rainstorms. The limestone PB sub-catchment showed significantly higher pH ($p < 0.05$) than
19
20 286 Q, ES and E, but median values over the 10 storms were 7.6, 7.4, 7.3 and 7.1, respectively,
21
22 287 and ~~thus all within the~~ slightly alkaline ~~range~~.
23
24

26 288 Significant differences in COD (dissolved phase) between sites were recorded ($p < 0.05$), with
27
28 289 lowest median concentration in the least urban Q (9.5 mg L^{-1}), intermediate values at PB
29
30 290 (12.0 mg L^{-1}) and E (13.0 mg L^{-1}), and highest median COD in the most urbanized ES sub-
31
32 291 catchment (17.8 mg L^{-1}) (Fig. 2). Ranges in values were substantial at all sites, with minima
33
34 292 ~~at~~ of $2.0 - 8.0 \text{ mg L}^{-1}$ and maxima of $48.5 - 62.5 \text{ mg L}^{-1}$ at E, PB and Q and 83.5 mg L^{-1} ~~in~~
35
36 293 ES.
37
38
39

40 294 Kjeldhal nitrogen in dissolved phase varied little between study sites, but was slightly higher
41
42 295 at E ($0.52 - 2.62 \text{ mg L}^{-1}$) and Q ($0.50 - 2.83 \text{ mg L}^{-1}$), where cattle-rearing occurs in fields
43
44 296 adjacent to the stream, than at ES ($0.50 - 2.54 \text{ mg L}^{-1}$) and PB ($0.47 - 2.54 \text{ mg L}^{-1}$) (Fig. 2).
45
46 297 PB, however, ~~displayed~~ experienced more than twice as many pollution occasions (12 values
47
48 298 $> 2.0 \text{ mg L}^{-1}$, DL236/98) than the other sites (~~12 vs~~ 5 ~~in~~ E and Q and 4 ~~in~~ ES). Pollution
49
50 299 thresholds and concentrations were ~~exceeded~~ reached in storm 9 (winter) at all sites, in storms
51
52 300 7 (after summer) and 8 (winter) at E and PB, and storms 1 (after summer) and 5 (winter) at
53
54 301 PB.
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302 Similarly to Nk-N, slightly higher NH₄-N concentrations were recorded at E (0.04 - 1.63 mg
303 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)
304 (p>0.05, Fig. 2). The water quality standard for NH₄-N (1.0 mg L⁻¹, DL236/98) was always
305 ~~complied with~~fulfilled at ES, but ~~exceeded~~surpassed for 7, 3 and 1 samples collected at E,
306 PB and Q, respectively. These pollution occasions were recorded during storms 7 (late
307 summer) and 8 (winter) ~~in~~at E, and storm 1 (late summer, after ~~a very dry period~~iest settings)
308 ~~in~~at PB, as recorded for Nk-N, but in addition in storm 6 (spring) at PB and Q. ~~A+~~Relatively
309 strong and statistically significant positive correlations ~~were~~as found between NH₄-N and
310 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).

311 Slightly lower NO₃-N concentrations were recorded at the least urbanized Q (0.04 – 3.47 mg
312 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.
313 2). Correlations with COD, Nk-N and NO₃-N were weak albeit significant at all sites
314 (r<0.350, p<0.05).

315 In contrast to nitrogen compounds, TDP varied significantly between sites (p<0.05), with
316 median concentrations being greater at E and PB (0.07 mg L⁻¹) than at ES (0.06 mg L⁻¹) and
317 Q (0.04 mg L⁻¹). Minimuma concentrations were 0.01 mg L⁻¹ at all sites, and maxima were
318 ~~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).
319 Phosphore~~us~~ was not a pollutant threat, ~~since~~as all values were far below the Portuguese
320 water quality standard (1.0 mg L⁻¹). TDP was positively correlated with COD and Nk-N
321 concentrations ~~at~~in PB (r=0.459 and 0.552, p<0.05). ~~In~~At ES and Q, TDP was only
322 significantly correlated with Nk-N (r=0.483 and 0.467, p<0.01).

323 Water quality displayed differences in concentrations of major cations between monitoring
324 sites (p<0.05), ~~distinct from previous chemical parameters~~ (Fig. 3). Sodium concentrations

325 were significantly lower at PB (median ~~values of~~ 5.7 mg L⁻¹, ~~although ranging from~~ 0.7 –
326 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)
327 and Q (11.9 mg L⁻¹, 1.1 – 28.1 mg L⁻¹). Calcium concentrations were significantly higher at
328 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
329 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
330 concentrations were higher (p<0.05) at ES (median 10.4 mg L⁻¹, 3.6 – 19.3 mg L⁻¹), than at
331 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 –
332 27.8 mg L⁻¹).

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

338 As regards ~~to~~ heavy metals, median dissolved Zn concentrations ~~in~~ the study storm
339 events were slightly higher at PB (0.140 mg L⁻¹) ~~than~~ at Q, E and ES (~~0.140 mg L⁻¹,~~
340 0.114 mg L⁻¹, 0.113 mg L⁻¹ and 0.088 mg L⁻¹, respectively) (Fig. 3). Highest ~~e~~ concentrations
341 exceeded Zn water quality standards (0.5 mg L⁻¹) in 7 samples at E (0.53 - 0.91 mg L⁻¹), 2
342 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
343 (maximum only 0.40 mg L⁻¹). Pollutant level ~~s~~ concentrations of Zn were attained after
344 summer ~~in~~ at E and PB (storm 7), but also during winter ~~at~~ PB (storm 8), E and Q (storm
345 9). A strong positive correlation was recorded between Zn and Nk-N concentrations at E
346 (r=0.682, p<0.01), whereas at PB and Q, Zn correlated significantly with TDP (r=0.524 and
347 0.564, p<0.01). At ES and Q, Zn was significantly ~~t~~ statistically correlated with both Nk-N and
348 TDP (r=0.544 and 0.638, p<0.01).

1 349 Median ~~copper~~Cu concentrations ~~for over~~the study ~~storm events~~period were slightly higher
2
3 350 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)
4
5
6 351 (p>0.05) (Fig. 3). Highest Cu concentrations were 0.200 mg L⁻¹ at ES, 0.174 mg L⁻¹ at E,
7
8 352 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)
9
10 353 were ~~recorded~~~~ached~~ only for one sample at E and one sample at ES, during storms 9 and 10,
11
12
13 354 respectively.

14
15
16 355 ~~Copper~~ and ~~Zinc-zinc~~ were positively correlated ~~with each other at~~ all monitored sites (r
17
18 356 ranged from 0.365 to 0.532, p<0.05). ~~In~~At ES and PB, Cu was significantly correlated with
19
20
21 357 Nk-N (r=0.481 and 0.579, p<0.01) and NH₄-N (r=0.481 and 0.501, p<0.01). ~~In~~At Q, Cu only
22
23
24 358 correlated significantly with Nk-N (r=0.536, p<0.01).
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27 359

30 31 360 ***4.2.2 Between-storm variation over the study period***

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33
34 361 Between-storm differences in water quality responses are apparent at the monitoring sites in
35
36 362 Figures 2 and 3. Generally, COD and nutrients displayed higher concentrations in storms
37
38
39 363 recorded in late summer (1, 2 and 7) ~~and~~with decreasing values over the wet season,
40
41
42 364 achieving lowest concentrations in late winter (storms 5 and 10) (Fig. 2). Seasonal differences
43
44 365 in COD were greater for PB than for Q, ES and E.

45
46
47 366 Nk-N concentration varied less with season, with median concentrations for late summer
48
49 367 storms being less than twice as high than for late winter storms. Greater seasonal differences
50
51
52 368 were recorded for NH₄-N concentrations, with storm medians being 3-4 times greater for late
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55 369 summer than late winter storms at ES, E and PB, but only 1.4 times ~~as~~ high at the least
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57 370 urbanized Q sub-catchments.
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371 As regards ~~nitrate~~ (NO₃-N), PB, Q and E displayed higher storm median concentrations
372 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
373 vs 0.36 mg L⁻¹ and 1.35 mg L⁻¹ vs 1.01 mg L⁻¹, respectively), whereas ES displayed 3 times
374 higher storm median concentrations in late winter than late summer storms (1.63 mg L⁻¹ vs
375 0.86 mg L⁻¹).

376 TDP concentrations were twice higher in PB and E in late summer than late winter storms,
377 but differences were much smaller at Q and ES. Lowest TDP concentrations were
378 ~~measured~~ recorded in storm 3, with the greatest rainfall intensity, and storm 4, with the wettest
379 antecedent conditions (Table 23).

380 ~~In contrast to previous water quality parameters~~, major cations exhibited higher
381 concentrations in wetter than drier settings (Fig. 3). Median Na concentrations measured
382 during storms 6 and 10, with greatest antecedent rainfall in previous 7 days (42.5 mm and
383 47.3 mm) were 2.5-, 1.8-, 1.5- and 1.3- folds higher than during storms after the summer
384 (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
385 (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
386 were found for Ca and ES, but no specific temporal pattern was recorded at E and Q.

387 The heavy metals Zn and Cu tended to show higher concentrations in late summer than late
388 winter storms. Thus, median Zn concentrations were 2.5- in E (0.140 mg L⁻¹ vs 0.055 mg L⁻¹
389 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
390 1.4-times higher (0.084 mg L⁻¹ vs 0.058 mg L⁻¹) in ES during late summer (storms 1, 2 and
391 7) than late winter storms (5 and 10). Similar patterns were recorded for Cu. Some pollutant-
392 level values of Zn and Cu were also recorded (see section 4.2.1).

394 **4.2.3 Hydrochemistry dynamics during storms**

1 395 Changes in water quality during a storm event showed distinct patterns during storms
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3
4 396 recorded after summer (storms 1, 2 and 7) than ~~in~~ remaining storms later in the wet season.
5
6 397 Given the extent of the dataset, this section focuses on intra-storm variation of three chemical
7
8 398 parameters included in the Portuguese water quality standards: NH₄-N (which is strongly
9
10
11 399 correlated with Nk-N at E and ES), Zn (which is strongly correlated with Cu) and TDP, for
12
13 400 the late summer storm 7 and winter storm 9. Storm 7 was a multiple storm event with two
14
15 401 peaks in rainfall five hours apart (Fig. 4). It also includes the first runoff recorded in ES and
16
17
18 402 Q after the 2012 summer dry season. Storm 9 is a typical winter season event (Fig. 5).
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21 403
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23
24
25 404 *NH₄-N storm dynamics*
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27
28
29 405 During storm 7 (Fig. 4), highest NH₄-N concentrations were recorded at baseflow (prior to
30
31 406 rainfall) in E, and with the initial storm runoff in PB and Q, with concentrations then
32
33 407 decreasing as discharge increased ~~with increasing peak flow~~. After the first discharge peak,
34
35 408 NH₄-N rose as discharge ~~fa~~ ell inat E, whereas inat PB it remained low. In Q, samples in storm
36
37
38 409 7 are too few to deduce the pattern, but in storm 2 (not shown) rose as discharge fall, as at E.
39
40
41 410 Changes in NH₄-N concentration at ES were small, though the number of samples were few.
42
43
44 411 After an initial flush of higher concentrations in the rising limb of the hydrograph, NH₄-N
45
46 412 concentrations ~~recorded~~ in the winter storm 9 ~~show~~ varied an ~~inversely~~ ~~pattern to~~ with
47
48 413 streamflow (Fig. 5), ~~with an initial flush of higher concentrations in the rising limb of the~~
49
50 414 ~~hydrograph, before decreasing with peak discharge and increasing again over the falling limb~~
51
52 415 ~~of the hydrograph. Nevertheless,~~ Whereas peak concentrations inat E and PB were reached
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54
55 416 during the initial storm runoff, ~~whereas~~ inat ES and Q they were attained in the falling limb.
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1 | 417 ~~At~~ E, however, a clear difference between both storms was noticed at pre-storm baseflow,
2
3 | 418 with high and low concentrations ~~in~~prior to the late summer and winter storms, respectively.
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7 | 419 Similar patterns to NH₄-N were in general recorded for Nk-N (not shown), in storms 7 and
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9 | 420 9.

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13 | 421
14
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16 | 422 *TDP storm dynamics*
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19

20 | 423 TDP concentrations, albeit never exceeding Portuguese national guidelines, changed within
21
22 | 424 storms differently from NH₄-N and Nk-N concentrations. In storm 7 (Fig. 4), TDP was low
23
24 | 425 at baseflow in E and increased progressively over the first storm peak, attaining highest
25
26 | 426 concentrations on the falling limb, before a sharp fall. Nevertheless, with rainfall restart
27
28 | 427 during storm 7, TDP concentration tended to follow discharge, with a peak at peakflow,
29
30 | 428 followed by a progressive decline to pre-event level on the falling limb of the hydrograph. In
31
32 | 429 ES, however, TDP concentration increased on the rising limb to a peak at peak flow-, before
33
34 | 430 declining ~~After the peak, TDP concentration first decreased~~ as discharge ~~fa~~ell. There were
35
36 | 431 too few samples to define patterns during the second peak. ~~On the other hand~~In contrast, at
37
38 | 432 PB and Q, peak TDP concentrations were recorded on the initial rising limb, with lowest
39
40 | 433 concentrations at peak flow. After rainfall restart during storm 7, TDP concentrations at PB
41
42 | 434 followed discharge variation, with values in late falling limb lower than those recorded in the
43
44 | 435 second rising limb and peak flow.
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52 | 436 In winter storm 9 (Fig. 5), ~~at~~ E and PB experienced a marked peak in TDP in the rising limb
53
54 | 437 before falling to low values at peak flow and in the falling limb. At ES, however, peak TDP
55
56 | 438 was recorded after peak discharge and TDP values throughout the storm hydrograph were
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1 | 439 higher ~~at post~~ than at pre-storm baseflow. At PB, high TDP concentration was also recorded
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3 | 440 by the end of the falling limb.
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10 | 442 *Dissolved Zn storm dynamics* 11 | 12 | 13 |

14 | 443 ~~Regarding to Zn, h~~High-magnitude and distinct temporal changes in dissolved zinc were
15 |
16 | 444 recorded in the late summer storm (Fig. 4). Generally, Zn concentrations were low at pre-
17 |
18 | 445 storm baseflow and reached multiple peaks at peak flow and during the falling limb. Only at
19 |
20 | 446 Q were Zn concentrations higher during the rising limb. In the wet season storm (Fig. 5), Zn
21 |
22 | 447 displayed massive peaks at E and Q, both in the rising and again in the falling limb of the
23 |
24 | 448 hydrograph, but only in the rising limb at PB. Changes were more muted at ES, with peak
25 |
26 | 449 concentration recorded at peak discharge.
27 |
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31 |
32 | 450 Although Cu concentrations followed similar intra-storm variation as Zn, pollutant levels
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34 | 451 were only recorded in winter storms (Fig. 3), also after peak discharge.
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41 | 453 **5 Discussion** 42 | 43 | 44 |

45 | 454 **5.1 Differences in hydrological responses between sites** 46 | 47 |

48 | 455 Before discussing the water quality results, differences in hydrological response between the
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50 | 456 sub-catchments are explained. Urbanization and the associated increase in impervious
51 |
52 | 457 surfaces have been widely reported to enhance runoff (e.g. Zhang and Shuster 2014; Yao et
53 |
54 | 458 al. 2015). Nevertheless, for the 10 storms studied, the storm runoff coefficient in the 40%
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56 | 459 urbanized Ribeira dos Covões catchment ranged only between 1.6% and 5.5%. In part this
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1 460 reflects the high permeability of the catchment provided by the sandstone and limestone
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3 461 bedrock (Ferreira et al. *this issue a*).
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6
7 462 Within the study catchment, PB (39% urban area and 15% impervious) displayed both the
8
9 463 greatest storm runoff coefficients (2.5% - 11.8%) and quickest response times (5-35 minutes).
10
11 464 In contrast, the more highly urbanized ES sub-catchment (49% urban, 27% impervious)
12
13 465 experienced lower storm runoff coefficients (2.4% to 6.7%) and slightly higher response
14
15 466 times (10-40 minutes). This is thought to be a consequence of distinct drainage systems. In
16
17 467 PB, part of the runoff from downslope impervious surfaces is directly piped into the stream,
18
19 468 leading to enhanced connectivity between overland flow sources and the stream network. In
20
21 469 ES, however, runoff from paved surfaces is mostly diverted into pervious soils, and/or piped
22
23 470 into downslope woodland areas, favouring water retention and infiltration, hence reducing
24
25 471 the storm runoff response of the stream.
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32 472 Such an explanation would conform to findings of previous studies highlighting the
33
34 473 significance of storm drainage systems (not simply % of impervious area) enhancing
35
36 474 flashiness of storm runoff (e.g. Yang et al. 2011, Miller et al. 2014) and much reduced effects
37
38 475 of impervious surfaces when not connecting to a storm sewer system (e.g. Hammer 1972).
39
40
41
42
43 476 In Q sub-catchment, containing the largest woodland area (73%) and the smallest impervious
44
45 477 ~~are cover~~ (5%), storm runoff coefficients were the lowest (0.8% - 4.9%). ~~This findings are in~~
46
47 478 ~~accordance with previous studies reporting lower runoff in forested than agriculture and~~
48
49 479 ~~urban catchments, due to higher transpiration and interception losses (e.g. Wang et al. 2013).~~
50
51
52
53 480 Storm runoff coefficients in Q, however, were only a little lower than in ES, possibly because
54
55 481 overland flow from paved surfaces in the enterprise park, located within Q, is piped into a
56
57 482 detention basin and then released direct into the stream network, rather than being directedly
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1 483 into pervious soils as within ES. Contrary to the typical flashy hydrographs with greater peak
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3 484 flows found in highly urbanized areas (e.g. Vidon et al. 2009), ES displayed longer-duration
4
5 485 hydrographs, sometimes without a clear peak flow (Figs. 4 and 5), in contrast to the quicker
6
7
8 486 response times of Q, even in small events (Table 34).

10
11
12 487 That higher storm runoff coefficients for Q were found in storms following driest antecedent
13
14 488 weather conditions may indicate that normally pervious soil is also providing overland flow,
15
16 489 because of the low infiltration capacity induced by water repellency, particularly given the
17
18
19 490 73% extent of woodland ~~areas~~ in the catchment (e.g. Ferreira et al. 2016).

22
23 491 Differences in hydrological response between monitoring sites in Ribeira dos Covões may
24
25 492 also reflect ~~difference~~similarities in lithology. In PB, underlain by~~overlying~~ limestone,
26
27 493 baseflow represented ~~less than 16~~55% of event runoff, whereas in ES and Q, the sandstone
28
29
30 494 sub-catchments, it is ~~greater than 55~~94% and 49-85% respectively (Table 34).

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37 496 **5.2 Influence of urban pattern on water quality**

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39
40 497 The Ribeira dos Covões results suggest that areas with different urbanization pattern have
41
42 498 distinct impacts on surface water quality, particularly in terms of COD, TDP, major cations
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44
45 499 and pH ($p < 0.05$). Nitrogen (~~Nk~~N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) and heavy metals (Zn and Cu),
46
47
48 500 however, did not show significant differences between sites over the study period ($p > 0.05$),
49
50 501 but nevertheless at least~~achieved~~ occasionally exceeded water quality standards ~~pollutant~~
51
52 502 concentrations in~~at~~ the four monitoring sites.

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56 503

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 NO₃-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 surfaces (Table 1). Enhanced COD and NO₃-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, ~~treatedment plant~~ effluent would not seem to be a major pollutant source. COD and NO₃-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.

NO₃-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 NO₃-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 NO₃-N recorded during storms in late summer (Fig. 2).

