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A simple model to separately simulate point and diffuse nutrient signatures in stream flows

Andrew R. Slaughter and Denis A. Hughes

ABSTRACT

A simple model has been developed to simulate the relationships between stream flow and point and diffuse nutrient concentrations. The point source component is based on a mechanistic approach (including uncertainty), while the diffuse component relies on a statistical regression model. The model is explained and its application illustrated using flow and nutrient data from the South African Department of Water Affairs national monitoring database. The study sites represent a wide range of different combinations of point and diffuse source contributions to the total nutrient signature. The model has been successfully calibrated against the observed data and the study concludes that the point source component offers opportunities for use as a scenario assessment management tool, largely related to its mechanistic basis. However, further research is required to link the parameters of the diffuse source model to diffuse load causative factors so that the model can be used effectively in un-gauged situations or to assess management scenarios.

Key words | diffuse sources, flow, nutrient model, point sources, South Africa

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INTRODUCTION

The introduction of nutrients into aquatic systems through point and diffuse sources, caused by an increase in urbanisation and agriculture, has led to a range of environmental, social and economic problems (Withers & Jarvie 2008). Environmental problems include an increase in periphyton growth in shallow, fast running streams, while slower moving streams have been affected by surface algal scum, low oxygen conditions and low light penetration (Withers & Jarvie 2008) and by a high abundance of floating macrophytes within very slow moving streams and impoundments (van Wyk & van Wilgen 2002).

The management of nutrient influx into aquatic systems to prevent the problems listed above can be facilitated by water quality models. Water quality models provide the link between observed environmental problems in rivers, data observed from the field and laboratory and current scientific understanding (Thomann 1998). A water quality model can also be used to estimate how water quality constituents of interest will change over temporal and spatial scales in the absence of observed data (Rouch *et al.* 1998) and can provide some understanding of the underlying processes (Glaser & Bridges 2007). It is not feasible to observe how rivers react for all pollutant loading scenarios and models can provide a way of investigating hypothetical scenarios (Glaser & Bridges 2007) related to water resources management decisions or environmental change. There is therefore a need for models that can simulate the effects of diffuse and point source inputs on in-stream nutrient concentrations, to act as management tools for decision makers.

There has been some debate in the literature regarding the usefulness of large, complex deterministic models in relation to the management of water resources. Deterministic models have advantages for management, as the simulation of real-life processes is useful for indicating the sources of pollutants, and therefore, where measurements can be taken, and where ameliorative action can be implemented. However, many authors have argued for the use of simpler models that include some estimate of uncertainty (Beck 1987; McIntyre *et al.* 2003; Reckhow 1994; Young *et al.* 1996). While, in the past, water quality models

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have tended to ignore uncertainty, there has been an increasing momentum to incorporate uncertainty into water quality models, which is partly a reflection of the maturation of the science underlying water quality modelling (Beck 1987). It is true that complex deterministic models that attempt to simulate many natural processes can be more accurate than simpler deterministic models. However, in reality, the large amount of data required to accurately calibrate large models and the expertise required to operate these complex models, effectively excludes their use for water resources management (Reckhow 1994). Complex models with many parameters are also prone to the problem of equifinality (McIntyre *et al.* 2003), where different combinations of parameter values can generate similar model results, resulting in possibly inaccurate model simulations when the model is applied to future scenarios. It can also be difficult to incorporate uncertainty into large complex models. Complex models are archives of hypotheses that attempt to simulate as many of the cause–effect relationships in natural processes as possible and are therefore impossible to falsify (Beck 1987). As model complexity increases, the ability to evaluate uncertainty in these models will decrease due to the large number of uncertain model components (McIntyre *et al.* 2003). Therefore, relatively simple models that give approximate solutions may be more appropriate than extremely complex models, as it is possible to incorporate an indication of the predictive uncertainty associated with the use of the model (McIntyre *et al.* 2003).

