



**Flow pathways and  
nutrient transport  
mechanisms drive  
hydrochemical  
sensitivity**

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**Flow pathways and nutrient transport  
mechanisms drive hydrochemical  
sensitivity to climate change across  
catchments with different geology and  
topography**

**J. Crossman<sup>1,2</sup>, M. N. Futter<sup>3</sup>, P. G. Whitehead<sup>2</sup>, E. Stainsby<sup>4</sup>, H. M. Baulch<sup>5</sup>,  
L. Jin<sup>6</sup>, S. K. Oni<sup>3</sup>, R. L. Wilby<sup>7</sup>, and P. J. Dillon<sup>1</sup>**

<sup>1</sup>Chemical Sciences, Trent University, Peterborough, ON, Canada

<sup>2</sup>Oxford University Centre for the Environment, Oxford University, Oxford, UK

<sup>3</sup>Department of Aquatic Science and Assessment, Swedish University of Agricultural Science, Uppsala, Sweden

<sup>4</sup>Ontario Ministry of Environment, Etobicoke, ON, Canada

<sup>5</sup>School of Environment and Sustainability and Global Institute for Water Security, University of Saskatchewan, Saskatoon, SK, Canada

<sup>6</sup>Department of Geology, State University of New York College at Cortland, Cortland, NY, USA

<sup>7</sup>Department of Geography, Loughborough University, Leicestershire, UK

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Correspondence to: J. Crossman (jillcrossman@trentu.ca)

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## Abstract

Hydrological processes determine the transport of nutrients and passage of diffuse pollution. Consequently, catchments are likely to exhibit individual hydrochemical responses (sensitivities) to climate change, which is expected to alter the timing and amount of runoff, and to impact in-stream water quality. In developing robust catchment management strategies and quantifying plausible future hydrochemical conditions it is therefore equally important to consider the potential for spatial variability in, and causal factors of, catchment sensitivity, as to explore future changes in climatic pressures. This study seeks to identify those factors which influence hydrochemical sensitivity to climate change. A perturbed physics ensemble (PPE), derived from a series of Global Climate Model (GCM) variants with specific climate sensitivities was used to project future climate change and uncertainty. Using the Integrated Catchment Model of Phosphorus Dynamics (INCA-P), we quantified potential hydrochemical responses in four neighbouring catchments (with similar land use but varying topographic and geological characteristics) in southern Ontario, Canada. Responses were assessed by comparing a 30 year baseline (1968–1997) to two future periods: 2020–2049 and 2060–2089. Although projected climate change and uncertainties were similar across these catchments, hydrochemical responses (sensitivity) were highly varied. Sensitivity was governed by soil type (influencing flow pathways) and nutrient transport mechanisms. Clay-rich catchments were most sensitive, with total phosphorus (TP) being rapidly transported to rivers via overland flow. In these catchments large annual reductions in TP loads were projected. Sensitivity in the other two catchments, dominated by sandy-loams, was lower due to a larger proportion of soil matrix flow, longer soil water residence times and seasonal variability in soil-P saturation. Here smaller changes in TP loads, predominantly increases, were projected. These results suggest that the clay content of soils could be a good indicator of the sensitivity of catchments to climatic input, and reinforces calls for catchment-specific management plans.

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## 1 Introduction

Phosphorus (P) is an essential nutrient in riverine and lotic ecosystems (Jarvie et al., 2002), however when present in concentrations surplus to requirement it can result in eutrophication, where death and decay of excess algal matter leads to reduction in stream oxygen concentrations (Nicholls, 1995; Jarvie et al., 2006). Eutrophication is now a pressing concern in many water bodies around the world, where nutrient monitoring and management are increasingly important.

There are numerous sources and pathways of P to rivers, which may travel either in the dissolved (DP) or particulate (PP) form. As PP may be rapidly converted to bioavailable DP, the movement of both forms (total phosphorus; TP) is generally monitored. Delivery to streams may be direct through sewage effluent, or more diffuse through soils (overland flow and leaching). Leaching may be a significant P transport mechanism where the ability of soil to absorb P is low (e.g. shortly after fertiliser applications), and where leachate rarely comes into contact with absorption sites (e.g. through macropore flow) (Haygarth et al., 1998; Hooda et al., 1999; Borling, 2003).

Nutrient transport pathways are influenced by hydrology, which is in turn driven by topography, geology and climate. Changes in climate, therefore, have far reaching implications for the future of watersheds, with increasing temperatures and altered precipitation patterns affecting the timing and magnitude of runoff and soil moisture, changing lake levels, groundwater availability and river discharge regimes (Gleik, 1989; Bates et al., 2008). It follows, therefore, that individual catchments are likely to respond to climate change in different ways (van Roosmalen et al., 2007). The extent to which the hydrology and nutrient concentrations of a catchment respond to alterations in climate drivers can be termed its “sensitivity” to climate change (Bates et al., 2008). In developing robust management strategies and quantifying plausible future ranges of hydrology and water quality it is important to explore possible changes in climatic and non-climatic pressures (Whitehead et al., 2009), but equally so to consider the potential for spatial variability in, and causal factors of, catchment sensitivity.

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A complicating factor when determining future conditions is climatic uncertainty. This stems from a wide range of sources, including natural variability, the inability to predict future emissions of greenhouse gases, and an imprecise understanding of the climate systems (modelling uncertainty) (Goddard and Baethgen, 2009). The unknown physics of climate systems introduces a significant source of uncertainty into Global Climate Models, known as parameter uncertainty (Wilby and Harris, 2006; Meehl and Stocker, 2007), whereby GCMs developed by different scientists may predict various outcomes under similar conditions. It is therefore important to explore a range of different plausible futures, to provide a better understanding of the vulnerability of watersheds (McSweeney and Jones, 2010), including possible threshold effects. Only recently have credible techniques become available to more fully quantify the uncertainty stemming from parameter uncertainty. These methods include multi-model- and perturbed physics ensemble (PPE). The former explores uncertainties stemming from differences in model structure by combining outputs from multiple GCMs (Collins et al., 2006). The PPE alters the physical parameterisation of a single GCM, within scientifically accepted ranges, to create an array of model variants with specific climate sensitivities (UKCP, 2012). As alterations are made to the GCM in a systematic way, the effects of different sensitivities on climate projections can be quantified (Collins et al., 2006), and a wider range of physically plausible future climates explored (McSweeney and Jones, 2010).

This study explores the underlying determinants of catchment hydrochemical sensitivity to climate change by applying a PPE to hydrological and water quality models of four major sub-watersheds with contrasting geological characteristics. Objectives include (a) comparing the hydrological and water quality sensitivity (to climate uncertainty) across catchments with different geology and topography and (b) generating likelihood estimates of future water quality, having accounted for uncertainty in GCM parameters. These analyses are intended to support adaptive management responses. We apply five variants of the regionally downscaled Met Office Hadley Centre PPE, to sub-watersheds of a large lake in Southern Ontario, Canada (Lake Simcoe).

This region was chosen for study as 50 years of research has been undertaken into the sources and pathways of phosphorous. Agricultural practices, urbanisation, wetland drainage and sewage effluent have all been linked to increasing P levels in the Lake (Evans et al., 1996; LSRCA, 2009; Jin et al., 2013), and associated with depleted oxygen concentrations and decreasing populations of Trout, Herring and Whitefish (LSEMS, 1995).

## 2 Methods

### 2.1 Site description

Lake Simcoe is situated in Southern Ontario, approximately 45 km north of Toronto, Canada. It drains north into the Severn River, and ultimately into Georgian Bay (Fig. 1). The total catchment area is 2914 km<sup>2</sup> (with a lake area of 720 km<sup>2</sup>), comprised of 21 sub-watersheds. The four focus catchments (referred to in this study as Holland, Pefferlaw, Beaver and Whites) are situated in the south, and contribute some of the most significant P-inputs to the Lake (Winter et al., 2002, 2007). The combined east and west branches of the Holland forms the largest area at 614 km<sup>2</sup>. The Pefferlaw and Beaver are a similar size at 444 and 325 km<sup>2</sup>; and the Whites is smallest at 85 km<sup>2</sup>. All catchments are characterised by a dominance of agricultural landuse (Table 1), though the Beaver and Whites have the highest coverage at over 65%. The Holland has the greatest degree of urbanisation at ~ 20%. There are three sewage treatment works (STW) in the Holland, two in the Beaver, and one in the Pefferlaw. Being much smaller there are no STWs within the boundaries of the Whites.

A proportion of the headwaters of each catchment are located in the Oak Ridges Moraine, an important area of groundwater recharge (Johnson, 1997), characterised by steep slopes, high infiltration capacity and relatively low surface overland flow (LSRCA, 2012a). The lower reaches of each catchment flows through the Peterborough drumlin fields, Algonquin Plains and Rolling Plains (Johnson, 1997). These are characterised

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by low slopes, and clayey-till soils (LSRCA, 2012a). This transition in topography and soil permeability creates areas of water logging and marshlands proximal to the Lake (Miles, 2012).

The contrasting soil properties lead to variations in surface overland flow and soil water residence times, and the catchments can be split into two distinct typologies. In the Beaver and Whites, rapid through-flow and nutrient transport have been recorded (Miles, 2012), due to the higher coverage of low-permeability clayey soils (27.5 % in the Beaver and 41.9 % in the Whites) (Agriculture and Agri-Food Canada, 2010), and a high density of tile drains (LSRCA, 2012a). Such characteristics are often associated with high runoff rates and a high percentage of macropore flow (Huang, 1995; Burt and Pinay, 2005) respectively. The saturation excess threshold of these soils is low, particularly in the northern end of the catchment, where wetlands dominate (Miles, 2012). In the Holland and Pefferlaw there is a much lower coverage of clayey soils (8.3 and 12.6 % respectively), and a greater dominance of sandy-loams. Here there are larger proportions of matrix flow (less runoff), longer soil water residence times, and transport of water through these catchments is slower (LSRCA, 2012c). This may be attributed to the higher soil storage capacity, and in the Pefferlaw may be ascribed to a more limited number of tile drains and low percentage of impervious surfaces (LSRCA, 2012b) and in the Holland to extensive seasonal drainage of wetlands (LSRCA, 2012c). Wetland drainage increases soil bulk density, which results in greater soil water retention capacity, and reduction of hydraulic conductivity and of overland flow (Burke, 1967, 1975; Schlotzhauer and Price, 1999). In the Holland, over 50 % of the former marshlands are now drained in spring for agricultural purposes, resulting in extensive modification to the catchment hydrology (Nicholls and MacCrimmon, 1975; LSRCA, 2012c). Urbanisation has had little influence on surface overland flow (LSRCA, 2012c), which has been attributed to township locations in the more permeable sediments of the Oak Ridges Moraine, where high infiltration capacities counteract the effect of impervious surfaces (Oni et al., 2014).