5.2.2 Kjeldhal nitrogen and ammonium

1 527 Higher concentrations of Nk-N and NH₄-N were recorded at the catchment outlet at E and at
2
3 528 Q, which has the lowest urban land-use (22%), than at ES and PB. In At both E and Q sites,
4
5
6 529 organic compounds were the dominant form of nitrogen, given the relatively low NO₃-N
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8 530 concentrations (median values of 1.01 mg L⁻¹ and 0.35 mg L⁻¹) and the small percentage of
9
10 531 NH₄-N in relation to Nk-N (34% and 25%, respectively). Extensive cattle rearing in the
11
12 532 agricultural fields located upslope and channel-margin locations in E and Q sampling sites,
13
14
15 533 and surrounding water channel, is thought to be a major source of Nk-N and NH₄-N, and may
16
17 534 explain why the pollutant concentrations measured often exceeded pollution guidelines
18
19
20 535 (maximum concentrations of 1.87 mg L⁻¹ of Nk-N and 1.32 mg L⁻¹ of NH₄-N, Fig. 2) often
21
22
23 536 exceeded pollution guidelines.
24
25
26 537 An Additional Nk-N and NH₄-N sources may arise occasionally before untreated domestic
27
28 538 wastewater. Contamination by leaks in the sewage drainage system, was observed
29
30 539 occasionally, through the colour and smell of surface water. Sewage leaks, however, are
31
32
33 540 prone to influence water quality in all the study sites. In Q sub-catchment, past soil
34
35 541 contamination from the abandoned WWTP, which received domestic wastewater from
36
37 542 upslope urban cores and spread it downstream without treatment until few years ago 2012,
38
39
40 543 may also be a potential source of Nk-N and NH₄-N concentrations. These soil contamination
41
42
43 544 sources may explain why the pollutant level concentrations were exceeded reached only
44
45
46 545 in late winter storms (Fig. 2), because of greater connectivity with stream network, favoured
47
48 546 by increasing the higher soil moisture content at that time. Great concentrations of NH₄-N can
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50
51 547 be toxic to aquatic organisms (e.g. Lin et al. 2014).

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55 56 57 549 **5.2.3 Total dissolved phosphorus**

1 550 Highest concentrations of TDP were found ~~at~~ E and PB (median values of 0.07 mg L⁻¹ ~~at~~
2
3 551 both sites, p<0.05). Phosphorus in urban areas is usually associated with household sources,
4
5
6 552 such as laundry and dishwasher detergents, as well as organic matter biodegradation in
7
8 553 domestic wastewater (e.g. Carey et al. 2013), but it can also derive from garden fertilizers.
9
10 554 Apart from sewage leaks already discussed, pavement and car washes were ~~often~~usually
11
12 555 observed within PB, which forms an~~located~~ upstream part of E. In PB, high concentrations
13
14 556 of TDP could possibly~~may~~ also be ~~also~~ associated with ~~soil properties, given~~ the clay content
15
16 557 ~~nature~~ of the limestone soils. ~~Thus, in~~ Xujiawan catchment, Southwest China, phosphorus
17
18 558 enters the runoff and open water bodies mainly through transport ~~in the~~with clay and fine silt
19
20
21
22
23 559 fractions (Yang et al. 2009).

24
25
26 560 Although TDP concentrations ~~never exceeded~~~~were always below~~ the Portuguese water
27
28 561 quality standard (1 mg L⁻¹), all ~~the sites~~ recorded~~attained~~ concentrations above the 0.1 mg L⁻¹
29
30 562 ¹ established as the critical phosphorus level in runoff for eutrophication (US EPA 1986).
31
32
33 563 This critical level was surpassed in 32% of the samples collected in PB, 21% in E, 7% in ES
34
35 564 but only 3% in the least urbanized Q sub-catchment which is 73% woodland (maximum
36
37
38 565 concentrations of 0.25 mg L⁻¹, 0.39 mg L⁻¹, 0.17 mg L⁻¹ and 0.14 mg L⁻¹, respectively).
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43 44 45 567 **5.2.4 Heavy metals**

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49 568 Although draining the smallest urban cover, Q displayed higher median concentrations of Cu
50
51 569 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
52
53 570 ¹ and 0.14 mg L⁻¹, respectively). Heavy metals are typically associated with vehicular traffic
54
55 571 and road runoff in urban situations (e.g. [Crabtree et al. 2006](#); [Herrera 2007](#)). ~~Ferreira et al.~~
56
57
58 572 ~~this issue in press~~ b). In Ribeira dos Covões catchment, a complementary study also

1 573 ~~investigated of heavy metals concentrations in runoff collected in~~ from four ~~distinct~~ roads
2
3 574 ~~provided direct evidence of the capacity of road runoff to generate heavy metal pollution in~~
4
5
6 575 ~~the catchment (Ferreira et al. in press b). Although heavy metal concentrations varied~~
7
8 576 ~~through were variable over the time, they and displayed a direct relationship with vehicular~~
9
10 577 ~~traffic intensity, with dissolved concentrations of Cu and Zn recording maxima attained of 0.2~~
11
12 578 ~~mg L⁻¹ and 0.5 mg L⁻¹, respectively. Nevertheless, heavy metals in road runoff were mostly~~
13
14 579 ~~in particulate form, since as total concentrations of Cu and Zn reached 0.7 mg L⁻¹ and 5.0 mg~~
15
16 580 ~~L⁻¹, respectively. These results highlight the capacity of road runoff to threat surface water~~
17
18 581 ~~quality within the study site.~~

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23
24 582 ~~The H~~higher concentrations ~~recorded at~~ Q probably result from road runoff from the
25
26 583 enterprise park area being piped directly to the detention basin and diverted into the stream
27
28 584 network, i.e. high connectivity between source and stream network. In PB, road runoff,
29
30 585 ~~particularly from the major national road.~~ is ~~in partially~~ piped to fields ~~adjacent to~~ nearby the
31
32 586 stream, ~~particularly from the major national road.~~ Increasing ~~Higher~~ moisture content in soils
33
34 587 receiving road runoff (~~as in prolonged wet weather~~) may favour ~~the~~ connectivity with the
35
36 588 stream network, and ~~been responsible for~~ ~~led to~~ the occasional pollutant concentrations ~~that~~
37
38 589 ~~were recorded~~ (maximum Zn of 0.59 mg L⁻¹ and Cu of 0.10 mg L⁻¹) (Fig. 3).

40
41 590 ES, ~~despite~~ draining the largest impervious cover (27%), recorded lower Zn and Cu
42
43 591 concentrations (Fig. 3), possibly because road runoff is diverted into pervious soils, located
44
45 592 at ~~a~~ greater distance ~~from the~~ stream network than at PB. These contrasts highlight the
46
47 593 importance of ~~variations in~~ the stormwater drainage system characteristics ~~and those~~
48
49 594 ~~variations~~ in controlling urban runoff quantity and quality, ~~rather than~~ ~~not~~ simply %
50
51 595 urbanization, as found also to be the case in Tucson, Arizona (Gallo et al. 2013).

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5.2.5 Major cations and pH

~~Despite~~Although not included in Portuguese water quality standards, major cations 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 ~~Lower~~ concentrations of Na, Ca and Mg ~~recorded~~measured in PB, ~~despite it~~overlaying limestone lithology, ~~however~~, may be associated with its lower baseflow fractions (Table 34). 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, $p < 0.05$).

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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

1 617 flow connectivity between source areas and the stream (e.g. Yang et al. 2009; Zhao et al.
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3 618 2015).
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6
7 619 COD, nutrients (Nk-N, NH₄-N, NO₃-N and TDP) and heavy metals (Zn and Cu) displayed
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9 620 higher median concentrations in storms recorded in late summer than in the wet seasons
10
11 621 (Figures 2 and 3), possibly due to two mechanisms: (i) pollutant accumulation ~~during dry~~
12
13 622 ~~periods~~ and subsequent flushing during the first rainfall events after long dry ~~periods~~settings,
14
15 623 although no statistically significant correlations with antecedent rainfall were identified
16
17 624 (p>0.05); and (ii) decreased dilution effect provided by (a) lower summer baseflow
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19 625 component, which is typically associated ~~with~~ better water quality than surface water (e.g.
20
21 626 Carey et al. 2013); and (b) lower storm runoff volume.
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27 627 During dry conditions ~~S~~solutes ~~precipitated~~deposited during dry conditions and accumulated
28
29 628 within ~~the~~ catchment and sub-catchment soils due to water table drawdown and reduced soil
30
31 629 water content, leading to restrictions on biogeochemical activity. Accumulated solutes are
32
33 630 than available for mobilization during rainfall and subsequent runoff (Vidon et al. 2009;
34
35 631 Gallo et al. 2013). The flushing process recorded in late summer led to higher NH₄-N and
36
37 632 Nk-N during the rising limb of the hydrograph in E, PB and Q (Fig. 4), exceeding on a few
38
39 633 occasions the water quality standards. Higher NO₃-N concentrations in late summer than wet
40
41 634 season storms may be also a consequence of their greater availability ~~associated~~ with crop
42
43 635 and garden fertilizer application in spring and early summer, in association with -Portuguese
44
45 636 Mediterranean climatic setting. The first flush effect ~~on higher concentrations~~ after extended
46
47 637 dry periods have been also reported in urban settings by previous authors (e.g. Barco et al.
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49 638 2008).
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1 639 Phosphorus and heavy metals (Zn and Cu), however, seem to be less easily mobilized than
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3 640 NH₄-N and Nk-N, ~~assimee~~ peak concentrations were reached after peak flows (Fig. 4). Peak
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5
6 641 concentrations of Zn, in a few cases exceeded water quality standards in PB and E
7
8 642 (maxim~~um~~ of 0.59 mg L⁻¹ and 0.55 mg L⁻¹, respectively). The later timing of peak
9
10 643 concentrations of TDP, Zn and Cu can be possibly associated with soil absorption capacity
11
12
13 644 and the difficulty to be detached/dissolved and transported by overland flow, as noted by
14
15 645 Yang et al. (2009). The delayed peak in Zn and and Cu also suggests that soil sources
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17 646 adjacent to roads and development of connectivity between roads, soil and the stream
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19 647 network are of greater significance than simply quick runoff from the roads.
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24 648 In PB, overland flow from paved surfaces seems to be the major runoff and pollutant source,
25
26 649 explaining quicker runoff and solute responses than at the other monitoring sites (Fig. 4).
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29 650 Although in Q there is also ~~a~~ partial piping of overland flow from paved surfaces, solute
30
31 651 transport may have been delayed by the detention basin.
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34
35 652 The overall higher COD and nutrient concentrations in late summer storms are also thought
36
37 653 to be a consequence of lower dilution by reduced summer baseflows (Table 34). ~~Lower~~
38
39 654 ~~baseflow provide minor dilution of solutes washed off by stormflow,~~ as recorded elsewhere
40
41
42 655 by Wilbers et al. (2014). This is ~~supported~~~~corroborated~~ by the negative correlations found
43
44 656 between all nutrient concentrations and baseflow (p<0.05), at most of the sites. In E, however,
45
46
47 657 peak concentrations of NH₄-N and Nk-N were measured under baseflow conditions, before
48
49 658 rainfall start, and recession limb, with few samples exceeding water quality standards. This
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51
52 659 highlights a combination of possible contamination from baseflow and, ~~thus,~~ a potential
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54 660 dilution by cleaner~~from~~ stormflow. ~~This D~~dilution effect provided by stormflow is also
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661 notice~~abled~~ in NH₄-N and Nk-N ~~responses~~~~loops~~, ~~that show~~~~linked with~~ decreasing
662 concentrations with increasing runoff volume (Fig. 4).

663 In ES, however, increasing runoff volume during storms observed in late summer does not
664 seem to have an important ~~diluting influence~~~~role~~ on nutrients concentrations, ~~as In turn~~, NH₄-
665 N, Nk-N and TDP concentrations ~~increased with discharge~~ ~~followed discharge tendency~~ and
666 attained highest ~~values~~~~concentrations~~ ~~at~~~~with~~ peak flow. These distinct solute ~~responses~~~~loops~~
667 compared with those ~~at~~~~from~~ other monitored sites may be linked to the greatest storm runoff
668 coefficients of ES (Table 34). Stormflow, however, only showed a statistically significant
669 positive correlation with NH₄-N concentrations (p<0.05).

670 ~~In~~~~At~~ E and ES, higher concentrations of Nk-N and NH₄-N were recorded on the recession
671 limb than at the beginning of late summer storms. In E and PB in the summer storms (Fig. 4)
672 and in E and Q in the winter storm (Fig. 5) Zn concentration showed marked peaks both on
673 the rising limb and the recession limb. This may indicate that lateral movement of Zn (and
674 Cu, which behaved similarly), Nk-N and NH₄-N in soil by ~~slower~~ throughflow may be
675 providing the delayed second peak, ~~whereas to add to~~ the ~~smaller~~ initial peak ~~derives~~ from
676 flushing by overland flow and road runoff, ~~as reported elsewhere by Yang et al. (2009)~~.

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

681 During winter storms, Nk-N, NH₄-N and TDP exhibited similar ~~responses~~~~loops~~ to those
682 experienced in late-summer storms, namely increased concentrations during the rising limb,
683 lower values at peak flow and increasing concentrations over the falling limb of the

1 684 hydrograph. In PB, concentrations of NH₄-N, Nk-N, Zn and Cu during the falling limb were
2
3 685 usually lower than at the beginning of storm runoff.
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7 686 High concentrations of nutrients (Nk-N, NH₄-N, NO₃-N and TDP) and heavy metals (Zn and
8
9 687 Cu) during winter storms may be a result of greater flow connectivity between solute sources
10
11 688 and the stream network (rather than just the arrival of slower throughflow, as suggested
12
13 earlier). ~~Thus, in E, a larger number of samples displayed Zn exceeded pollution levels and~~
14 689 ~~concentrations more frequently in~~ during winter than in late--summer storms. In Q, Zn
15
16 690 concentrations only exceeded water quality standards in winter storms (Fig. 3). The increased
17
18 691 flow connectivity resulted from increasing soil moisture over the wet season in the catchment
19
20 692 leading to decreasing infiltration and surface water retention capacity (Ferreira et al. 2015),
21
22 693 thus favouring runoff and solute transfer into downslope areas.
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30 695 In ES, highest NH₄-N, Nk-N and Cu concentrations measured during the falling limb of
31
32 696 winter storms (sometimes exceeding water quality standards) (Fig. 5), may be provided by
33
34 697 upslope urban areas lacking a storm drainage system. In E and Q, higher NH₄-N and Nk-N
35
36 698 also reached pollutant concentrations in the falling limbs of a few winter storms (Fig. 2) and
37
38 699 pollutant concentrations of Zn were reached in Q only during winter storms (Fig. 3). The
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40 700 increased concentrations of these nitrogen forms and heavy metals in Q over the wet season,
41
42 701 may partly result from possible leaching of soils polluted by the abandoned WWTP.
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51 703 **6 Conclusions**

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55 704 The results of this study of the small, peri-urban Ribeira dos Covões catchment in central
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57 705 Portugal, suggest that (i) storm rainfall, antecedent rainfall and seasonal Mediterranean
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1 706 rainfall regime and (ii) urbanization pattern, notably the extent, location and degree of
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3 707 continuity of impervious surfaces and type of storm drainage system, together largely
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5
6 708 determine ~~runoff response and~~ temporal dynamics of pollutant and solutes ~~dynamics~~ transport
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8 709 during storm events via their influences on runoff responses, thereby, influencing catchment
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10 710 water quality and aquatic ecosystem sustainability.

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14 711 Significant increases in COD and TDP with increasing urban area of the monitored catchment
15
16 712 and sub-catchments were recorded. The Quinta (Q) sub-catchment, with lowest urban cover
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18 713 (22%) and largest woodland (73%), displayed lowest COD concentrations than the other
19
20 714 more urbanized (39-49%) catchments. Together with Espírito Santo (ES), this sub-catchment
21
22 715 also showed lower TDP concentrations than ~~recorded~~ measured in at the catchment outlet (E)
23
24 716 and at Porto Bordalo (PB). ES, however, drains the largest urban area (49%) and impervious
25
26 717 cover (27%), but the upslope location of most impervious surfaces and the dispersion of
27
28 718 overland flow in downslope pervious soils (in woodland and agricultural fields) minimizes
29
30 719 the potential impacts on streamflow. Nevertheless, the ES urban pattern, characterized
31
32 720 mainly by detached houses surrounded by green spaces, may have led to higher NO₃-N
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34 721 concentrations than in the other sites, due to high applications of fertilizer to lawns and
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36 722 gardens.

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44 723 The sub-catchments (PB and Q) with Uurban areas characterized by storm drainage systems
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46 724 connecting road runoff directly to the stream network ~~(PB and Q)~~, displayed higher
47
48 725 concentrations of heavy metals (Zn and Cu), typically associated with vehicular traffic.
49
50 726 Hence Highgreater connectivity between the stream network and surrounding land-use may
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52 727 be also an important parameter affecting water quality. Thus, in E and Q, higher Nk-N and
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1 728 NH₄-N concentrations are thought to result from ~~be a consequence of extensive~~ cattle-rearing
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3 729 in agricultural fields adjacent to their stream networks.

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7 730 Generally, median concentrations of COD, nutrient parameters and heavy metals were
8
9 731 greater in late summer than winter storms. This pattern was attributed to (i) the accumulation
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11 732 of pollutant sources ~~located on and in surface soil and on roads in the surface~~ during prolonged
12
13 733 dry periods and ~~the~~ subsequent flushing during the first rainfall and runoff events, and (ii)
14
15 734 the lower dilution effect provided by low summer baseflow~~streamflow~~. These mechanisms
16
17 735 led to concentrations of Nk-N and NH₄-N exceeding pollution thresholds in some ~~a few~~
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19 736 samples at all the monitored sites, mostly in the rising limb of the hydrograph in late summer
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24 737 storm events.

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27 738 Storm events over the wet season, however, led to increasing soil moisture ~~contents~~ that
28
29 739 enhanced the connectivity between pollutant sources, runoff processes and the stream
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31 740 network. Greater wet-season connectivity may explain pollutant level~~se~~concentrations of Zn
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33 741 attained in PB and Q, mostly during the falling limb of the hydrograph, as well as pollutant
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35 742 concentrations of Cu in ES and E.

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40 743 Intra- and inter-storm variations over the study period demonstrate that solute (including
41
42 744 pollutant) transport in an urban Mediterranean environment may not be effectively predicted
43
44 745 using simple relationships with hydrological conditions or rainfall. This study has
45
46 746 demonstrated that a larger storm event dataset, covering all seasons and a range of storm
47
48 747 sizes and antecedent weather, is needed to understand the impact of different urban patterns,
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50 748 and complex land-use mosaics in peri-urban areas, on hydrochemical response of the
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52 749 catchment and its sub-catchments to storm events. This study, however, covered only
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57 750 selected pollutant and solute parameters; in particular, additional monitoring of dissolved

1 751 oxygen and microbial contamination parameters should be added to give a fuller picture of
2
3 752 the impact of urban activities.