Many water quality models require measured nutrient data before they can be accurately calibrated (Beck 1981; Oreskes *et al.* 1994; Shanahan *et al.* 1998; Thomann 1998; Chapra 2003). Unfortunately, while many countries have reasonably extensive flow gauging networks, there is often a paucity of equivalent water quality data (McDonnel 2008). However, models that can be considered useful from a management perspective would be required to 'accurately' simulate in-stream nutrient concentrations using whatever data are available, as time and budgetary constraints often preclude the collection of additional site-specific data. Management requirements of 'accuracy' are linked to specific management issues, and may not be the same as the conventional scientific view of accuracy within modelling as being a good match between model simulations and observed data. In some cases, the accurate representation of the frequency of occurrence of unacceptably high nutrient concentrations under different management scenarios may be considered sufficient.

Bowes *et al.* (2008) created models based on an understanding of the responses of total phosphorus to flow. Their understanding was that total phosphorus, introduced primarily through point sources into a river, would show a decreasing concentration with increasing flow. This is because the load of pollutants generated by point sources was considered to be relatively constant over time compared to that emanating from diffuse sources and because higher natural flows dilute effluent from point sources, leading to lower in-stream nutrient concentrations. In contrast, Bowes *et al.* (2008) found that rivers dominated by diffuse sources would show increasing concentrations with increasing flow. This is because the mobilisation of phosphorus is dependent on flow processes, such as surface runoff from urban areas (Hughes & van Ginkel 1994), or soil water drainage from agricultural areas subject to fertiliser applications (Malan & Day 2002). The models of Bowes *et al.* (2008) sought to separate the diffuse and point source phosphate signatures in rivers using a non-linear regression equation.

Initial investigations using the available historical flow and water quality monitoring data in South Africa (Slaughter 2011) for sites where known point sources exist (mostly wastewater treatment works (WWTW)) revealed that there are rarely clear asymptotic decreases in phosphorus concentrations with increasing flow as suggested by Bowes *et al.* (2008). While the South African data show similar trends, there is typically considerable scatter in the flow-concentration relationship at low flows. This could be a consequence of point sources releasing effluent that has a highly variable nutrient concentration and/or a highly variable flow rate which may be related to the rates of spillage from the final settling ponds of WWTW (partly related to variations in effluent treatment volumes as well as pond evaporation rates and local rainfall inputs). Some of the high concentrations and high effluent release rates could be related to the exceedance of the treatment capacity of the works, which is a recognised problem in many WWTW in the country (Department of Water Affairs

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(DWA) 2009). For those sites where nutrient concentrations increased with increasing flow, the diffuse source model proposed by Bowes *et al.* (2008) appeared to be generally applicable, although with considerable scatter in the relationships.

For these reasons, the use of the non-linear regression models proposed by Bowes *et al.* (2008) to the South African nutrient data met with little success and an alternative approach has been adopted in this study. The concept of the revised method was to make use of the same underlying mechanisms that form the basis of the Bowes *et al.* (2008) approach, but to apply a combined mechanistic/statistical approach that may be more appropriate for South African conditions. This model was applied to phosphate as well as nitrite plus nitrate data, with the assumption that nitrite plus nitrate signatures would display the same response to flow as phosphate. Phosphate (PO_4-P) and nitrite plus nitrate (NO_2-N + NO_3-N) were chosen as these are the dissolved inorganic species of phosphorus and nitrogen respectively and therefore the most bio-available. These nutrient species are also relatively well represented within the available historical monitoring data.

METHODS

Data used

The South African DWA maintains records of daily flow data for many gauging stations on rivers throughout the country. Associated with many of these gauging stations are also water quality observations, but these are sparse in comparison with the flow data, with some readings being taken weekly while, in some cases, consecutive readings show much larger temporal gaps of over a year. From the perspective of understanding the relationships between flow and diffuse source concentrations, very few nutrient concentration observations are available for high flow conditions. The data provided do not include some of the water quality variables (e.g. the concentrations of nitrogen species such as organic nitrogen) that would be typically required for complex nutrient modelling (Wimberley & Coleman 2005). The data used are available via the DWA Resource Quality Services website (http://www.dwa.gov.za/iwqs/default.asp).