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The climate of the study regions (1968–1997) has a distinct seasonal cycle with 30 year seasonal average peak temperatures in the summer (June–August) of between 17 to 20 °C. Minimum temperatures occur in winter (December–February) of between –4 to –6 °C. Precipitation is greatest in summer and in autumn (September–November) with between 2.90 and 3.40 mm day<sup>-1</sup> and least in spring (March–May) with between 1.95 and 2.32 mm day<sup>-1</sup>. There is a strong seasonal input of snow to the Simcoe watershed, with local meteorological stations recording a 30 year average of 92.34 cm of snow falling during winter, and 26.45 cm during spring.

## 2.2 Dynamic modelling of hydrology and phosphorus using INCA-P

The Integrated Catchment Model of Phosphorus Dynamics (INCA-P) has been applied to over 40 catchments across Europe and North America (Wade et al., 2002a; Whitehead et al., 2011, 2014; Jin et al., 2013; Baulch et al., 2013 inter alia). It is a dynamic, process-based model, which uses a semi-distributed approach to simulate the flow of water and nutrients through the terrestrial system to river reaches, differentiated by land use type. The model can simulate fully branched river networks, with unlimited numbers of tributaries and stream orders. Information flows through the model from the individual process equations, via the sub-catchment comprised of up to six land-use types, to a network of multiple reaches and tributaries. A full mass balance is imposed at each level (Fig. S11 in the Supplement).

The flow of water and phosphorus through INCA is modelled through four storage zones (Fig. S12 in the Supplement), using a series of detailed process equations, solved using numerical integration routines (Wade et al., 2002a, b, 2007a). By analysing phosphorus inputs from diffuse sources, sewage treatment works (STW), sediment interactions and biological processes (Wade et al., 2002a) the model estimates a variety of parameters both in the terrestrial and aquatic phase. Terrestrial outputs used in this study include soil export coefficients, and daily concentrations of both soil water TDP and labile P. Aquatic outputs include daily flow amounts, and daily

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concentrations of in-stream total phosphorus (TP), total dissolved phosphorus (TDP), and particulate phosphorus (PP).

INCA-P requires a daily input time series of precipitation, temperature, hydrologically effective rainfall (HER) and soil moisture deficit (SMD). Precipitation and temperature are obtained from local meteorological stations, and HER and SMD from the rainfall–runoff model HBV (Hydrologiska Byråns Vattenbalansavdelningen). There are five main storage components within HBV, and the physical processes operating within and between these zones are represented through simplified mathematical expressions which can be adjusted through a series of parameters to within recommended ranges, to attain a best fit compared with observed river flow records (Oni et al., 2011). An individual HBV model was created for each of the study catchments.

Locally observed daily temperature, precipitation and flow data for the calibration period was input into each HBV model (PWQMN, 2009; LSEMS, 2010; LSRCA, 2010; Environment Canada, 2013; D. Woods, personal communication, 2013), and the derived HER and SMD were used to complete the daily time series required for INCA-P. For each catchment, the most proximal meteorological station data was used (Fig. 1). Where station record length was insufficient, the nearest available records were used and adjusted to the local baseline conditions using bias correction techniques of Futter et al. (2009).

Each of the four study catchments was subdivided into their constituent sub-catchment network using hydrological flow data, developed from a 2 m vertical resolution DEM (Global LandCover Facility, 2002). Landuses were grouped into five cover classes; urban, intensive agricultural, non intensive agricultural, wetlands and forest, derived from Ecological Land Classification of Ontario data (Ontario Ministry of Natural Resources, 2007).

Parameter inputs for model calibration were then calculated. P-inputs from fertilisers ( $\text{kg P day}^{-1}$ ) were calculated using the methods of Wade et al. (2007b) and Baulch et al. (2013), from local recommended P-Application rates (OMAFRA, 2009) and crop types (Statistics Canada, 2011). Application rates of P from livestock waste were

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calculated using current livestock assessment numbers (Statistics Canada, 2011) combined with Ontario livestock phosphorus nutrient coefficients (Bangay, 1976). Based on OMAFRA recommendations, model fertiliser inputs were extended over a 60 day period to intensively cropped areas, and a 120 day period to non-intensive agricultural lands beginning in late April (Baulch et al., 2013; Whitehead et al., 2011). In addition to effluent from STWs (Table 2), a large proportion of households contribute P loads through septic systems. Input loads were determined using methods of Scott et al. (2006) and Paterson et al. (2006), calculated as a function of annual P input per person, combined with septic system usage. Data used included Greenland International Consulting (2006) GIS information on households connected to septic systems, household population data (Statistics Canada, 2011), and the average TP load from excretion ( $2.6 \text{ g TP person}^{-1} \text{ day}^{-1}$ , Stephens, 2007). As the efficiency of P removal is estimated at 57 % (Whitehead et al., 2011), only 43 % of the calculated septic TP load was input to the model.

Initial soil P concentrations were based on values measured by Fournier et al. (1994), and soil equilibrium coefficients calibrated using the methods of Lepistö et al. (2013). Laboratory-derived equilibrium phosphorus concentration (EPC) and freudlinch isotherm values for different soil types (Peltouvouri et al., 2002; Väänänen, 2008; Koski-Vähälä, 2001) were applied to the dominant soil types of each land use (Olding et al., 1950; Agriculture and Agri-Food Canada, 2010). Average catchment values for EPC ranged from 0.01 in the Beaver to 0.08 in the Holland, and are consistent with those used by Baulch et al. (2013) and Whitehead et al. (2011). An overview of key input variables and sources is given in Table 2, with model structures provided in Fig. S13 in the Supplement.

### 2.3 Climate modelling using Perturbed Physics Ensemble

The PPE used in this study is designed to quantify uncertainty in model predictions (QUMP) (McSweeney and Jones, 2010), and originated from the HADCM3 SRES-A1B scenario. As suggested by McSweeney and Jones (2010), a subset of the available 17

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members were chosen which cover the fullest range of climate sensitivities (Table 3; Collins et al., 2006), whilst continuing to represent regional climatic behaviours. Members Q3 and Q10 were deemed the members of maximum sensitivity appropriate for use in the Simcoe watershed, as the temperature and precipitation patterns of high-sensitivity QUMP scenarios were less representative of the observed regional climate over a 1968–1997 baseline period.

The five members were dynamically downscaled by the Institute for Energy, Environment and Sustainability (IEESC, 2012) to 25 km<sup>2</sup> grid cells using the regional climate model PRECIS (Providing Regional Climates for Impacts Studies). Complete details of the model components within PRECIS and of its application to Southern Ontario are given in Jones et al. (2004), and IEESC (2012). PRECIS was run from 1968 to 2100, and daily outputs of mean temperature and total precipitation obtained for each ensemble member. Output grid cells from PRECIS were selected for analysis which covered the respective Simcoe Watersheds. At this resolution most watersheds fall within a single grid cell; where two or more PRECIS outputs were available for a single catchment, that which was geographically closest to the watershed's observed monitoring station was selected.

Whilst GCM outputs are not intended to be weather forecasts it is important that each ensemble member provides plausible climate information (Futter et al., 2009). The standard climatic baseline for Southern Ontario has been established as the 30 year period of 1968–1997 (IEESC, 2012). Therefore to establish the suitability of each scenario, monthly average comparisons for both temperature and precipitation were made between QUMP outputs and observed data over this baseline period. Although reproduction of temperature by QUMP members was highly successful (Fig. 2), with an average monthly  $R^2$  value of 0.99, precipitation was less accurate with an  $R^2$  of only 0.23 (Fig. 3). The distinctive seasonal patterns of minimum winter, and maximum summer precipitation values are well represented by ensembles Q0, Q13 and Q15; whereas ensemble members Q3 and Q10 present inverse seasonal patterns. Whilst removing these less accurate members from the study would restrict the range

of future conditions applied in the analysis, use of a bias correction is also questionable. This would alter the future change of each member to different extents, and in so doing would render the study incapable of directly assessing impacts of climate variability (originating from internal GCM parameter uncertainty) upon catchment responses.

In order to ensure plausible projections for the Simcoe region under all ensemble members, whilst incorporating the maximum range of conditions in the study, the Delta Change ( $\Delta$  Change) method was chosen.  $\Delta$  Change is an established technique for directly assessing impacts of climate change, and was the primary method used to generate future scenarios in the US National Assessment (Hay et al., 2000). Rather than the “direct forcing” of bias correction, which perturbs future simulations to account for biases detected during the baseline period (Lenderink et al., 2007), the  $\Delta$  Change method perturbs a time series of observed meteorological data to match projected future changes. Where there are discrepancies between baseline observed and baseline GCM data, this method assumes that the GCM is better able to simulate relative change than it is to provide absolute values (Hay et al., 2000). In the case of the PPE it also preserves the original relationship between QUMP ensemble members.

The average monthly difference between each ensemble baseline (1968–1997) and future 30 year period is analysed as the monthly  $\Delta$  Change. Future periods selected here were 2020–2049 (the 2030s), and 2060–2089 (the 2070s). These differences are applied to the observed meteorological conditions of the baseline period, so that each month in the observed dataset has undergone the same degree of change in climate as was originally demonstrated by the particular ensemble member. These new datasets are now a  $\Delta$  Change version of the original QUMP outputs from PRECIS, whereby the local conditions of each catchment are better represented.