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7 753 Understanding the impact of urbanization pattern and storm drainage systems on
8
9 754 hydrochemical dynamics is both relevant and crucial to helpguide policymakersdecision-
10 makers and policy actors design and to implement the most appropriatesuitable solutions to
11 755
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14 756 achieve good water quality and preserve aquatic ecosystems. Pollution control policies
15
16 757 should include urban planning and be adjusted to fit changes over space and time, focusing
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19 758 on (1) pollutant flushing in late-summer storms and (2) increasing flow connectivity through
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21 759 the wet season. Upslope urban cores and dispersed urban patterns should favour runoff
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24 760 dispersion in downslope pervious soils. This will favour not only overland flow retention and
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26 761 infiltration but also preventing 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 ~~involves~~ construction sites, parking zones, courtyards and sidewalkspavements; 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
<i>Impervious</i>	17	15	27	5
<i>Semi-pervious</i>	11	9	7	10
<i>Pervious</i>	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 \(DL236/98\), regarding to chemical parameters measured in the current study.](#)

<u>pH</u>	<u>N_{K-N}</u>	<u>NH_{4-N}</u>	<u>TDP</u>	<u>Zn</u>	<u>Cu</u>
<u>(mg L⁻¹)</u>					
<u>5.0-9.0</u>	<u>2.0</u>	<u>1.0</u>	<u>1.0</u>	<u>0.5</u>	<u>0.1</u>

[Table 2-3](#) – Rainfall characteristics for the 10 storm events monitored (I_{mean}: mean intensity, I₆₀: maximum hourly rainfall intensity, API₇: 7-day antecedent rainfall, and AP₁₄: 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

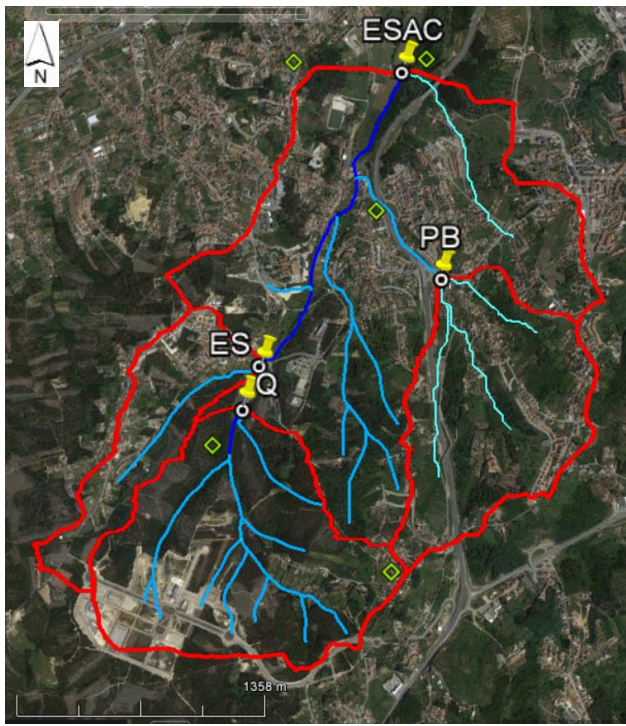
Table 3-4 – Streamflow responses to the 10 rainstorms at the catchment outlet (E: ESAC) and the three sub-catchments (E: Espírito Santo and Q: Quinta).

Storm	Peak discharge (L s ⁻¹)				Mean discharge (L s ⁻¹)				Baseflow fraction (%)				Storm runoff coefficient (%)			
	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



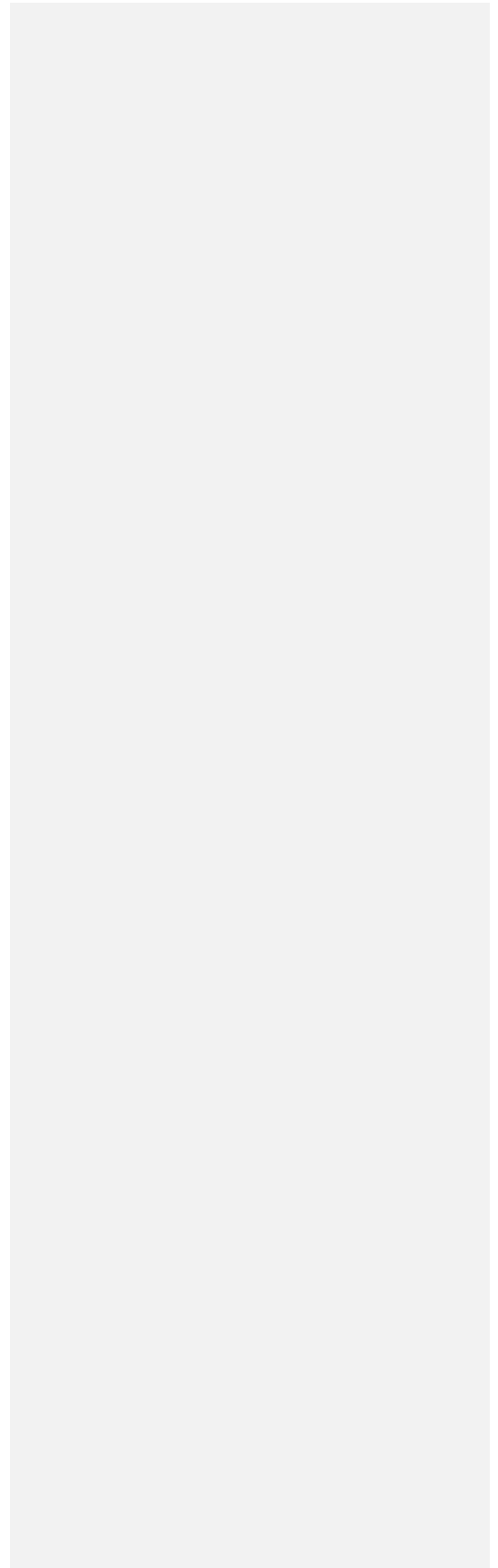
- Legend**
- ★ Sampling sites
 - Drainage area
 - Stream network
 - Perennial
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 - Ephemeral

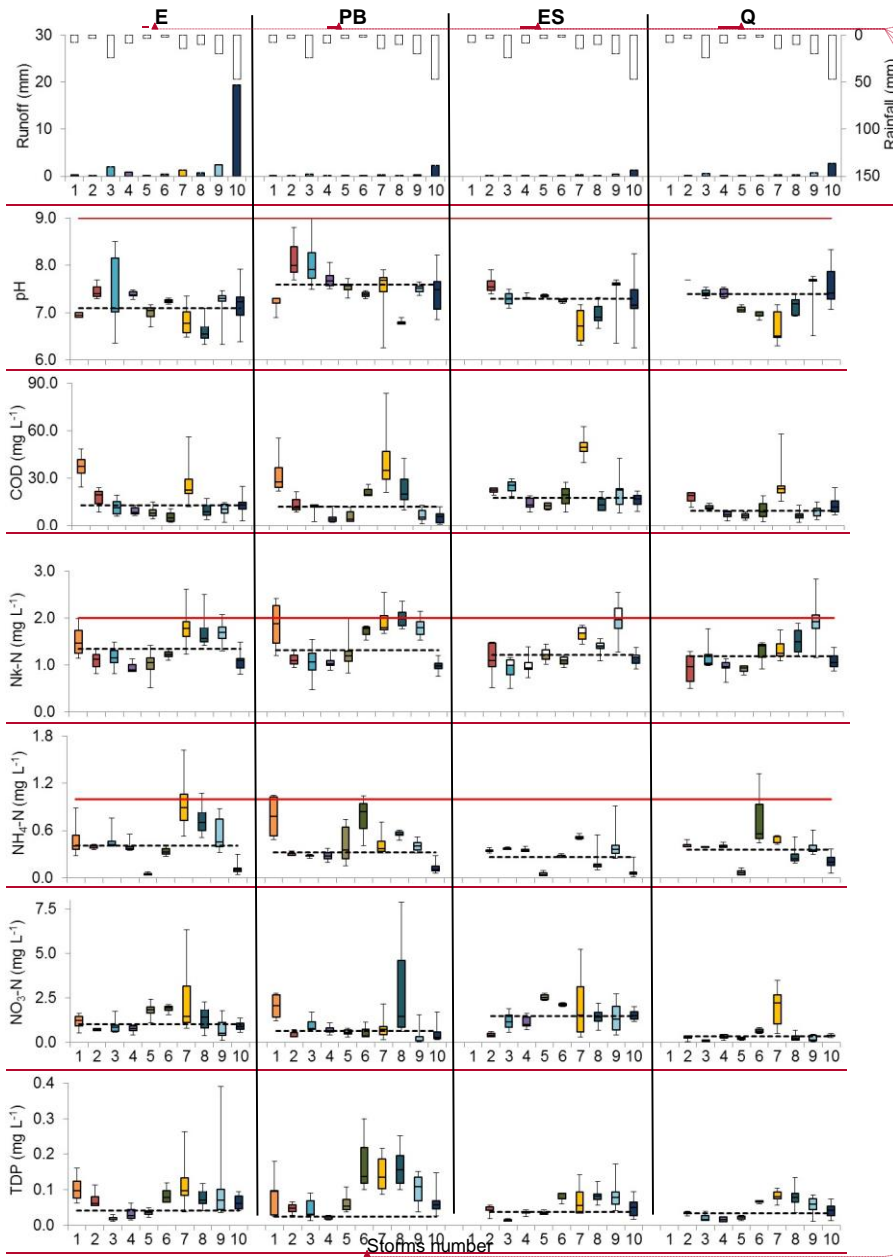


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| ★ Sampling sites | Hydrological network | Stream network |
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| | ◇ Rainfall gauges | — Intermittent |
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Figure 1 - Ribeira dos Covões catchment 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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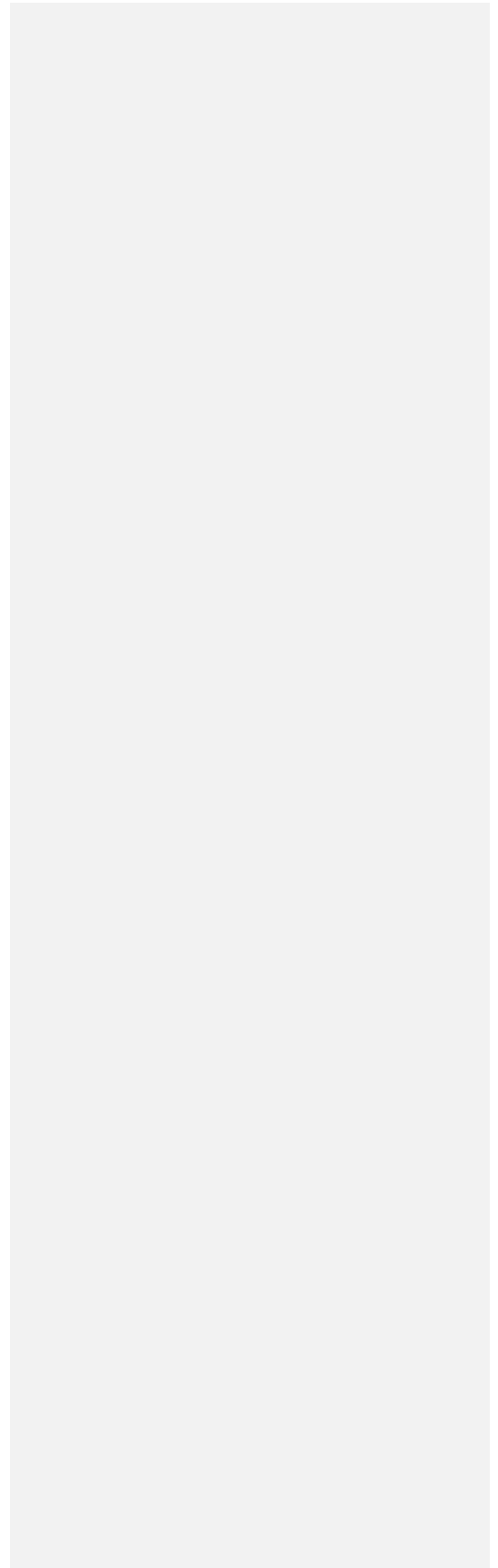
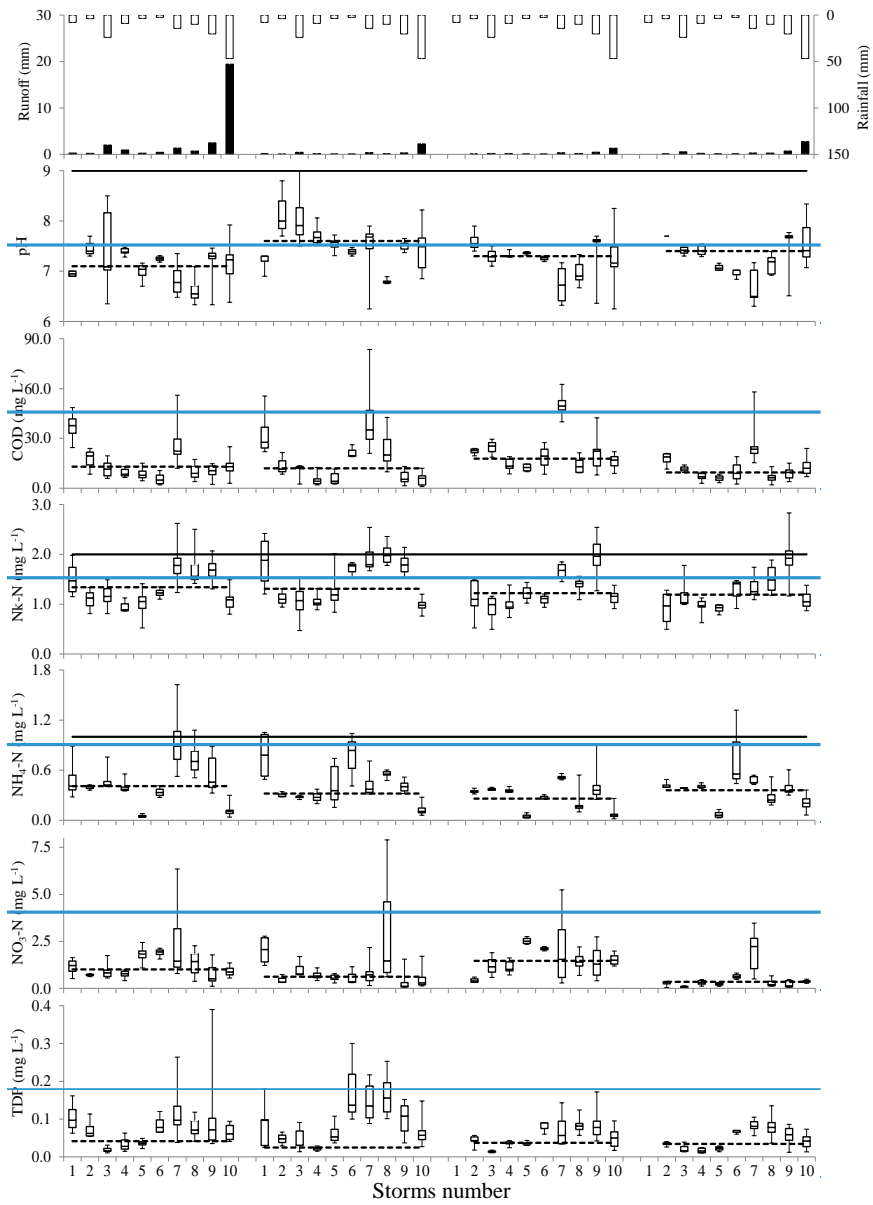
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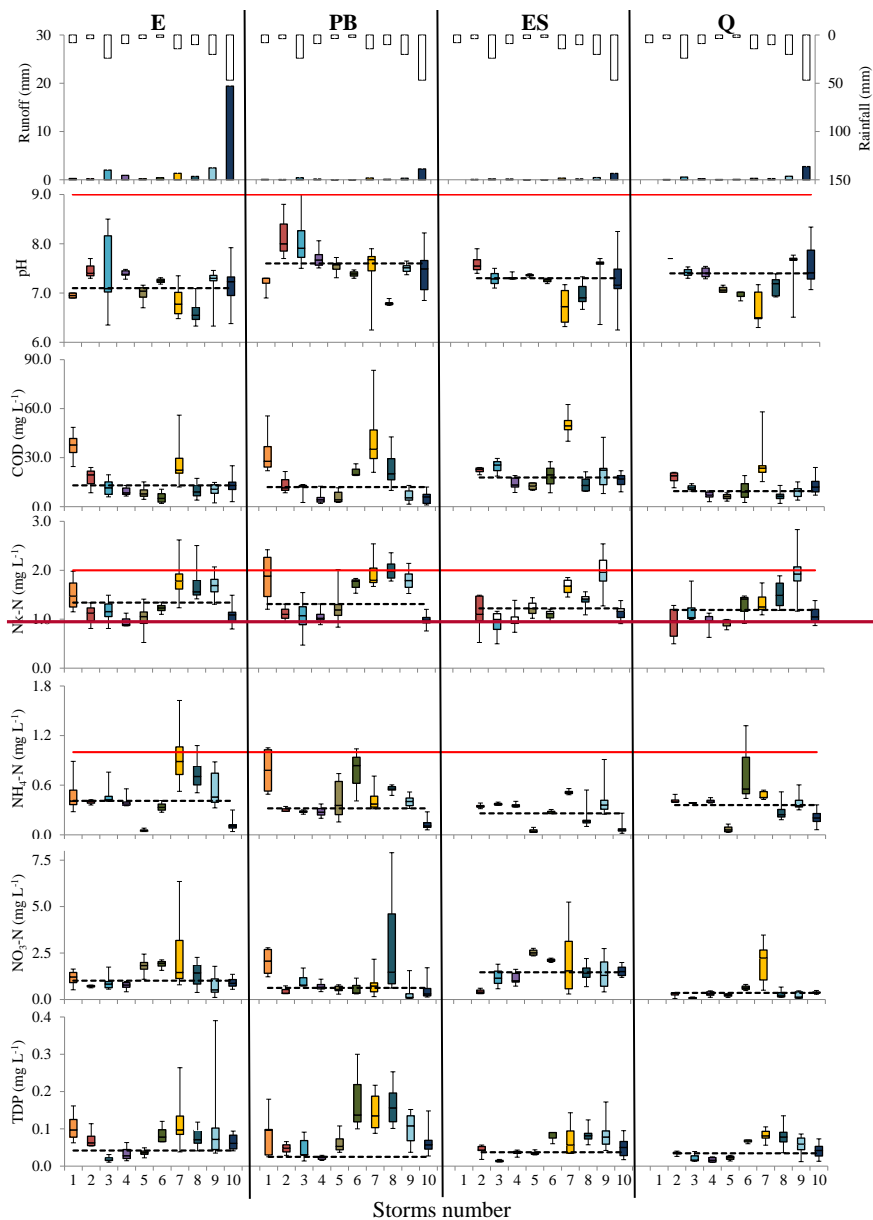
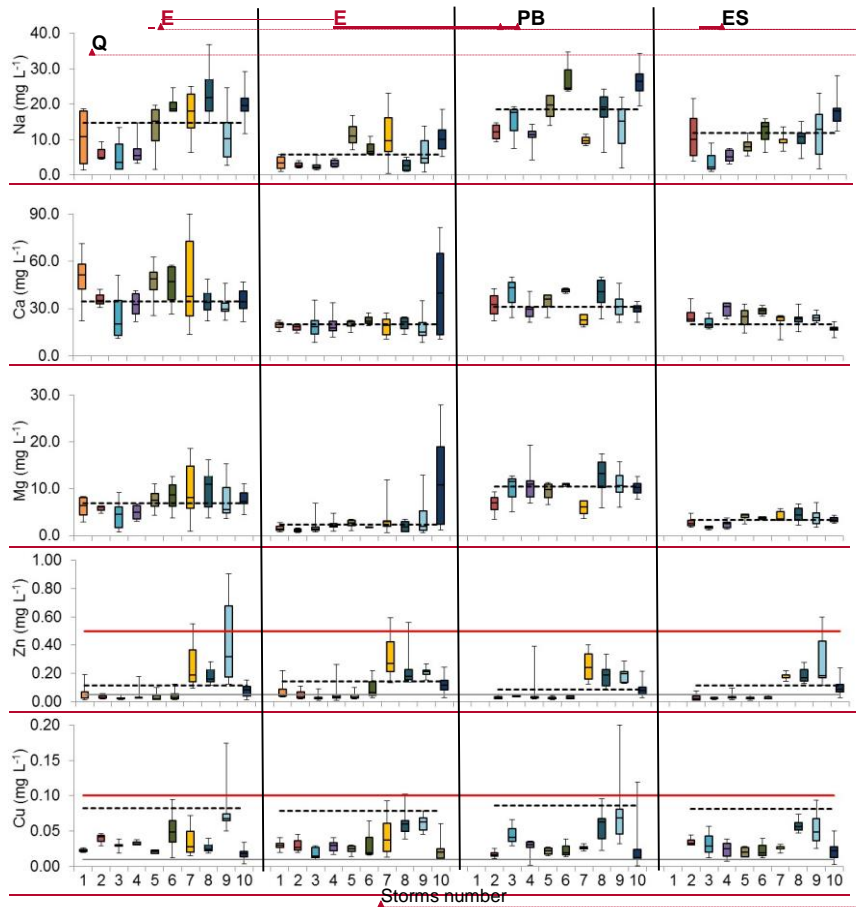


