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Hydro-climatological non-stationarity shifts patterns of nutrient delivery to an estuarine system

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Abstract

The influence of hydro-climatological variability on catchment nutrient export was assessed by a retrospective analysis of rainfall, discharge, and total and dissolved nutrient loads for three sub-basins (Serpentine, Murray and Harvey) of the Peel–Harvey catchment, Western Australia. Both, temporal trends and their variability for different hydrological conditions (dry, normal or wet years) were analyzed from 1984 to 2011. Rainfall declined below median values for the study period over the last two decades and runoff decreased significantly in two of the three main rivers. Since Nitrogen (N) and Phosphorus (P) loads were strongly correlated with river discharge, nutrient exports decreased. However, when nutrient loads were flow-adjusted, increases in Total P (TP) and Total N (TN) were observed in the Serpentine and Murray rivers respectively, suggesting new sources of TP and TN and that the flow–export relationship is non-stationary. Dissolved Inorganic Phosphorus (DIP), showed a decreasing tendency in the last decade; but the trend in DIN loads is not clear and it appears to show a decreasing trend until 2004 and an increasing trend from 2004, accompanied with large inter-annual variability. The analysis of TP, TN, DIP and DIN in relation to dry and wet years, indicated that there is a significantly higher load in wet years for all three rivers, except for DIP in the Murray sub-catchment, explained by a higher proportion of soils with a higher Phosphorus Retention Index (PRI). Hydrological conditions, specific sub-catchment characteristics (e.g. soil type) and chemical properties of the nutrients altered the degree of nutrient partitioning (defined as dissolved inorganic to total nutrient concentration). For example, DIP increased to more than 50 % of TP in wet years in Harvey and Serpentine but not in the Murray sub-catchment due to a higher PRI, while DIN behaved more randomly and did not show a link to discharge or the catchment soil type. We also found a mild association between nutrient partitioning and the rate of population growth which indicates that rapid change in population growth is accompanied by an increase in nutrient dissolved species. Changes in hydrological conditions between seasons did result in changes in the TN : TP and DIN : DIP ratio, but on an

annual scale these ratios were not sensitive to whether a year was classified as wet or dry. The findings indicate that the quantity and nature of nutrient export varies in response to climate variability, which is superimposed on effects from changing land-use characteristics.

1 Introduction

Disentangling nutrient pathways within river basins and determining the relationship between nutrient export and the quality of receiving waters (e.g. lakes, rivers and estuaries) remains a central issue for management and research agencies around the world (Bartley and Speirs, 2010). Whilst internal processing of nutrients within water bodies can shape water quality trends, it is widely accepted that external loading, especially of Nitrogen (N) and Phosphorus (P), from the surrounding basin is the key determinant that links catchment condition with the quality of the aquatic ecosystem. The problem of non-point source nutrient contributions is a major focus of research efforts and there is an ongoing need to understand the factors that control rates of nutrient export (Chambers et al., 2012; Lewis et al., 2011; Smith et al., 2003; Carpenter et al., 1998; Valiela, 1992).

In general terms, catchment nutrient dynamics are affected by: (i) hydrological processes, such as climate-driven rainfall-runoff processes, (ii) the physical characteristics of the basin, including geomorphological factors, soil types, and vegetation, and (iii) anthropogenic influences related to land development that create altered hydrological regimes and modified nutrient budgets. In relation to hydrological processes, the linear association of runoff and nutrient export has been demonstrated from local (e.g. Robson et al., 2008) to continental scales (Alexander et al., 1996; Lewis et al., 1999, 2002). In relation to the catchment characteristics, Smith et al. (2005) studied the effect of catchment size on the export of dissolved nutrient loads (Dissolved Inorganic Nitrogen – DIN – and Dissolved Inorganic Phosphorus – DIP), and found a more variable response of nutrient fluxes in small catchments than intermediate sized ones, and soils and vegetation distribution have been found to be important by Kosten et al. (2009). In relation to human induced changes, numerous studies have demonstrated how the degree of human influence manifests in nutrient export, both in terms of the degree of land-use change and population expansion (for example: Peierls et al., 1991; Caraco, 1995; Smith et al., 2005; Howarth et al., 1996; Howarth, 1998; Caraco and Cole, 1999; Dowining et al., 1999; Harris, 2001; Bennett et al., 2001).

Whilst these factors are clearly important, the effect of climate is not as clearly understood. Climate is the key driver of hydrological processes and consequently climate change has the potential to significantly alter nutrient export via shifts in temperature and rainfall (Meyer et al., 1999; Marshall and Randhir, 2008). Several studies of different catchments across a range of latitudes have demonstrated that climate differences can affect nutrient dynamics. For example, in Nordic catchments, Bouraou et al. (2004) observed an increase in N and P losses because of the increase in winter runoff under a warming climate. In Europe, Zweimüller et al. (2008) indicated that changes in temperature and discharge will shift the seasonal pattern of nitrate export within the Danube River and that the dependence of nitrate concentration on temperature was altered by river discharge. In New Zealand, Caruso (2001) evaluated 12 different catchments and concluded that the effects of drought on river ecosystems were "river specific".

Hydrological responses to changes in climate vary regionally and small changes in temperature and precipitation can be amplified into significant changes in runoff. In mid-latitude regions specifically, water resources are especially sensitive to climate shifts, and climatic models for this region predict an increase in drought frequency and a decrease in streamflow (Milly et al., 2005; Bates et al., 2008). It remains unclear though what affect this will have on net nutrient export, and whether existing flow–export relationships remain stable. A persistent reduction in rainfall can alter the balance of surface and groundwater contribution to river flows and potentially also the timing and variability of flow regimes (Kingsford, 2011). This may further alter hyporheic zone processes, and the ability of river systems to transport, retain and transform nu-

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trients originating from upslope regions (Seitzinger et al., 2002), in addition to other water quality attributes such as suspended sediment (Marshall and Randhir, 2008). Superimposed on this, changes in temperature will not only affect the water balance but also affect rates of nutrient transformation. For example an increase in temperature can strongly increase nitrification rates (Kosten et al., 2009), and in stream nitrogen attenuation (Donner et al., 2004). Therefore, shifts in climate may not only influence rates of export, but also potentially impact on the ratio of the total to dissolved nutrient load (nutrient "partitioning"), as well as the stoichiometry of nutrient loads (N : P).

In this study we take advantage of a long term (28 yr) hydrological and water quality dataset for the Peel–Harvey catchment system in south-west of Western Australia (SWWA) to investigate the impacts of different hydrological conditions, categorised as dry, normal and wet, on nutrient export. The Peel–Harvey has been the focus of significant research and management efforts since the 1970s to combat excessive nutrient export loads and eutrophication pressures brought about by rapid land-use development (Hornberger and Spear, 1980; Potter et al., 1983; Hodgkin and Birch, 1986). Since the implementation of a management plan in the 1990s, the primary goal has been to reduce nutrients, particularly P, transported to the estuary via its tributaries (Summers et al., 1999). Whilst some trend analysis has been conducted (WRC, 2000; EPA, 2008; Kelsey et al., 2011) to assess the effectiveness of management actions in the catchment, the relationship between climate variability, land use changes and nutrient export is not understood. This is particularly important, since climate models for SWWA predict that the 15 % decline in rainfall that has been observed to date since 1975 (Petrone et al., 2010), will decline by up to by 20–30 % (from the 1975 average) by 2030 (Hick, 2006). This would have a dramatic impact on runoff, with an estimated 64 % reduction in annual flow (Hick, 2006; Bates et al., 2008), and the resulting pattern of nutrient export and ecological function of the associated aquatic ecosystems could be severely impacted by such a shift.

Specifically, this paper conducts an analysis of catchment nutrient export of the three Peel–Harvey sub-catchment monitoring datasets to determine trends in Total Nitro-

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gen (TN), Total Phosphorus (TP), Dissolved Inorganic Nitrogen (DIN), and Dissolved Inorganic Phosphorus (DIP) export, in addition to the nutrient partitioning and stoichiometry. We subsequently attempt to determine to what extent this change can be explained by the reduction in flows over the past decade and/or by changes in land use in the context of increasing development pressure within the catchment and nutrient management practices.

The second objective is to identify the dynamics of the nutrient loads and their interrelationship in the context of wet and dry years. We test the hypothesis that dry years significantly differ from wet years in terms of nutrient export, nutrient partitioning processes and nutrient stoichiometry in the catchment, and seek to explain the reasons behind these differences.

The findings demonstrate how variability and non-stationarity in climate can affect loads to receiving water systems, and help us understand how future changes in climate may impact on water quality of river systems, particularly relevant to Mediterranean and semi-arid regions.

2 Materials and methods

2.1 Study area

The coastal catchment of the Peel–Harvey Estuary is located approximately 75 km south of Perth and is drained by three major river systems: the Serpentine, Murray and Harvey Rivers, with some minor drains also discharging directly to the estuary (Fig. 1, Table 1). The cumulative area of the catchment is approximately 11 930 km^2 (Kelsey et al., 2011) and it experiences a Mediterranean climate characterized by hot dry summers and mild wet winters. Rainfall predominantly falls between May and October with a long-term average annual rainfall range of 700–800 mm along the coastal zone (WRC, 2000), with less falling in the eastern most parts of the catchment. Approximately 95 % of runoff from the total catchment area enters the estuary via the three

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rivers during the main rainfall period: May–October. Most streams experience little or no flow between December through to April, and most flow in this period is comprised from groundwater input.

The catchment can be divided into three broad regions: the coastal plain, the forested region, and the broad-acre agricultural region, with the latter two regions situated on the Darling Scarp or further inland. The land use on the coastal plain is mainly rainfed and irrigated agriculture, urban and peri-urban developments, and small areas of mining (Kelsey et al., 2011). A large proportion of the soils of the coastal plain are deep infertile sands that are naturally deficient in P and have a low P retention index (PRI). They vary greatly in character, with fourteen different soil associations being identified, but the dominant soil categories recognized with respect to their varied ability to retain or release P are: loams and clays, deep grey sands, sands over clays (duplex soils) and brown and yellow sands (Weaving, 1999; Hodgkin et al., 1985).

2.2 Data sources and treatment

The study considers hydro-climatological data including flow and rainfall from the three major rivers, and water quality data including dissolved and total nutrient concentrations. Rainfall data was obtained from the Western Australia Department of Water (DoW) and the Australian Bureau of Meteorology (BoM) from meteorological stations within close proximity to the river gauging stations and were selected based on the completeness of the data series over the period of interest. The rainfall stations chosen were Serpentine Dog Hill (DoW 509295), Pinjarra (BoM 009596) and Waroona (BoM 009614).

Mean daily discharges from the three rivers were obtained from DoW. For the Serpentine and Harvey Rivers, flow records date back to 1979 and 1982 respectively at the gauging stations of Dog Hill (AWRC Reference 614030) and Clifton Park (613052), also respectively. However for the Murray River at the Pinjarra gauging station (614065), river flow data only commenced in 1994. Therefore, in order to estimate the flows for the missing time period (1984–1993), non-linear correlation between flows of the upstream

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gauging station, Baden Powell (614006), and Pinjarra was used (for the existing flow data set 1994–1996). The correlation of 4531 values for the period 1994–2006 showed an $R^2 = 0.9802$ for flow rates and $R^2 = 0.9795$ for daily total discharges. For the regression, values below 0.1 $m^3 s^{-1}$ at Pinjarra, as well as those values identified as poor quality, were discarded. Values below 0.1 $m^3 s^{-1}$ were eliminated because they were likely to be affected by the weir at the gauging station, which holds back the lower flows and by the large number of householders and small property owners who extract water from the weir pool. To validate the 1984–1993 regression model the observed data for Baden Powell for the 2007–2010 period was used to estimate the flow/discharge data for Pinjarra. The model predicted well when compared to the actual data for Pinjarra 2007–2010.

Water quality has been monitored by DoW at these same gauging stations with variable frequency over the study period. Water quality parameters considered in this study were: TP, TN, DIN (= $N\text{-}NH_4^+ + N\text{-}NO_3^- + N\text{-}NO_2^-$ or = TN – TON, where TON is Total Organic Nitrogen), and DIP, which corresponds to Filterable Reactive P or Soluble Reactive Phosphorus (SRP, also reported as $P\text{-}PO_4^{3-}$). When values for TN were absent, they were calculated as the sum of Kjedalhl Nitrogen (TKN) and $N\text{-}NO_3^-$ and $N\text{-}NO_2^-$ ($TN = TKN + NO_x$); for example, such an estimation was used for Murray River station 614065 between 1996 and 1997. Only grab and surface (0 to 0.5 m) samples were considered. Monitoring commenced in 1983 (WRC, 2000), however, the sampling frequency has changed over time from two samples per season to approximately monthly in the summer months and fortnightly in the winter months. Prior to 1995 samples for TP and TN were analysed at the Chemistry Centre Western Australia (CCWA). However, the majority of the samples collected after 1995 were analyzed by a segmented flow analyzer at the National Measurement Institute (WA) (DoW, personal communication, 2010). Water quality data reported as "below the detection limit" (< DL; censored data) make it difficult to compute simple statistics, but a common approach in these cases is to set censored values as half of the reported DL (Gilbert, 1987). Note that these filled values were not considered as estimates for specific samples, but only used

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collectively with the data above the detection limit to compute statistics, as described below. Values reported as $< 0.4\,\mathrm{mg\,L^{-1}}$ for TP were not used, as they were considered faulty due to the colorimetric method being only applicable for concentration ranges between 0.5–0.010 $\mathrm{mg\,L^{-1}}$ (Wetzel and Likens, 2000; APHA, 1998; Murphy and Riley, 1962). Similarly, one outlier TP value of 18 $\mathrm{mg\,L^{-1}}$ was not used, as it was well above the overall TP average (average ± standard deviation: $0.224 \pm 0.885\,\mathrm{mg\,L^{-1}}$). Values of TP reported to be below the respective SRP value at a particular location and time, were also considered mistaken and were assumed to be a recording error and discarded (e.g. TP value for 19 June 1996 at Dog Hill).

2.3 Data analysis approach

2.3.1 Hydro-climatological analysis and classification of wet and dry years

A period of 28 yr (1984–2011) of daily and monthly data was available for this study. This study focused on annual rainfall and runoff, calculated as the sum over the calendar year of daily rainfall and total daily discharge, respectively, but a monthly analysis was also done to search for changes in seasonality.