$\Delta$  Change was applied individually to each catchment in the study, using the associated gridded PRECIS outputs and observed meteorological data. The formula used to determine the  $\Delta$  Change adjusted QUMP time series for future daily temperature ( $T_f$ , daily) and future daily precipitation ( $P_f$ , daily) follows Akhtar et al. (2008):

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$$T_f, \text{ daily} = T_o, \text{ daily} + (T_f, \text{ monthly} - T_b, \text{ monthly}) \quad (1)$$

$$P_t, \text{ daily} = P_o, \text{ daily} \times \frac{P_f, \text{ monthly}}{P_b, \text{ monthly}} \quad (2)$$

where  $T_{o, \text{ daily}}$  and  $P_{o, \text{ daily}}$  are the observed daily temperature and precipitation;  $T_{f, \text{ monthly}}$  and  $P_{f, \text{ monthly}}$  are the mean monthly QUMP simulated future temperature and precipitation;  $T_{b, \text{ monthly}}$  and  $P_{b, \text{ monthly}}$  are the mean monthly QUMP simulated baseline temperature and precipitation. Monthly  $\Delta$  change values of precipitation (%) and temperature ( $^{\circ}\text{C}$ ) are provided in Figs. SI4 and SI5 in the Supplement for reference. The new  $\Delta$  Change-adjusted temperature and precipitation time series were then passed through respective HBV catchment models to derive associated SMD and HER. Eleven time series were generated for each catchment; five ensemble members over two different future 30 year time periods, and one baseline 30 year period of observed meteorological data. Finally, these time series of temperature, precipitation, SMD and HER were used as input for the INCA-P models to generate future values of water quality (TP) and flow.

Future change in variables (TP concentrations, TP loads and hydrology) are assessed as a percentage difference between current and future time periods. In this way INCA-P model deficiencies are removed, as model errors are presumed to be similar under both current and future scenarios. The ensemble cumulative distribution function (CDF) of outputs for each variable was calculated to identify the likelihood of a change being less than a certain amount, having accounted for the projections from all ensemble members. Here, uncertainty can be calculated as the range of values projected by ensemble members at any specific probability level (Fig. 4), and “average uncertainty” is calculated as the mean value of uncertainty across *all* CDF probability levels. In addition, a metric was derived to assess catchment sensitivity independent of between-catchment variance in input climate drivers. The catchment response variables of change in hydrology ( $\text{m}^3 \text{s}^{-1}$ ) and in phosphorus concentration ( $\text{mg L}^{-1}$ ) were

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divided by change in precipitation (mm), giving an output of “catchment response per unit change in precipitation”. A similar metric was not established for unit change in temperature due to insignificant variance in this driving variable between catchments. Sensitivities were compared across catchments to provide an indicator as to which underlying factors might contribute to their responses. A greater understanding of catchment sensitivity would be highly beneficial, where management strategies could focus on reducing the extent of hydrochemical responses to climatic variability, as opposed to a project-then-act approach, which relies upon the accuracy of individual climate projections.

### 3 Results

#### 3.1 INCA-P model calibration

Calibration periods were selected that maximise available spatial resolution and temporal longevity of observed data. This helps to ensure that parameterisation is plausible across as wide a range of conditions as possible, and has proven most effective in application of water quality models to predictive studies (Larsen et al., 2007). As a result, the calibration period for each catchment varied according to availability of data (Fig. SI3 in the Supplement). The short observed record for the Whites (2010–2012) limited calibration to three years, however intensive monitoring over 17 sites enabled a detailed calibration across the whole catchment. A summary of model coefficients is provided in Table 4, an example daily model output given in Fig. 5, and spatial variability of model fit throughout the catchment provided in Fig. 6. The Pefferlaw is not included within the latter, due to the limited spatial distribution of in-stream records (Fig. SI3 in the Supplement), where sampling has been conducted predominantly within the main channel.

During calibration periods there was considerable spatial variability in TP concentration model coefficients within each catchment (Fig. 6). In general, model accuracy

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was greatest in catchment outflows and lower in tributaries. In the Holland the greatest accuracy was achieved for flow near this outflow, with  $R^2 = 0.95$ , and model error =  $-24.78\%$ . The accuracy of TP concentrations was also highest in the main channel, with an  $R^2 = 0.72$ , and model error =  $-4.36\%$ . TP loads are well represented at the downstream extent where  $R^2 = 0.74$ . In the Pefferlaw, model coefficients within the main channel range from  $R^2 = 0.92$  to  $0.65$  for flow, and model error from  $14.06$  to  $46.28\%$ . Near the outflow, explained variance in annual TP concentrations is fair ( $R^2 = 0.37$ ) with an error of  $-23.41\%$ . This need not be interpreted as a poor model fit as accuracy varied significantly with season, where model error is as low as  $-12.97\%$  in winter, but as high as  $-35.97\%$  in spring and can be attributed to difficulty in representing occasional peaks in TP during March and April. Model accuracy in reproducing annual loads is excellent with  $R^2 = 0.71$ .

In the Beaver, the greatest model flow accuracy was found in the upstream tributaries, where flow  $R^2 = 0.98$ , and error was as low as  $-15.30\%$ .  $R^2$  of TP concentrations =  $0.79$  and error was  $+4.4\%$ . The amount of explained variance for TP load was also high (up to  $0.82$ ). At the downstream extent, flow variability was simulated well, with  $R^2 = 0.85$ , though model error was  $+33.50\%$ . Although the fit to TP concentrations at this site were poor ( $R^2 = 0.05$  and model error =  $-58.37\%$ ) that of TP loads remained good ( $R^2 = 0.81$ ). Despite the shorter duration of observed data available for the Whites, the amount of explained variance at the outflow for TP concentrations, flow and TP loads were  $0.92$ ,  $0.33$  and  $0.87$  respectively. Average annual flow error at this site was only  $3.03\%$ . The model marginally under-predicts TP concentrations with an annual error of  $-18.56\%$ , which is lowest during autumn and spring ( $-6.60$  and  $7.56\%$  respectively) and highest during summer ( $-36.23\%$ ). In headwaters and tributaries,  $R^2$  of flow and TP loads of up to  $0.90$  and  $0.94$  were achieved. Success in modelling TP concentrations was highly spatially variable (Fig. 6), with a maximum  $R^2 = 0.47$ .

## 3.2 Export coefficients

Average export coefficients were calculated for each catchment landuse type by dividing INCA source apportionment outputs ( $\text{kg TP km}^{-2}$ ) over the years of model runs ( $\text{kg TP km}^{-2} \text{ year}^{-1}$ ). Values were highly variable between sites, ranging from 3.43  $\text{kg km}^{-2} \text{ year}^{-1}$  in the Beaver, to 13.05  $\text{kg km}^{-2} \text{ year}^{-1}$  in the Holland (Table 5). These findings are consistent with previous studies of these catchments (Thomas and Sevean, 1985; Winter et al., 2007; Baulch et al., 2013), although higher modelled exports have previously been reported for the Holland (Winter et al., 2007). This could be attributed to the larger spatial domain used in this study (covering both East and West branches of the river), plus a recent decline in TP exports due to implementation of best management practices.

In each catchment, the highest exports of TP originated from agricultural soils, ranging from 3.71  $\text{kg km}^{-2} \text{ year}^{-1}$  (Beaver) to 16.13  $\text{kg km}^{-2} \text{ year}^{-1}$  (Holland). The lowest exports of TP originated from Sewage treatment works, with the lowest outputs from the Whites (no output) and the greatest from the Holland (0.76  $\text{kg km}^{-2} \text{ year}^{-1}$ ). It is notable that in the Holland exceptionally high export coefficients were found in wetlands (14.41  $\text{kg ha}^{-1} \text{ year}^{-1}$ ). This could be attributed to the recent drainage of former wetlands and use for intensive agriculture.

The percentage contribution of each source to TP output from the catchment was calculated by multiplying each coefficient by landuse area, and (in the case of STWs) by calculating the load differences resulting from models run with and without STW inputs (Table 5). In the Whites, Beaver and Pefferlaw, agriculture was by far the major source of TP (ranging from 64.39 to 69.86%). In the Holland, although agricultural sources dominate, there is also a large contribution from urban areas and STW (14.22 and 4.25 %, respectively).

Terrestrial model outputs indicate significant seasonal variability in soil TDP concentrations within the agricultural areas of each catchment, with large increases in summer following fertiliser additions, and associated increases in the soil labile pool.

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Models also exhibited a seasonal minimum of labile P concentrations during winter and spring, following plant uptake and exhaustion of TDP surface pools (Fig. SI6 in the Supplement).

### 3.3 Climate change

Projected changes in temperature and precipitation for 10, 50 and 90 % likelihood levels indicate that changes will become progressively more extreme and more likely between the 2030s and 2070s (Fig. SI7 in the Supplement). Notably, there is very little difference between catchments in projected climatic drivers; by 2070 at the 50 % likelihood level there is a cross catchment range of only 0.07 °C (temperature) and 4.18 % (precipitation). The average temperature uncertainty within all catchments was low (Table 6), at < 1 °C in 2030, and < 2 °C in 2070. Average precipitation uncertainty was higher, at < 19 % in 2030 and < 23 % in 2070. Of note is the similarity in uncertainty between catchments (Fig. 7a–d), with a cross-catchment range in average temperature uncertainty of only 0.03 (2030) and 0.08 (2070) (Table 6), and cross-catchment range in average precipitation uncertainty of only 3.5 % (2030) and 1.05 % (2070) (Table 6).

Seasonal changes in climate drivers (Figs. SI8 and SI9 in the Supplement) demonstrate that the largest increases in temperature generally occur during winter. Average seasonal changes in temperature were similar between catchments, with a maximum cross-catchment range occurring during winter (0.18 °C in 2070). The Pefferlaw was, however, consistently projected to experience the greatest winter increases (+3.00 °C in 2030 and +5.90 °C in 2070), and the Whites the least (+2.94 °C in 2030 and 5.80 °C in 2070). The largest changes in precipitation were projected to occur during winter and spring, with lower increases and modest reductions during summer and autumn. Seasonal precipitation changes varied more markedly between catchments than did temperature, with a maximum cross-catchment range during winter of 10.88 % (2070). The largest changes in winter precipitation are projected to occur in the Holland (12.17 %, 2030 and 26.20 %, 2070), and the lowest in the Pefferlaw (5.80 %, 2030 and 15.32 %, 2070). The largest reductions in summer precipitation are projected for the Whites

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(−0.68 % in 2030 and −9.23 % in 2070), and the lowest for the Holland (+2.84 % in 2030 and −2.44 % in 2070).