Figure 2 - Rainfall and runoff, as well as and box plots (median, upper (75) and lower (25) quartiles, maximum and minimum) showing pH, COD, N_{k-N} , NH_4-N , NO_3-N and TDP concentrations in at ESAC (E), Porto Bordalo (PB), Espírito Santo (ES) and Quinta (Q) for the ten storms monitored between October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

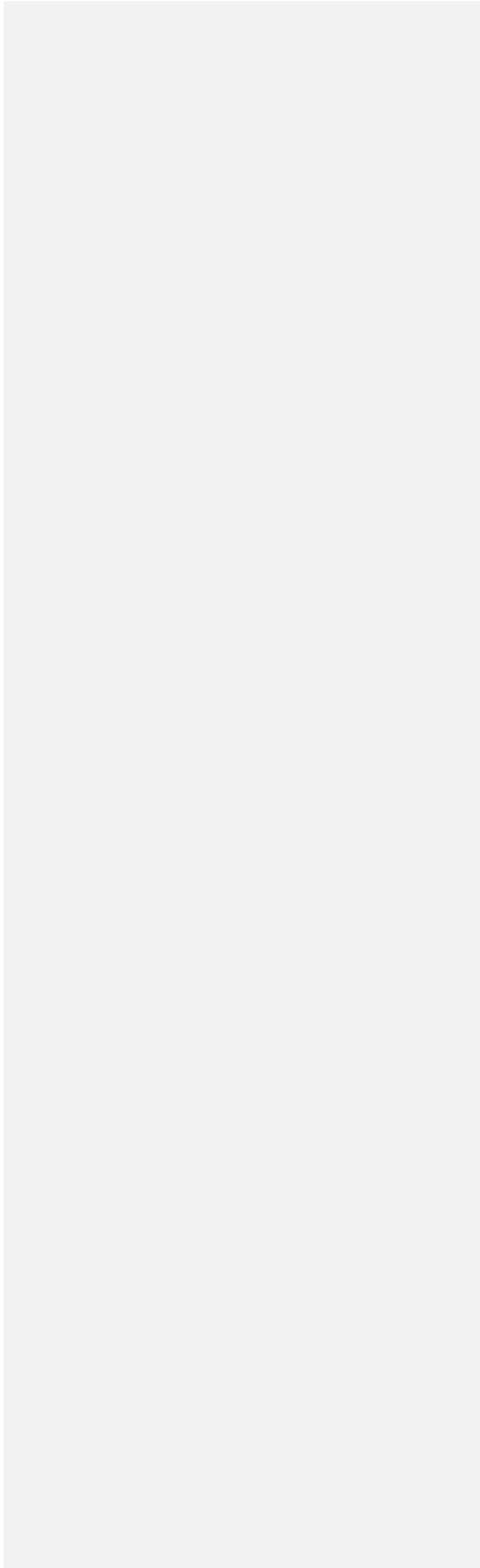
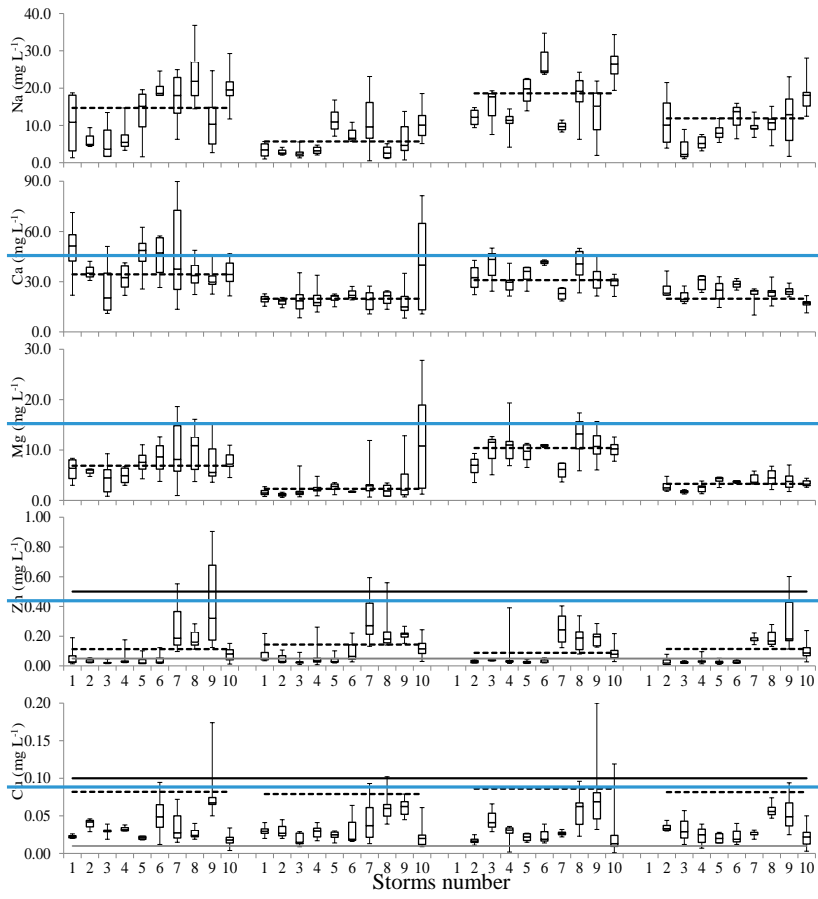
TDP is 1.0 mg L⁻¹ and is not shown as it is above the scale of the graphs represented because it is out of range.



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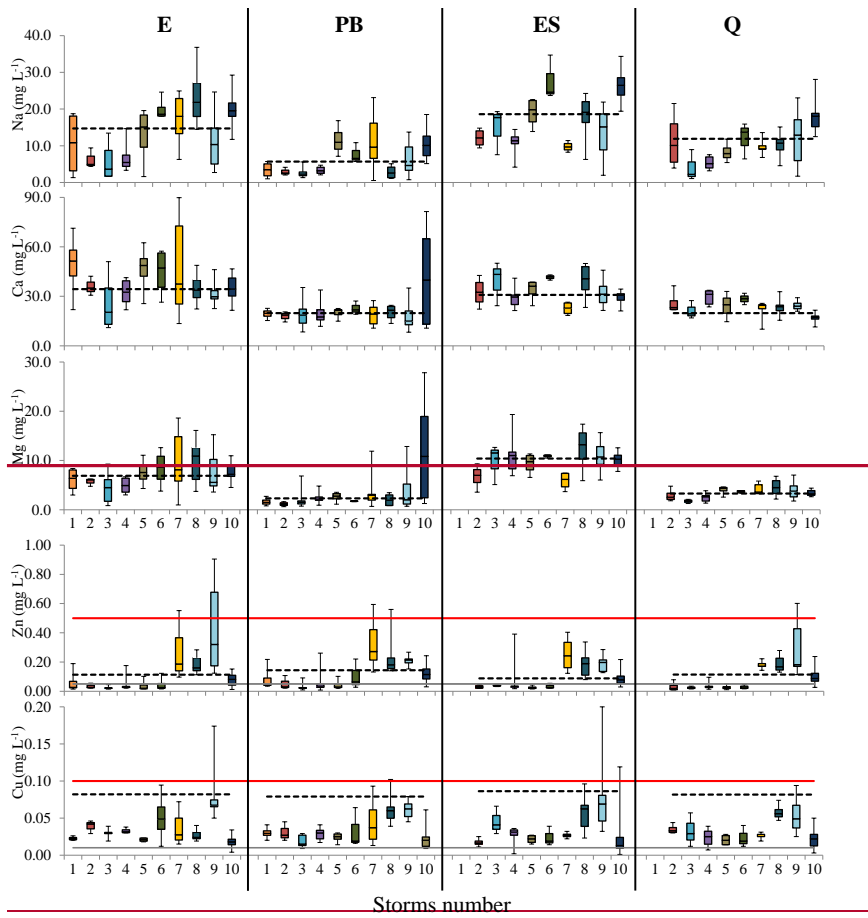
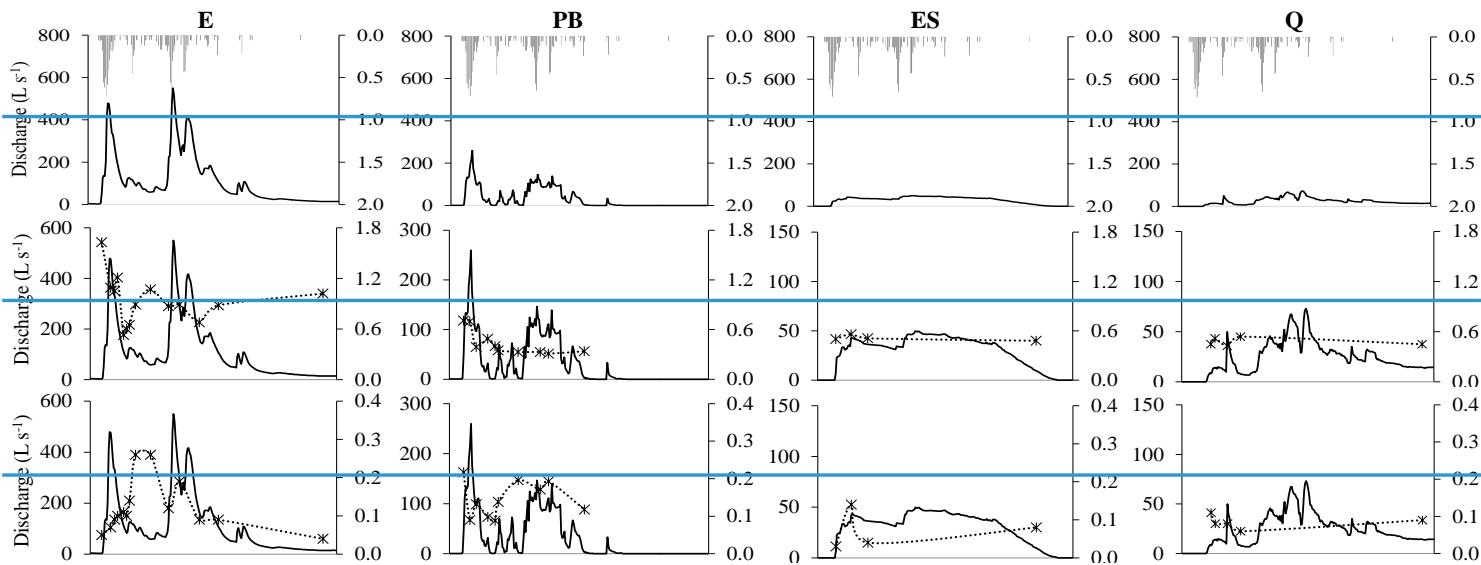
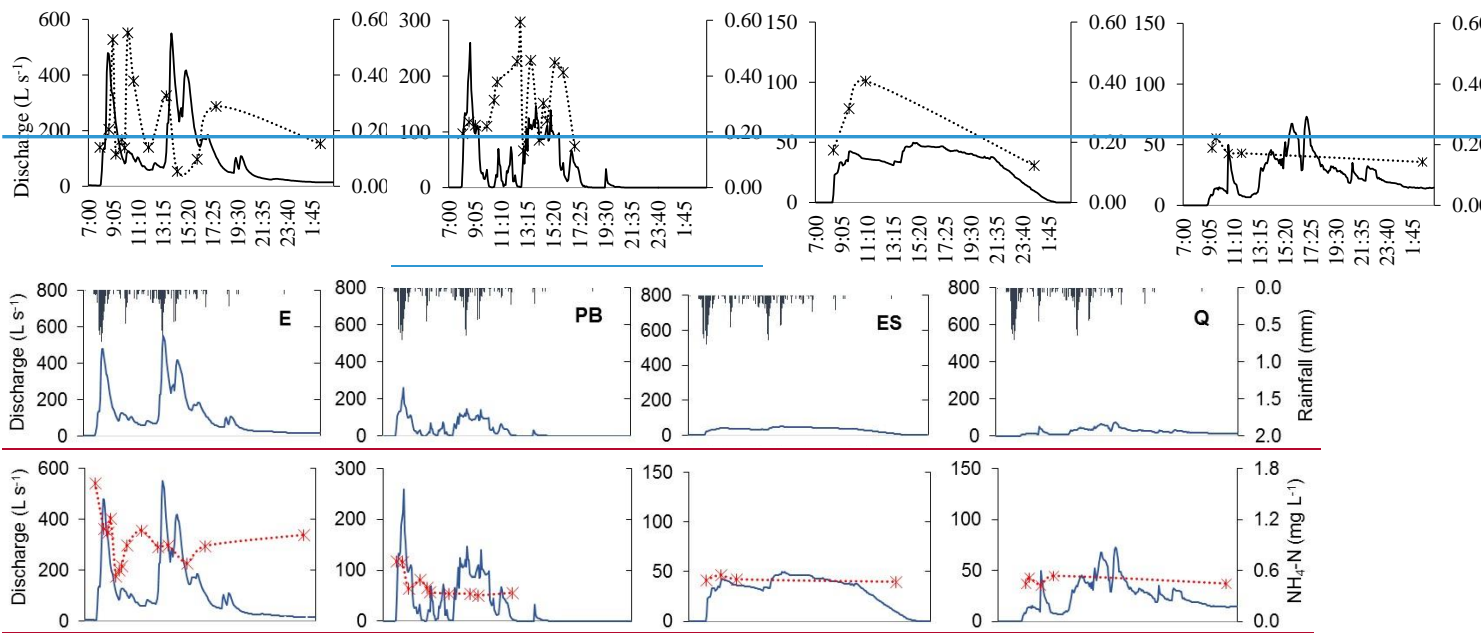


Figure 3 - Box plots (median, upper (75) and lower (25) quartiles, maximum and minimum) showing major cations (Na, Ca and Mg) and heavy metals (Zn and Cu) concentrations in at ESAC (E), Porto Bordalo (PB), Espírito Santo (ES) and Quinta (Q) for the ten storms monitored between October 2011 and March 2013. Black dashed lines represent median concentration 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.





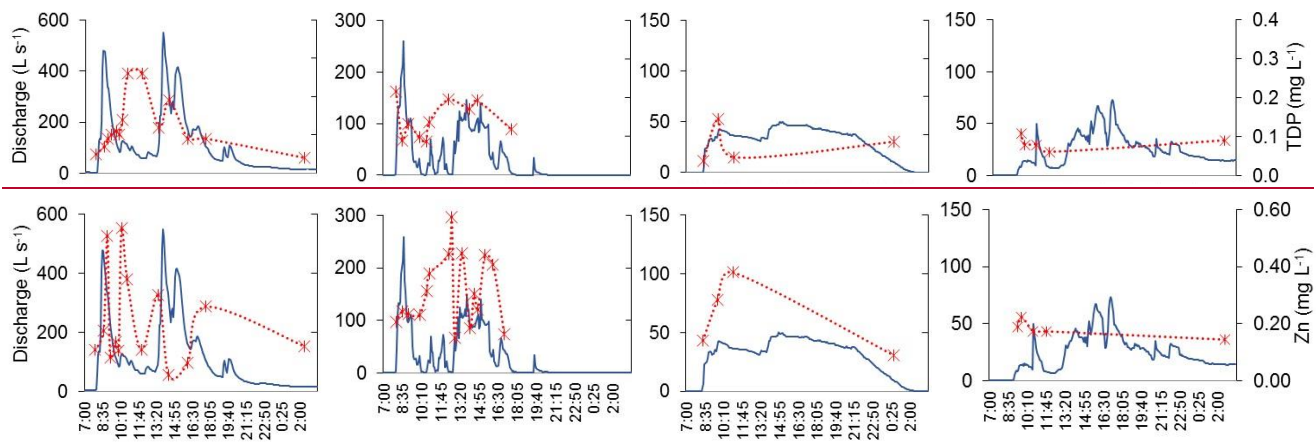
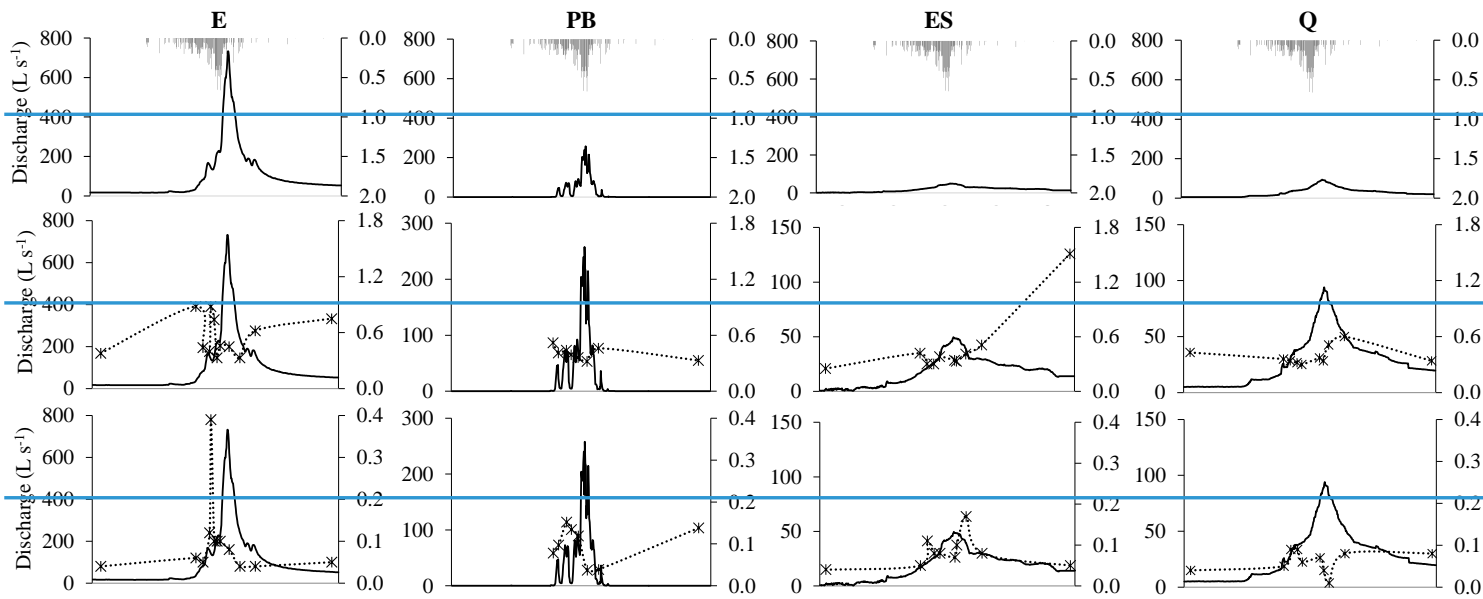
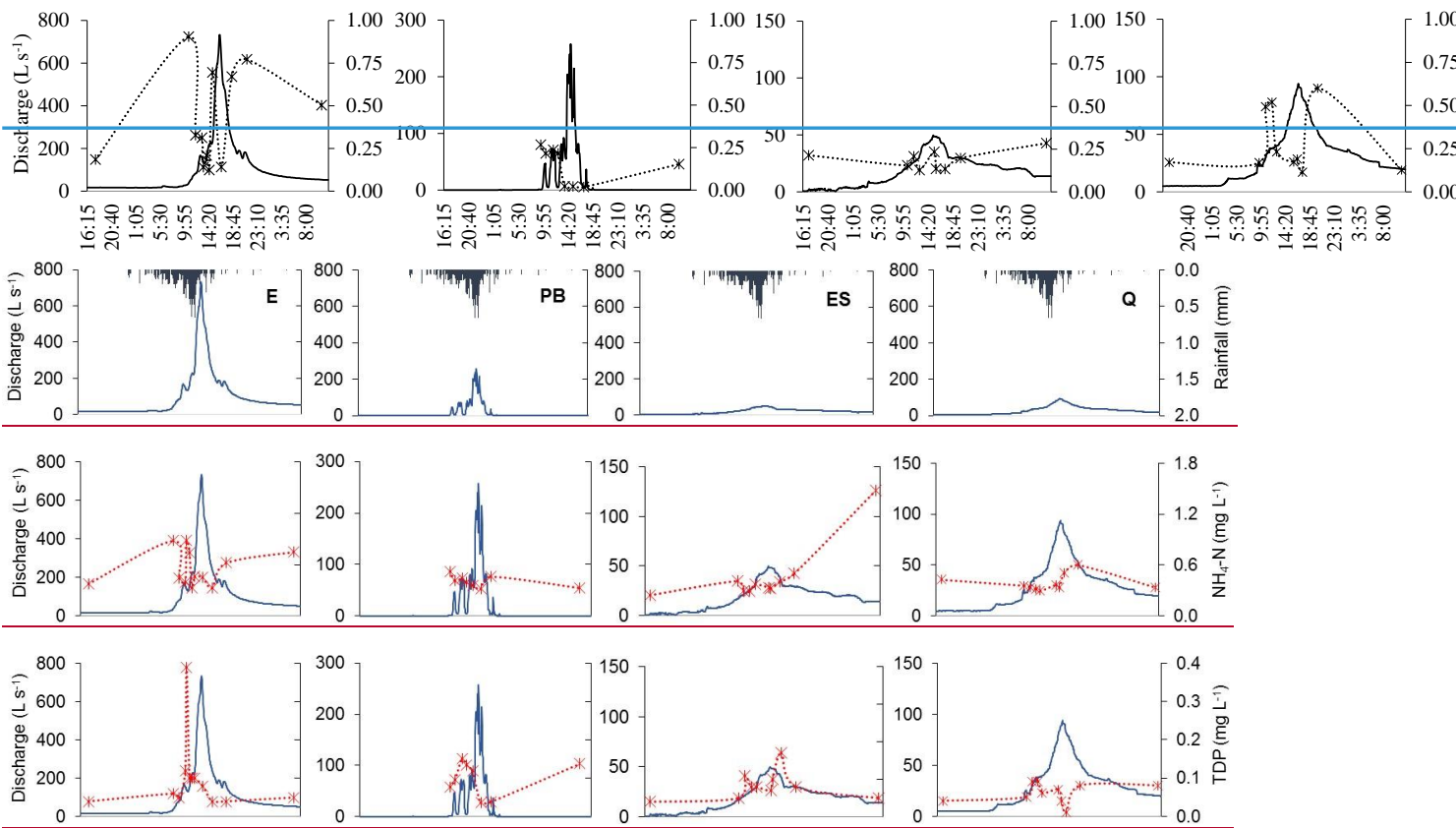


Figure 4 – Ammonium nitrogen ($\text{NH}_4\text{-N}$), total dissolved phosphorus (TDP) and zinc (Zn) responses (dotted green/red lines) to the late-summer 25-26 Sept 2012 rainstorm event (storm 7) at the four catchment sites (E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and Q: Quinta) in relation to rainfall and discharge.