The DWA provides phosphorus measures as dissolved PO_4-P concentration in mg l^{-1}, and nitrogen measures as dissolved NO_2-N plus NO_3-N concentration in mg l^{-1}. Only flow and water quality data measured after 1990 were used for the analysis and monitoring points were only selected if there were >50 water quality observations after 1990. Flow data and corresponding water quality data were ignored when flow was zero, as the aim of the model is to relate changes in water quality to changes in flow. In addition, as the model outlined here is a simple lumped mechanistic/statistical model, monitoring points considered to be very distant from upstream point sources were excluded to avoid the possible influence of processes that the model does not attempt to explain, such as nutrients re-introduced to the water column through scouring of the river bed, the degradation of nitrate through the process of nitrification, and the uptake of nutrients by flora. The data were analysed for seasonal bias, and the gauging station data were rejected where the number of data points was biased more than 70:30 in favour of either the summer (September–February) or winter season (March–August). Table 1 lists the gauging site data used in this study.

Land cover data for the case study catchments were derived from the DWA Groundwater Resource Directed Measures Database (Parsons & Wentzel 2006). A limited amount of WWTW nutrient concentration data were also obtained from the DWA flow and water quality database.

Model description

The model was implemented in Microsoft Office 2003 Excel. To illustrate the model, flow and PO_4-P data from the DWA gauging station B3H021 are used. This station is situated on the Elands River in the Limpopo Province and is located close to human settlements as well as areas of irrigation, suggesting that the water quality is likely to be influenced by both point and diffuse sources.

The point source component of the model simulates the point source signature of the data using four parameters. Q_{pmax} and Q_{pmin} ($m^3\ s^{-1}$) represent the maximum and minimum possible flow contributions from all point sources influencing the data at the monitoring point, while C_{pmax}

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Table 1 | Details of the South African Department of Water Affairs (DWA) gauging station data used in developing a simple mechanistic nutrient model

				Data availability		
Gauging station	**River name**	**Latitude**	**Longitude**	**From**	**To**	**Catchment area (km^2)**
A2H106	Pienaars	−25.13111	27.81111	1990	2010	6,139
A7H001	Sand	−22.90833	29.61417	1990	1999	7,703
A9H001	Luvuvhu	−23.11167	30.38972	1990	2006	915
B3H021	Elands	−24.92528	29.32444	1994	1998	6,119
C5H035	Modder	−24.63833	29.02861	1993	2006	17,313
K1H004	Brandwagrivier	−34.03194	22.05333	1990	2008	215
K3H001	Kaaimans	−34.10306	22.07194	1990	1996	47
R2H010	Buffalo	−32.94056	27.46139	1990	2005	668
S7H001	Gcuwa	−32.32750	28.14472	1998	2008	724
T5H002	Bisi	−30.40806	29.90000	1990	2008	867
W2H009	Wit-Mfolozi	−27.89722	30.88389	1990	2008	432
W5H026	Ngwempisi	−26.67750	30.70194	1992	2007	1,392
X2H015	Elandsrivier	−25.48778	30.69750	1990	2008	1,554
X3H006	Sabie	−25.03000	31.12667	1990	2000	766

and C_{pmin} (mg l^{-1}) represent the maximum and minimum possible concentrations of either phosphate or nitrite + nitrate of the effluent being released from the point sources. The model is based on mean daily flows and concentrations to correspond with the daily time step of the observed flow data. The model generates two uniformly distributed random numbers ($R\ andQ_i$ and $RandC_i$: with values between 0 and 1) to estimate the point source effluent flow ($Q_{\mathrm{psim_}i}$) and the point source nutrient concentration ($C_{\mathrm{psim_}i}$)

$$Q_{\mathrm{psim_}i} = R\,andQi \times \left(Q_{\mathrm{pmax}} - Q_{\mathrm{pmin}}\right) + Q_{\mathrm{pmin}} \quad (1)$$

$$C_{\mathrm{psim_}i} = RandC_i \times \left(C_{\mathrm{pmax}} - C_{\mathrm{pmin}}\right) + C_{\mathrm{pmin}} \quad (2)$$