### 3.4 Sensitivity of hydrology and water quality

#### 3.4.1 Hydrologically effective rainfall and river flow

5 Similar to temperature and precipitation, the likelihood and extent of flow changes increased between the 2030s and 2070s (Fig. S110 in the Supplement). There were, however, markedly greater differences in projected flow changes than for corresponding climatic drivers. At the 50 % likelihood level there is a cross catchment range of 23.37 % by 2070, where projected changes are significantly smaller in the Holland and Pefferlaw (−5.82 and −8.20 %) compared to the Whites and Beaver (−29.19 and −20.35 %) respectively (Fig. 8a). The average flow uncertainty within each catchment was also generally higher than that of temperature and precipitation, reaching up to 43.15 % (2030) and 40.07 % (2070) (Table 6). In contrast to climatic drivers, average uncertainty in projected flow varied considerably between catchments, with a cross-catchment range of 19.89 % (2030) and 12.46 % (2070), and was consistently largest in the Whites and lowest in the Pefferlaw.

15 Seasonal changes in HER and flow (Figs. S111 in the Supplement and 12) demonstrate that, similar to precipitation, the largest increases occur during winter, with reductions occurring during summer and autumn. In spring, however, in contrast to the increases projected by precipitation, large reductions are projected for both HER and flow. Similar to precipitation, the maximum cross-catchment range occurred in winter, though seasonal variability in HER and flow between catchments was notably greater than that of climatic drivers, with a winter HER range of 38.98 % (2030) and 68.11 % (2070) and flow range of 21.73 % (2030) and 46.78 % (2070). Similar to precipitation, 20 the Holland projects the largest mean seasonal increases in winter HER and flow (of up to 96.08 % HER and 84.63 % flow), whilst the Pefferlaw and Beaver project the smallest, with projected change as low as 27.97 % (HER) and 37.95 % (flow). The largest mean 25

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seasonal reductions in summer flow and HER occur in the Whites, and the smallest in the Holland and Pefferlaw.

Seasonal changes in soil moisture deficit (SMD) were also analysed. Annually, SMD increased in all catchments, though increases in the Whites and Beaver (up to 45.84%) were up to four times greater than those in the Holland and Pefferlaw (up to 11.03%). Seasonally, the largest SMD increases were projected during spring, and were consistently higher in the Beaver and Whites than those in the Holland and Pefferlaw.

To determine the sensitivity of catchment HER to precipitation input, the HER generated per unit change in precipitation was calculated (Table 7). On average, the Holland and Pefferlaw yield the least HER in response to changes in precipitation, whilst the Beaver and Whites generate the most. During the baseline period, a greater proportion of HER flowed as surface runoff in the Beaver and Whites than in the Holland and Pefferlaw (up to 82% in the Whites compared to less than 46% in the Pefferlaw and Holland). This difference amplified under future climate conditions, where flow through the soil matrix increased by up to 24% in the Holland and Pefferlaw, but by less than 13% in the Beaver and Whites. Proportions of overland and subsurface flow varied by landuse type, with highest runoff proportions in saturated wetlands and urban areas, and lowest in forests and intensively farmed (and drained) agricultural lands.

### 3.4.2 Water quality

By 2070 total annual TP loads were projected to decrease in the Beaver and Whites by -14.70 and -13.13% respectively, but lower reductions, or even increases were projected for the Holland and Pefferlaw, of 14.69 and -1.03% respectively (Table 8). Projections varied considerably between catchments with a range of 14.59% (2030) to 29.39% (2070).

Again projected changes in monthly TP concentrations and loads at the 10, 50 and 90% likelihood levels amplify between 2030 and 2070 (Fig. SI13 in the Supplement) and indicate that larger changes are more likely by 2070. The cross-catchment range of TP loads is considerable, and at 32.67% (2070 at the 50% likelihood level) is wider

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than that of all other variables. Similarly there is a larger difference between catchments in TP concentration changes than for corresponding climatic drivers (8.88 % by 2070). Reductions in TP concentration are projected at the 50 % likelihood level, and are more extreme in the Whites and Beaver than in the Holland and Pefferlaw. Similarly, at the 50 % likelihood level markedly higher monthly reductions in TP loads are projected for the Whites and Beaver (−39.66 % by 2070) compared to the Holland and Pefferlaw (−11.15 by 2070).

In some catchments (Holland and Pefferlaw) the average uncertainty for TP concentrations was lower than that of the corresponding climatic driver. However, similar to flow, uncertainty varied significantly between catchments (Table 6), with a cross-catchment range of 14.97 % (2030) and 16.50 % (2070). In contrast, the average uncertainty for TP loads within each catchment was markedly higher than corresponding catchment drivers, flow and TP concentrations, at 30.94 % in 2030, and 20.4 % in 2070. Average uncertainty of TP concentrations was consistently highest in the Whites and Beaver (Table 6). Similarly, uncertainty in TP loads is highest in the Whites and lowest in the Pefferlaw.

Seasonal changes in TP concentrations demonstrate that the largest increases are projected during winter (up to +7.63 %) and the largest reductions during summer and autumn (up to −26.63 %) (Fig. 10), and during this period are positively associated with changes in HER and flow. In spring, however, only in the Beaver and Whites did projected TP reductions (up to −9.03 %) correspond with projected reductions in HER and flow. In contrast, increases in spring TP concentrations are projected for the Holland and Pefferlaw (up to 3.85 %), and are negatively associated with projected hydrological changes (flow reductions). Accordingly, the spring cross-catchment range of projections was high (9.31 % in 2030 and 12.88 % in 2070). Ensemble average seasonal changes in TP concentration varied to a greater extent between catchments than did corresponding seasonal climatic drivers with a maximum cross-catchment range in autumn of 22.28 % (2070).

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Seasonal changes in TP loads demonstrate that, similar to HER and flow, increases are projected during winter and reductions projected during spring, summer and autumn. Similar to hydrological and climatic variables, the maximum cross-catchment range occurs during winter (26.40 % in 2030, and 53.23 % in 2070), and minimum in spring (12.36 % in 2030, and 19.1 % in 2070). The degree of difference in TP loads between catchments is, however, notably higher than for all other variables, suggesting additional factors are influencing TP loads. In winter, corresponding with climatic and hydrological changes, markedly higher increases in TP load are projected for the Holland (56.16 % in 2030, and 97.01 % in 2070), than for the Beaver (29.76 % in 2030 and 43.78 % in 2070). In summer, greater reductions in TP loads are projected for the Beaver and Whites, (9.61 and -14.75 % in 2030 respectively; -40.03 and -45.93 % in 2070), than for the Pefferlaw and Holland (-2.21 and -6.62 % in 2030 respectively; -15.07 and -20.93 % in 2070). This large cross-catchment difference in seasonal balances likely accounts for a significant portion of the difference in projections of annual loads between the Pefferlaw and Holland (increases) and Beaver and Whites (reductions).

An analysis of change in TP ( $\text{mg L}^{-1}$ ) per unit change in precipitation was undertaken, to determine catchment sensitivity to climate drivers (Table 9). The Beaver and Whites had a higher sensitivity to changes in precipitation throughout the year (0.06 and  $0.14 \text{ mg L}^{-1}$  TP generated per unit of change in precipitation), compared to the Holland and Pefferlaw ( $0.02$  and  $0.01 \text{ mg L}^{-1}$  TP per unit change in precipitation). In the Beaver and Whites the majority of changes in TP export occurred during spring and winter, in contrast to the Holland and Pefferlaw where greater changes occurred during summer and autumn.

## 4 Discussion

### 4.1 Impact of a changing climate on hydrology and water quality

Climate change and variability presents long term water management challenges both now, and persisting into the future. Results show that changes in climatic drivers (temperature and precipitation) become progressively more likely and extreme between the 2030s and 2070s, increasingly perturbing catchment hydrology and water quality from present conditions. Whilst changes in climatic drivers were similar in each study catchment, responses in HER and flow varied considerably between sites. With a significant seasonal snowmelt influence, catchments such as those within the Lake Simcoe watershed may be very sensitive to climatic inputs (Barnett et al., 2005), where even small changes in climate may have large implications for catchment hydrology (Hamlet et al., 2005; Barnett et al., 2005), specifically with respect to the magnitude and timing of snowfall and snowmelt. With the greatest increases both in temperature and in precipitation projected to occur during winter, larger quantities of precipitation previously falling as snow might in future fall as rain, which could result in an earlier snowmelt of reduced magnitude (Regonda et al., 2005; Crossman et al., 2013a, b). Projected soil moisture deficits (SMD) suggest that whilst in winter these higher inputs of rain (as opposed to snow) and an earlier snowmelt will limit rises in SMD, in spring a marked increase is to be expected, due in part to the earlier depletion of frozen water stores.

Seasonally, the direction of change in projected HER and flow did not always match those of climatic drivers. Although all indicated more extreme and likely changes between the 2030s and 2070s, spring reductions in HER and flow contrast markedly to projected precipitation increases. HER and flow are affected by a number of variables, including evapotranspiration and preceding soil moisture conditions. It is likely, therefore, that spring reductions in HER and flow are due to the increases in spring SMD, the magnitude of which was not offset by increases in spring rainfall.

The response of TP concentrations to climatic drivers also varied between catchments. In the Beaver and Whites the direction of change in TP concentration was

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consistently positively associated with that of HER and flow; whereas in the Holland and Pefferlaw a negative association was demonstrated in spring. These different hydrological and water quality responses to very similar climatic drivers are significant in terms of annual TP loads, where large annual reductions were projected for the Beaver and Whites, compared to much smaller reductions, and even some increases, projected in the Holland and Pefferlaw. Differences in hydrological flow pathways and mechanisms of nutrient delivery are a possible explanation for these different responses.