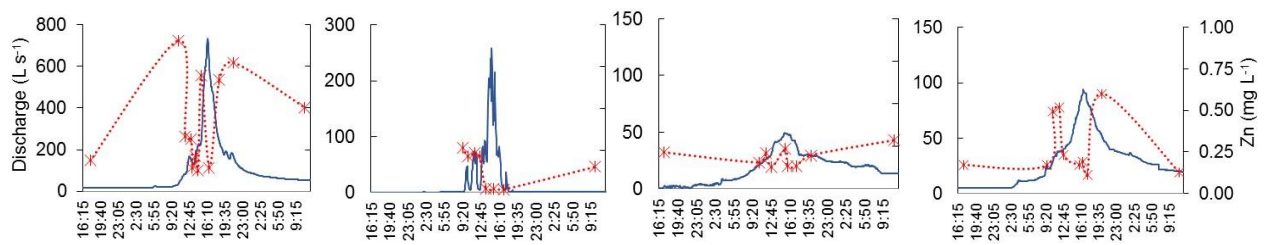


Figure 5 - Ammonium nitrogen ($\text{NH}_4\text{-N}$), total dissolved phosphorus (TDP) and zinc (Zn) responses (dotted green/red lines) in to the late-winter 15-17 Jan 2013 rainstorm event (storm 9) at the four catchment sites (E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and Q: Quinta) in relation to rainfall and discharge.

1 1 URBAN SOILS AND SEDIMENTS

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6 3 **Dynamics of surface water quality driven by distinct urbanization patterns and**
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9 4 **storms in a Portuguese peri-urban catchment**

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11 5 **Carla Sofia Santos Ferreira^{1,2} • Rory Peter Dominic Walsh³ • Maria de Lourdes**
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1 19 **Abstract**

2 20 *Purpose:* Although influences of urban land-use on water quality have been widely investigated, the
3 21 impacts of different urbanization patterns, particularly in Mediterranean environments, are not well
4 22 understood. Focussing on a Portuguese peri-urban catchment with 40% urban cover, this paper
5 23 explores (i) the impact of areas with differing urban extent and storm drainage system on streamwater
6 24 quality, and (ii) temporal variations driven by season and storm events of differing magnitude,
7 25 intensity and antecedent weather.

8 26 *Materials and methods:* Water quality was assessed at the catchment outlet (E) and for three upstream
9 27 tributaries: (1) Porto Bordalo (PB), 39% urban with a new major road and piping of some overland
10 28 flow from impervious surfaces directly into the stream, (2) Espírito Santo (ES), 49% urban, mostly
11 29 comprising detached houses surrounded by gardens, and with overland flow infiltrating into
12 30 downslope pervious soils; and (iii) Quinta (Q), 22% urban with partial piping of overland flow from
13 31 a recent enterprise park area. Water samples were collected at different stages in storm hydrograph
14 32 responses to ten rainfall events in October 2011 to March 2013. Water quality variables analysed
15 33 included chemical oxygen demand (COD), nutrients (kjeldahl nitrogen [Nk-N], ammonium [NH₄-N],
16 34 nitrate [NO₃-N] and total dissolved phosphorus [TDP]) and heavy metals (zinc [Zn] and copper [Cu]).

17 35 *Results and discussion:* Urban areas had great impact on COD, with highest median concentrations
18 36 in ES and lowest in Q. In ES, fertilizing lawns and gardens may have been responsible for its higher
19 37 median NO₃-N concentrations. High concentrations of heavy metals were recorded in PB and Q,
20 38 probably due to piping of road runoff directly into the stream. Generally, higher pollutant
21 39 concentrations were recorded in the first storm events after the summer drought, due to flushing of
22 40 accumulated solutes and a lower dilution effect, with Nk-N and NH₄-N exceeding water quality
23 41 standards. Over the wet season, increasing soil moisture favoured greater flow connectivity between
24 42 runoff processes from pollutant sources and the stream network, leading to a higher proportion of
25 43 samples exceeding pollution thresholds.

26 44 *Conclusions:* No direct relationship was identified between urban extent and water quality, possibly
27 45 due to the overriding impact of different storm drainage systems and flow connectivities of different
28 46 urban patterns. Hydrological regime, linked to seasonal changes, also exerted a major influence on
29 47 water quality dynamics. Information on the spatiotemporal dynamics of pollutants, linked to different
30 48 urban patterns and storm drainage systems, should help enable urban planners to minimize adverse
31 49 impacts of urbanization on aquatic ecosystems.

32 50
33 51 **Keywords** Flow connectivity • Heavy metals • Mediterranean climate • Storm events • Urban pattern
34 52 • Urban water quality
35 53

1 54 **1 Introduction**

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4 55 Population growth is a worldwide phenomenon and in the Mediterranean region population
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6
7 56 is likely to have more than doubled by 2020 compared with 1960 (Zdruli 2014). The increase
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10 57 of population is generally accompanied by the loss of forest and agricultural land to urban
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12 58 expansion, and the integration of fragmented rural areas surrounding growing cities into the
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14 59 urban system (e.g. Binns et al. 2003). The abandonment of the mountains and urbanization
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16 60 process influences landscape characteristics, such as its structure, function and dynamics
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19 61 (Çakir et al. 2008; Keestra et al. 2009), leading to major environmental and water resources
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21 62 impacts (e.g. Alphan 2003), including both hydrological processes (e.g. Shuster et al. 2005;
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24 63 Fletcher et al. 2013) and water quality (e.g. Tu 2011; Barco 2008).

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27 64 Urban areas are typically associated with many pollutants, including heavy metals (e.g.
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30 65 cadmium [Cd], copper [Cu], chromium [Cr], iron [Fe] and zinc [Zn]) (e.g. Yu et al. 2014),
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32 66 organic compounds (e.g. biochemical oxygen demand, ammonium, polycyclic aromatic
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34 67 hydrocarbons, polychlorinated byphenils, oil and grease) (Gilbert and Clausen 2006; Dias-
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36
37 68 Ferreira et al. *in press*), nutrients (e.g. nitrates, phosphates) (Lin et al. 2014), and faecal
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40 69 coliforms (Mallin and Wheeler 2000). These pollutants are mainly provided by (i) industrial
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42 70 activities (Yu et al. 2014) and vehicular traffic (e.g. Carey et al. 2013); (ii) wastewater
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44 71 contamination, including from septic tanks and sewage system leaks (Le Pape et al. 2013),
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47 72 diffuse sources, and treated and untreated effluent from wastewater treatment plants and
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50 73 storm sewer overflows (Yu et al. 2014); and (iii) lawns and gardens maintenance, due to
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52 74 inappropriate fertilization and irrigation activities (Lin et al. 2014).

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55 75 Although the type of urban development (e.g. industrial, commercial, residential, and
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57
58 76 recreational) determines the nature of pollutants released (e.g. Tu 2011), urban runoff

1 77 generally has been considered a major non-point source of pollutants within catchments (e.g.
2
3 78 Yu et al. 2016). Direct relationships have been reported between pollutant concentrations and
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5 79 percentage urban surface (e.g. Sliva and Williams 2001), with for example total impervious
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8 80 area being considered an indicator of aquatic ecosystem conservation status (e.g.
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11 81 Rautengarten 2006; Kuusisto-Hjort and Hjort 2013).

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14 82 Other authors, however, suggest that the location of pollutant sources within the catchment,
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16 83 and the distance to the stream network, are better indicators of water quality (e.g. Yu et al.
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19 84 2016). Urban areas located downslope may provide runoff flowing into the stream network,
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21 85 whereas runoff from upslope areas may be infiltrated and retained in downslope pervious
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24 86 soils (e.g. Ferreira et al. 2015), preventing pollutants from reaching aquatic ecosystems. In
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26 87 catchments comprising mosaics of urban and non-urban land-uses, typical of peri-urban
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29 88 catchments, the connectivity between runoff/pollutant sources and water resources can vary
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31 89 greatly and have been little researched to date, particularly in Mediterranean environmental
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34 90 settings. Furthermore, there is a general lack of studies exploring the dynamics of pollutant
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36 91 concentrations and fluxes in peri-urban catchments (Rodríguez-Blanco 2013).

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39 92 In order to address these research gaps, this study investigates the spatial and temporal
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42 93 dynamics of aspects of streamwater chemistry in a peri-urban catchment in Portugal, and
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44 94 explores in particular the influence of landscape pattern on flow and pollutant connectivity
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47 95 in storm events at different seasons and following differing antecedent weather associated
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50 96 with the Mediterranean climate. The study aims to assess the impact of different urban
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52 97 patterns, in forms of different impervious cover and spatial arrangement of pervious and
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54 98 impervious surfaces, on surface water quality and discharge chemistry dynamics in a typical
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57 99 Portuguese peri-urban catchment. The specific objectives are to (i) assess water quality

1 100 differences between three sub-catchments with distinct urbanization patterns and the
2
3 101 catchment outlet, as regards to pH, chemical oxygen demand (COD), nutrients (kjeldahl
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5 102 nitrogen [Nk-N], ammonium [NH₄-N], nitrate [NO₃-N] and total dissolved phosphorus [TDP]),
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7 103 heavy metals (Cu and Zn) and major cations (calcium [Ca], magnesium [Mg] and sodium
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9 104 [Na]); (ii) explore temporal variations in water quality between and within storm events at
10
11 105 different times of year; and (iii) investigate whether pollutant threshold levels (according to
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13 106 Portuguese water quality standards) were exceeded and under which weather conditions. A
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15 107 better understanding of the impact of urban patterns on water quality should enable urban
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17 108 planners to minimize adverse impacts of urbanization on stream ecosystems.
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110 **2 Study site description**

111 The study was carried out in the small (6.2 km²), peri-urban Ribeira dos Covões catchment
112 on the outskirts of the city of Coimbra in central Portugal (Fig.1). The catchment is
113 characterized by sandstones with Fluvisols and Podsoles in west and limestone with Leptic
114 Cambisols in the east (WRB 2006).

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

1 123 Catchment land-use comprises urban areas (40%) dispersed within woodland (56%) and
2
3 124 agricultural land (4%). The woodland is dominated by eucalyptus, but with some pine
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5 125 plantations and a relict oak stand. Agricultural land-use consists of a few olive plantations,
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8 126 pasture areas for cattle along part of the main stream, and small family farms with vegetables.
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10 127 Urban land-use mainly comprises residential areas, some small supermarkets and shops,
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12 128 educational and health services, including a central hospital, and a few facilities (garage
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14 129 shops, sawmill and a pharmaceutical factory). An enterprise park, covering 5% of the
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16 130 catchment area, is under construction in the headwaters in the extreme southwest of the
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18 131 catchment (clearly visible in Fig.1). A network of roads extends across the catchment and
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20
21 132 includes a recent motorway. Residential areas differ greatly in urbanization style, comprising
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23 133 (i) areas of single-family houses, surrounded by gardens, and (ii) recent row-houses and
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25 134 apartment blocks. These distinct residential areas house approximately 26,700 inhabitants,
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28 135 with population densities ranging from <25 inhabitants km^{-2} to >9900 inhabitants km^{-2} (Pato
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31 136 et al. 2015).
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36 137 In the newer urban areas, of high population density, part of the runoff from impervious
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38 138 surfaces is collected in culverts and gutters and routed or piped direct to the stream network.
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41 139 In contrast, in urban settlements surrounded by gardens, agricultural and woodland soils,
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43 140 stormwater tends to dissipate in adjacent areas of high permeability.
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47 141 Domestic effluent, however, is piped to a large, modern wastewater treatment plant (WWTP),
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49 142 located outside the catchment. However, a small WWTP, installed in around 1985, served an
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51 143 upslope urban core in Quinta sub-catchment until 2012, but was very inefficient and effluent
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53 144 from it was released into a downslope woodland area and into a tributary. In 2012 the
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55 145 wastewater was linked to the larger sewerage network and the small WWTP was disabled.
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147 **3 Methodology**

148 **3.1 Research design**

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

152 T sites comprised the catchment outlet at ESAC (E) and three upstream sites in sub-
153 catchments of distinct urban cover and pattern (Table 1). These were: (i) Espírito Santo (ES),
154 the most urbanized (49% urban) sub-catchment containing areas of high impervious cover in
155 upslope sites and lower impervious cover (detached houses surrounded by gardens), mainly
156 in downslope locations; (ii) Porto Bordalo (PB), with 39% urban cover extending over the
157 sub-catchment in strip fashion, with row-house areas upslope and detached houses with
158 greater impervious cover or only small gardens downslope) and part of the motorway; and
159 (iii) Quinta (Q), 22% urban, mainly in upslope locations, comprising a small residential area
160 (4%) and the enterprise park under construction (18%). Differences between urban patterns
161 also include dissimilarities in the storm drainage system: (i) in ES, overland flow from
162 impervious surfaces is dissipated in adjacent downslope pervious soils; (ii) in PB, storm
163 runoff from upslope urban areas is diverted into pervious soils, whereas from downslope
164 impervious surfaces it is piped into the stream tributary or nearby abandoned fields; and (iii)
165 in Q runoff from the residential area dissipates in downslope woodland, whereas runoff from
166 impervious surfaces within the new enterprise park is piped into a detention basin, which
167 delays its flow into the stream network. Additional differences are linked to physical
168 properties of the sub-catchments. In terms of lithology, ES and Q are sandstone sub-

1 169 catchments and PB a limestone sub-catchment, with the entire catchment at E being 56%
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3 170 sandstone, 41% limestone and 3% alluvial (Table 1).

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7 171 Water samples were collected at intervals manually at each site during each of 10 storm
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9 172 events. This was facilitated by the small size of the catchment, the proximity of sampling
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11 173 sites, the use of a car and multiple personnel. Selection of storm events was aided by use of
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13 174 weather forecasts and focus on the first rainstorms after the summer (storms 1, 2 and 7) and
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15 175 on storm events of different magnitudes over the wet season, including autumn (storms 3, 4
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17 176 and 5), winter (storms 8, 9 and 10) and spring (storm 6), in order to cover seasonal differences
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19 177 in response over the year.
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28 179 **3.2 Water sampling**

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32 180 Three to fifteen samples covering the rising limb, peak and falling limb of storm responses
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34 181 at the four sites were collected during each of 10 storm events, monitored between October
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36 182 2011 and March 2013. Whenever possible, the first sample of the event was collected
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38 183 immediately before rainfall started, if stream was flowing, to provide preceding baseflow
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40 184 water quality. Storm events were assumed to have stopped when no rainfall was recorded for
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42 185 6h. In total 76 samples were collected at E, 75 at PB, 56 at ES and 58 at Q. Samples were
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44 186 collected in acid-washed 250 mL glassware and 2 L polyethylene bottles, placed in a dark
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46 187 chilled cooler (~4°C) and taken to the laboratory.
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52 188 Hydrological data of 5-minute resolution were provided by an existing network of flow
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54 189 gauging stations at each site and five rainfall gauges distributed across the catchment (Figure
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1 190 1). The Thiessen Polygon method was used to calculate the weighted mean rainfall, assumed
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3 191 to be constant over the catchment.
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10 193 **3.2 Laboratory analysis**

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14 194 Water samples were immediately analysed for pH by electrometry (Hach, Sension Portable
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16 195 case). Sample aliquots were filtered through 0.45 µm membranes (Millipore MF) and stored
17
18 196 for later chemical analyses: (i) aliquots for dissolved nitrite (NO₂-N) and nitrate (NO₃-N);
19
20 197 (ii) aliquots for dissolved chemical oxygen demand (COD), kjeldahl nitrogen (Nk-N),
21
22 198 ammonium (NH₄-N) and total dissolved phosphorus (TDP) were acidified with sulphuric
23
24 199 acid (pH <2); (iii) aliquots for dissolved ions [sodium (Na), calcium (Ca) and magnesium
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26 200 (Mg)] and heavy metal analyses [zinc (Zn) and copper (Cu)] were acidified with nitric acid
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28 201 (pH 2-3). All aliquot samples were stored surrounded by ice and defrozen at room
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30 202 temperature before analysis.
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37 203 Nitrite and nitrate concentrations were measured simultaneously with an automated
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39 204 segmented flow analyser (SAN⁺⁺ system), using the cadmium reduction method (Skalar
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41 205 method 461-322; Skalar, 2004a). Given the normally very low nitrite concentration in rivers
42
43 206 the analytical results are examined only as NO₃-N. Ammonium concentration was also
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45 207 determined by an automated segmented flow analyser, but using a modified Berthelot
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47 208 reaction (Skalar method 155-316; Skalar, 2004b). Kjeldahl nitrogen, including organic
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49 209 nitrogen, ammonia and ammonium, was measured after sulphuric acid digestion with a
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51 210 selenium catalyser, followed by distillation and titration with hydrochloric acid (Standard
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53 211 Method 4500-Norg B; APHA 1998).
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1 212 COD and TDP were analysed using a multiparameter water quality instrument (Hach DR
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3 213 2000). COD was determined colorimetrically after acid digestion and oxidation with
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5 214 dichromate, in accordance with ISO 15705:2002 standards (HI 93754A vials, Hanna
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7
8 215 Instruments). TDP was quantified, after persulfate acid digestion, colorimetrically by
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10 216 reacting with molybdate ascorbic acid and antimony potassium tartrate, adapted from 4500-
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12
13 217 P Standard Methods (HI 93758A vials, Hanna Instruments).