To assess the effect of hydro-climatological variability on nutrient delivery, years were classified as wet, normal and dry. Unlike other studies that base the classification on rainfall, this classification was based on annual discharge because the aim of this study is to assess the effect of discharge variability on nutrient loads. Annual discharge data shows a normal distribution, therefore data were standardized according to the average flow, $\overline{Q}$, and standard deviation (SD):

$$Q_{si} = \frac{Q_i - \overline{Q}}{\mathrm{SD}} \quad (1)$$

where, Q_{si} is standardized annual discharge for the i-th year, Q_i is annual discharge and SD is the standard deviation of annual discharges. The categorization of the years

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as dry, normal (denoted as "nor" below) and wet conditions was based on: dry for $Q_{si} \leq (-1)$, wet for $Q_{si} \geq 1$ and normal for $-1 < Q_{si} < 1$.

2.3.2 Assessment of changes in nutrient loads

Calculation of daily nutrient loads: nutrient loads were calculated by assuming a linear interpolation between available data points, a method used previously in Western Australia (Degens and Donohue, 2002), and elsewhere (Preston et al., 1989), according to:

$$L = \sum_{i=1} [Q_i C_i] \qquad (2)$$

where, L is the annual load [t yr^{-1}], Q_i is the daily flow [m^3 d^{-1}], C_i is the daily (measured or interpolated) nutrient concentration [g m^{-3}]. A main source of error in calculating mass loads is associated with sampling frequency; precision and accuracy of mass load measurements are improved by higher sampling frequencies (Degens and Donohue, 2002; Rose, 2003). Here the data set is comprised of two types of samples, grab and composite, both with variable frequency. When both types are considered for nutrient load calculation, the sampling frequency of nutrient concentration data is high and the load calculation is less biased. However, composite samples were not taken in all years of the study period; therefore year-to-year comparisons would be biased. To evaluate the error introduced by the sampling approach, nutrient loads were calculated separately for grab samples and for grab and composite samples together. In the Serpentine River, annual loads calculated only with grab samples underestimated loads by up to between 68 % and in the Harvey River, by up to 50 %. Since the aim of this study is to compare annual loads under dry and wet hydrological conditions and because the number of grab samples collected per year in each river is less variable, only grab samples were considered for statistical assessment of changes in annual loads. Years with less than four samples per year were not considered in the analysis. Although the nutrient loads estimated using only grab samples are less accurate (underestimated),

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the comparison among years is considered to be less biased than comparing annual mass calculations that combine grab and composite samples.

Shifts in N : P *ratios*: the ratio between TN and TP was compared against the Redfield (1958) mass ratio of 7.22 N to 1 P to indicate which nutrient may be limiting or in oversupply. A ratio greatly in excess of 12 indicates P may be limiting (or N in oversupply) while a ratio of much less than 7 indicates that N may be limiting (or P in oversupply) (Overbeck, 1988; Forsberg and Ryding, 1980). The temporal variability in the total and dissolved N : P mass ratio was evaluated annually and monthly.

2.3.3 Land-use change assessment

The assessment of the impact of changes in land-use on nutrient trends is complex, and in this study we approached it in three different ways: (1) spatial assessment of change in the dominant land-use categories between 1993 and 2006; (2) evaluation of population trend of the four main shires covering the three sub-catchments, and (3) evaluation of the temporal trend in the runoff coefficient. The approach for these three are summarised below.

Spatial land-use assessment: in order to undertake the comparative analysis of land-use change in the three sub-catchments, we used available data sets, which were limited to a 1993 study, and a more recent Department of Agriculture and Food of Western Australia (DAFWA) study in 2006. The 1993 data set was sourced from a once-off investigation of land-use undertaken by DAFWA on behalf of the Peel–Harvey Catchment Support Group, and the 2006 data set was the Land Use v7 also from DAFWA. Categories of land-use that were compared included: conservation, plantation forestry, grazing, intensive agriculture, intensive urban, mining and water. Prior to undertaking the intersection of the spatial data and attributes between these two snapshots, a data cleaning processes was required to ensure compatibility.

Evaluation of resident population: national population censuses are held every five years by the Australian Bureau of Statistics (ABS) in order to estimate population numbers in-between years. Yearly residential population data since 1999 (measured and

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predicted) was obtained from the Peel Development Commission and ABS website. Before 1999, 5 yearly data was obtained from the Western Australia Planning Commission (WAPC, 2000). In addition to examining population numbers, we additionally estimated the annual rate of population change, calculated as the difference between consecutive years.

2.3.4 Statistical analysis

Non-parametric methods have high power when data is normally or non-normally distributed (Esterby, 1996; Helsel and Hirsch, 2002). The non-parametric smoothing technique LOWESS, was used to explore trends in data time-series and the Mann Kendall test was used to identify a statistically significant change. Nutrient data series contain several sources of variation: flow variation, seasonal variation, trend and random components (Hipel and McLeod, 2005). To remove the effect of flow variability, nutrient data trends were analysed after nutrient loads were flow adjusted. The relationship between annual nutrient load and annual discharge was modelled using linear regression and the difference or "residuals" between the observed and the linear modelled loads were defined as the flow-adjusted loads. The rate of change in the annual nutrient loads was determined using a Sen slope estimator. Non-parametric summary statistics were calculated for the water quality data in dry, wet and normal years. The median value was used to summarise the centre of the dataset and the interquartile range (IQR, 75th percentile minus the 25th percentile) used to represent the data spread. The significance of differences in water quality between dry and wet years was determined using the non-parametric Kruskal–Wallis test (Helsel and Hirsch, 2002). All statistical tests were performed using R software (http://CRAN.R-project.org) with the "Rcmdr", "Kendall" and "mblm" packages used to calculate algorithms for Kruskal–Wallis, Mann Kendal and Sen-slope estimators, respectively.

3 Results

3.1 Hydro-climatological data

The trend in annual rainfall for the study period was similar for all three sub-catchment stations, with the moving average decreasing below the median values (medians: Serpentine = 786 mm, Murray = 849 mm, Harvey = 906 mm). Although there are some missing data, a significant trend was detected in the Murray and Harvey sub-catchments using parametric and non-parametric statistical trend tests (Fig. 2). Similarly, the annual discharges of Serpentine and Harvey rivers show a decreasing trend ($p < 0.05$); annual discharges remained below or very close to the median value for the last 10 yr. The Serpentine flows decreased between 50–59 % and Harvey between 54–56 % respectively, based on the non-parametric and parametric estimation. The Murray discharges however did not exhibit any trend, although visually a downward trend is evident. A separate analysis of summer and winter daily discharges highlights a marked downward trend in the Serpentine and Harvey rivers and no trend for Murray.

Analysis of the annual hydrograph for three different decades showed that July has the largest absolute reduction in flow in all three rivers. The annual runoff peak has moved from July to August between 1984–2003 and 2003–2011 (Fig. 3).

3.2 Nutrients

3.2.1 Dynamics of nutrient delivery

Nutrient loads are linearly correlated with total discharge (Fig. 4). For TP, a unit of change in annual discharge (GL) leads to a 0.31 and 0.23 t yr^{-1} change for the Serpentine and Harvey Rivers respectively. In contrast, for the Murray River, a unit change in discharge led to a much smaller change in TP loads of 0.03 t yr^{-1}. The TN load relationship is different however; a unit of change in discharge brings a similar magnitude change in all three rivers (Serp = 1.89, Murr = 1.68, Harv = 2.34 t yr^{-1}). The largest absolute TP exports are from Harvey catchment, whilst the largest absolute TN exports are from the Murray catchment. Analysis of the TN : TP ratio of loads indicates that the ratio is not highly correlated with discharge (Fig. 4c). In annual terms, both nutrients are non-limiting in the Serpentine and Harvey rivers (7 < TN : TP < 12). However, potential P limitation is evident in the Murray River (18 < TN : TP < 70). For the Murray River the ratio appears to increase with discharge, although the trend was not significant. Dissolved nutrients loads (Fig. 4d–f), show higher variability in their relationship with discharge, and poorer predictability. In particular, the high spread in the DIN loads, and the DIN : DIP ratio for the Murray River showed non-linearity.

Analysis of nutrient concentration rating curves gives some insight into the dynamics of nutrient delivery in each catchment (Fig. 5). In the Serpentine River, TP and TN concentrations increase as streamflow increases from zero to approximately 10 $m^3 s^{-1}$, after which it seems that increasing flow exerts a dilution effect rather than being the source of more nutrients. In the Murray River, the trend is different with TP at low flows showing dilution of relatively high P concentrations as flow increases. In contrast, at higher flows TP concentration is driven by flow, that is, the higher the flow the higher the concentration. Again in the Murray River, TN concentrations are driven by flow but not in a clear linear relationship. In Harvey, the dependency of TN and TP on discharge is simpler, following a linear pattern, with higher concentrations corresponding to higher flows.

The N : P coupling and stoichiometry is very dynamic and, different again, in Murray River (Fig. 5g–i). Murray River predominantly exhibits P limitation, while Serpentine and Harvey show seasonal differences. During periods of high flow there is tendency towards N limitation.

3.2.2 Temporal trends of total nutrients

Temporal trends of TP and TN loads show reductions in the Serpentine and Harvey Rivers during the study period (Figs. 6a, c and 7a, c), with percentages of reduction in TN and TP shown in Table 2. A statistically significant trend was detected in Harvey

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for TP but no significant trend was detected for TP in Serpentine, or for both in the TN loads. The Murray River behaves differently, with an upward tendency from 1998 for TP and TN (Figs. 6b and 7b). Due to the high correlation of nutrient load with discharge, a reduction in discharge proportionally influences nutrient load. Therefore, to account for discharge variation over the study period, TN and TP loads were flow-adjusted. The analysis of flow-adjusted TP loads (Fig. 6d–f) indicated a significant upward trend of TP load in the Serpentine River ($p < 0.05$) but not a significant trend ($p > 0.05$) in the Murray and Harvey Rivers. Despite the lack of a significant trend in the Murray and Harvey River, there was a slight increase evident in the flow-adjusted TP loads from the 1990s. The analysis of flow-adjusted TN loads indicates an increase in TN delivery over the last 15 yr in Murray and Harvey (Fig. 7e, f).

3.2.3 N : P ratios: temporal and hydrological shifts

The TN : TP ratio does not show any trend over the study period (Fig. 8a–c). In the Serpentine and Harvey rivers, the stoichiometric relationship remains close to the Redfield ratio over time, but it is well above the Redfield ratio in Murray River. At an annual time-scale, the TN : TP ratio seems to be unaffected by dry, normal or wet hydrological conditions, however, there is seasonal variability (Fig. 8d–f), particularly in the Serpentine River. In contrast to the ratio of total nutrients which does not vary significantly with time, the DIN : DIP ratio clearly rose from 2004 (Fig. 8g–i), after a period of mild N-limiting conditions in the Serpentine and Harvey Rivers.

3.2.4 Trends in nutrient partitioning

The ratio of the dissolved fractions to the total nutrient loads (SRP : TP, DIN : TN) shows large variability, particularly in the Murray River (Fig. 9). There is a significant ($p < 0.05$, not for Murray) downward trend in DIP as percentage of TP, indicating a decrease in biologically available P. The proportion of DIP in the TP load changed in the last 20 yr, from being about 60 % of the TP to be about 30 % in the Harvey and Ser-

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pentine Rivers (Fig. 9a, c), on an annual basis. In the Murray River, DIP increased until the year 2000 with an important decrease in the last 10 yr. Conversely, over this time the % DIN shows an increase particularly in the Murray River, but also in the other two rivers (Fig. 9d–f).

3.3 Effect of hydrological condition on nutrient delivery

The analysis of water quality data for dry, normal and wet years shows that the median TP and TN loads in the Serpentine, Murray and Harvey Rivers significantly change between dry and wet years (Table 3 and Fig. 10). Total P loads in wet years are always above the target load, and median loads are more than double those in dry years. No significant ($p < 0.05$) change associated with annual hydrological conditions was observed in the TN : TP ratio, which were on average near Redfield stoichiometry in the Serpentine and Harvey Rivers, but well above Redfield ratio in the Murray River (Fig. 10h). Only in the Serpentine River the TN : TP ratio values showed more variability under wet conditions.

The loads of dissolved nutrients (DIP, DIN) also show a significant ($p < 0.05$) difference between dry and wet years with the lowest values in dry years, approximately 10 % the level of the wet years (Table 3 and Fig. 11). Large increases in DIP loads occurred in the rivers, particularly in the Serpentine and Harvey Rivers, where the median DIP load during the wet years (23.6 and 25.57 $t\,yr^{-1}$ respectively) was approximately ten times higher than in dry years (respectively 1.92 and 3.30 $t\,yr^{-1}$, $p < 0.05$). Dissolved inorganic N levels in Murray were very high compared to the other rivers, and a particularly sharp increase in the load was noticed in wet years. Therefore the Serpentine and Harvey rivers showed more sensitivity to hydrological conditions and P export. However, the Murray showed more sensitivity to hydrological conditions and N export. The ratio of the dissolved fractions (DIN/DIP) shows no significant differences when considering annual medians. However, they are different at the monthly level for Serpentine and Murray. Harvey River does not show a significant difference either in annual or monthly terms (monthly data not shown).

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Notable increases in the proportion of DIP compared with TP (i.e. DIP : TP) occurred during the wet years (Fig. 12a–c), particularly in the Serpentine and when using the monthly averages in Harvey. The proportion of DIP during wet years (∼ 60 %) was approximately twice as much as for dry years (∼ 35 % $p < 0.05$). This trend is not evident in the Murray River data. As with the total loads highlighted above, the different behavior between Murray and the other rivers is also evident in the DIN : TN fraction (Fig. 12d–f) with Murray responding greatly to high flows (based on one high flow year data), with ratio reaching 0.9.

3.4 Land-use change assessment: 1993 to 2006

Over the three sub-catchments, around 10 to 15 % of land (expressed as a proportion of total sub-catchment area) experienced some form of land use change (Figs. 13–16): Serpentine 10.2 %; Murray 14.8 %; Harvey 14.5 %).

In the Serpentine sub-catchment the majority of land use change between census years was experienced in the following categories: (a) over a quarter reduction in the area under conservation, (b) a six-fold decrease in grazing, (c) an 80-fold increase in urbanisation, and (d) over a 100-fold increase in mining. Plantation forestry appeared as a new land use. Agriculture and water land uses remained much the same.

In the Murray sub-catchment the majority of land use change between census years was experienced in the following categories: (a) a 17-fold decrease in areas under grazing, (b) a three-and-a-half-fold decrease in agriculture, (c) a five-fold increase in the area under conservation, and (d) a nearly two-fold increase in mining. Plantation forestry appeared as a major new land use (nearly four percent). There was a small increase in urbanisation and a small decrease in water land uses.