Model calibrations demonstrated that in each catchment TDP soil water concentrations and labile P concentrations increased in summer where fertilisers and plant decomposition enrich stores (Haygarth et al., 1998). When TDP is present in excess of plant requirements, it is transported from these pools to increase in-stream concentrations via overland and subsurface flow of soil water in highly fertilised organic soils, with low phosphorus sorption capacities i.e., shortly after the application of fertilisers in areas of shallow water tables e.g. wetlands (Borling, 2003). By late autumn, the surface pools of TDP have been exhausted. Lower concentrations of TDP are delivered through subsurface flows, and the soils release P to re-establish an equilibrium. By winter, the labile pool is at a seasonal minimum (Weaver et al., 1988; Fig. SI6 in the Supplement), and the soil sorption capacity is high (Hoseini et al., 2013), due to excess summer leaching, and loss of organic matter which opens up additional P-binding sites in the soil. The soil matrix therefore becomes depleted in TDP and the leachate that reaches the stream in spring and winter is less P-enriched than it was during the summer months.

Where catchments, such as the Beaver and Whites, have significant overland and macropore flow contributions, or tile drainage (where rapid flow mobilises PP, and bypasses P-binding sites in the soils, Hooda et al., 1999), TP continues to be delivered directly to the streams from soils in spring (Heathwaite and Dils, 2000), and a positive relationship between HER and TP is maintained. Under future climates, spring flow and TP concentrations are reduced simultaneously. However, where catchment pathways

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are dominated by soil matrix flow, the dilute leachate enhanced by spring meltwater has a significant impact on in-stream TP concentrations (Borling, 2003), and a negative relationship between HER and TP is created. When future spring HER is reduced (and less dilute leachate delivered to streams), the in-stream TP concentrations increase.

5 This effect may be further enhanced in the Holland and Pefferlaw catchments due to dilution of sewage treatment work contributions (point sources).

The large reductions in annual TP loads of the Whites and Beaver are projected due to large scale reductions in flow and TP concentrations in spring, summer and autumn, combined with only small scale increases in winter flow and TP concentrations. In contrast, spring flow reductions in the Holland and Pefferlaw enhance TP concentrations, which in combination with larger scale winter flow and TP concentrations (and smaller scale summer flow reductions), leads to projections of annual increases in TP loads.

The earlier thawing of frozen soils in spring under a changing climate may also influence nutrient flow pathways. The projected increase in proportion of subsurface flow under a future climate could lead to further interactions with the soil matrix. In the Holland and Pefferlaw, where there are longer residence times, this may be an additional factor behind the dilution of the spring and winter leachate. However, in the Beaver and Whites, the macropore flow and tile drainage means that additional subsurface flow has a limited effect on soil water concentrations reaching the stream. A final consideration is the drainage of wetlands (polders) in the Holland River during spring (Burke, 1967, 1975), where artificial drainage of soils can significantly increase levels of P lost through subsurface leaching (McDowell et al., 2001). This practice might therefore contribute to the negative HER associated with TP during spring, where the addition of artificial drainage waters with high TP concentrations will in future be less diluted by flows with a lower spring melt contribution.

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### 4.2 Sensitivity of hydrology and water quality to changing climatic drivers

In all catchments, uncertainty in temperature is low (across the range of QUMP scenarios generated by the PPE), and similar between catchments. As is common amongst



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climate change studies, uncertainty in precipitation is higher (Hawkins and Sutton, 2011; Maskey et al., 2004), though remains relatively consistent between sites. Importantly, hydrological (HER and flow) uncertainty is considerably higher than corresponding climatic drivers, and varies more significantly between catchments. The catchment-specific response can be defined by the quantity of HER generated per unit of precipitation input (Table 7). This relative index of HER sensitivity to climate change normalises the catchment response from differences in original driving forces (precipitation). On average, the Beaver and Whites catchments demonstrated a greater HER sensitivity to precipitation change ( $> 0.93$  mm) than the Holland and Pefferlaw ( $< 0.55$  mm). This sensitivity might be attributed to shorter soil water residence times in the Beaver and Whites, whereby more rapid soil drainage through macropores and tile drains results in prompt responses of soil moisture content to changes in precipitation; and the dominance of overland flow results in greater exposure to evaporation and rising temperatures. As a result, reductions in summer and autumn precipitation have a greater impact upon SMD in the Beaver and Whites (as indicated by model results) and thus upon HER and flow. Similarly, reductions in spring-melt waters within these catchments have a greater impact on SMD, as soils with a dominant overland flow component would previously have responded most rapidly and significantly to snowmelt input (Dunne and Black, 1971).

In contrast, in the Holland and Pefferlaw projected changes in SMD are lower, and the impact of a changing climate upon hydrology less extreme, due to a higher soil storage capacity, longer soil water residence times, and a greater proportion of water directed through the soil matrix. Slow passage of waters through soils in the Holland and Pefferlaw reduces its response rate to precipitation changes and meltwater reductions, and its exposure to evaporation (Dunne and Black, 1971; van den Hurk et al., 2004), meaning soil moisture deficits can be recharged with a lesser affect upon HER and stream flow.

The sensitivity of TP concentrations to changing climate also varies considerably between catchments, with a greater response of TP per unit change in precipitation in

the Whites and Beaver (up to 0.14 mg L<sup>-1</sup>) than in the Holland and Pepperlaw (up to 0.02 mg L<sup>-1</sup>). In Simcoe this variance between catchments appears to be associated with flow pathways and timings of nutrient export which may act as a buffer to uncertainty within some catchments. For instance, in the Holland and Pepperlaw, the majority of changes in TP export are associated with changes in future summer and autumn precipitation (Table 9), despite there being smaller absolute changes in water volumes during these periods. This is likely due to the high mobility of soil TP in the Holland and Pepperlaw at this time of fertiliser applications, with high initial P soil concentrations, and limited P sorption capacities. As the uncertainty of future climate change is lowest during this period, these are the catchments for which the lowest TP uncertainty is calculated. During the periods of high climate uncertainty (winter and spring), TP mobility is low, and the effects of the climate change uncertainty upon water quality are buffered. In the Beaver and Whites, a much larger proportion of the changes in TP export occurs during winter and spring. This is likely due to the high runoff rates and macropore flow, which facilitates movement of TP directly to the stream during all seasons. Climate uncertainty is highest during the large projected spring and winter changes, therefore uncertainty in future TP concentrations are higher in these catchments. Given that nutrient loads are directly derived from a combination of flow and TP concentrations, it follows that the uncertainty from each propagates up into the load estimations. As such, uncertainty of future TP loads is also greatest in the Whites.

It is evident then that the future certainty in both hydrology and water quality depends not only upon climatic inputs (between which there is little difference in these catchments), but also largely upon the relative sensitivity of a catchment to changing drivers. Results from this study suggest that catchment sensitivity is strongly influenced by geology, seasonal P-inputs and P-saturation thresholds. Sensitivity to climatic drivers was highest in clayey catchments, dominated by overland flow, with little influence of P-saturation (Beaver and Whites); it was lowest in sites with greater contributions from soil matrix flow, and where seasonal variability in soil P-saturation had a marked influence on water quality (Holland and Pepperlaw). It is likely that these characteristic drivers

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of sensitivity will be applicable to other catchments. For instance, van der Hurke (2004) determined that future interannual variability in wintertime runoff in the Rhine was smallest in catchments with high storage capacities, whilst van Roosmalen et al. (2007) determined across a range of geological sites in Denmark, that sites with clayey soils responded to precipitation change with the highest increases in stream discharge and overland flow proportions. The consistency of driving forces behind catchment sensitivity to climate change requires further investigation, but indicates that the clay content of soils might be used as an indicator of catchment hydrochemical sensitivity to climate change.

The overall outcome of this study indicates that management strategies might focus on internal processes dynamics that define the extent of hydrochemical responses to changes in climatic input, and as such reinforces the call for catchment-specific management plans. In the Holland and Pefferlaw, where the majority of P export appears to be derived from leachate during summer and autumn, a reduction in labile P concentrations and an increase in soil sorption capacity would be beneficial. It has been shown that soil P levels can take over 20 years to fully recover from extensive periods of excess fertiliser applications (McCollum, 1991; McLauchland, 2006), but may gradually be achieved through methods such as avoidance of nutrient applications in excess of plant requirements (Whitehead et al., 2011), and establishing nutrient vulnerable zones where use is no longer required. In the Beaver and Whites, where the majority of export appears to be derived from surface runoff and soil erosion, a more appropriate strategy might include efforts to reduce rates of surface runoff from fertilised fields, through injecting fertiliser directly to the root zone, constructing vegetated riparian areas (Sharpley et al., 2001), restricting fertiliser applications to periods of higher soil moisture deficit (Westerman and Overcash, 1980; Sharpley et al., 2001), and limiting tile drainage.

## 5 Conclusions

Accounting for climate modelling uncertainty, this study suggests that in the Beaver and Whites, large scale reductions in annual TP loads could result from reductions in flow and TP concentrations in spring, summer and autumn, combined with minor increases in winter. In contrast, much smaller reductions and even some increases in annual TP loads are expected in the Holland and Pefferlaw, due to much smaller scale reductions in summer and autumn flow and TP concentrations, combined with larger scale increases in winter, and enhanced spring TP concentrations. These findings indicate that all changes will become more extreme and more likely between 2030 and 2070.

Uncertainty in future projections of climate change impacted those of hydrology and water quality to different extents within each catchment. This impact depended upon (a) catchment characteristics which determine the sensitivity of a catchment to climate drivers and (b) the degree of projected climate change within each catchment. Influential catchment characteristics include geology, seasonal P-inputs and P-saturation thresholds. Catchment sensitivity to climatic drivers was relatively high where catchments had large proportions of overland flow and a direct association between TP concentrations, loads and HER was established. Catchment sensitivity to climate uncertainty was lower in catchments with larger proportions of soil matrix flow, and where seasonal variability in soil P-saturation influenced water quality; here internal catchment processes had a greater impact on hydrology and water quality.