14
15
16 218 Cation and heavy metal analyses were made after digestion with nitric acid (Standard Method
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19 219 3030-E; APHA 1998), by atomic absorption spectrophotometry (Perkin Elmer AA300), with
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21 220 direct air-acetylene flame and hollow cathode lamps (Standard Method 3111-B; APHA
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24 221 1998). Detection limits for Zn and Cu were 0.05 mg L^{-1} and 0.01 mg L^{-1} , respectively.

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27 222 Reagent blanks and duplicate samples were used for quality control purposes and mean
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30 223 concentration values (repeated analysis of each sample) were used for data analysis.

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34 35 36 37 225 **3.3 Data analysis**

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40 226 The hydrological regime of the ten sampled storms was characterized in terms of rainfall and
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42
43 227 stream discharge. For each storm event, the rainfall amount, duration and intensity were
44
45 228 calculated. Rainfall intensity was described in terms of the event mean (Imed), and the
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48 229 maximum in 60- minutes (I_{60}). Seven-day and 14-day antecedent precipitation (API_7 and
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50 230 API_{14}) for each storm event were calculated using weighted mean rainfall data. Streamflow
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53 231 parameters used included instantaneous discharge (at the time of water sampling) and event
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55 232 peak and mean discharges. Stormflow and baseflow components were separated for
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57 233 individual events, using a mathematical digital filter (Nathan and McMahon 1990). The
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1 234 storm runoff coefficient for each event was calculated as the ratio of total storm runoff
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3 235 (discharge normalized by area) divided by event rainfall. The time to peak was defined as the
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5
6 236 time from the centroid of the rainfall to peak flow (Lana-Renault et al. 2011).
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8
9 237 Water quality values for the ten rainfall events were compared with Portuguese standards of
10
11 238 minimum surface water quality (DL236/98) (Table 2). Portuguese standards do not exist for
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13
14 239 the monitored parameters COD, NO₃-N and major cations (Na, Ca and Mg).
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17 240 The statistical significance of differences in parameters between the four sites were
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20 241 investigated using the non-parametric Kruskal-Wallis test. Whenever significant spatial
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22 242 and/or temporal water quality differences were identified ($p < 0.05$), they were further
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25 243 investigated using the post-hoc Fisher's Least Significant Difference test, at the 0.05
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27 244 significance level. For each site, relationships between different water quality parameters,
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30 245 and between these parameters and streamflow properties, were explored using Spearman's
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32 246 rank correlation coefficient (r), at 0.05 and 0.01 significance levels. Data analysis was
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35 247 performed using IBM SPSS Statistics 22 software.
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41 249 **4 Results**

42 250 **4.1 Storm characteristics and streamflow response to storm events**

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45 251 Rainfall characteristics for the 10 storms sampled between October 2011 and March 2013
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48 252 are shown in Table 3. Storm totals ranged from 2.4 mm (storm 6) to 46.8 mm (storm 10),
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50
51 253 which had a return period of less than 2 years, but the return period of the maximum hourly
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54 254 intensity for storm 3 (15.6 mm h^{-1}) was 3 years.
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1 255 Streamflow responses at the four monitored sites are summarized in Table 4 and Figure 2.
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3 256 Storm 1, recorded at the end of summer (23-24/10/2011) was not enough to trigger discharge
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5
6 257 in ES and Q. For the 10 storms, the mean storm runoff coefficient at PB (6.1%) was twice as
7
8 258 high as at E (3.0%) and Q (2.7%), and also greater than at ES (4.4%). In the monitored storms,
9
10 259 baseflow comprised 46%-87% of event flows at E, 51%-85% at Q and 58%-94% at ES,
11
12 260 whereas at PB it was 16%-55%. The catchment and sub-catchments have a flashy behaviour,
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14 261 with response times ranging from 5-35 min at PB, 10-40 min at ES, 10-65 min at Q and 25-
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16 262 85 min at E.
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26 264 **4.2 Water quality**

27 265 *4.2.1 Overview of water quality in the ten events at the four sites*

28
29 266 Fig. 2 uses box plots to summarise water quality responses at each of the four sites to the ten
30
31 267 rainstorms. The limestone PB sub-catchment showed significantly higher pH ($p < 0.05$) than
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33 268 Q, ES and E, but median values over the 10 storms were 7.6, 7.4, 7.3 and 7.1, respectively,
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35 269 and thus slightly alkaline.
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40 270 Significant differences in COD (dissolved phase) between sites were recorded ($p < 0.05$), with
41
42 271 lowest median concentration in the least urban Q (9.5 mg L^{-1}), intermediate values at PB
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44 272 (12.0 mg L^{-1}) and E (13.0 mg L^{-1}), and highest median COD in the most urbanized ES sub-
45
46 273 catchment (17.8 mg L^{-1}) (Fig. 2). Ranges in values were substantial at all sites, with minima
47
48 274 of $2.0 - 8.0 \text{ mg L}^{-1}$ and maxima of $48.5 - 62.5 \text{ mg L}^{-1}$ at E, PB and Q and 83.5 mg L^{-1} at ES.
49
50 275 Kjeldhal nitrogen in dissolved phase varied little between study sites, but was slightly higher
51
52 276 at E ($0.52 - 2.62 \text{ mg L}^{-1}$) and Q ($0.50 - 2.83 \text{ mg L}^{-1}$), where cattle-rearing occurs in fields
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54 277 adjacent to the stream, than at ES ($0.50 - 2.54 \text{ mg L}^{-1}$) and PB ($0.47 - 2.54 \text{ mg L}^{-1}$) (Fig. 2).
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1 278 PB, however, experienced more than twice as many pollution occasions (12 values >2.0 mg
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3 279 L⁻¹, DL236/98) than the other sites (5 at E and Q and 4 at ES). Pollution thresholds were
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6 280 exceeded in storm 9 (winter) at all sites, in storms 7 (after summer) and 8 (winter) at E and
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8 281 PB, and storms 1 (after summer) and 5 (winter) at PB.

10 282 Similarly to Nk-N, slightly higher NH₄-N concentrations were recorded at E (0.04 - 1.63 mg
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12
13 283 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)
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15 284 (p>0.05, Fig. 2). The water quality standard for NH₄-N (1.0 mg L⁻¹, DL236/98) was always
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17
18 285 complied with at ES, but exceeded for 7, 3 and 1 samples collected at E, PB and Q,
19
20 286 respectively. These pollution occasions were recorded during storms 7 (late summer) and 8
21
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23 287 (winter) at E, and storm 1 (late summer, after a very dry period) at PB, as recorded for Nk-
24
25 288 N, but in addition in storm 6 (spring) at PB and Q. Relatively strong and statistically
26
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28 289 significant positive correlations were found between NH₄-N and Nk-N at E (r=0.623, p<0.01)
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30 290 and ES (r=0.340, p<0.05), but not at Q and PB (p>0.05).

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33
34 291 Slightly lower NO₃-N concentrations were recorded at the least urbanized Q (0.04 – 3.47 mg
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36 292 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.
37
38 293 2). Correlations with COD, Nk-N and NO₃-N were weak albeit significant at all sites
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40
41 294 (r<0.350, p<0.05).

42
43
44 295 In contrast to nitrogen compounds, TDP varied significantly between sites (p<0.05), with
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46 296 median concentrations being greater at E and PB (0.07 mg L⁻¹) than at ES (0.06 mg L⁻¹) and
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49 297 Q (0.04 mg L⁻¹). Minimum concentrations were 0.01 mg L⁻¹ at all sites, and maxima were
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51
52 298 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).
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54 299 Phosphorus was not a pollutant threat, as all values were far below the Portuguese water
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56
57 300 quality standard (1.0 mg L⁻¹). TDP was positively correlated with COD and Nk-N
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1 301 concentrations at PB ($r=0.459$ and 0.552 , $p<0.05$). At ES and Q, TDP was only significantly
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3 302 correlated with Nk-N ($r=0.483$ and 0.467 , $p<0.01$).
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5
6 303 Water quality displayed differences in concentrations of major cations between monitoring
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8 304 sites ($p<0.05$) (Fig. 3). Sodium concentrations were significantly lower at PB (median 5.7
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10 mg L^{-1} , range $0.7 - 23.1 \text{ mg L}^{-1}$) than at ES (18.6 mg L^{-1} , $2.0 - 34.7 \text{ mg L}^{-1}$), E (14.7 mg L^{-1} ,
11
12 $1.3 - 29.3 \text{ mg L}^{-1}$) and Q (11.9 mg L^{-1} , $1.1 - 28.1 \text{ mg L}^{-1}$). Calcium concentrations were
13
14 306 significantly higher at E (median 34.4 mg L^{-1} , $11.0 - 89.9 \text{ mg L}^{-1}$) and ES (30.9 mg L^{-1} , 18.4
15
16 307 $- 49.9 \text{ mg L}^{-1}$) than at Q (22.6 mg L^{-1} , $10.0 - 36.4 \text{ mg L}^{-1}$) and PB (19.8 mg L^{-1} , $8.3 -$
17
18 308 81.4 mg L^{-1}). Mg concentrations were higher ($p<0.05$) at ES (median 10.4 mg L^{-1} , $3.6 -$
19
20 309 19.3 mg L^{-1}), than at E (6.9 mg L^{-1} , $0.8 - 18.6 \text{ mg L}^{-1}$), Q (3.3 mg L^{-1} , $1.3 - 7.0 \text{ mg L}^{-1}$) and
21
22 310 PB (2.3 mg L^{-1} , $0.6 - 27.8 \text{ mg L}^{-1}$).
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24 311 Sodium increased with increasing Mg, but with a stronger correlation at E ($r=0.709$, $p<0.01$)
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26 312 than at PB, ES and Q ($r=0.569$, 0.391 and 0.358 , $p<0.01$). Sodium displayed significant
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28 313 positive correlations with Ca only at E and PB ($r=0.464$ and 0.423). Calcium and magnesium
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30 314 were strongly correlated with each other at all sites ($r= 0.633 - 0.735$, $p<0.01$) except Q.
31
32 315 As regards heavy metals, median dissolved Zn concentrations in the study storm events were
33
34 316 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
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36 317 0.088 mg L^{-1} , respectively) (Fig. 3). Concentrations exceeded Zn water quality standards
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38 318 (0.5 mg L^{-1}) in 7 samples at E ($0.53 - 0.91 \text{ mg L}^{-1}$), 2 samples at PB ($0.56 - 0.59 \text{ mg L}^{-1}$) and
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40 319 2 samples at Q ($0.52 - 0.60 \text{ mg L}^{-1}$), but none at ES (maximum only 0.40 mg L^{-1}). Pollutant
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42 320 levels of Zn were attained after summer at E and PB (storm 7), but also during winter at PB
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44 321 (storm 8), E and Q (storm 9). A strong positive correlation was recorded between Zn and Nk-
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46 322 N concentrations at E ($r=0.682$, $p<0.01$), whereas at PB and Q, Zn correlated significantly
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1 324 with TDP ($r=0.524$ and 0.564 , $p<0.01$). At ES and Q, Zn was significantly correlated with
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3 325 both Nk-N and TDP ($r=0.544$ and 0.638 , $p<0.01$).

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6 326 Median copper concentrations for the study storm events were slightly higher at Q than at
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8 327 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).

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10 328 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
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13 329 and 0.094 mg L^{-1} at Q. Pollutant levels of Cu ($>0.10 \text{ mg L}^{-1}$, DL236/98) were recorded only
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15 330 for one sample at E and one sample at ES, during storms 9 and 10, respectively.

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19 331 Copper and zinc were positively correlated with each other at all monitored sites (r ranged
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21 332 from 0.365 to 0.532 , $p<0.05$). At ES and PB, Cu was significantly correlated with Nk-N
22
23 333 ($r=0.481$ and 0.579 , $p<0.01$) and $\text{NH}_4\text{-N}$ ($r=0.481$ and 0.501 , $p<0.01$). At Q, Cu only
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25 334 correlated significantly with Nk-N ($r=0.536$, $p<0.01$).

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31 32 33 336 ***4.2.2 Between-storm variation over the study period***

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37 337 Between-storm differences in water quality response are apparent at the monitoring sites in
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39 338 Figures 2 and 3. Generally, COD and nutrients displayed higher concentrations in storms
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41 339 recorded in late summer (1, 2 and 7) with decreasing values over the wet season, achieving
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43 340 lowest concentrations in late winter (storms 5 and 10) (Fig. 2). Seasonal differences in COD
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45 341 were greater for PB than for Q, ES and E.

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50 342 Nk-N concentration varied less with season, with median concentrations for late summer
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52 343 storms being less than twice as high than for late winter storms. Greater seasonal differences
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54 344 were recorded for $\text{NH}_4\text{-N}$ concentrations, with storm medians being 3-4 times greater for late
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1 345 summer than late winter storms at ES, E and PB, but only 1.4 times as high at the least
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3 346 urbanized Q sub-catchment.
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6 347 As regards nitrates ($\text{NO}_3\text{-N}$), PB, Q and E displayed higher storm median concentrations in
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8 348 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
9
10 349 0.36 mg L^{-1} and 1.35 mg L^{-1} vs 1.01 mg L^{-1} , respectively), whereas ES displayed 3 times
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13 350 higher storm median concentrations in late winter than late summer storms (1.63 mg L^{-1} vs
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15 351 0.86 mg L^{-1}).
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18 352 TDP concentrations were twice higher in PB and E in late summer than late winter storms,
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20 353 but differences were much smaller at Q and ES. Lowest TDP concentrations were recorded
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23 354 in storm 3, with the greatest rainfall intensity, and storm 4, with the wettest antecedent
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25 355 conditions (Table 3).
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28 356 In contrast, major cations exhibited higher concentrations in wetter than drier settings (Fig.
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30 357 3). Median Na concentrations measured during storms 6 and 10, with greatest antecedent
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32 358 rainfall in previous 7 days (42.5 mm and 47.3 mm) were 2.5-, 1.8-, 1.5- and 1.3- fold higher
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35 359 than during storms after the summer (storms 1, 2 and 7) for ES (26.3 mg L^{-1} vs 10.4 mg L^{-1}),
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37 360 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}),
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39
40 361 respectively. Similar patterns were found for Ca and ES, but no specific temporal pattern
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42 362 was recorded at E and Q.
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45 363 The heavy metals Zn and Cu tended to show higher concentrations in late summer than late
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47 364 winter storms. Thus, median Zn concentrations were 2.5- in E (0.140 mg L^{-1} vs 0.055 mg L^{-1}),
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49 365 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
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52 366 1.4-times higher (0.084 mg L^{-1} vs 0.058 mg L^{-1}) in ES during late summer (storms 1, 2 and
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54 367 7) than late winter storms (5 and 10). Similar patterns were recorded for Cu. Some pollutant-
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57 368 level values of Zn and Cu were also recorded (see section 4.2.1).
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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: NH₄-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).

NH₄-N storm dynamics

During storm 7 (Fig. 4), highest NH₄-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, NH₄-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 NH₄-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, NH₄-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

1 391 noticed at pre-storm baseflow, with high and low concentrations prior to the late summer and
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3 392 winter storms, respectively.

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7 393 Similar patterns to $\text{NH}_4\text{-N}$ were in general recorded for Nk-N (not shown), in storms 7 and
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16 396 *TDP storm dynamics*

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20 397 TDP concentrations, albeit never exceeding Portuguese national guidelines, changed within
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22 398 storms differently from $\text{NH}_4\text{-N}$ and Nk-N concentrations. In storm 7 (Fig. 4), TDP was low
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24 399 at baseflow in E and increased progressively over the first storm peak, attaining highest
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26 400 concentrations on the falling limb, before a sharp fall. Nevertheless, with rainfall restart
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28 401 during storm 7, TDP concentration tended to follow discharge, with a peak at peakflow,
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30 402 followed by a progressive decline to pre-event level on the falling limb of the hydrograph. In
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32 403 ES, however, TDP concentration increased on the rising limb to a peak at peak flow, before
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34 404 declining as discharge fell. There were too few samples to define patterns during the second
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36 405 peak. In contrast, at PB and Q, peak TDP concentrations were recorded on the initial rising
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38 406 limb, with lowest concentrations at peak flow. After rainfall restart during storm 7, TDP
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40 407 concentrations at PB followed discharge variation, with values in late falling limb lower than
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42 408 those recorded in the second rising limb and peak flow.

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50 409 In winter storm 9 (Fig. 5), E and PB experienced a marked peak in TDP in the rising limb
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52 410 before falling to low values at peak flow and in the falling limb. At ES, however, peak TDP
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54 411 was recorded after peak discharge and TDP values throughout the storm hydrograph were

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1 412 higher than at pre-storm baseflow. At PB, high TDP concentration was also recorded by the
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3 413 end of the falling limb.
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10 415 *Dissolved Zn storm dynamics*
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14 416 High-magnitude and distinct temporal changes in dissolved zinc were recorded in the late
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16 417 summer storm (Fig. 4). Generally, Zn concentrations were low at pre-storm baseflow and
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18 418 reached multiple peaks at peak flow and during the falling limb. Only at Q were Zn
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20 419 concentrations higher during the rising limb. In the wet season storm (Fig. 5), Zn displayed
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22 420 massive peaks at E and Q, both in the rising and again in the falling limb of the hydrograph,
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24 421 but only in the rising limb at PB. Changes were more muted at ES, with peak concentration
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26 422 recorded at peak discharge.
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32 423 Although Cu concentrations followed similar intra-storm variation as Zn, pollutant levels
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34 424 were only recorded in winter storms (Fig. 3), also after peak discharge.
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41 426 **5 Discussion**
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45 427 **5.1 Differences in hydrological responses between sites**
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48 428 Before discussing the water quality results, differences in hydrological response between the
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50 429 sub-catchments are explained. Urbanization and the associated increase in impervious
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52 430 surfaces have been widely reported to enhance runoff (e.g. Zhang and Shuster 2014; Yao et
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54 431 al. 2015). Nevertheless, for the 10 storms studied, the storm runoff coefficient in the 40%
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56 432 urbanized Ribeira dos Covões catchment ranged only between 1.6% and 5.5%. In part this
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1 433 reflects the high permeability of the catchment provided by the sandstone and limestone
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3 434 bedrock (Ferreira et al. *this issue a*).
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7 435 Within the study catchment, PB (39% urban area and 15% impervious) displayed both the
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9 436 greatest storm runoff coefficients (2.5% - 11.8%) and quickest response times (5-35 minutes).
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11 437 In contrast, the more highly urbanized ES sub-catchment (49% urban, 27% impervious)
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13 438 experienced lower storm runoff coefficients (2.4% to 6.7%) and slightly higher response
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15 439 times (10-40 minutes). This is thought to be a consequence of distinct drainage systems. In
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17 440 PB, part of the runoff from downslope impervious surfaces is directly piped into the stream,
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19 441 leading to enhanced connectivity between overland flow sources and the stream network. In
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21 442 ES, however, runoff from paved surfaces is mostly diverted into pervious soils, and/or piped
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23 443 into downslope woodland areas, favouring water retention and infiltration, hence reducing
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25 444 the storm runoff response of the stream.
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32 445 Such an explanation would conform to findings of previous studies highlighting the
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34 446 significance of storm drainage systems (not simply % of impervious area) enhancing
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36 447 flashiness of storm runoff (e.g. Yang et al. 2011, Miller et al. 2014) and much reduced effects
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38 448 of impervious surfaces when not connecting to a storm sewer system (e.g. Hammer 1972).
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43 449 In Q sub-catchment, containing the largest woodland area (73%) and the smallest impervious
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45 450 cover (5%), storm runoff coefficients were the lowest (0.8% - 4.9%). Storm runoff
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47 451 coefficients in Q, however, were only a little lower than in ES, possibly because overland
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49 452 flow from paved surfaces in the enterprise park, located within Q, is piped into a detention
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51 453 basin and then released direct into the stream network, rather than being directed into
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53 454 pervious soils as within ES. Contrary to the typical flashy hydrographs with greater peak
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55 455 flows found in highly urbanized areas (e.g. Vidon et al. 2009), ES displayed longer-duration
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1 456 hydrographs, sometimes without a clear peak flow (Figs. 4 and 5), in contrast to the quicker
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3 457 response times of Q, even in small events (Table 4).
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7 458 That higher storm runoff coefficients for Q were found in storms following driest antecedent
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9 459 weather conditions may indicate that normally pervious soil is also providing overland flow,
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11 460 because of the low infiltration capacity induced by water repellency, particularly given the
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13 461 73% extent of woodland in the catchment (e.g. Ferreira et al. 2016).
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17 462 Differences in hydrological response between monitoring sites in Ribeira dos Covões may
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19 463 also reflect differences in lithology. In PB, underlain by limestone, baseflow represented
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21 464 55% of event runoff, whereas in ES and Q, the sandstone sub-catchments, it is 58-94% and
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23 465 49-85% respectively (Table 4).
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31 32 467 **5.2 Influence of urban pattern on water quality** 33 34

35 468 The Ribeira dos Covões results suggest that areas with different urbanization pattern have
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37 469 distinct impacts on surface water quality, particularly in terms of COD, TDP, major cations
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39 470 and pH ($p < 0.05$). Nitrogen (Nk-N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) and heavy metals (Zn and Cu),
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41 471 however, did not show significant differences between sites over the study period ($p > 0.05$),
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43 472 but nevertheless at least occasionally exceeded water quality standards at the four monitoring
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45 473 sites.
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54 475 **5.2.1 Chemical oxygen demand and nitrates** 55 56 57 58 59 60 61 62 63 64 65

1 476 The ES sub-catchment, with largest urban land-use (49%) and imperviousness, displayed
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3 477 higher concentrations of COD and NO₃-N (median values of 18.0 mg L⁻¹ and 1.46 mg L⁻¹)
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6 478 than E, PB and Q (Fig. 2), with concentrations increasing with percentage impervious surface
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8 479 (Table 1). Enhanced COD and NO₃-N values elsewhere are usually attributed to wastewater
9
10 480 contamination (e.g. Wilbers et al. 2014). However, given the separate sewage and storm
11
12 481 runoff drainage systems in Ribeira dos Covões, as well as the location of the WWTP outside
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14 482 the catchment, treated effluent would not seem to be a major pollutant source. COD and NO₃-
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16 483 N can be provided by diffuse sewage sources and road runoff, which can be an important
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18 484 pollutant source due to the high runoff volumes that can be involved (e.g. Crabtree et al.
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20 485 2006; Pereira et al. 2015). Both these sources may be significant in the Ribeira dos Covões
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22 486 catchment.