In the Harvey sub-catchment the majority of land use change between census years was experienced in the following categories: (a) more than two-fold decrease each for grazing and agriculture respectively, (b) a one third increase in areas under conservation, and (c) a two-fold increase in urbanisation. Water and mining remained about the same.

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4 Discussion

4.1 Hydro-climatological non-stationarity

Persistent shifts observed over the period from 1984–2011 support the idea of a transitional hydrological period characterised by a non-stationary phase. A declining trend in total annual rainfall was evident in the three major sub-catchments, with a statistically significant reduction in the Murray and Harvey sub-catchments of 39 and 29 % respectively. A reduction was also noticed in Serpentine; however, it was not as significant. Several other recent analyses have highlighted a persistent drop in rainfall based on data from a variety of locations across Southwest Australia, and in particular a major downward shift in the mid-1970s (Petrone et al., 2010; Samuel et al., 2011; Silberstein et al., 2012). In these studies a second small shift in the 1990s is also discussed and this is consistent with the trend observed over this period.

In parallel, the mean annual discharge rates decreased significantly in the Serpentine and Harvey Rivers (approximately 55 %). As such the decline in stream flow in these rivers has been greater than the respective declines in recorded rainfall. (This pattern was not observed in the Murray River.) A similar amplification was found in nearby forested catchments by Petrone et al. (2010), who reported runoff coefficients also reducing in tandem with rainfall decline. Some of the reduction could also be due to a higher rate of water extraction by irrigators in response to more frequent dry years. Some expansion of vegetation cover was seen in terms of plantation forestry (Figs. 13–15) and this could also cause reductions in runoff. However, this is unlikely since only a small percentage of the Harvey (5 %) and Serpentine (1 %) sub-catchments were converted to plantation forerstry. For the Murray River the situation is different, with the notable reduction in rainfall not yet manifesting as a similar reduction in river flow. This could be potentially due to two reasons: (1) the fact that this sub-catchment is dominated by heavier soils it may take longer for the catchment to achieve a new hydrological equilibrium; or (2) the fact that the Pinjarra rainfall station is a long way from the majority of the Murray catchment and as such most of the runoff is being driven by

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the very large inland catchment east of the scarp, where rainfall may have only recently been declining. This may explain the most recent reductions in flow. On the other hand the noted rainfall decline over the very small coastal catchment is having little influence on overall catchment runoff.

In an attempt to assess the importance of regional climatic drivers, the annual rainfall and flow from the three rivers was statistically compared to several major climatic indices known to be important for Australian rainfall (Table 4). Here a general linear model (GLM) was estimated for the rainfall/flow records as a function of four climatic indices (SOI, SAM, IOD, IPO). Statistically significant relationships over the study period were identified predominantly with SAM, and to a lesser extent with the IOD. Together these two indices explained up to 30 % of the variance in rainfall and streamflow data.

Along with the decline in flow, the seasonal pattern of river discharges, including both summer and winter, showed a general decreasing trend, particularly in the Serpentine and Harvey Rivers. Furthermore, the hydrograph peak has shifted from July to August, and this was observed in all three rivers. These shifts may respond to a change in the catchment storage potential with a reduction in autumn rains reducing the rate of moisture accumulation prior to the winter rains. Following Smettem et al. (2013), who analysed runoff decline in forested catchments south of the study area, we conducted an analysis of low summer flows over time as an indicator of the decline in base flow contributions (Fig. 17). This highlighted the dramatic decline in summer discharge in the Serpentine River relative to its winter discharge, and to a lesser extent in the Harvey and Murray Rivers. Whilst Ali et al. (2012) reported limited significant change in groundwater for the part of the region analysed here from 1980–2007, the analysis conducted at this scale points to a decline in groundwater storage and base flow contribution over the past decade.

4.2 Catchment characteristics and nutrient export

Whilst all three sub-catchments had a clear relationship between flow and nutrient export, (i.e. for TP, R^2 for Serpentine = 0.86, Murray = 0.61 and Harvey = 0.85), there

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were notable differences between them. Variation in geology, lithology and vegetative cover, as well as variation in hydrological and biogeochemical pathways, are known to lead to variability in nutrient export relationships (Meyer, 1999). Murray River displayed the lowest sensitivity in TP delivery in response to discharge fluctuations. The Murray River exported ~ 9 times less TP per unit discharge as compared to the Serpentine, and ~ 6 times less than the Harvey. However, there was practically no difference in the annual N export rates from all three sub-catchments. Consequently, on an annual basis, the Murray River is notably P limited, while the Serpentine and Harvey Rivers are neither N nor P-limited. This difference highlights the importance of different soil conditions in the upper reaches of the Murray River compared to the other sub-catchments, which lead to a higher retention of P, particularly as a result of the presence of soils with high Phosphorus Retention Indices (PRI > 10) (McPharlin et al., 1990; McComb and Lukatelich, 1995; Kelsey et al., 2011; Summers et al., 1999). With the majority of the sediments derived from high PRI soils east of the scarp (and travelling over greater distances and through nutrient-poor Jarrah systems), by the time they reach the coast plain there exists the potential for coastal P to be retained in the river system either through direct sorption onto suspended sediments and/or by the process of sedimentation after interaction with sediments suspended in the water column.

The Murray River also displays different patterns of P export, with two phases evident: a dilution-driven phase and a flow-driven phase (Fig. 5). The "dilution" effect (i.e. dilution-driven phase) may be due to the capacity for in-stream retention at relatively low flows where sedimentation can occur from the increasing inputs of sediment up to a point, at which time the sediment is no longer able to be dropped out (i.e. the start of the flow-driven phase). Unlike the other two river systems the Murray has a very long drainage system coursing from the east through the Jarrah forest and along the scarp. This may affect river flow dynamics. As such the sedimentation effect (which could explain the dilution-driven phase) could be overwhelmed by flow stopping sedimentation and indeed scouring previously deposited sediment into flows recorded downstream (and hence the start of the flow-driven phase).

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A distinctive aspect of potential nutrient limitation results when looking at the soluble inorganic fractions (DIN : DIP). The Serpentine River is N-limited in terms of the ratio of available nutrients, but not when considering the ratio of total nutrients. The Murray River is P-limited when considering total nutrients and this limitation is further magnified when considering the available nutrient ratio (i.e. DIN : DIP is twice the TN : TP ratio). This reinforces the fact that the sediments derived from the Murray's upper catchment have high affinity for DIP and that these higher-PRI soils east of the scarp make up the vast majority of the Murray catchment. This is further influenced by the long transit time that these sediments experience in travelling from the source to the gauging station. Harvey is less variable with both TN : TP and DIN : DIP ratios remaining within the limits of natural variability of the Redfield ratio. Differences between TN : TP and DIN : DIP has been noted by other authors. For example, Kosten et al. (2009) observed that TN : TP ratios can lead to erroneous interpretation of P-limitation since TN is largely comprised of non-bioavailable DON, and Harris (2001) also cautioned that annual estimates for TN : TP may not adequately represent subtle changes in TN : TP stoichiometry.

4.3 Temporal trends in nutrient export

Over the study period, TP, TN and DIP loads in the Serpentine and Harvey Rivers fell substantially (> 25 %, though not a statistically significant decrease in some cases), and consequently there was lower downstream export of dissolved and particulate material into the estuary. The Murray River again exhibited a different behavior, showing no trend in TP and an upward tendency of TN over the last twelve years (1999–2011). The significant reduction in load in tandem with the observed flow decreases was expected due to an intimate association between flow and nutrient loads being reported elsewhere (Alexander et al., 1996), including for catchments in the region (Robson et al., 2008; McComb and Humphries, 1992). This is what Basu et al. (2008) refer to as relative "biogeochemical stationarity", whereby the rate of nutrient export scales predictably with runoff. The question however remains whether there is also a declining trend of nutrient export but without the effect of the flow variability. For total nutrient loads, this analysis indicated that flow-adjusted TP and TN displayed notable upward trends over the last two decades (Figs. 6d–f and 7e, f), with a statistically significant trend for flow-adjusted TP in the Serpentine River. This suggests that new P sources and/or land use change are continuing to exceed the rate of P reduction that might be achieved through the various nutrient control measures in the region.

Unfortunately the flow-adjusted dissolved nutrient load data were available only for the two last decades (1990–2013). Nonetheless, as TP showed an increasing trend, we expected similar behavior in DIP. However, flow-adjusted DIP experienced a reduction in the Harvey and Murray Rivers with a less clear pattern for Serpentine. This reduction in flow-adjusted DIP is difficult to explain. One possible reason coming from anecdotal observations is that the decreasing flow-adjusted DIP may be caused by an overall reduction in fertilizer application in the catchment, driven perhaps by increasing fertilizer costs and falling commodity prices. Such anecdotal information requires further investigation.

Trends in DIN export differ from the other variables. In all rivers there were no clear trends in DIN loads over time, though it appeared to decrease until 2004, after which it rose again with large inter-annual variability. Overall, there has been a decrease in the DIN load (which was magnified due to an extremely high value in the wet year of 1996), but the pattern is not linear. The flow-adjusted DIN load, on the other hand, decreased from the mid-1990s and started to rise again from 2004 onwards. This trend was also seen by Smith et al. (2005), who observed that linear extrapolation of DIN loads for different flows is not appropriate because N exports show a complex pattern particularly at low flows. This may be partly explained by changing land-use, since DIN (particularly NO_3^-) is known to be a sensitive indicator to anthropogenic disturbance (Wang et al., 2013). Our analysis of yearly population growth rates for each sub-catchment (Fig. 18b) shows a similar trend to flow-adjusted DIN (see discussion below).

A changing contribution of base-flow and hyporheic zone interactions may lead to changes in NO_3^- export. Donohue et al. (2001) found in the nearby Swan Estuary

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a seasonal signal of groundwater contribution and Ocampo et al. (2006) highlighted that NO_3^- "flushing" following rainfall is dependent on shallow groundwater connectivity and antecedent conditions. The changing hydrological dynamics can therefore potentially explain the decoupling of DIN export relationships at low flows. Other natural factors that can affect nutrient fluxes between years include average annual soil and water temperature (Zweimüller et al., 2008), which can affect mineralization of organic matter and denitrification (Peters, 2001; Pinay et al., 2007; Herrman et al., 2008). Land-use can also change denitrification rates; for example, Smith (2005) found that the degree to which a basin denitrifies is strongly controlled by land use.

From the point of view of nutrient partitioning, we surprisingly found a large decrease in DIP : TP over time. This behavior could be explained by hydrological factors and economic circumstances. In reality, both factors are probably at play here: an increasingly drier climate is driving reductions in DIP concentrations through increased time for in-stream processing, while historical economic changes (vis a vis the deregulation of the dairy industry in the 1990s) may have reduced overall fertilizer usage.

In contrast to DIP : TP, the DIN : TN ratio shows an increase from 2004 for all three sub-catchments (Fig. 9d–f), which is consistent with Harris (2001), who demonstrated a rapid increase of available fractions of N as N export increases with land use change on the east coast of Australia.

Whilst changes in average concentration and partitioning were reported, the stoichiometry of annual loads was quite resilient to change, with TN : TP ratios constant over the study period. The stoichiometric ratio of the dissolved nutrients did however show an upward trend in all three rivers. This could be attributed primarily to increased catchment urbanization. For example, Harris (2001) found that exports from urban catchments are not only higher than forested catchments but they also have relatively more inorganic nitrogen. Marshall and Randhir (2008) suggest that a watershed system could change from N to P limited and vice versa under different climate change scenarios. However, in this study the link between hydrologic change and nutrient stoichiometry is not strong.

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4.4 Hydrologic change or land-use change?

Whilst we have seen a clear drying trend in the three sub-catchments, the nature of the biogeochemical response appears relatively complex, particularly when looking beyond TN and TP loads. Over the period of hydro-climatological change the catchment has also been undergoing a rapid expansion of population. Much of the original forest clearing however, occurred prior to the study period. Therefore the questions that remain are: how much of the change in riverine water quality and nutrient loads can be explained by climate variability; and what is the result of land-use change and associated policy?

As expected, the statistical comparison of dry and wet years indicated that wet years bring significantly more total and dissolved nutrients than dry years (with some exceptions e.g. DIP in the Murray sub-catchment). There was no significant difference in either TN : TP or DIN : DIP in terms of dry and wet years. However, the fact that there were only a few dry and wet years to compare made the assessment less powerful, and consequently a parallel analysis of monthly values was conducted. This analysis did show a significant difference in nutrient stoichiometry in wet and dry conditions for the Serpentine and Murray Rivers but not the Harvey River. The lower DIN : DIP ratio under wet conditions in the Serpentine River is possibly due to the increase in the proportion of DIP in wet years, or may have resulted from increased denitrification in riparian areas following periods of extended water logging. Conversely, in the Murray River this is potentially associated with denitrification in the anoxic bottom waters of the river. In contrast, the ratio of total : dissolved nutrient loads was significantly affected by flow variability but also seemed to be influenced by properties of the catchment and land-use changes. The variability in the proportion of dissolved fraction differs in each sub-catchment. The increase in the proportion of DIP under wet conditions is higher in the Serpentine than in the Harvey and it is not observed in Murray. The increment in the proportion of DIP may partly be explained by application of fertilizers before winter rains or from the P stored in the soils from the long history of fertilizer applications

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(Weaver et al., 1988a,b). Other plausible reasons for increased DIP in wet conditions are that drying of marginal river sediments has increased the biologically available P for release following rainfall (Kerr et al., 2010).

The flow adjusted TP showed a predominantly upward trend in the last two decades (statistically significant in the Serpentine sub-catchment) and this suggests that new sources of P are continuing to exceed the rates of P reduction that might be achieved through the various nutrient control measures in the region. Analysis of population data indicated that growth rates for the Serpentine Jarrahdale Shire were the highest of those in the Peel Region and second only to the state's capital city in the last decade (the rate of growth in population was 5.7 % between 2004 and 2009). Land-use changes from small rural residential into more intensive peri-urban residential developments are common (Serpentine Jarrahdale Shire, 2013). Comparisons of land-use change between the years 1993 and 2006 indicated that in the Serpentine sub-catchment there was a 3 % reduction in the land designated to conservation and approximately 6 % of other land changed into more intense anthropogenic disturbances i.e. urban expansion and mining activity (Figs. 13–16). This supports the idea that rapid urbanization is the cause of the TP concentration increase and it is in agreement with Harris (2001), who reported an increase in P exports as a function of altered land use and urbanization.