The model is therefore based on the assumption that the point source flows and nutrient concentrations are independently uncertain and that the uncertainty can be defined by a uniform distribution between two extreme values. The simulated concentration of phosphate (or nitrite + nitrate) within the river due to point sources is then estimated using a simple mechanistic dilution model:

$$C_{\mathrm{sim_}i} = \left(C_{\mathrm{psim_}i} \times Q_{\mathrm{psim_}i}\right)/Q_i \quad (3)$$

where $C_{\mathrm{sim_}i}$ (mg l^{-1}) represents the simulated concentration of phosphate (or nitrite + nitrate) in the river due to point sources and Q_i (m^3 s^{-1}) represents the total flow in the river. The total flow values would be obtained from observed data for situations where the model is being tested at gauged sites, while these values could be simulated by a hydrological model at un-gauged sites. Even in gauged situations, the actual values of the point source parameters may not be available from observational data and the parameters Q_{pmax}, Q_{pmin}, C_{pmax} and C_{pmin} are manually adjusted to achieve a degree of scatter in the simulated flow-concentration relationship that is similar to the observed scatter. It should be noted that automatic calibration approaches cannot be used in this model because of the random uncertainty associated with Equations (1) and (2). There is no expectation that the daily simulated concentrations will match the observed concentrations on the same day, only that the patterns of scatter in the observed and simulated flow–concentration relationships are similar. If it is assumed that the point sources represent the dominant channel flow and nutrient load at low flows, the highest and lowest observed nutrient concentrations can be used to approximately quantify C_{pmax} and C_{pmin} respectively, while the lowest observed

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flow can be used to quantify Q_{pmin}. This leaves the value of Q_{pmax} as the main parameter to be calibrated. These assumptions would only be expected to be valid in relatively small, semi-arid catchments where the natural channel flows are very low during dry low-flow periods. The assumptions would not be valid where the catchment flow contributions upstream of the point source are the dominant source of flow and additional information would be required to be able to satisfactorily quantify the point source parameters. Some of the required information for point sources related to WWTW should be available from information about the capacity of the treatment works. Actual monitored WWTW effluent flow and nutrient concentration would of course be the most useful data for calibrating the point source component of the model, but in most cases, these data are not easily available.

The calibration process can be based on selecting the highest and lowest nutrient concentrations in the historical data for C_{pmax} and C_{pmin} respectively (but ignoring any assumed diffuse source concentrations that occur at higher flows in the data set), while the lowest flow in the historical data set is chosen for Q_{pmin}. The value of Q_{pmax} is then adjusted until a visual fit between the observed and simulated data is obtained. The basis for the visual fit is to achieve a similar degree of scatter in the observed and simulated concentrations, as well as similar maximum concentrations for different in-channel flow rates (Figure 1).

The y axes of the graphs in Figure 1 are shown using a logarithmic scale so as to better demonstrate the low-flow calibration in more detail. C_{pmax} and C_{pmin} were set at 0.12 and 0.005 mg l^{-1} respectively, while Q_{pmin} was set at 0.001 $m^3 s^{-1}$ and Q_{pmax} adjusted during the calibration