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29 487 NO₃-N is the dominant nitrogen form in ES (median values of 1.46 mg L⁻¹), and may be
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31 488 linked with use of fertilizer in the mainly detached houses with gardens and lawns, covering
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33 489 15% of the urban pattern of ES (Table 1), as found in such detached house areas elsewhere
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35 490 (e.g. Lin et al. 2014; Carey et al. 2013). Some of the NO₃-N in ES may also have derived
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37 491 from the small agricultural area adjacent to the stream channel. Fertilizer application in both
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39 492 urban and agricultural areas is usually carried out during spring and summer, which may in
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41 493 part explain the high concentrations of NO₃-N recorded during storms in late summer (Fig.
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43 494 2).

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53 496 ***5.2.2 Kjeldhal nitrogen and ammonium***

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56 497 Higher concentrations of N_k-N and NH₄-N were recorded at the catchment outlet at E and at
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58 498 Q, which has the lowest urban land-use (22%), than at ES and PB. At both E and Q sites,

1 499 organic compounds were the dominant form of nitrogen, given the relatively low $\text{NO}_3\text{-N}$
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3 500 concentrations (median values of 1.01 mg L^{-1} and 0.35 mg L^{-1}) and the small percentage of
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5
6 501 $\text{NH}_4\text{-N}$ in relation to Nk-N (34% and 25%, respectively). Extensive cattle rearing in
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8 502 agricultural fields in upslope and channel-margin locations in E and Q, is thought to be a
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10 503 major source of Nk-N and $\text{NH}_4\text{-N}$, and may explain why concentrations often exceeded
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12 504 pollution guidelines (maxima of 1.87 mg L^{-1} Nk-N and 1.32 mg L^{-1} $\text{NH}_4\text{-N}$, Fig. 2).

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16 505 An additional Nk-N and $\text{NH}_4\text{-N}$ source may occasionally be untreated domestic wastewater.
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18 506 Contamination by leaks in the sewage drainage system was observed occasionally through
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20 507 the colour and smell of surface water. Sewage leaks, however, are prone to influence water
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22 508 quality in all the study sites. In Q sub-catchment, past soil contamination from the abandoned
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24 509 WWTP, which received domestic wastewater from upslope urban cores and spread it
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26 510 downstream without treatment until 2012, may also be a potential source of Nk-N and $\text{NH}_4\text{-}$
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28 511 N . These soil contamination sources may explain why pollution levels were exceeded only
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30 512 in late winter storms (Fig. 2), because of greater connectivity with stream network, favoured
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32 513 by the higher soil moisture content at that time. Great concentrations of $\text{NH}_4\text{-N}$ can be toxic
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34 514 to aquatic organisms (e.g. Lin et al. 2014).

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43 44 45 516 ***5.2.3 Total dissolved phosphorus***

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48 517 Highest concentrations of TDP were found at E and PB (median values of 0.07 mg L^{-1} at both
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50 518 sites, $p < 0.05$). Phosphorus in urban areas is usually associated with household sources, such
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52 519 as laundry and dishwasher detergents, as well as organic matter biodegradation in domestic
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54 520 wastewater (e.g. Carey et al. 2013), but it can also derive from garden fertilizers. Apart from
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56 521 sewage leaks already discussed, pavement and car washes were often observed within PB,
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1 522 which forms an upstream part of E. In PB, high concentrations of TDP could possibly also
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3 523 be associated with the clay content of the limestone soils. Tus, in Xujiawan catchment,
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5 524 Southwest China, phosphorus enters the runoff and open water bodies mainly through
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8 525 transport in the clay and fine silt fractions (Yang et al. 2009).
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11 526 Although TDP concentrations never exceeded the Portuguese water quality standard (1 mg
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14 527 L⁻¹), all sites recorded concentrations above the 0.1 mg L⁻¹ established as the critical
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16 528 phosphorus level in runoff for eutrophication (US EPA 1986). This critical level was
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19 529 surpassed in 32% of the samples collected in PB, 21% in E, 7% in ES but only 3% in the
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21 530 least urbanized Q sub-catchment which is 73% woodland (maximum concentrations of 0.25
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24 531 mg L⁻¹, 0.39 mg L⁻¹, 0.17 mg L⁻¹ and 0.14 mg L⁻¹, respectively).
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30 31 533 **5.2.4 Heavy metals**

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34 534 Although draining the smallest urban cover, Q displayed higher median concentrations of Cu
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36 535 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
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39 536 ¹ and 0.14 mg L⁻¹, respectively). Heavy metals are typically associated with vehicular traffic
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41 537 and road runoff in urban situations (e.g. Crabtree et al. 2006; Herrera 2007). In Ribeira dos
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43
44 538 Covões catchment, a complementary study of heavy metals in runoff collected from four
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47 539 roads provided direct evidence of the capacity of road runoff to generate heavy metal
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49 540 pollution in the catchment (Ferreira et al. *in press* b). Although heavy metal concentrations
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51 541 varied through time, they displayed a direct relationship with vehicular traffic intensity, with
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54 542 dissolved Cu and Zn recording maxima of 0.2 mg L⁻¹ and 0.5 mg L⁻¹, respectively.
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56 543 Nevertheless, heavy metals in road runoff were mostly in particulate form, as total
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59 544 concentrations of Cu and Zn reached 0.7 mg L⁻¹ and 5.0 mg L⁻¹, respectively.
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1 545 The higher concentrations recorded at Q probably result from road runoff from the enterprise
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3 546 park area being piped directly to the detention basin and diverted into the stream network,
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6 547 i.e. high connectivity between source and stream network. In PB, road runoff, particularly
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8 548 from the major national road, is in part piped to fields adjacent to the stream. Higher moisture
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10 549 content in soils receiving road runoff (as in prolonged wet weather) may favour connectivity
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13 550 with the stream network, and been responsible for the occasional pollutant concentrations
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15 551 that were recorded (maximum Zn of 0.59 mg L⁻¹ and Cu of 0.10 mg L⁻¹) (Fig. 3).
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19 552 ES, despite draining the largest impervious cover (27%), recorded lower Zn and Cu
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21 553 concentrations (Fig. 3), possibly because road runoff is diverted into pervious soils, located
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24 554 at a greater distance from the stream network than at PB. These contrasts highlight the
25
26 555 importance of variations in stormwater drainage system characteristics in controlling urban
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29 556 runoff quantity and quality, rather than simply % urbanization, as found also to be the case
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31 557 in Tucson, Arizona (Gallo et al. 2013).
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38 559 *5.2.5 Major cations and pH*

41 560 Although not included in Portuguese water quality standards, major cation concentrations
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43
44 561 (Na, Ca and Mg), do not constitute a water quality problem. These solutes are usually
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46 562 associated with rock composition, explaining the significant positive correlations with
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48
49 563 baseflow ($p < 0.05$). In Ribeira dos Covões, Ca and Mg concentrations (Fig. 3) were in
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51 564 accordance with those found in streamwater of forest catchments at Colorado, overlaying
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54 565 sedimentary rocks including, among others, sandstone and limestone. In these Colorado
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56 566 catchments, Miller (2002) reported Ca, Mg and Na concentrations ranging from 41 mg L⁻¹ to
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59 567 101 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
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1 568 concentrations of Na, Ca and Mg recorded in PB, despite its limestone lithology, may be
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3 569 associated with its lower baseflow fraction (Table 4). Higher Na concentrations than those
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6 570 reported by Miller (2002) may be linked to higher evapotranspiration. The limestone
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8 571 lithology of PB may explain its highest pH (median of 7.6, $p < 0.05$).
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15 573 **5.3 Temporal dynamics in water quality parameters**

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19 574 Streamwater quality varied considerably seasonally and within storm events. Several factors
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21 575 of the hydrological regime can affect temporal dynamics including storm and antecedent
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23 576 rainfall characteristics, stream discharge, the proportions of baseflow and storm runoff, and
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26 577 flow connectivity between source areas and the stream (e.g. Yang et al. 2009; Zhao et al.
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28 578 2015).
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32 579 COD, nutrients (Nk-N, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and TDP) and heavy metals (Zn and Cu) displayed
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34 580 higher median concentrations in storms recorded in late summer than in the wet season
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37 581 (Figures 2 and 3), possibly due to two mechanisms: (i) pollutant accumulation and
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39 582 subsequent flushing during the first rainfall events after long dry periods, although no
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42 583 statistically significant correlations with antecedent rainfall were identified ($p > 0.05$); and (ii)
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44 584 decreased dilution effect provided by (a) lower summer baseflow component, which is
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47 585 typically associated with better water quality than surface water (e.g. Carey et al. 2013); and
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49 586 (b) lower storm runoff volume.
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52 587 During dry conditions solutes precipitate and accumulate within catchment and sub-
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55 588 catchment soils due to water table drawdown and reduced soil water content, leading to
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57 589 restrictions on biogeochemical activity. Accumulated solutes are than available for
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1 590 mobilization during rainfall and subsequent runoff (Vidon et al. 2009; Gallo et al. 2013). The
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3 591 flushing process recorded in late summer led to higher $\text{NH}_4\text{-N}$ and Nk-N during the rising
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5 592 limb of the hydrograph in E, PB and Q (Fig. 4), exceeding on a few occasions the water
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7 593 quality standards. Higher $\text{NO}_3\text{-N}$ concentrations in late summer than wet season storms may
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9 594 be also a consequence of their greater availability with crop and garden fertilizer application
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11 595 in spring and early summer, in association with Portuguese Mediterranean climatic setting.
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13 596 The first flush effect after extended dry periods have been also reported in urban settings by
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15 597 previous authors (e.g. Barco et al. 2008).
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21 598 Phosphorus and heavy metals (Zn and Cu), however, seem to be less easily mobilized than
22
23 599 $\text{NH}_4\text{-N}$ and Nk-N , as peak concentrations were reached after peak flows (Fig. 4). Peak
24
25 600 concentrations of Zn, in a few cases exceeded water quality standards in PB and E (maxima
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27 601 of 0.59 mg L^{-1} and 0.55 mg L^{-1} , respectively). The later timing of peak concentrations of
28
29 602 TDP, Zn and Cu can be possibly associated with soil absorption capacity and the difficulty
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31 603 to be detached/dissolved and transported by overland flow, as noted by Yang et al. (2009).
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33 604 The delayed peak in Zn and and Cu also suggests that soil sources adjacent to roads and
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35 605 development of connectivity between roads, soil and the stream network are of greater
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37 606 significance than simply quick runoff from the roads.
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44 607 In PB, overland flow from paved surfaces seems to be the major runoff and pollutant source,
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46 608 explaining quicker runoff and solute responses than at the other monitoring sites (Fig. 4).
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48 609 Although in Q there is also partial piping of overland flow from paved surfaces, solute
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50 610 transport may have been delayed by the detention basin.
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55 611 The overall higher COD and nutrient concentrations in late summer storms are also thought
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57 612 to be a consequence of lower dilution by reduced summer baseflows (Table 4), as recorded
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1 613 elsewhere by Wilbers et al. (2014). This is supported by the negative correlations found
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3 614 between all nutrient concentrations and baseflow ($p < 0.05$), at most of the sites. In E, however,
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5 615 peak concentrations of $\text{NH}_4\text{-N}$ and Nk-N were measured under baseflow conditions, before
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8 616 rainfall start, and recession limb, with few samples exceeding water quality standards. This
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10 617 highlights a combination of possible contamination from baseflow and potential dilution by
11
12 618 cleaner stormflow. This dilution effect provided by stormflow is also noticeable in $\text{NH}_4\text{-N}$
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14 619 and Nk-N responses, that show decreasing concentrations with increasing runoff volume
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18 620 (Fig. 4).

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21 621 In ES, however, increasing runoff volume during storms observed in late summer does not
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23 622 seem to have an important diluting influence on nutrient concentrations, as $\text{NH}_4\text{-N}$, Nk-N
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25 623 and TDP concentrations increased with discharge and attained highest values at peak flow.
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27 624 These distinct solute responses compared with those at other monitored sites may be linked
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29 625 to the greatest storm runoff coefficients of ES (Table 4). Stormflow, however, only showed
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31 626 a statistically significant positive correlation with $\text{NH}_4\text{-N}$ concentration ($p < 0.05$).

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37 627 At E and ES, higher concentrations of Nk-N and $\text{NH}_4\text{-N}$ were recorded on the recession limb
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39 628 than at the beginning of late summer storms. In E and PB in the summer storms (Fig. 4) and
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41 629 in E and Q in the winter storm (Fig. 5) Zn concentration showed marked peaks both on the
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43 630 rising limb and the recession limb. This may indicate that lateral movement of Zn (and Cu,
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45 631 which behaved similarly), Nk-N and $\text{NH}_4\text{-N}$ in soil by slower throughflow may be providing
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47 632 the delayed second peak, whereas the smaller initial peak derives from flushing by overland
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50 633 flow and road runoff.

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55 634 Over the course of the wet season, repeated storm events appear to have led to progressive
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57 635 exhaustion of COD, nutrient and heavy metal sources, evidenced by much lower
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1 636 concentrations in late winter than in summer storms (Figures 2 and 3), as reported in other
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3 637 catchments with a Mediterranean climate (e.g. Bowes et al. 2009; Siwek et al. 2012).

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7 638 During winter storms, Nk-N, NH₄-N and TDP exhibited similar responses to those
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9 639 experienced in late-summer storms, namely increased concentrations during the rising limb,
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11 640 lower values at peak flow and increasing concentrations over the falling limb of the
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14 641 hydrograph. In PB, concentrations of NH₄-N, Nk-N, Zn and Cu during the falling limb were
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16 642 usually lower than at the beginning of storm runoff.

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20 643 High concentrations of nutrients (Nk-N, NH₄-N, NO₃-N and TDP) and heavy metals (Zn and
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22 644 Cu) during winter storms may be a result of greater flow connectivity between solute sources
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25 645 and the stream network (rather than just the arrival of slower throughflow, as suggested
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27 646 earlier). Thus, in E Zn exceeded pollution levels more frequently in winter than in late-
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30 647 summer storms. In Q, Zn concentrations only exceeded water quality standards in winter
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32 648 storms (Fig. 3). The increased flow connectivity resulted from increasing soil moisture over
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35 649 the wet season in the catchment leading to decreasing infiltration and surface water retention
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37 650 capacity (Ferreira et al. 2015), thus favouring runoff and solute transfer into downslope areas.

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41 651 In ES, highest NH₄-N, Nk-N and Cu concentrations measured during the falling limb of
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43 652 winter storms (sometimes exceeding water quality standards) (Fig. 5), may be provided by
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45 653 upslope urban areas lacking a storm drainage system. In E and Q, higher NH₄-N and Nk-N
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48 654 also reached pollutant concentrations in the falling limbs of a few winter storms (Fig. 2) and
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50 655 pollutant concentrations of Zn were reached in Q only during winter storms (Fig. 3). The
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53 656 increased concentrations of these nitrogen forms and heavy metals in Q over the wet season,
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55 657 may partly result from possible leaching of soils polluted by the abandoned WWTP.

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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 $\text{NO}_3\text{-N}$ 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

1 682 parameter affecting water quality. Thus, in E and Q, higher Nk-N and NH₄-N concentrations
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3 683 are thought to result from cattle-rearing in agricultural fields adjacent to their stream
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6 684 networks.

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9 685 Generally, median concentrations of COD, nutrient parameters and heavy metals were
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11 686 greater in late summer than winter storms. This pattern was attributed to (i) the accumulation
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14 687 of pollutant sources in surface soil and on roads during prolonged dry periods and subsequent
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16 688 flushing during the first rainfall and runoff events, and (ii) the lower dilution effect provided
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19 689 by low summer baseflow. These mechanisms led to concentrations of Nk-N and NH₄-N
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21 690 exceeding pollution thresholds in some samples at all the monitored sites, mostly in the rising
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24 691 limb of the hydrograph in late summer storm events.

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27 692 Storm events over the wet season, however, led to increasing soil moisture that enhanced the
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30 693 connectivity between pollutant sources, runoff processes and the stream network. Greater
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32 694 wet-season connectivity may explain pollutant levels of Zn attained in PB and Q, mostly
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35 695 during the falling limb of the hydrograph, as well as pollutant concentrations of Cu in ES and
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37 696 E.

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41 697 Intra- and inter-storm variations over the study period demonstrate that solute (including
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43 698 pollutant) transport in an urban Mediterranean environment may not be effectively predicted
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46 699 using simple relationships with hydrological conditions or rainfall. This study has
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48 700 demonstrated that a larger storm event dataset, covering all seasons and a range of storm sizes
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51 701 and antecedent weather, is needed to understand the impact of different urban patterns, and
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53 702 complex land-use mosaics in peri-urban areas, on hydrochemical response of the catchment
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55 703 and its sub-catchments to storm events. This study, however, covered only selected pollutant
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58 704 and solute parameters; in particular, additional monitoring of dissolved oxygen and microbial
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1 705 contamination parameters should be added to give a fuller picture of the impact of urban
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3 706 activities.