In the Harvey River sub-catchment, the process of urbanization has not been as rapid as in Serpentine (2 % of land was assigned to conservation purposes and this was accompanied by a reduction in agriculture and a small increment in plantation forestry; Figs. 13–16). The decrease in DIP : TP (Fig. 9c) may correspond to a reduction in superphosphate use due to the combined effects of increased fertilizer costs and reduced commodity prices. Model simulations of management scenarios with reduction in fertilization over a 10 yr period in surrounding rural catchments indicated the potential for a linear decrease in P exports with reduced fertilization (Zammit et al., 2005). In the present analysis, TP did not decrease, but the proportion of the soluble fraction did. On the other hand, Donohue (2001) analysed 12 yr of TP concentrations on nearby rural

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and urban catchments and argued that the temporal changes in TP concentrations caused by management of non-point sources may be similar to the natural temporal variation. Nevertheless, in terms of nutrient load, the results of this study indicate that there is a significant reduction ($p < 0.05$) in the proportion of DIP, accompanied by a decline in flow-adjusted DIP inputs to the Harvey River.

In terms of N, we observed that the yearly population growth rate shows very similar trend to flow-adjusted DIN. Unlike the findings from other authors (Harris, 2001; Peierls et al., 1991), we found no correlation of DIN and DIN : TN with population size (Fig. 19a–c). However, the DIN proportion rises as a function of the population growth rate (Fig. 19d–f). About 30 % of the variability in the proportion of DIN could be explained by population growth rates in the Serpentine and Harvey catchments, and about 40 % in Murray if the year 2000 is removed from the regression analysis due to its extremely large value (average ± sd for normal years = 41.52 ± 21). From anecdotal evidence this would be explained by the actions of land-use development leading to increased DIN export; for example, through groundwater pumping and surface drainage. Overall, the weak linearity observed between the DIN data and river discharge, together with the abovementioned association between DIN and population growth rates, point to the stronger effect that land-use changes have upon DIN export as opposed to the effects that hydro-climatological changes may have upon DIN export.

Therefore, whilst a continuation of the drying climate is expected (Silberstein et al., 2012), the historical rapid rate of development may also continue to accelerate and the trends reported here may be likely to continue. Therefore, while climate may drive a downward trend in overall nutrient export, urbanisation and agriculture will tend to drive a counter-trend of increases in inorganic nutrient export. It should be noted that there has been a far greater rate of urbanisation downstream of our study area and as such it would be reasonable to assume therefore that the effects observed in our study would be amplified downstream and would bring about further undesirable impacts in the lower reaches of the rivers and on the estuary itself.

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5 Conclusions

This study examined the effects of a non-stationary climate, reflected in stream flow, on the variation of catchment nutrient export into an estuarine system. There is evidence for a downward trend in nutrient load over the 28 yr of the study period that is associated with a higher frequency of dry years. Consequently, the estuary has experienced an average reduction of ~50, ~50, and ~80 % in TP, TN and DIP loadings respectively from the Serpentine and Harvey rivers, with no clear trend observed for DIN loading. When the effect of flow differences were removed, none of the flow-adjusted annual average nutrient loads significantly increased or decreased in the Murray and Harvey Rivers. In the Serpentine River, TP increased over the last decade indicating increasing inputs of TP, likely associated with the recent rapid urban development in this area. This is important to consider in future management strategies on nutrient control.

The variability of total nutrients (TP and TN) is strongly associated with variability in flows. However, the variability of dissolved nutrients (DIN and DIP) could only be partially explained by flow variability and other factors should be considered to explain DIN and DIP patterns. For example, the role of ground water inflows in supplying nutrients during the low-flow periods may be important. However, limited information exists about this component and should be the focus of future research.

Both the TN : TP and DIN : DIP stoichiometric ratios of the three rivers were not significantly affected by climate variability in annual terms, and therefore the physiographic and geomorphological characteristics of the sub-catchments was more important in determining this factor than flow variability. In particular, Murray River was P limited all year round, while Serpentine and Harvey were N limited. However, when conducting the analysis on a monthly or daily basis a significant relationship was noted in the Serpentine and Murray Rivers between stoichiometry and flow, indicating that the system tends to maintain the stability of this ratio over the hydrological year. This highlights the dynamic and complex interactions between hydrology, catchment inputs and biogeochemical processes, and the importance of the time scale used in the analysis.

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Notably, the variability of DIN : DIP over time suggests that this ratio is being affected more by changes in land use than by changes in climatic conditions. This complexity and diversity should be captured when considering management actions.

Analysis of nutrient partitioning indicated an increase in the proportion of the dissolved inorganic fraction with higher flows. However, P and N dissolved inorganic fractions responded differently to flow depending on the catchment. Total nutrients responded more to variability in flow conditions, whilst the dissolved component responded more to catchment type (e.g. DIP in Murray) and land-use (e.g. DIN in all three catchments). We also noted an association between DIN : TN and population growth rate, as opposed to absolute population numbers.

The disentangling of the effects of climatic variability from other human perturbations is therefore a difficult task. However, this work has demonstrated the application of statistical tools to isolate the effect of climate, and offers new information to assist in the development of future nutrient management programs. If the present downward trends in river flows persist, dry years will become more frequent and it is important to understand how possible future scenarios of nutrient delivery will affect changes in estuarine ecological function.

References

Alexander, R. B., Murdoch, P. S., and Smith, R. A.: Streamflow-induced variations in nitrate flux in tributaries to the Atlantic coastal zone, Biogeochemistry, 33, 149–177, 1996.
Ali, R., McFarlane, D., Varma, S., Dawes, W., Emelyanova, I., Hodgson, G., and Charles, S.: Potential climate change impacts on groundwater resources of south-western Australia, J. Hydrol., 475, 456–472, 2012.
APHA: Standard Methods for the Examination of Water and Waste Water, 20th Edn., American Public Health Association, Washington, D.C., 1998.
Bartley, R. and Speirs, W.: A review of sediment and nutrient concentration data from Australia for use in catchment water quality models, eWater Cooperative Research Centre

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Technical Report, available at: http://www.ewater.com.au/uploads/files/Water%20quality%20review_Bartley%20and%20Speirs_Final(2).pdf (last access: 5 August 2013), 2010.
Basu, N. B., Destouni, G., Jawitz, J. W., Thompson, S. E., Loukinova, N. V., Darracq, A., Zanardo, S., Yaeger, M., Sivapalan, M., Rinaldo, A., and Rao, P. S. C.: Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity, Geophys. Res. Lett., 37, L23404, doi:10.1029/2010GL045168, 2010.
Bates, B. C., Hope, P., Ryan, B., Smith, I., and Charles, S.: Key findings from the Indian Ocean Climate Initiative and their impact on policy development in Australia, Climatic Change, 89, 339–354, 2008.
Bennett, E. M., Carpenter, S. R., and Caraco, N. F.: Human impact on erodable phosphorus and eutrophication: A global perspective, Bioscience, 51, 227–234, 2001.
Bouraoui, F., Grizzetti, B., Granlund, K., Rekolainen, S., and Bidoglio, G.: Impact of climate change on the water cycle and nutrient losses in a Finnish catchment, Climatic Change, 66, 109–126, 2004.
Bradby, K.: Peel–Harvey – The Decline and Rescue of an Ecosystem, Greening the Catchment Taskforce (Inc.), Mandurah, 1997.
Caraco, N. F.: Influence of human populations on P transfers to aquatic systems: a regional scale study using large rivers, in: Phosphorus in the Global Environment: Transfers, Cycles and Management (SCOPE 54), edited by: Tiessen, H., Wiley, New York, 236–244, 1995.
Caraco, N. F. and Cole, J. J.: Human impact on nitrate export: an analysis using major world rivers, Ambio, 28, 167–170, 1999.
Caruso, B. S.: Regional river flow, water quality, aquatic ecological impacts and recovery from drought, Hydrolog. Sci. J., 46, 677–699, 2001.
Chambers, P. A., McGoldrick, D. J., Brua, R. B., Vis, C., Culp, J. M., and Benoy, G. A.: Development of environmental thresholds for nitrogen and phosphorus in streams, J. Environ. Qual., 41, 7–20, 2012.
Degens, B. P. and Donohue, R. D.: Sampling Mass Loads in Rivers – A Review of Approaches for Identifying, Evaluating and Minimising Estimation Errors, 48, Water and River Commission, Western Australia, 2002.
Donner, S. D., Kucharik, C. J., and Oppenheimer, M.: The influence of climate on in-stream removal of nitrogen, Geophys. Res. Lett., 31, L20509, doi:10.1029/2004gl020477, 2004.

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Donohue, R., Davidson, W. A., Peters, N. E., Nelson, S., and Jakowyna, B. N.: Trends in total phosphorus and total nitrogen concentrations of tributaries to the Swan-Canning Estuary, 1987 to 1998, Hydrol. Process., 15, 2411–2434, 2001.

Downing, J. A., McClain, M., Twilley, R., Melack, J. M., Elser, J., Rabalais, N. N., Lewis, W. M., Turner, R. E., Corredor, J., Soto, D., Yanez-Arancibia, A., Kopaska, J. A., and Howarth, R. W.: The impact of accelerating land-use change on the N-cycle of tropical aquatic ecosystems: current conditions and projected changes, Biogeochemistry, 46, 109–148, 1999.

EPA (Ed.): Water Quality Improvement Plan for the Rivers and Estuary of the Peel–Harvey System-Phosphorus Management, Environmental Protection Authority of Western Australia, Perth, Western Australia, 1–74, 2008.

Esterby, S. R.: Review of methods for the detection and estimation of trends with emphasis on water quality applications, Hydrol. Process., 10, 127–149, 1996.

Forsberg, C. and Ryding, S. O.: Eutrophication parameters and trophic state indexes in 30 Swedish water-water receiving lakes, Arch. Hydrobiol., 89, 189–207, 1980.

Gilbert, R. O.: Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold, New York, 1987.

Harris, G. P.: Biogeochemistry of nitrogen and phosphorus in Australian catchments, rivers and estuaries: effects of land use and flow regulation and comparisons with global patterns, Mar. Freshwater Res., 52, 139–149, 2001.

Helsel, D. R. and Hirsch, R. M.: Statistical Methods in Water Resources, USGS, United State of America, available at: http://water.usgs.gov/pubs/twri/twri4a3/, last access: 27 July 2013.

Herrman, K., Bouchard, V., and Moore, R.: Factors affecting denitrification in agricultural headwater streams in northeast Ohio, USA, Hydrobiologia, 598, 305–314, 2008.

Hick, P.: Understanding, quantifying and demonstrating the likely local effects of climate change and variability in the Peel–Harvey catchment, South West Catchment Council Funded Project Report L2.G4, South West Catchments Council & Peel–Harvey Catchment Council, Mandurah, Western Australia, 40 pp., 2006.

Hipel, K. W. and McLeod, A. I.: Time Series Modelling of Water Resources and Environmental Systems, available at: http://www.stats.uwo.ca/faculty/aim/1994Book/default.htm (last access: 27 June 2013), 2005.

Hodgkin, E. P. and Birch, P. B.: No simple solutions: Proposing radical management options for a eutrophic estuary, Mar. Pollut. Bull., 17, 399–404, 1986.

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Hodgkin, E. P., Birch, P. B., Black, R. E., and Hillman, K.: The Peel–Harvey Estuarine System: Proposals for Management, DEC Report No14, 51, Department of Conservation and Environment, Western Australia, 1985.
Hornberger, G. M. and Spear, R. C.: Eutrophication in Peel Inlet – 1. Problem-defining behavior and mathematical-model for the phosphorus scenario, Water. Res., 14, 29–42, 1980.
Howarth, R. W.: An assessment of human influences on fluxes of nitrogen from the terrestrial landscape to the estuaries and continental shelves of the North Atlantic Ocean, Nutr. Cycl. Agroecosys., 52, 213–223, 1998.
Howarth, R. W., Billen, G. B., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, R. J. A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, E. J., Kudeyarov, V. P., Murdoch, P., and Zhao-Liang, Z.: Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: natural and human influences, Biogeochemistry, 35, 75–139, 1996.
Johnson, A. H.: Estimating solute transport in streams from grab samples, Water. Resour. Res., 15, 1224–1228, 1979.
Kelsey, P., Hall, J., Kretschmer, P., Quinton, B., and Shakya, D.: Hydrological and nutrient modelling of the Peel–Harvey catchment, Water Science Technical Series, Report No. 33, Department of Water, Western Australia, 1–234, 2011.
Kerr, J. G., Burford, M., Olley, J., and Udy, J.: The effects of drying on phosphorus sorption and speciation in subtropical river sediments, Mar. Freshwater. Res., 61, 928–935, 2010.
Kingsford, R. T.: Conservation management of rivers and wetlands under climate change – a synthesis, Mar. Freshwater Res., 62, 217–222, 2011.
Kosten, S., Huszar, V. L. M., Mazzeo, N., Scheffer, M., Sternberg, L. D. S. L., and Jeppesen, E.: Lake and watershed characteristics rather than climate influence nutrient limitation in shallow lakes, Ecol. Appl., 19, 1791–1804, 2009.
Lewis, W. J., Melack, J. M., McDowell, W. H., McClain, M., and Richey, J. E.: Nitrogen yields from undisturbed watersheds in the Americas, Biogeochemistry, 46, 149–162, 1999.
Lewis, W. M.: Yield of nitrogen from minimally disturbed watersheds of the United States, Biogeochemistry, 57, 375–385, 2002.
Lewis Jr., W. M., Wurtsbaugh, W. A., and Paerl, H. W.: Rationale for control of anthropogenic nitrogen and phosphorus to reduce eutrophication of inland waters, Environ. Sci. Technol., 45, 10300–10305, 2011.