The different ranges of uncertainty demonstrated by the catchments indicate that in water quality management it is important to consider every catchment as a distinct hydrological unit. Effectiveness of management strategies will vary depending on the dominant sources and P transport mechanisms in each area. Significantly, although the hydrology and water quality of the Whites and Beaver Catchments are more sensitive to changes in climate, the majority of projections under the PPE indicate reductions in TP concentrations and loads. Although the Holland and Pefferlaw are less sensitive to

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change, the dominant response is an increase in annual TP loads; as such the latter catchments might be seen as priority target areas for nutrient management.

Estimates of catchment sensitivity might be influenced by parametric uncertainty within each INCA model (Wade et al., 2001; Starrfelt and Kaste, 2014). Although beyond the scope of this study, future work will explore the extent to which this type of uncertainty might contribute to catchment sensitivity. This further research will also explore the potential use of clay-content of soils as an indicator of catchment hydrochemical sensitivity, through the use of a larger range of catchments.

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doi:10.5194/hessd-11-8067-2014-supplement.**

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**Table 1.** Landuse cover of the four study catchments within the Lake Simcoe Watershed reported to 2 significant figures (s.f.).

Land Type		% Land Cover			
		Holland	Pefferlaw	Beaverton	Whites
Agriculture	Intensive	34.93	23.44	28.11	20.40
	Non Intensive	17.79	25.27	37.06	45.71
Urban		19.54	10.63	5.08	1.68
Wetland		10.84	18.19	19.26	21.19
Forest		16.90	22.47	10.49	11.02

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**Table 2.** Details of key parameters and data sources used in model calibration.

Parameter	Data description	Study Site				Data Source
		Holland	Pefferlaw	Beaverton	Whites	
Catchment characteristics	Catchment area (km <sup>2</sup> )	613.78	444.39	325.29	84.96	Modelled using a 2 m vertical resolution DEM (Global Land Cover Facility; 2002)
	Number of sub catchments	39	41	30	23	
Hydrological characteristics	Temperature (°C) daily data	7.38	7.28	7.28	7.28	Measurements from local Environment Canada meteorological stations
	Precipitation daily data	2.45	2.49	2.48	2.03	
	SMD (mm)	42.78	47.98	47.24	22.11	Derived from HBV model
	HER (mm)	0.48	0.89	1.07	0.70	
	Soil water residence time (days)	3.00	2.66	2.44	1.36	Calculations from flow hydrographs derived from field monitoring data (Dave Woods, personal communication; LSRCA (2010); LSEMS (2010); PWQMN (2009))
	Saturation excess threshold (m <sup>3</sup> s <sup>-1</sup> )	0.62	0.03	0.46	0.50	
Fertiliser and septic inputs to non-intensive Agriculture	Fertiliser inputs from grazing animals and applications to crops (kg ha <sup>-1</sup> year <sup>-1</sup> )	33.24	32.4	30	25.8	Calculations using data from Statistics Canada (2011); OMAFRA (2009); Bangay (1976) using methods of Wade et al. (2007b)
	Septic tank inputs (kg ha <sup>-1</sup> year <sup>-1</sup> )	1.20	0.78	0.24	0.21	
Fertiliser inputs to intensive Agriculture	Fertiliser inputs from grazing animals and applications to crops (kg ha <sup>-1</sup> year <sup>-1</sup> )	21.15	24	32.52	32.4	Calculations using data from Statistics Canada (2011); OMAFRA (2009); Bangay (1976) using methods of Wade et al. (2007b)
P inputs to whole catchments	Atmospheric Deposition: average regional values (kg ha <sup>-1</sup> year <sup>-1</sup> )	0.21	0.21	0.21	0.21	Regional monitoring data Ramwekellan et al. (2009)
Sewage (STW) P inputs to river reaches	Number of STWs Average Inputs (kg P year <sup>-1</sup> )	3 103.55	1 102.9	2 67.15	N/A N/A	XCG consultants Ltd (2010) and KMK consultants (2004)

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**Table 3.** QUMP members listed in order of climate sensitivity under a doubling of CO<sub>2</sub> concentrations (from Collins et al., 2006).

QUMP member	Equilibrium climate sensitivity (sK) ( $\delta = 0.07$ K)
Q5	2.2
Q9	2.2
Q1	2.6
<b>Q15</b>	<b>2.9</b>
Q16	3.0
Q2	3.1
Q14	3.1
<b>Q13</b>	<b>3.2</b>
Q11	3.2
Q7	3.3
Q	3.4
<b>Q0</b>	<b>3.5</b>
Q6	3.8
<b>Q3</b>	<b>3.8</b>
<b>Q10</b>	<b>3.9</b>
Q4	4.6
Q8	4.9
Q12	4.9

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**Table 4.** Model fit coefficients presented for locations of highest calibration accuracy (2.s.f.)  
\*Due to the different temporal resolution of sampling vs. modelled data “observed loads” are not directly comparable with modelled loads. Both are calculated using monthly means of flow and TP data, however, although degree of load variance explained by the model can be determined ( $R^2$ ), a direct quantification of over or under-estimation (model error) cannot be calculated.

Catchment	Model coefficient				
	Flow		TP Concentration		TP loads*
	$R^2$	Model Error (%)	$R^2$	Model Error (%)	$R^2$
Holland	0.95	−24.78	0.72	−4.36	0.74
Pefferlaw	0.91	+46.28	0.37	−23.41	0.71
Beaverton	0.98	−15.30	0.79	+4.40	0.82
Whites	0.92	+3.03	0.47	+32.50	0.94

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**Table 5.** Export coefficients ( $\text{kg km}^{-2} \text{yr}^{-1}$ ) of TP from diffuse and point sources, and contributions of each source as a percentage of total P export (2.s.f.).

Source		Coefficients ( $\text{kg km}^{-2} \text{yr}^{-1}$ )				Source (% contribution)			
		East/West Holland	Pefferlaw	Beaver	Whites	East/West Holland	Pefferlaw	Beaver	Whites
In-stream	STW	0.76	0.31	0.52	0.00	5.51	3.67	13.31	0.00
Soils	Urban	9.92	4.84	2.37	2.14	14.05	6.10	3.04	0.43
	Intensive Agriculture	16.13	8.31	3.71	8.71	40.78	23.05	26.33	21.18
	Non Intensive Agriculture	15.96	13.83	4.15	8.94	20.55	41.34	38.86	48.68
	Wetlands	14.41	5.10	2.49	8.08	11.31	10.98	12.13	20.41
	Forest	6.38	5.59	2.38	7.08	7.82	14.86	6.32	9.30
	<i>Average soils export</i>	<i>13.05</i>	<i>8.14</i>	<i>3.43</i>	<i>8.51</i>	<i>94.51</i>	<i>96.33</i>	<i>86.68</i>	<i>100</i>

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**Table 6.** PPE ensemble average model projections of uncertainty in temperature, precipitation, flow, TP concentrations and loads, where “average uncertainty” is a measure of the mean value of uncertainty across all probability levels within the Cumulative Distribution Function (2.s.f).

Date	Catchment	Average Uncertainty				
		Temperature (°C)	Precipitation (%)	Flow (%)	TP (%)	Loads (%)
2030	Holland	0.91	19.55	33.97	5.87	39.29
	Pefferlaw	0.92	16.22	23.26	7.73	27.93
	Beaverton	0.93	16.88	28.98	11.25	36.61
	Whites	0.94	19.72	43.15	20.84	58.87
	Range	0.03	3.50	19.89	14.97	30.94
2070	Holland	1.88	23.65	37.29	7.13	43.03
	Pefferlaw	1.89	23.14	27.61	11.14	33.41
	Beaverton	1.92	23.24	35.09	11.87	38.71
	Whites	1.96	22.60	40.07	23.63	53.81
	Range	0.08	1.05	12.46	16.50	20.40

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**Table 7.** Calculation quantity of HER (mm) generated per mm of precipitation (2.s.f.).

Catchment	Change in HER per mm change in precipitation		
	2030	2070	Average
Holland	0.49	0.55	0.52
Pefferlaw	0.80	0.93	0.87
Beaverton	0.89	0.99	0.94
Whites	0.86	1.02	0.94

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**Table 8.** Annual change in TP loads between baseline and future periods, for all ensemble members of the perturbed physics ensemble. Includes ensemble average (EA) change (2.s.f.).

	Mean annual % change in TP loads					
	Q0	Q3	Q10	Q13	Q15	EA
Holland	22.64	11.73	−8.03	10.80	3.68	<i>8.16</i>
Pefferlaw	13.53	10.48	−2.86	−3.63	−6.61	<i>2.18</i>
Beaver	4.52	0.18	−12.80	−7.64	−16.38	<i>−6.42</i>
Whites	13.51	2.42	−8.99	−4.20	−25.14	<i>−4.48</i>
Range						<i>14.59</i>
Holland	29.63	17.58	−1.96	20.91	7.31	<i>14.69</i>
Pefferlaw	13.23	9.08	−14.23	−5.71	−7.51	<i>−1.03</i>
Beaver	0.29	−7.18	−26.33	−16.45	−23.82	<i>−14.70</i>
Whites	6.95	−3.21	−30.46	−14.84	−24.11	<i>−13.13</i>
Range						<i>29.39</i>

**Table 9.** Estimation of average catchment sensitivity of water quality to uncertainty in precipitation: projected change in TP ( $\text{mgL}^{-1}$ ) per mm change in precipitation averaged over 2030 and 2070 (2.s.f.).