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7 707 Understanding the impact of urbanization pattern and storm drainage systems on
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9 708 hydrochemical dynamics is both relevant and crucial to help policymakers design and
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11 709 implement the most appropriate solutions to achieve good water quality and preserve aquatic
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13 710 ecosystems. Pollution control policies should include urban planning and be adjusted to fit
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15 711 changes over space and time, focusing on (1) pollutant flushing in late-summer storms and
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17 712 (2) increasing flow connectivity through the wet season. Upslope urban cores and dispersed
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19 713 urban patterns should favour runoff dispersion in downslope pervious soils. This will favour
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21 714 not only overland flow retention and infiltration but also prevent pollutants from reaching the
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23 715 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
<i>Impervious</i>	17	15	27	5
<i>Semi-pervious</i>	11	9	7	10
<i>Pervious</i>	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 (I_{mean}: mean intensity, I₆₀: maximum hourly rainfall intensity, API₇: 7-day antecedent rainfall, and AP₁₄: 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-catchments (E: Espírito Santo and Q: Quinta).

Storm	Peak discharge (L s ⁻¹)				Mean discharge (L s ⁻¹)				Baseflow fraction (%)				Storm runoff coefficient (%)			
	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

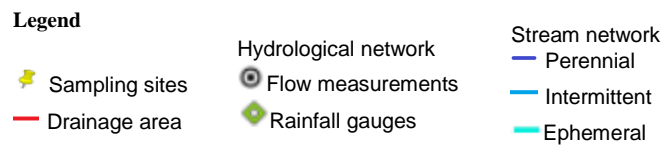
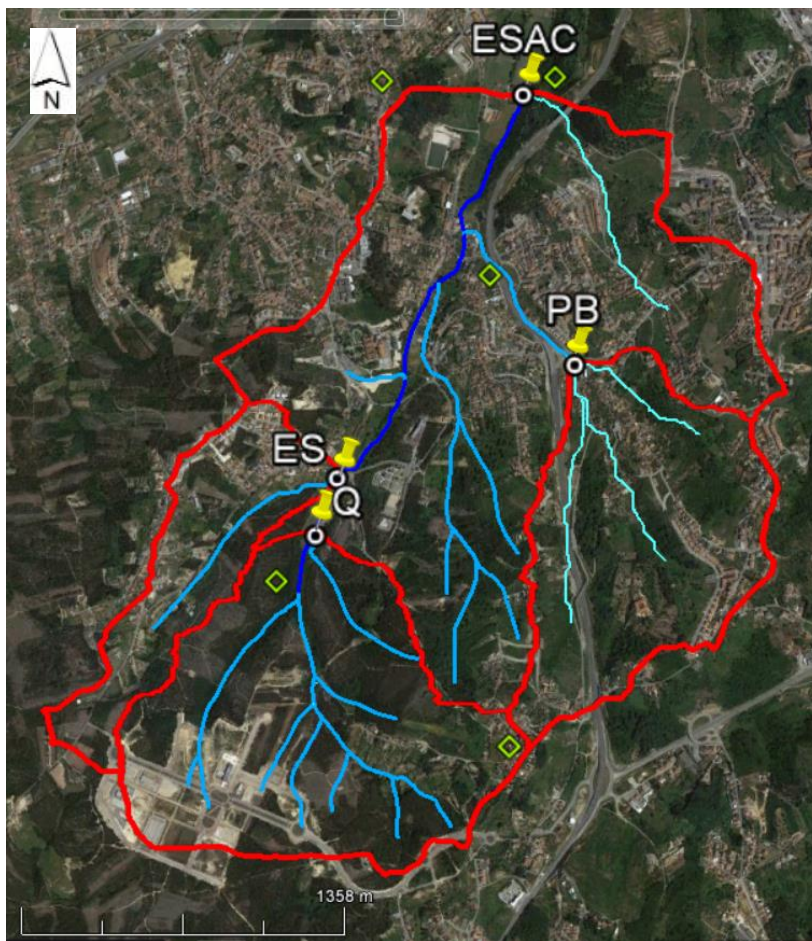


Figure 1 - Ribeira dos Covões catchment and location of the sampling sites – E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and Q: Quinta (adapted from Google Earth, 2014).

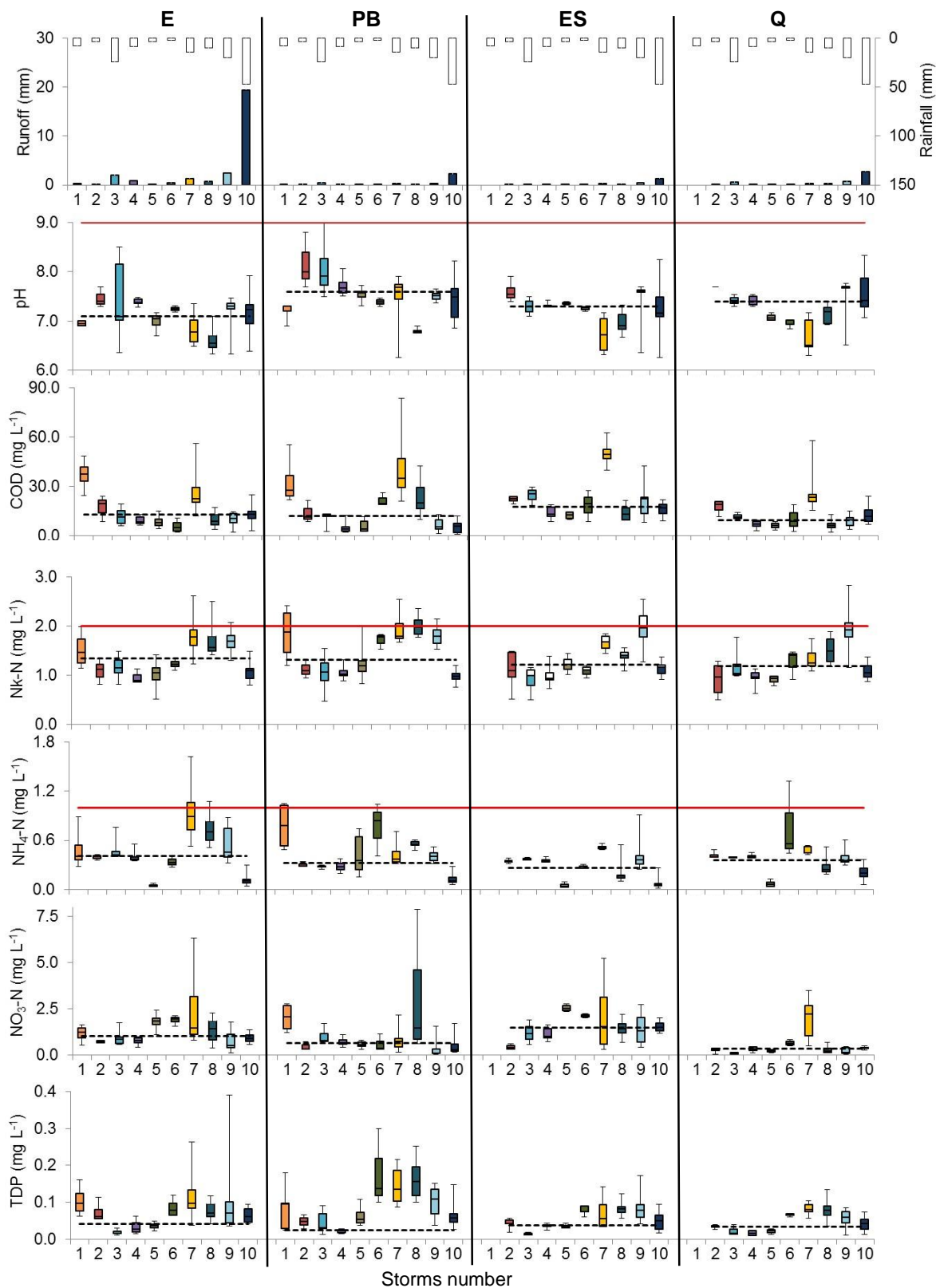


Figure 2 - Rainfall and runoff and box plots (median, upper (75) and lower (25) quartiles, maximum and minimum) showing pH, COD, N_K, NH₄-N, NO₃-N and TDP concentrations at ESAC (E), Porto Bordalo (PB), Espírito Santo (ES) and Quinta (Q) for the ten storms monitored between October 2011 and March 2013. 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.

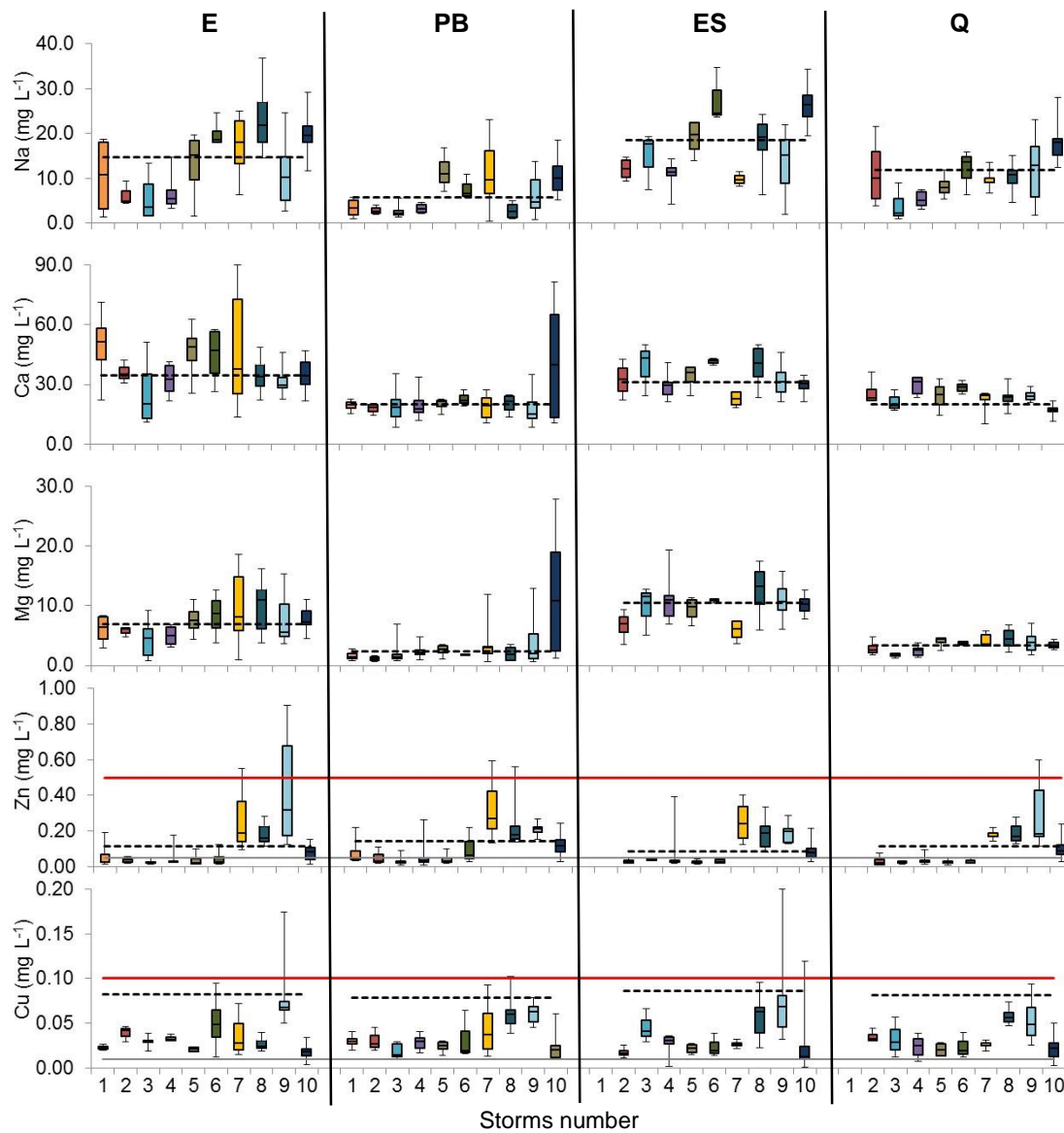


Figure 3 - Box plots (median, upper (75) and lower (25) quartiles, maximum and minimum) showing major cations (Na, Ca and Mg) and heavy metals (Zn and Cu) concentrations at ESAC (E), Porto Bordalo (PB), Espírito Santo (ES) and Quinta (Q) for the ten storms monitored between October 2011 and March 2013. 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.

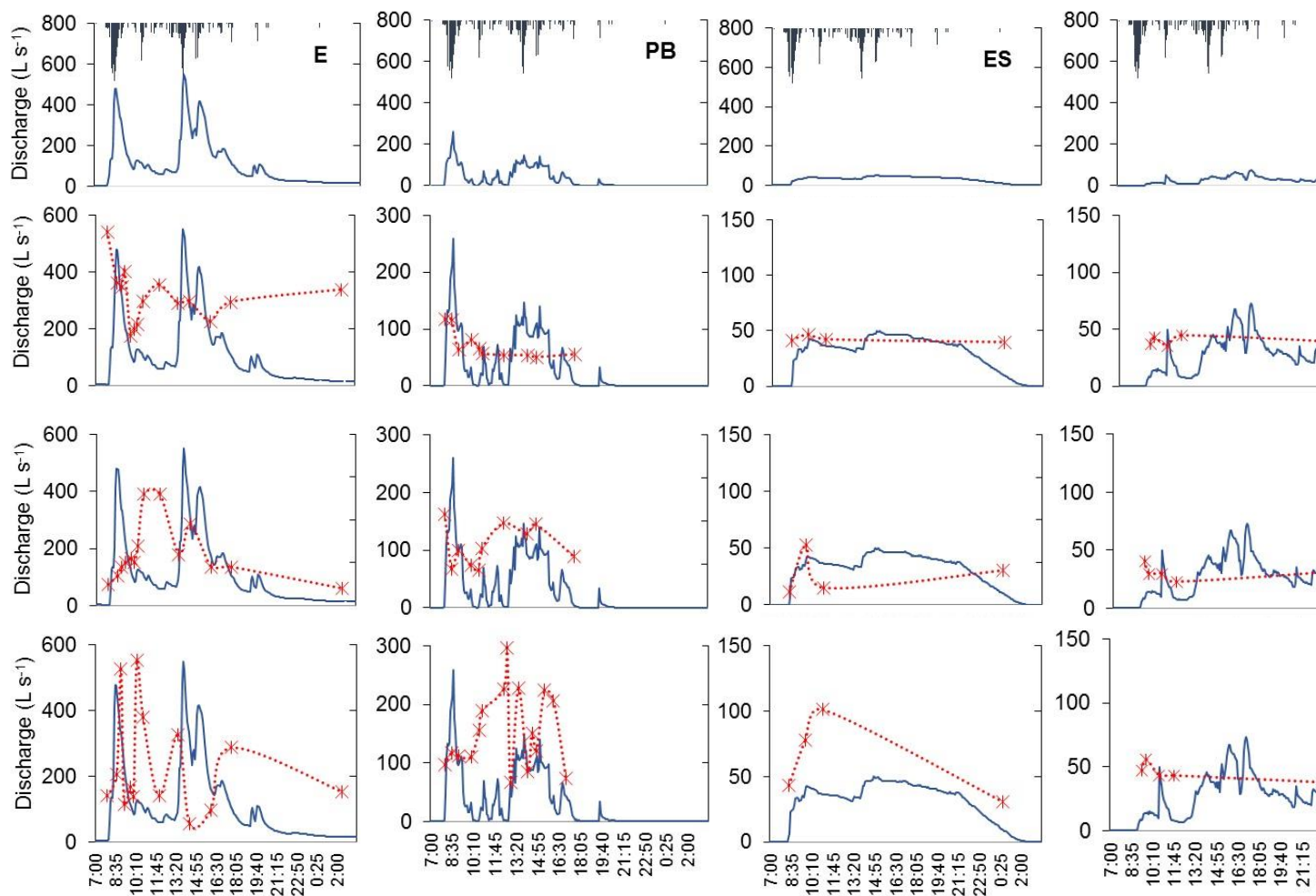


Figure 4 – Ammonium nitrogen ($\text{NH}_4\text{-N}$), total dissolved phosphorus (TDP) and zinc (Zn) responses (red lines) 2012 rainstorm event (storm 7) at the four catchment sites (E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and and discharge).

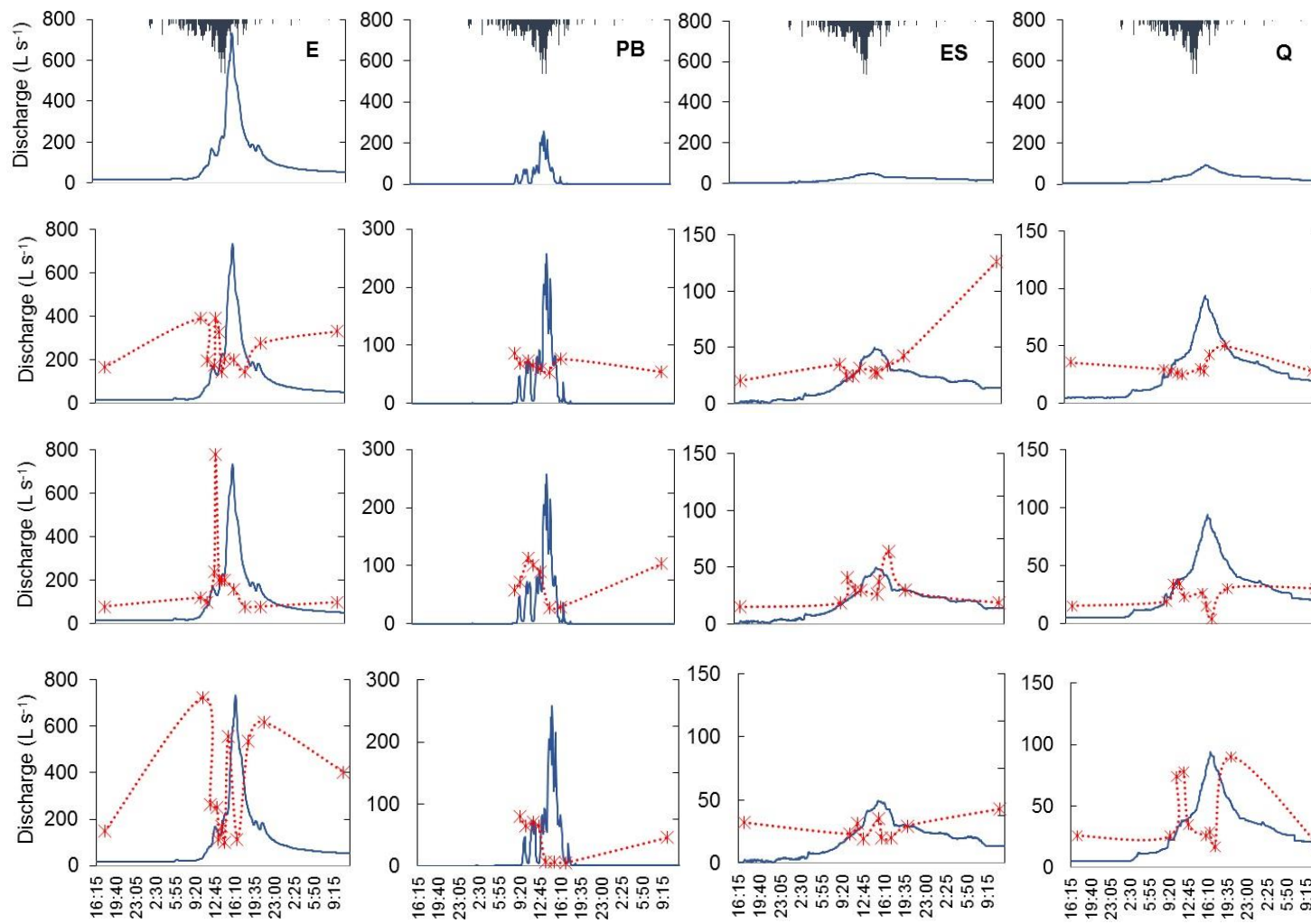


Figure 5 - Ammonium nitrogen ($\text{NH}_4\text{-N}$), total dissolved phosphorus (TDP) and zinc (Zn) responses (red lines) to a rainstorm event (storm 9) at the four catchment sites (E: ESAC, PB: Porto Bordalo, ES: Espírito Santo and Q: Q: discharge).