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Marshall, E. and Randhir, T.: Effect of climate change on watershed system: a regional analysis, Climatic Change, 89, 263–280, 2008.
McComb, A. J. and Humphries, R.: Loss of nutrients from catchments and their ecological impacts in the Peel–Harvey Estuarine System, Western Australia, Estuaries, 15, 529–537, 1992.
McComb, A. J. and Lukatelich, R. J.: Eutrophic Shallow Estuaries and Lagoons, CRC Press, Boca Raton, 1995.
McPharlin, I., Delroy, N., Jeffery, B., Dellar, G., and Eales, M.: Phosphorus retention of sandy horticultural soils on the Swan coastal plain, West. Aust. J. Agr., 31, 28–32, 1990.
Meyer, J. L., Sale, M. J., Muiholland, P. J., and LeRoy Poff, N.: Impacts of climate change on aquatic ecosystem functioning and health, J. Am. Water Resour. As., 35, 1373–1386, 1999.
Milly, P. C. D., Dunne, K. A., and Vecchia, A. V.: Global pattern of trends in streamflow and water availability in a changing climate, Nature, 438, 347–350, 2005.
Murphy, J. and Riley, J.: A modified single solution method for the determination of phosphorus in natural water, Anal. Chim. Acta, 27, 21–26, 1962.
Ocampo, C. J., Oldham, C. E., Sivapalan, M., and Turner, J. V.: Hydrological versus biogeochemical controls on catchment nitrate export: a test of the flushing mechanism, Hydrol. Process., 20, 4269–4286, 2006.
Overbeck, J.: Ecosystem concepts, in: Guidelines of Lake Management, Vol. 1 – Principles of Lake Management, edited by: Jorgensen, S. E. and Vollenweider, R. A., International Lake Environment Committee/UNEP, Otsu, Japan, 19–34, 1989.
Peierls, B. L., Caraco, N. F., Pace, M. L., and Cole, J. J.: Human Influence on river nitrogen, Nature 350, 386–387, 1991.
Peters, N. E. and Donohue, R.: Nutrient transport to the Swan-Canning Estuary, Western Australia, Hydrol. Process., 15, 2555–2577, 2001.
Petrone, K. C., Hughes, J. D., Van Niel, T. G., and Silberstein, R. P.: Streamflow decline in southwestern Australia, 1950–2008, Geophys. Res. Lett., 37, 11401–11407, 2010.
Pinay, G., Gumiero, B., Tabacchi, E., Gimenez, O., Tabacchi-Planty, A. M., Hefting, M. M., Burt, T. P., Black, V. A., Nilsson, C., Iordache, V., Bureau, F., Vought, L., Petts, G. E., and De Camps, H.: Patterns of denitrification rates in European alluvial soils under various hydrological regimes, Freshwater Biol., 52, 252–266, 2007.
Potter, I. C., Loneragan, N. R., Lenanton, R. C. J., and Chrystal, P. J.: Blue-green-algae and fish population-changes in a eutrophic estuary, Mar. Pollut. Bull., 14, 228–233, 1983.

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A. L. Ruibal-Conti et al.

Preston, S. D., Bierman, V. J., and Silliman, S. E.: An evaluation of methods for the estimation of tributary mass loads, Water. Resour. Res., 25, 1379–1389, 1989.
Redfield, A. C.: The biological control of chemical factors in the environment, Am. Sci., 46, 205–221, 1958.
Robson, B. J., Bukaveckas, P. A., and Hamilton, D. P.: Modelling and mass balance assessments of nutrient retention in a seasonally-flowing estuary (Swan River Estuary, Western Australia), Estuar. Coast. Shelf. S., 76, 282–292, 2008.
Rose, T.: Water Quality Monitoring Programme for the Peel–Harvey Coastal Catchment – a guiding document with strategies for establishing a monitoring network capable of accurately measuring nutrient loads, Coastal Catchment Initiative – Environment Australia, Western Australia, 1–35, 2003.
Samuel, J. M., Verdon, D. C., Sivapalan, M., and Franks, S. W.: Influence of Indian Ocean sea surface temperature variability on southwest Western Australian winter rainfall, Water. Resour. Res., 42, W08402, doi:10.1029/2005wr004672, 2006.
Seitzinger, S. P., Styles, R. V., Boyer, E. W., Alexander, R. B., Billen, G., Howarth, R. W., Mayer, B., and Van Breemen, N.: Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA, Biogeochemistry, 57, 199–237, 2002.
Serpentine Jarrahdale Shire Populations Forecasts: http://forecast2.id.com.au/Default.aspx?id=323&pg=5000, last access: 2 July 2013.
Silberstein, R. P., Aryal, S. K., Durrant, J., Pearcey, M., Braccia, M., Charles, S. P., Boniecka, L., Hodgson, G. A., Bari, M. A., Viney, N. R., and McFarlane, D. J.: Climate change and runoff in south-western Australia, J. Hydrol., 475, 441–455, 2012.
Smettem, K. R. J., Waring, R. H., Callow, J. N., Wilson, M., and Mu, Q.: Satellite-derived estimates of forest leaf area index in southwest Western Australia are not tightly coupled to inter-annual variations in rainfall: implications for groundwater decline in a drying climate, Global Change Biol., 19, 2401–2412, doi:10.1111/gcb.12223, 2013.
Smith, S. V., Swaney, D. P., Talaue-McManus, L., Bartley, J. D., Sandhei, P. T., McLaughlin, C. J., Dupra, V. C., Crossland, C. J., Buddemeier, R. W., Maxwell, B. A., and Wulff, F.: Humans, hydrology and the distribution of inorganic nutrient loading to the ocean, Bioscience, 53, 235–245, 2003.
Smith, S. V., Swaney, D. P., Buddemeier, R. W., Scarsbrook, M. R., Weatherhead, M. A., Humborg, C., Eriksson, H., and Hannerz, F.: River nutrient loads and catchment size, Biogeochemistry, 75, 83–107, 2005.

HESSD
10, 11035–11092, 2013

Hydro-climatological non-stationarity shifts patterns of nutrient delivery

A. L. Ruibal-Conti et al.

Summers, R. N., Van Gool, D., Guise, N. R., Heady, G. J., and Allen, T.: The phosphorus content in the run-off from the coastal catchment of the Peel Inlet and Harvey Estuary and its associations with land characteristics, Agr. Ecosyst. Environ., 73, 271–279, 1999.
Valiela, I., Foreman, K., Lamontagne, M., Hersh, D., Costa, J., Peckol, P., Demeoandreson, B., Davanzo, C., Babione, M., Sham, C. H., Brawley, J., and Lajtha, K.: Couplings of watersheds and coastal waters: sources and consequences of nutrient enrichment in Waquoit Bay, Massachusetts, Estuaries, 15, 443–457, 1992.
Wang, R., Xu, T., Yu, L., Zhu, J., and Li, X.: Effects of land use types on surface water quality across an anthropogenic disturbance gradient in the upper reach of the Hun River, Northeast China, Environ. Monit. Assess., 185, 4141–4151, 2013.
WAPC: Western Australia tomorrow: population projections for the statistical divisions, planning regions and local government areas of Western Australia, Western Australian Planning Commission, available at: http://www.planning.wa.gov.au/dop_pub_pdf/WA_Tomorrow_Population_Report_No._4_October_2000.pdf, last access: 5 August 2013, 141 pp., 2000.
Weaver, D. M., Ritchie, G. S. P., Anderson, G. C., and Deeley, D. M.: Phosphorus leaching in sandy soils, I. Short-term effects of fertilizer applications and environmental conditions, Aust. J. Soil Res., 26, 177–190, 1988a.
Weaver, D. M., Ritchie, G. S. P., and Anderson, G. C.: Phosphorus leaching in sandy soils, II. Laboratory studies of the long-term effects of the phosphorus source, Aust. J. Soil. Res., 26, 191–200, 1988b.
Weaving, S.: Peel–Harvey Catchment: Natural Resource Atlas, Spatial Resource Information Group, Agriculture Western Australia, Perth, 1999.
Wetzel, R. G. and Likens, G. E.: Limnological Analyses, 2nd Edn., Springer-Verlag, New York, 391 pp., 2000.
Western Australian Department of Water: Water Resources Information Catalogue, http://kumina.water.wa.gov.au/waterinformation/wric/SearchByCriteria.asp, last access: 7 July 2013.
WRC – Water and Rivers Commission: Nutrients in tributary inflows to the Peel–Harvey estuarine system: status and trend (1983–1998), Water Resource Technical Series, WRT 23, Water and Rivers Commission, Perth, Western Australia, 1–41, 2000.
Zammit, C., Sivapalan, M., Kelsey, P., and Viney, N. R.: Modelling the effects of land-use modifications to control nutrient loads from an agricultural catchment in Western Australia, Ecol. Model., 187, 60–70, 2005.

Zweimueller, I., Zessner, M., and Hein, T.: Effects of climate change on nitrate loads in a large river: the Austrian Danube as example, Hydrol. Process., 22, 1022–1036, 2008.

Table 1. Characteristics of the three main river basins in the Peel–Harvey catchment and summary of statistics of hydrological data over the period 1984 to 2011.

River	Catchment Area (km^2)	Mean Daily Flow ($m^3 s^{-1}$)	Median Flow ($m^3 s^{-1}$)	Flow Range ($m^3 s^{-1}$)	Land Use[c]	Dominant Soil Types[d]
Serpentine	1300[a]	2.06	0.28	0.00–112.77	Commercial and industrial, undergoing rapid urbanisation. Stock grazing, pasture production, horticulture, piggeries, poultry, dairies, floriculture.	Deep grey sands, brown and yellow sands, and sand over clay
Murray	7049[b] (292.15)	8.66	2.09	0.02–289.70	Several large townships. Some commercial areas and industry (refinery). Stock grazing, horticulture, pasture development, dairies. Forestry and plantations.	Deep grey sands, loams clay and peats, deep grey sands
Harvey	720[a]	4.53	1.03	0.03–121.12	Several townships. Some commercial areas and industry (mining). Dairies, horticulture, pasture development and stock grazing. Forestry and plantations.	Deep grey sands, brown and yellow sands, and sand over clay

[a] Data obtained as described in Sect. 2.1.
[b] Data obtained from the WA Water Resources Information Catalogue (Western Australian Department of Water, 2013). Note that the area in brackets is the area difference between the whole catchment and the catchment area at Baden Powell gauging station.
[c] Rose (2003).
[d] Hodgkin et al. (1985).

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Table 2. Nutrient load reductions: 1984 to 2011.

	Serpentine (t)	(%)	Murray (t)	(%)	Harvey (t)	(%)
TP load	12	50	*no change*		25	[a]55
TN load	50[np] to 98	38[np] to 57	*no change* (upward trend since 1998)		96[np] to 200	36[np] to 57
DIP load (1990–2011)	7.7	80[np]	3.4	[a]93[np]	24.6	[a]81[np]
DIN load (1995–2011)[b]	downward trend observed up to 2004/upward trend observed since 2004					

[a] Statistical significance $p < 0.05$.
[b] Data period for Serpentine only is 1993–2011.
[np] No parametric slope; "without indication" = parametric slope.
Note: Unless otherwise stated all amounts and percentages represent nutrient reductions.

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Table 3. Summary statistics for total and dissolved nutrient loads for different hydrological conditions (dry, normal, wet) at Serpentine, Murray and Harvey (p values only for significant differences between dry–wet years based on the Kruskall–Wallis test).

WQ Parameter		Serpentine			Murray			Harvey		
		Dry	Nor	Wet	Dry	Nor	Wet	Dry	Nor	Wet
TP load ($t\,yr^{-1}$)	n	5	18	5	4	19	3	3	14	5
	Median	4.87	17.92	35.16	3.16	8.06	18.62	9.05	32.43	47.39
	IQR	5.09	9.79	3.86	2.87	4.10	6.97	0.42	9.86	1.2
	p value		< 0.001			< 0.001			< 0.001	
TN load ($t\,yr^{-1}$)	n	5	17	4	4	18	3	4	16	4
	Median	34.91	121.9	220.7	111.40	299.0	957.0	74.35	216.5	347.3
	IQR	32.26	36.16	66.27	84.05	169.82	324.46	29.36	61.55	57.44
	p value		< 0.001			< 0.001			NS	
TN/TP	n	5	17	4	4	18	3	3	14	4
	Median	7.35	6.6	6.2	35.3	28.80	48.30	7.60	7.00	7.25
	IQR	0.57	1.2	2.15	4.5	12.2	2.1	0.3	1.3	0.55
	p value		– NS –			– NS –			– NS –	
DIP ($t\,yr^{-1}$)	n	5	14	3	3	15	2	3	14	3
	Median	1.92	7.8	23.6	0.47	2.30	3.55	3.30	14.69	24.56
	IQR	1.49	4.98	1.28	0.03	2.44	1.08	0.10	11.64	5.61
	p value		< 0.05			– NS –			< 0.05	
DIN ($t\,yr^{-1}$)	n	5	12	1	3	12	1	3	10	3
	Median	4.82	22.7	55.0	13.37	102.6	1020.2	18.40	59.74	129.77
	IQR	0.88	17.92	0.00	6.40	91.84	0.00	2.99	22.71	129.67
	p value		< 0.05			0.05			< 0.05	
DIN/DIP	n	5	12	1	3	12	1	3	10	3
	Median	2.98	3.36	2.33	29.85	37.10	219.99	0.46	3.02	3.16
	IQR	2.34	1.93	0.00	16.08	112.56	0.00	16.08	87.52	95.99
	p value		– NS –			– NS –			– NS –	
DIP/TP (%)	n	5	14	3	3	15	2	3	13	3
	Median	34.73	48.89	61.86	27.26	31.31	23.43	36.58	47.09	53.74
	IQR	22.07	12.91	3.74	13.63	26.59	3.39	2.85	14.66	6.22
	p value		< 0.05			– NS –			– NS –	
DIN/TN (%)	n	5	12	1	3	12	1	3	10	3
	Median	18.58	18.70	26.28	15.89	39.32	93.35	27.3	28.9	36.4
	IQR	8.39	7.08	0.00	1.85	18.5	0.00	5.40	10.90	19.65
	p value		– NS –			< 0.05			– NS –	

NS = not significant at 5 % level ($p > 0.05$).

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Table 4. Correlation between three relevant climatic modes (SOI, IOD, SAM) and rainfall and stream flow from 1984–2011. Relationships determined using annual averages of climate indices, rainfall and streamflow with a General Linear Model. Relationships with > 95 % confidence are in **bold**.