Catchment	Season	Projected change in TP ( $\text{mgL}^{-1}$ ) per mm of change in precipitation	Proportion of annual change (%)
Holland	spring	0.01	6.82
	summer	0.02	27.27
	autumn	0.05	61.36
	winter	> 0.01	4.55
	Annual Average	0.02	100
Pefferlaw	spring	0.01	11.91
	summer	0.02	55.95
	autumn	> 0.01	9.52
	winter	0.01	22.62
	Annual Average	0.01	100
Beaverton	Spring	0.20	88.08
	Summer	0.01	2.14
	Autumn	0.01	5.78
	Winter	0.01	6.00
	Annual average	0.06	100
Whites	spring	0.03	4.99
	summer	0.01	0.97
	autumn	0.02	3.15
	winter	0.52	90.89
	Annual Average	0.14	100

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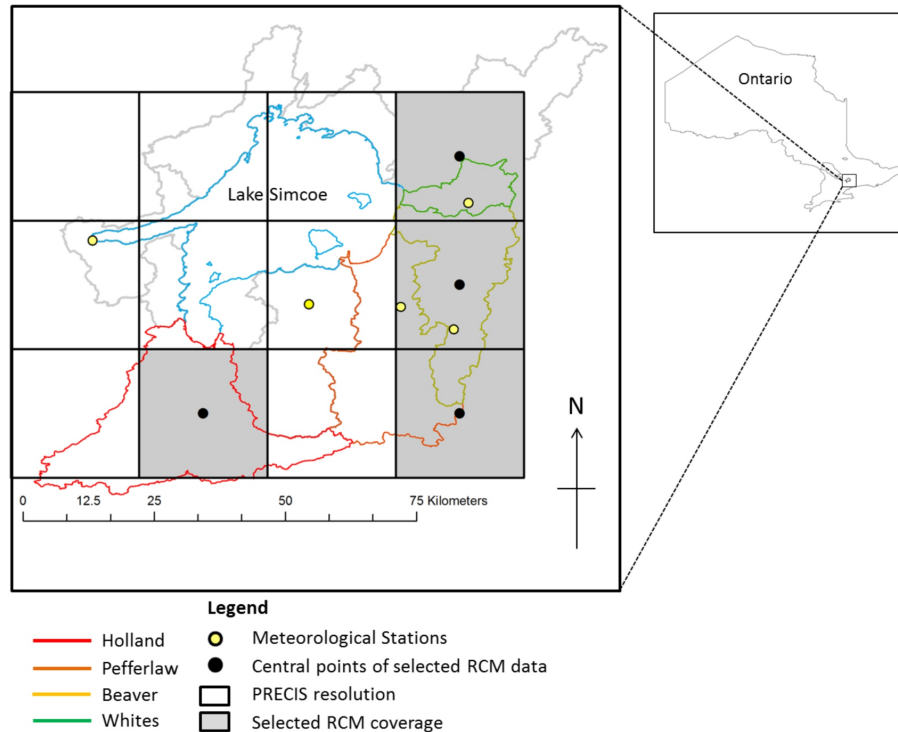
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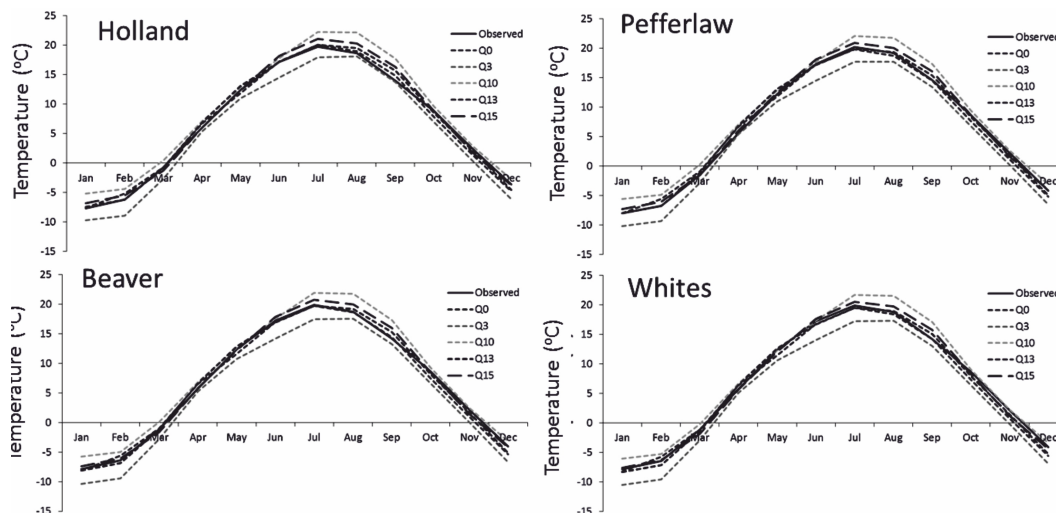
**Figure 1.** Map of 4 study watersheds within the Simcoe Basin, Southern Ontario, including analysis of regional climate model resolution in relation to watershed boundaries and available meteorological stations.

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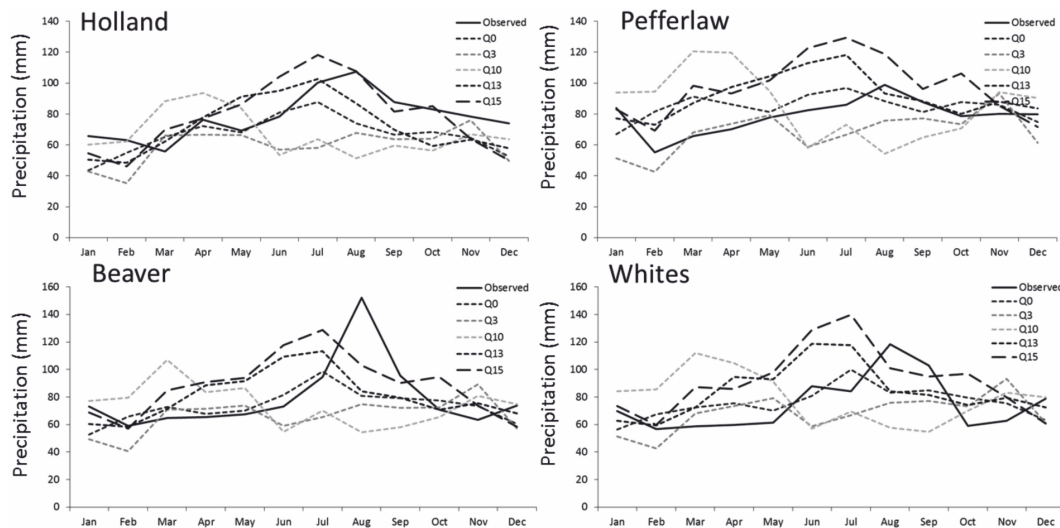


**Figure 2.** Comparison of monthly PRECIS regionally downscaled PPE temperature data to observed meteorological station data over 30 year baseline period (1968–1997).

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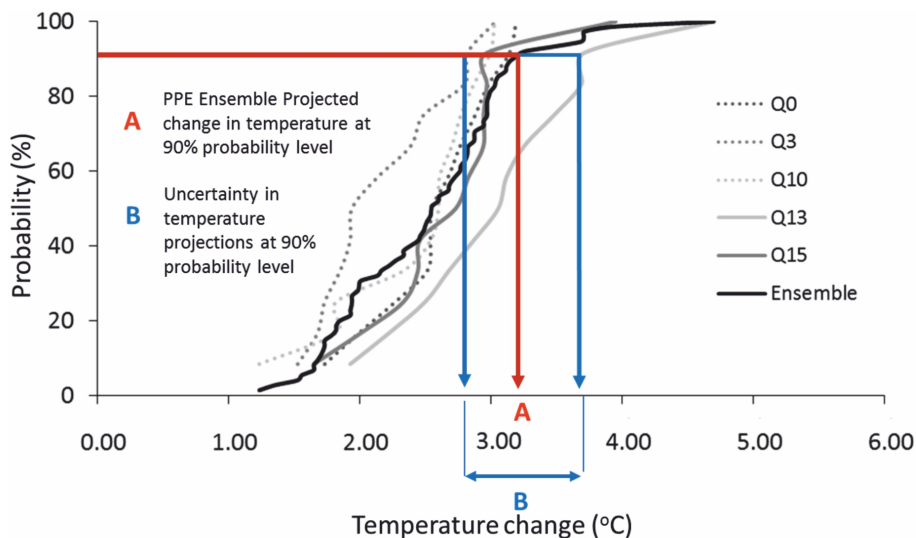


**Figure 3.** Comparison of monthly PRECIS regionally downscaled PPE precipitation data to observed meteorological station data over 30 year baseline period (1968–1997).

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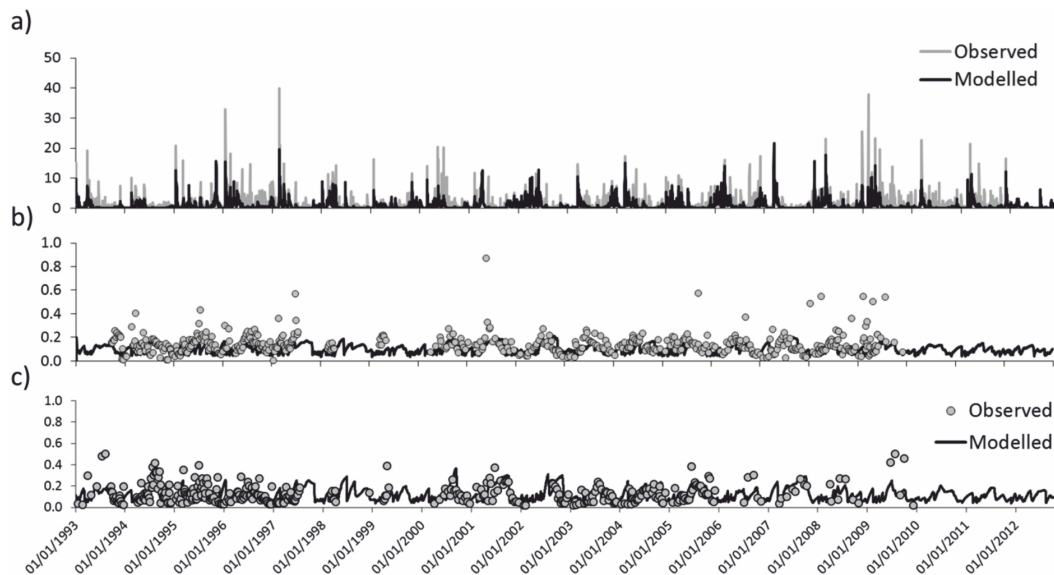


**Figure 4.** Calculations of (A) change in temperature and (B) projected uncertainty from Cumulative Distribution Functions of PPE temperature data of the Holland River in 2030.