	SOI: Southern Oscillation Index *p* value	IOD: Indian Ocean Dipole *p* value	SAM: Southern Annular Mode *p* value	GLM: General Linear Model R^2
Rainfall	0.502	0.272	**0.007**	0.31
Serpentine River Flow	0.770	0.163	**0.005**	0.33
Murray River Flow	0.892	0.083	**0.032**	0.27
Harvey River Flow	0.449	0.473	0.122	0.16

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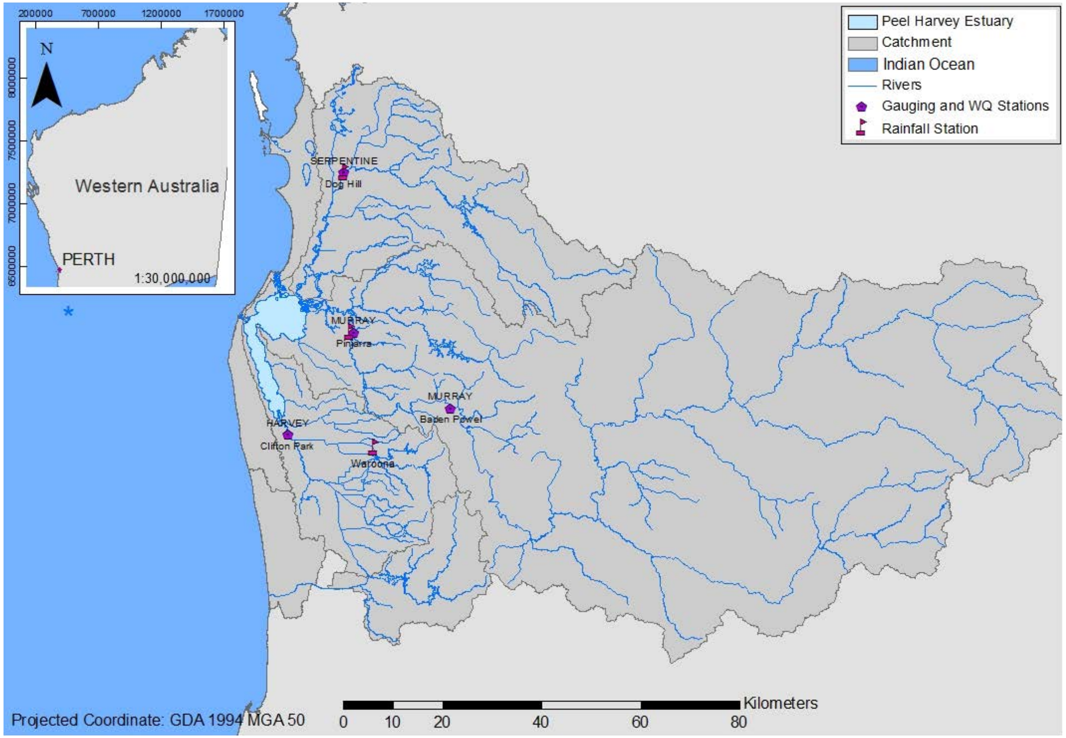

Fig. 1. Location of Peel–Harvey catchment, with sampling sites for river flow, water quality and rainfall.

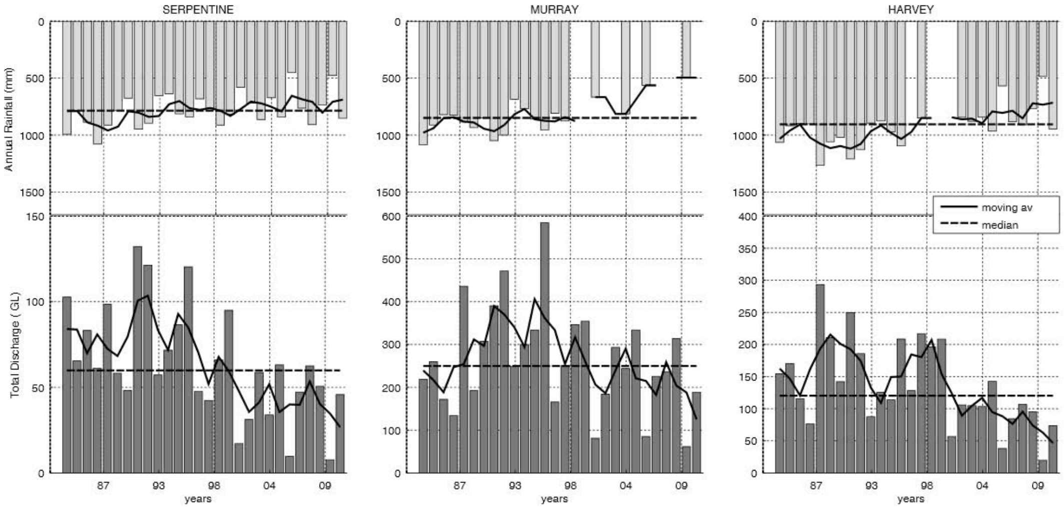

Fig. 2. Temporal variability of rainfall and surface runoff (1984–2009). Dashed black line represents the overall median; solid line represents the three year moving average. Note change of scale in Total Discharge between river catchments.

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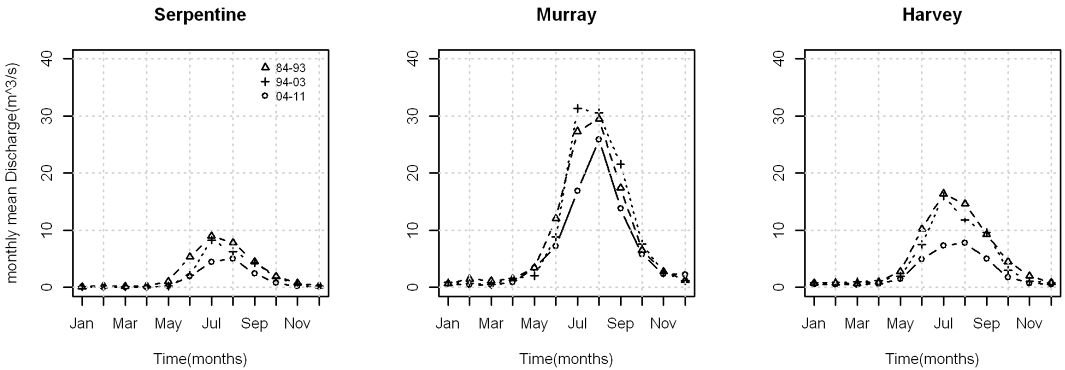

Fig. 3. Annual variability of the monthly mean discharge for three decadal periods (1984–1993, 1994–2003 and 2004–2011).

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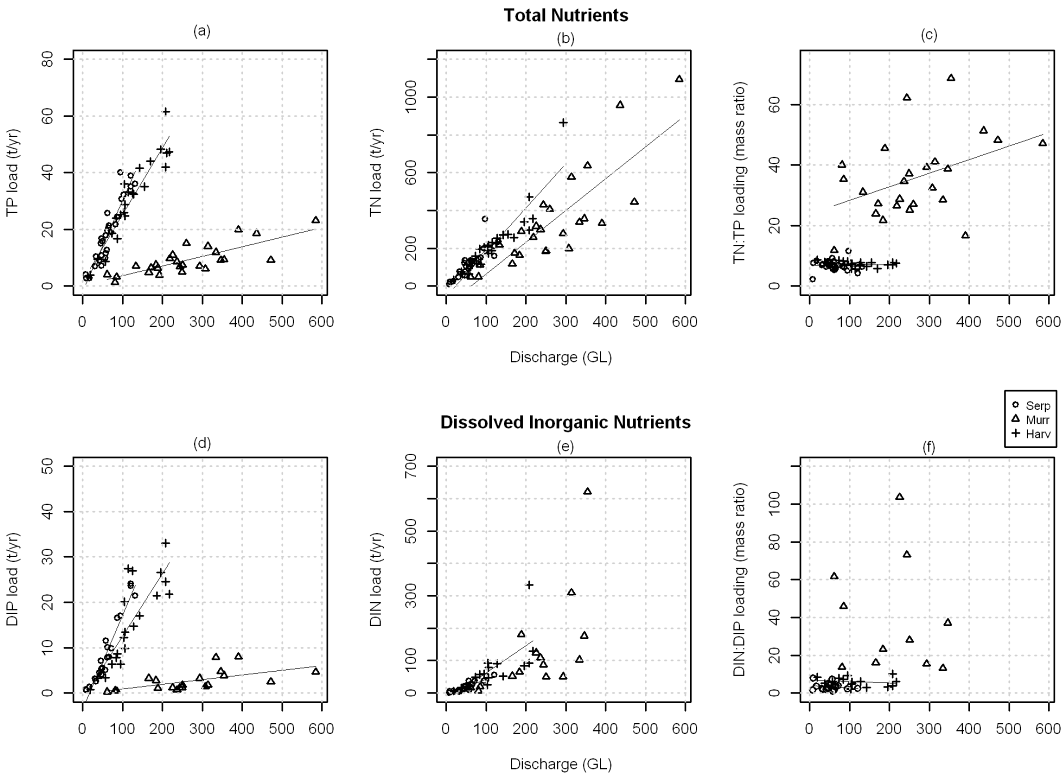

Fig. 4. Relationship between annual load of nutrients ($t\,yr^{-1}$) and annual total discharge (GL) over the study period 1984–2011.

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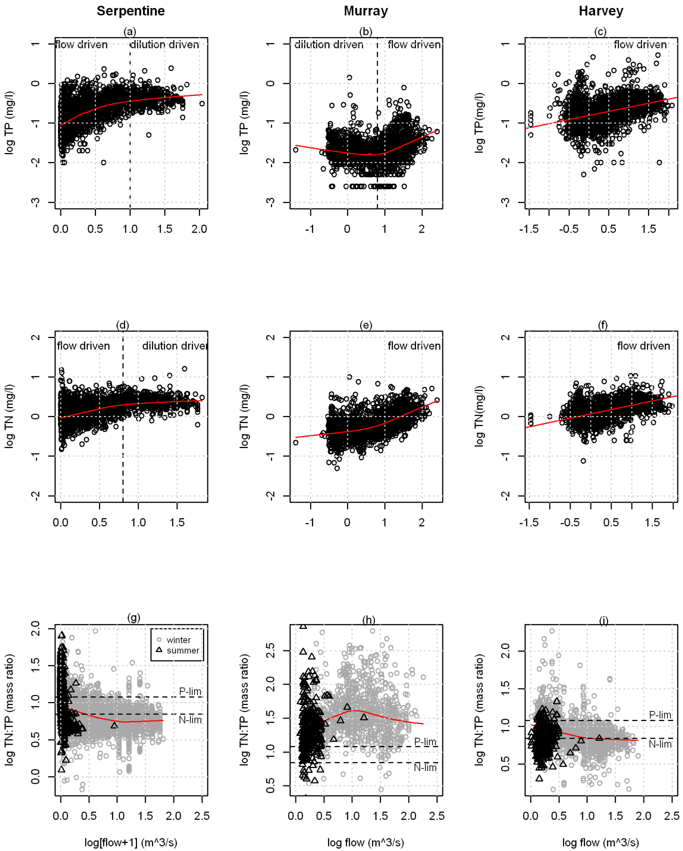

Fig. 5. Rating curves (nutrient concentration vs. flow) for TP & TN concentrations in the Serpentine, Murray and Harvey Rivers (1985–2009). The concentration vs. flow relationships are as described by Johnson (1979): (i) controlled by dilution, (ii) partially controlled by dilution and (iii) flow driven release pattern (Red line is LOWESS smoothing; Grab + comp = combination of data collected as grab sample and composite sample).

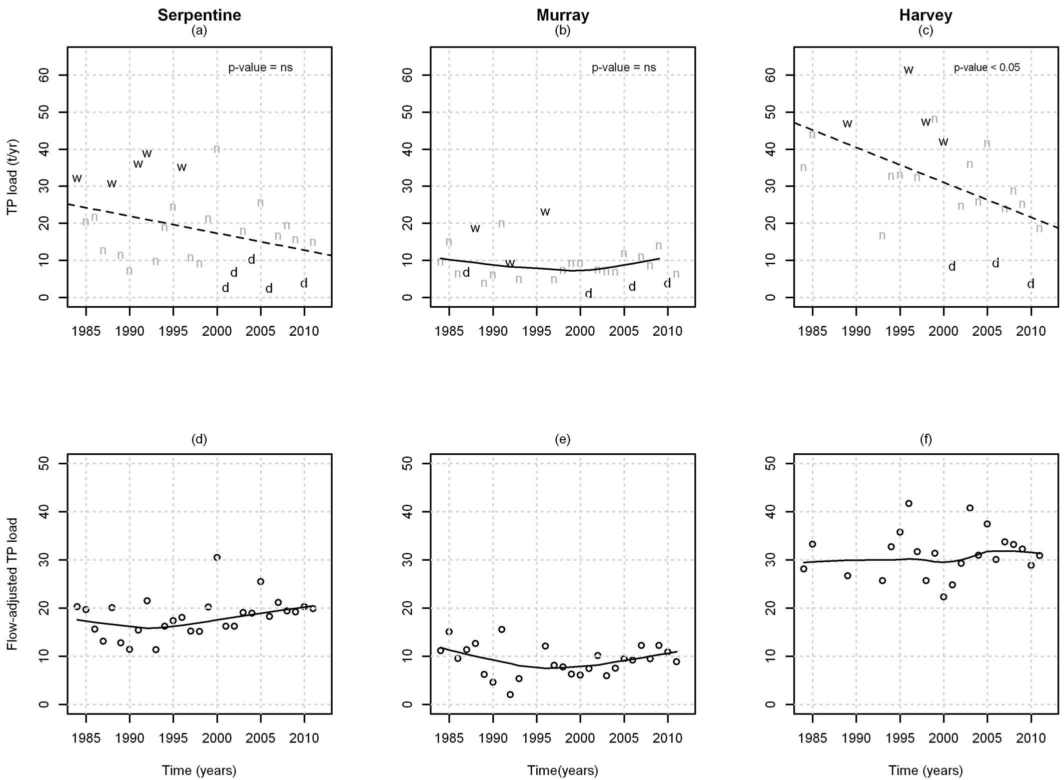

Fig. 6. Temporal variability in annual TP loads and flow-adjusted loads at Serpentine, Murray and Harvey Rivers from 1984–2011 (w = wet; d = dry; n = normal, dashed line = linear regression; solid line = LOWESS smoothing).

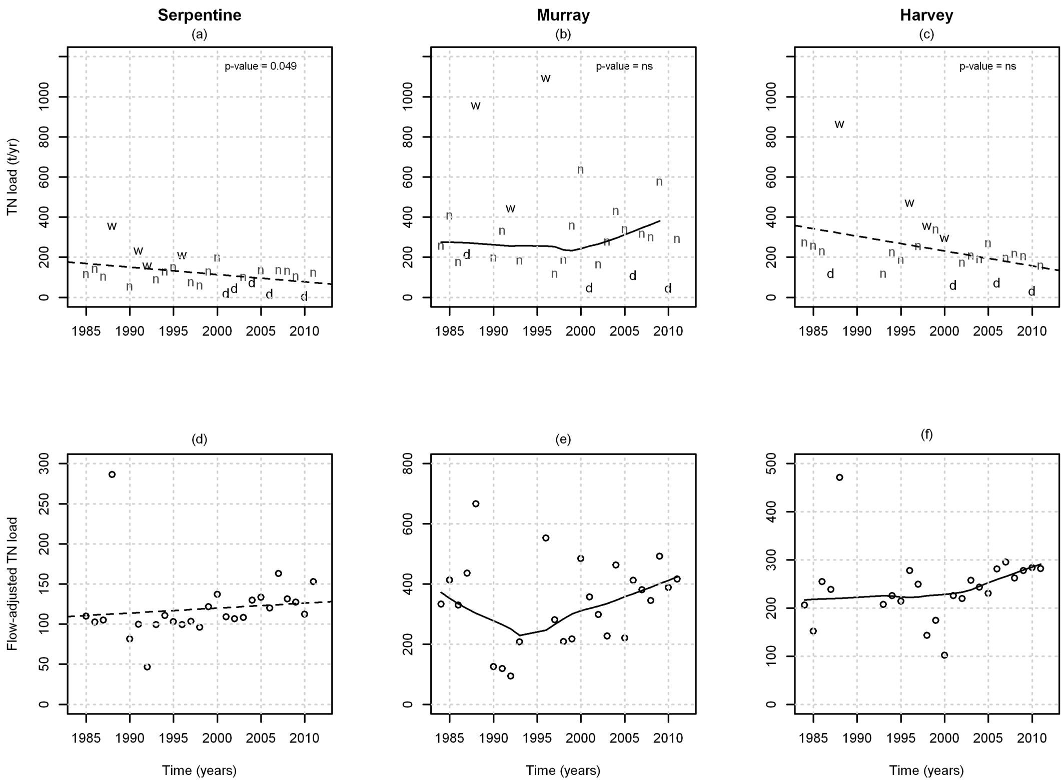

Fig. 7. Temporal variability in annual TN loads and flow-adjusted loads at Serpentine, Murray and Harvey Rivers from 1984–2011 (w = wet; d = dry; n = normal, dashed line = linear regression; solid line = LOWESS smoothing).

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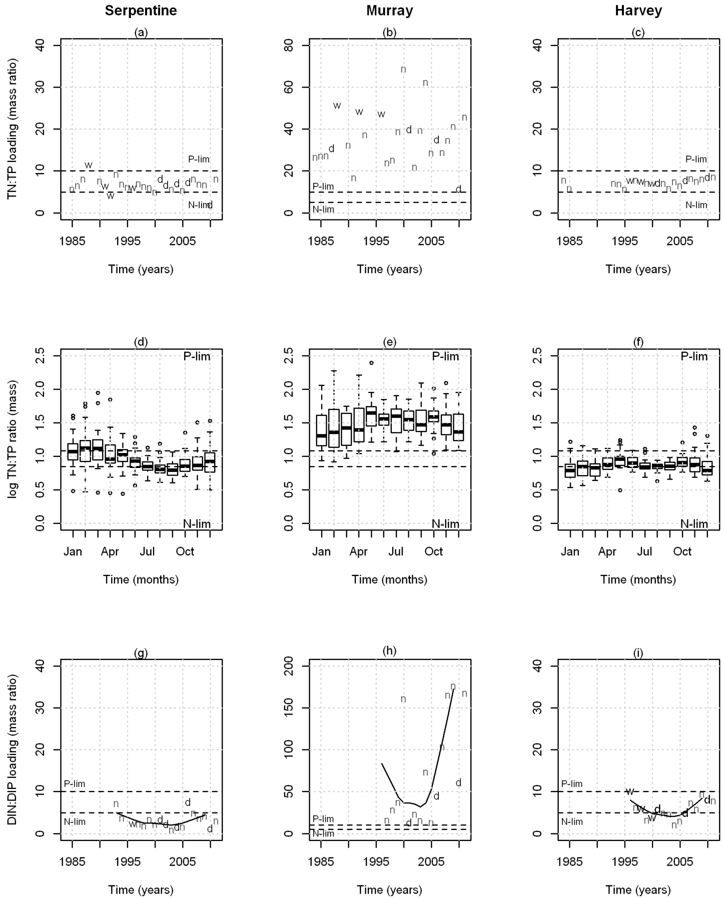

Fig. 8. (a)–(c) Time series of annual TN : TP mass ratio, **(d)–(e)** monthly variation in the TN : TP mass ratio, and **(e)–(f)** time series of annual DIN : DIP mass ratio. Dashed lines indicate the range of normal variability around the Redfield ratio.

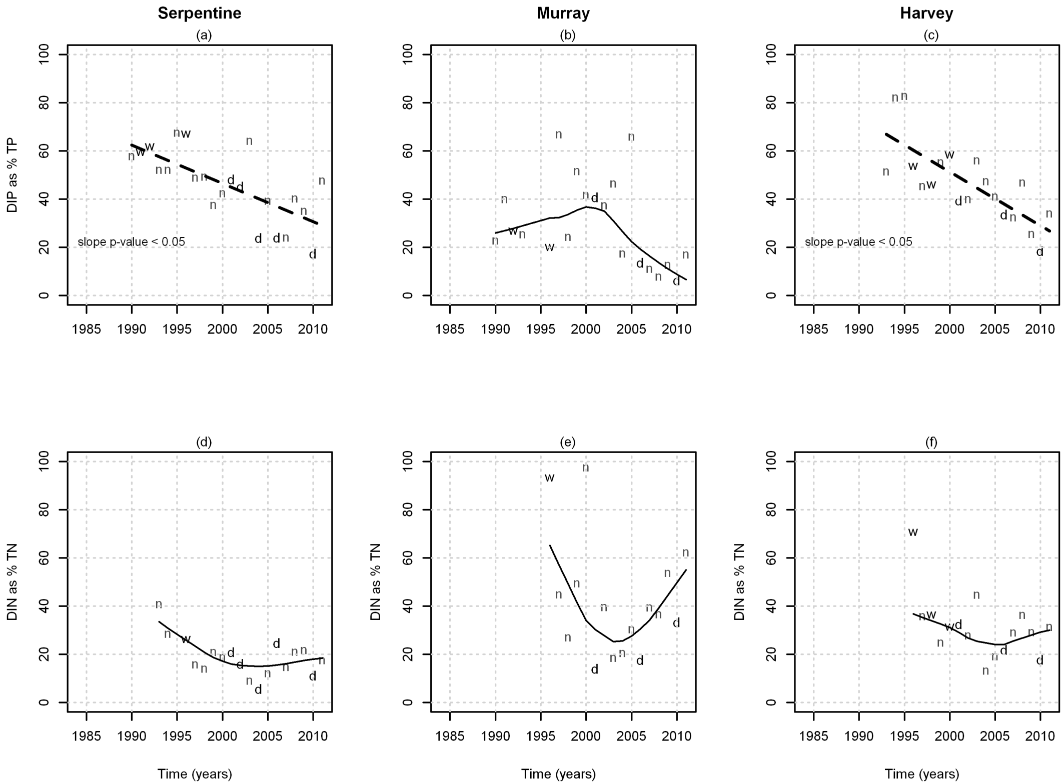

Fig. 9. Time variability in total vs. dissolved fractions for: P **(a–c)** and N **(d–f)** (w = wet; d = dry; n = normal, dashed line = linear regression; solid line = LOWESS smoothing).

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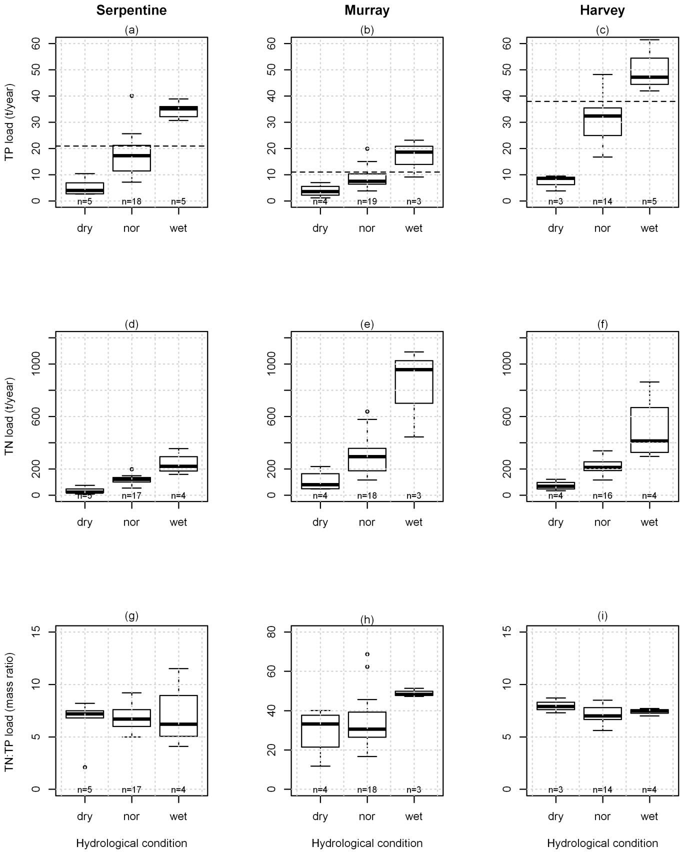

Fig. 10. Effect of hydrological condition – "dry", normal ("nor"), "wet" – on the annual load of **(a)**–**(c)** TP, **(d)**–**(f)** TN, and **(g)**–**(i)** the TN : TP mass ratio. Dashed horizontal line indicates the target value for TP loads specified by EPA (1992) as cited in Kelsey et al. (2011). Note: change of *y* scale in **(h)**.

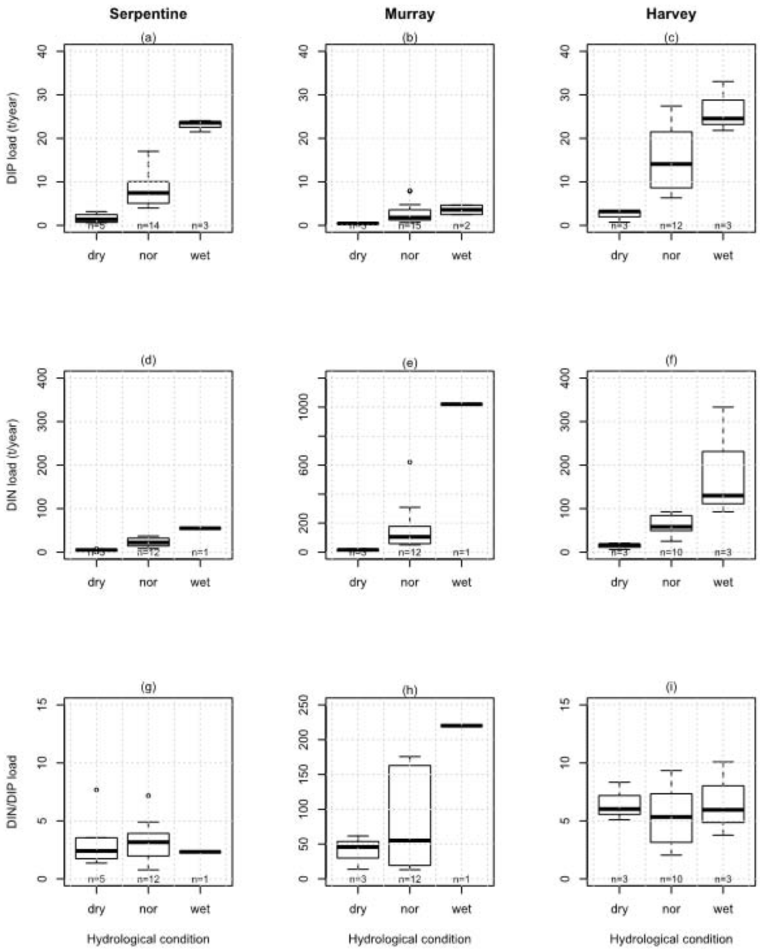

Fig. 11. Effect of hydrological condition – "dry", normal ("nor"), "wet" – on the annual load of: **(a)–(c)** DIP; **(d)–(f)** DIN; **(g)–(i)** DIN : DIP mass ratio. Note: change of y scale in **(e)** and **(h)**.

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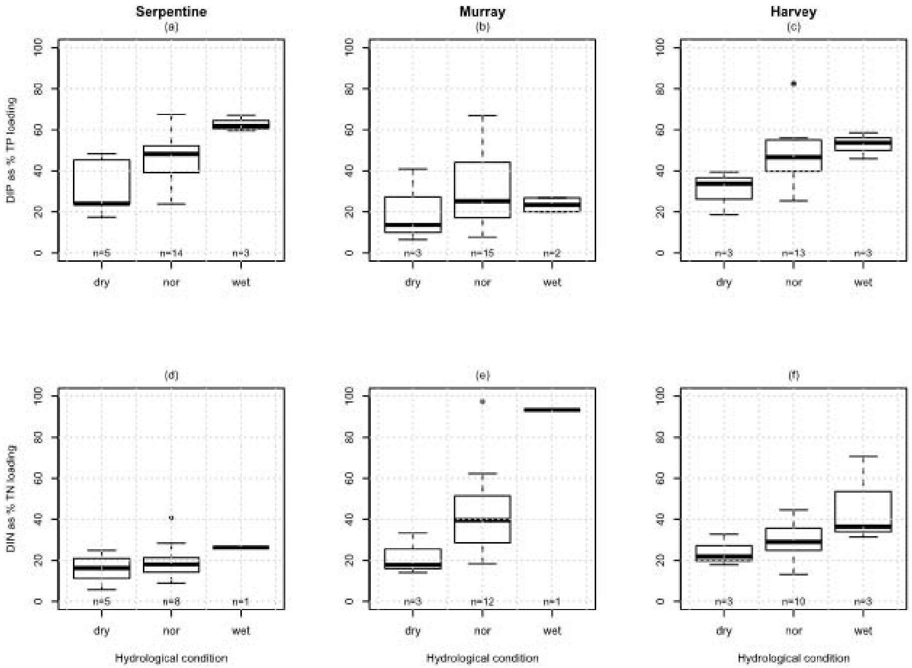

Fig. 12. Effect of hydrological condition – "dry", normal ("nor"), "wet" – on partitioning of: **(a)**–**(c)** P (DIP : TP); **(d)**–**(f)** N (DIN : TN).