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**Figure 5.** Example of INCA model output. Calibration results from Holland River comparing modelled and observed data of **(a)** flow at East Branch outflow **(b)** TP concentrations at East Branch outflow **(c)** TP concentration at West branch outflow.

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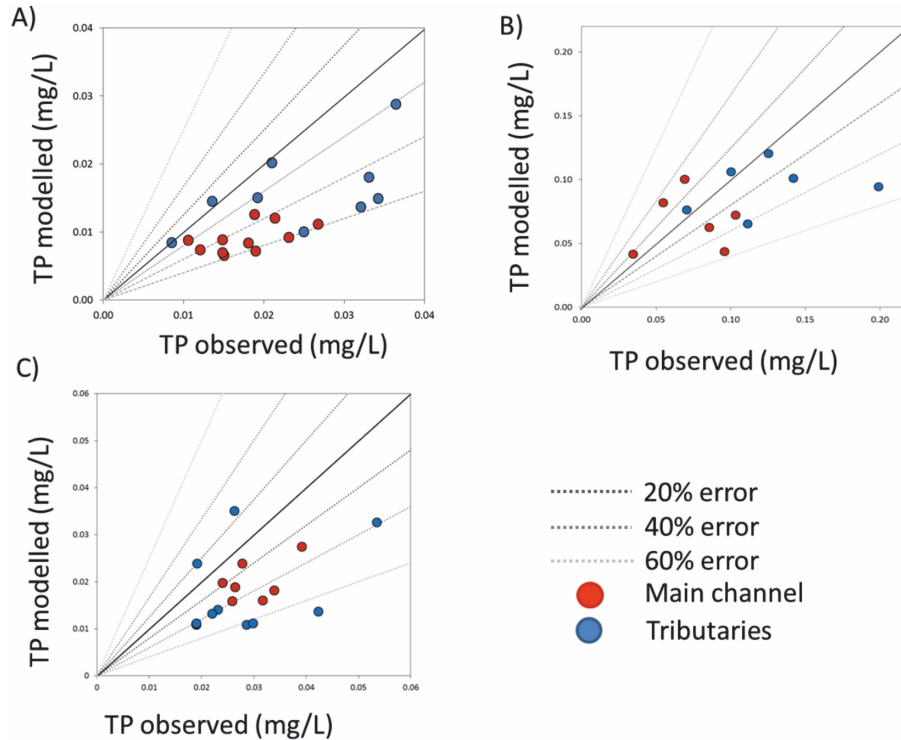
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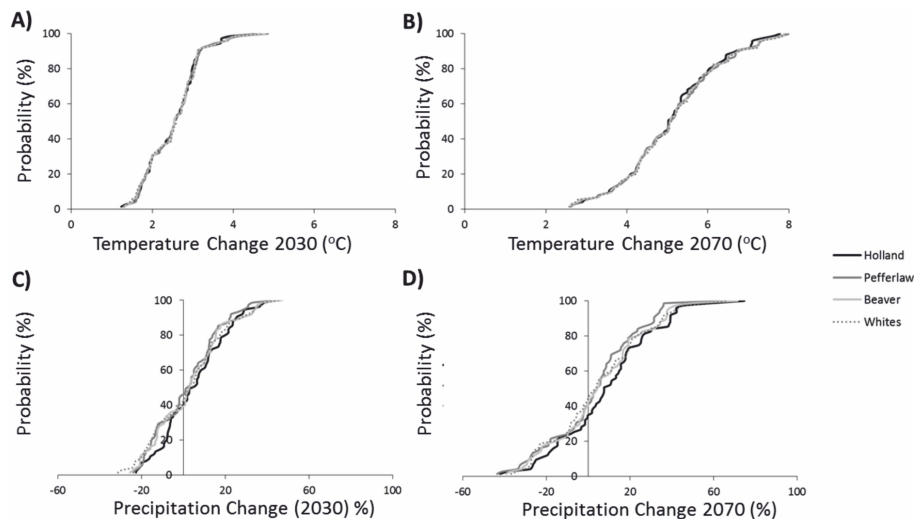
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**Figure 6.** Spatial variability in model accuracy of TP concentrations throughout INCA models calibrated across multiple reaches, illustrating relative model error in **(A)** Holland, **(B)** Beaver and **(C)** Whites catchments.

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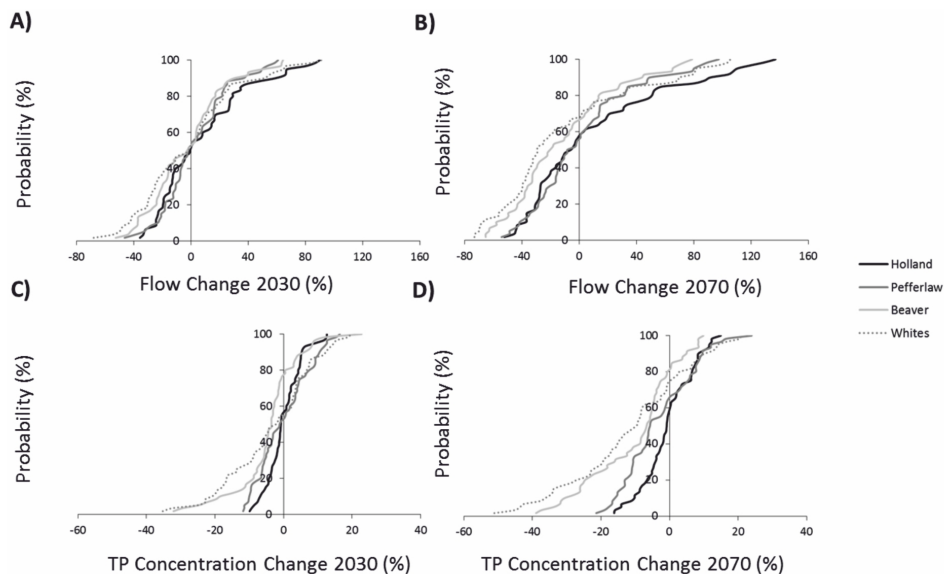
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**Figure 7.** Comparison between catchments of PPE ensemble CDF of **(A)** monthly change in temperature by 2030, **(B)** monthly change in temperature by 2070, **(C)** monthly change in precipitation by 2030 **(D)** monthly change in precipitation by 2070.

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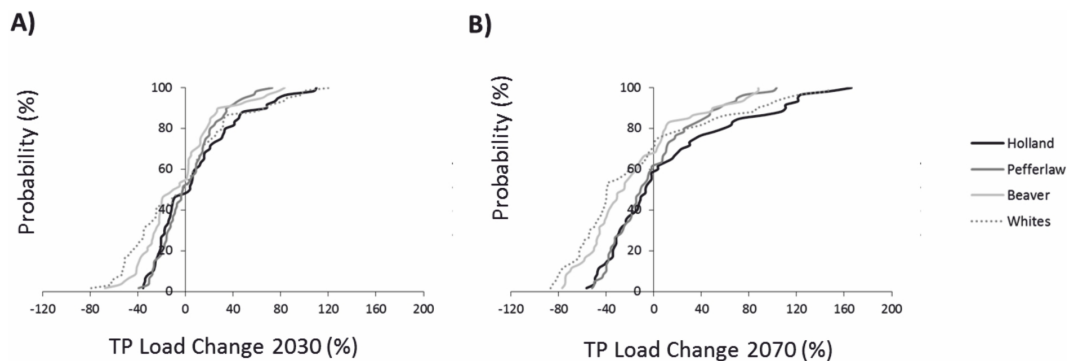


**Figure 8.** Comparison between catchments of PPE ensemble CDF of **(A)** monthly change in flow by 2030, **(B)** monthly change in flow by 2070, **(C)** monthly change in TP concentration by 2030, **(D)** change in TP concentration by 2070.

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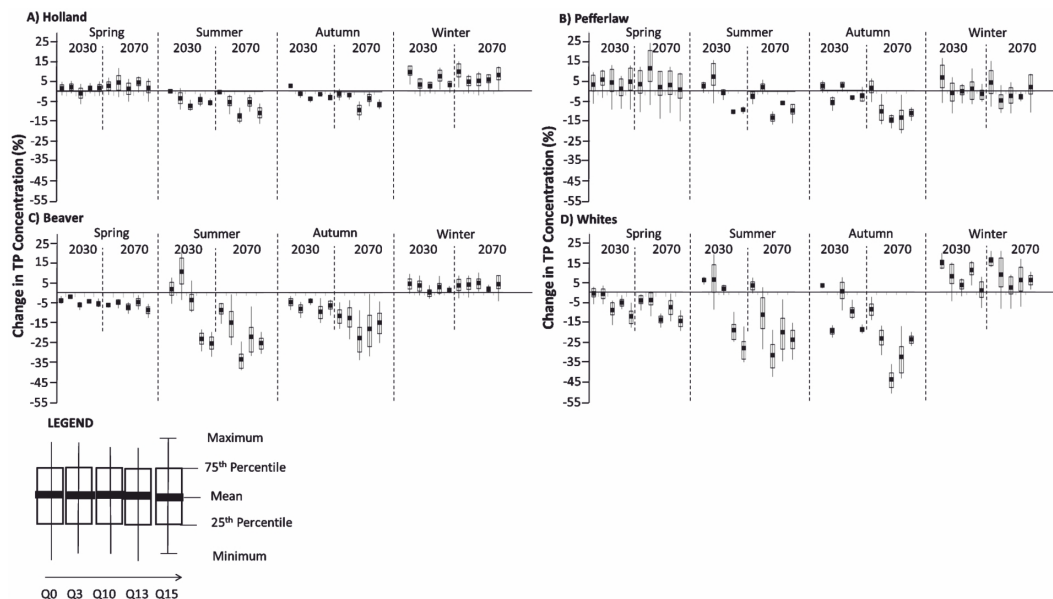
**Figure 9.** Comparison between catchments of PPE ensemble CDF of **(A)** change in TP loads by 2030, **(B)** change in TP loads by 2070.

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**Figure 10.** Boxplot of seasonal changes in TP concentrations across all QUMP members in **(A)** Holland **(B)** Pefferlaw **(C)** Beaverton and **(D)** Whites.

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