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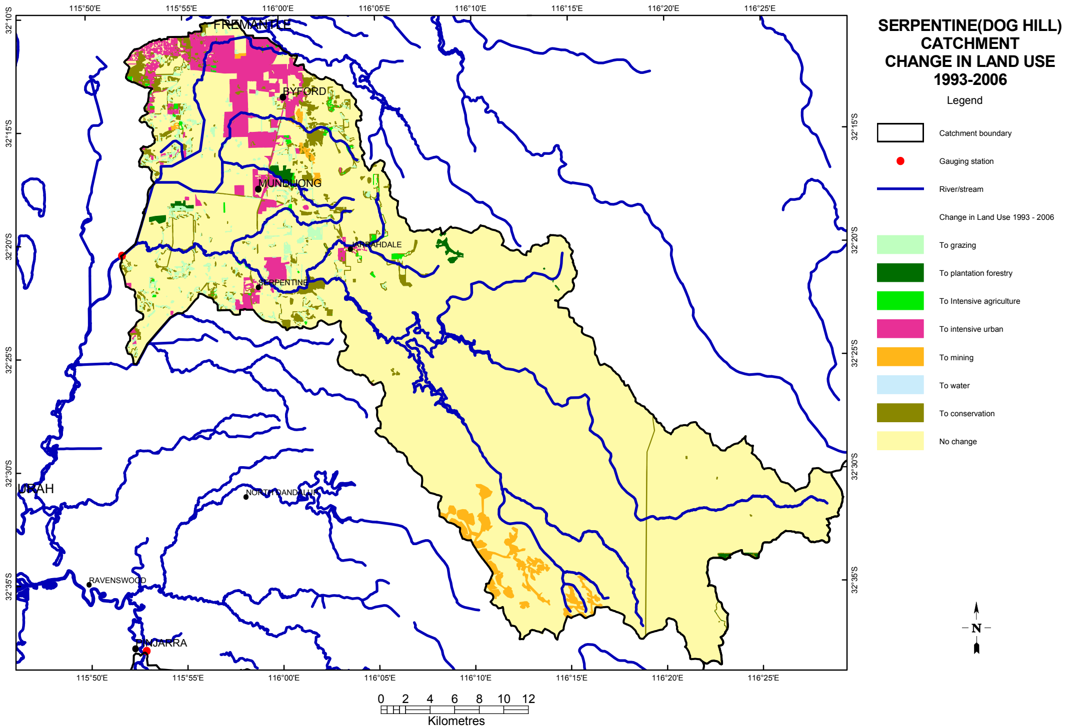

Fig. 13. Serpentine (Dog Hill) catchment: change in land use 1993 and 2006.

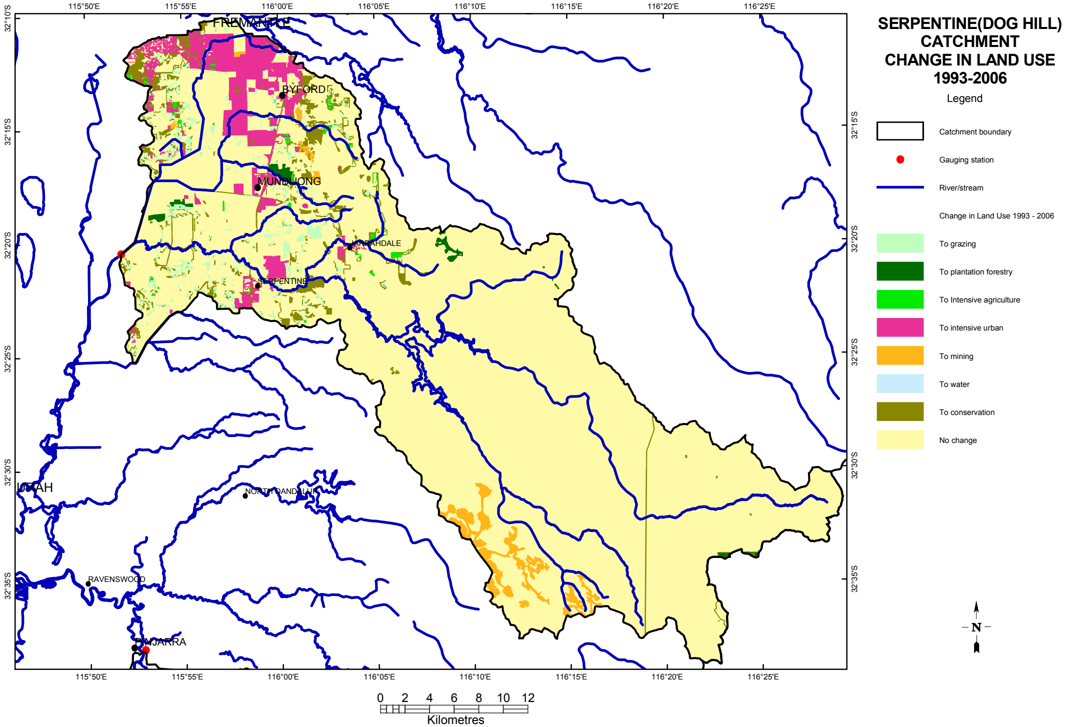

Fig. 14. Middle Murray (Pinjarra) catchment: change in land use 1993 and 2006.

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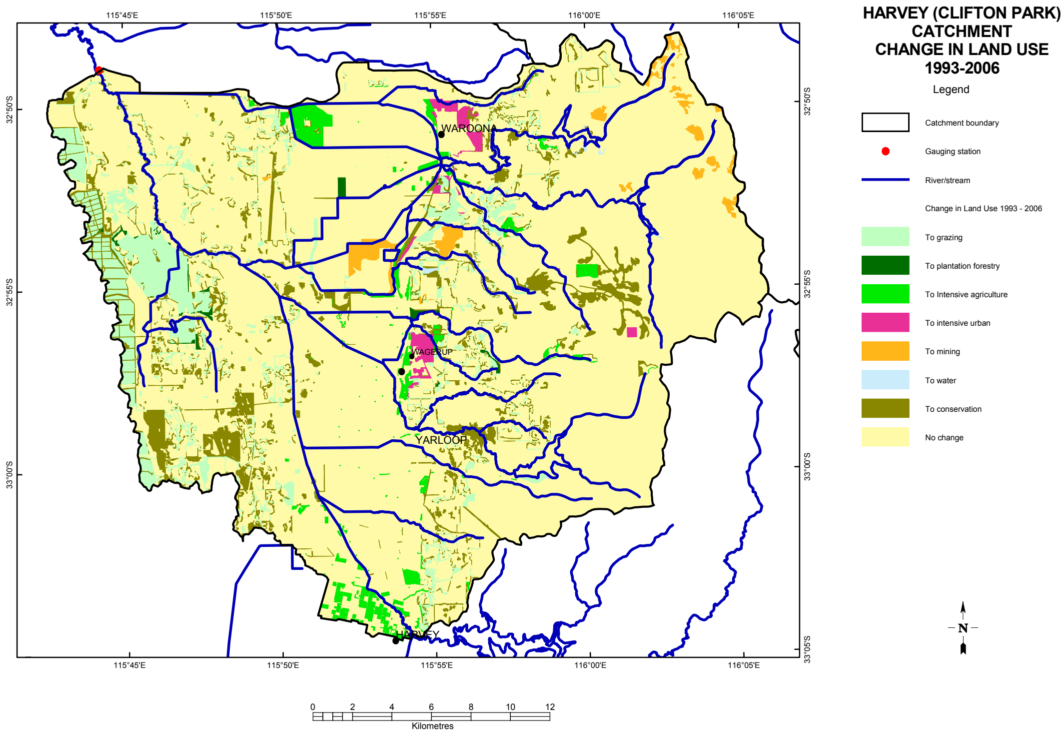

Fig. 15. Harvey (Clifton Park) catchment: change in land use 1993 and 2006.

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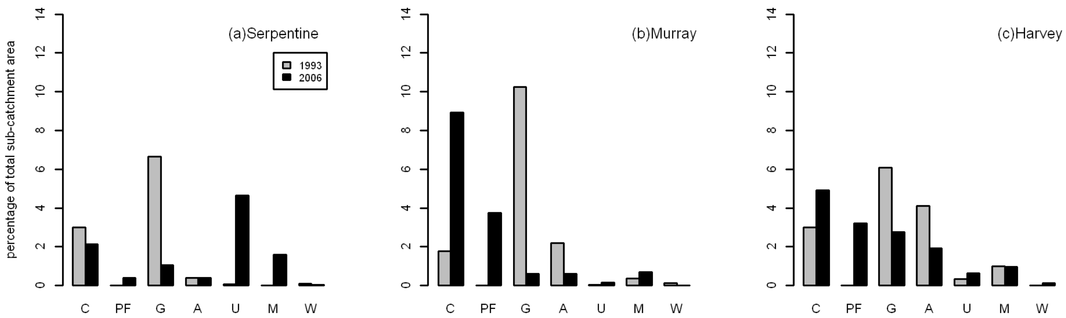

Fig. 16. Summary of land-use change between 1993 and 2006 for the three river sub-catchments (C = conservation, PF = plantation forestry, G = grazing, A = agriculture, U = urban, M = mining, W = water). Total areas considered: Serpentine = 133 333 ha, Murray = 302 208 ha (note: this represents about half of the catchment; comparable data was only available for this area); Harvey=72 700 ha.

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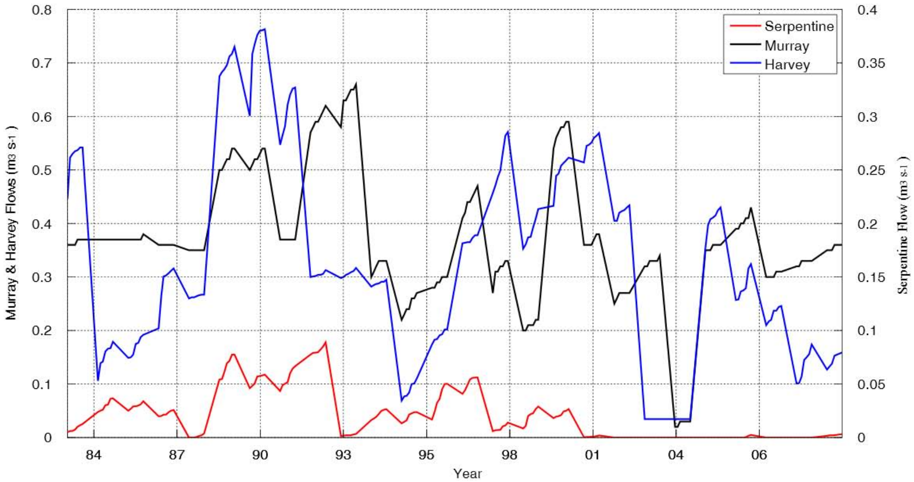

Fig. 17. Time series of the seven lowest flows per year indicating the base flow contributions for the Serpentine, Murray and Harvey Rivers.

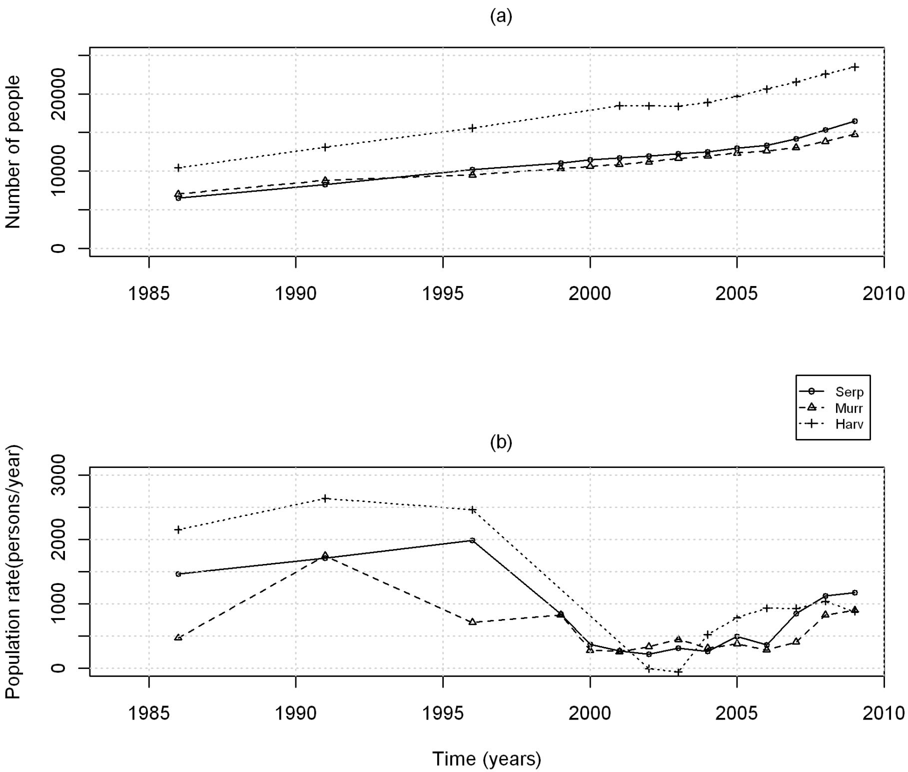

Fig. 18. Variability in **(a)** population; **(b)** population growth rate – in the three main shires of the river sub-catchments.

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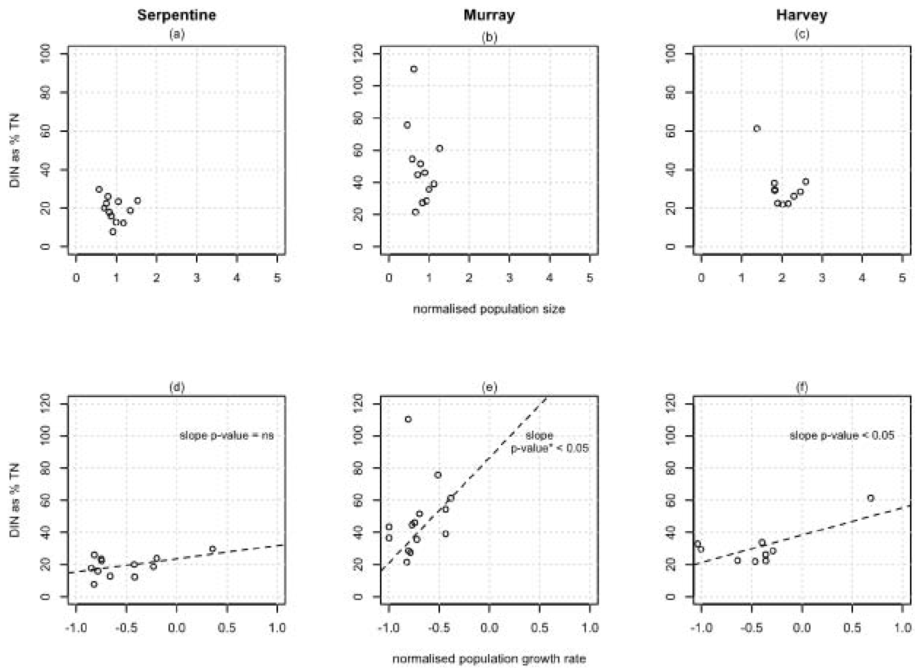

Fig. 19. Relationship between dissolved fraction of nitrogen load as a function of **(a)–(c)** the normalised population and **(d)–(f)** the normalised population growth rate (* indicates *p* value calculated without outlier).

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