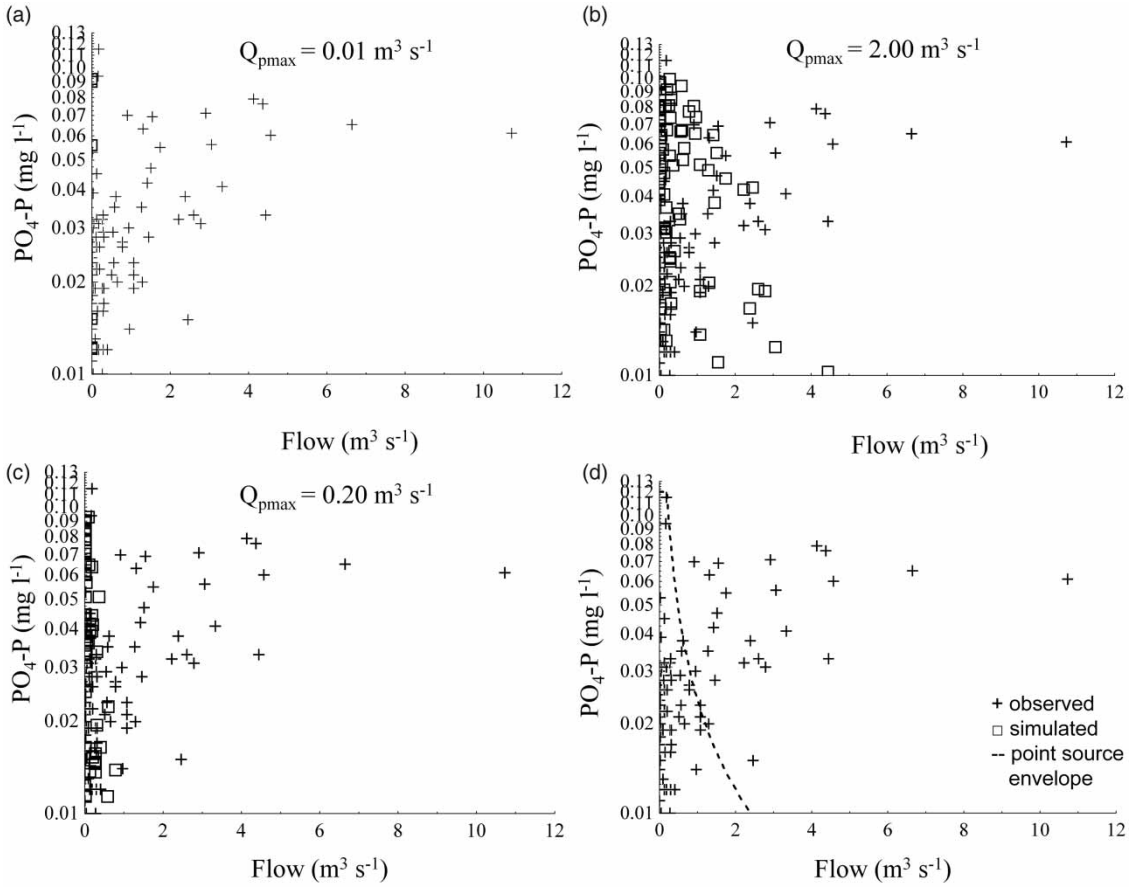

Figure 1 | Example calibration process for estimating the point source signal in the historical data for DWA monitoring point B3H021. Refer to text for further explanation.

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process. Figure 1(a) illustrates the result with a low maximum point source discharge ($Q_{pmax} = 0.01\ m^3\ s^{-1}$), while Figure 1(b) illustrates the opposite extreme of a very high Q_{pmax} parameter ($2.0\ m^3\ s^{-1}$). Neither of these reproduced the observed scatter of nutrient concentrations within the range of low flows. Figure 1(c) shows the result using a maximum point source discharge of $0.2\ m^3\ s^{-1}$, a value which gives the best visual fit to the observed variations in concentration at low flows. The envelope of maximum simulated point source concentrations at any flow rate is illustrated in Figure 1(d) and defined by:

$$C_{pmaxsim_i} = (C_{pmax} \times Q_{pmax})/Q_i \quad (4)$$

where $C_{pmaxsim_i}$ is the maximum concentration of nutrients for Q_i due to point sources.

The next step in the model calibration process is to isolate the diffuse source signature from the observed data, and this is achieved using the residual ratio of the observed concentrations to the expected maximum point source signature defined by Equation (4) (dashed line in Figure 1(d)):

$$C_{res_i} = Cobs_i / C_{pmaxsim_i} \quad (5)$$

where C_{obs_i} is the observed nutrient concentration and C_{res_i} is the residual ratio (which is the equivalent of the ratio of the total nutrient load to the maximum point source load). The value of C_{res_i} will be low for observations falling within the point source envelope, but higher for those which lie outside the envelope where the dominant influence is assumed to be diffuse sources (Figure 2).

The scatter of points in the low-flow parts of Figure 2(a) and 2(b) are assumed to be associated with the uncertainty in the point source signature and are therefore not considered useful for defining the diffuse source relationship with flow. Only those points that can be clearly identified as being associated with diffuse source effects (generally increasing concentration with flow – Bowes *et al.* 2008)

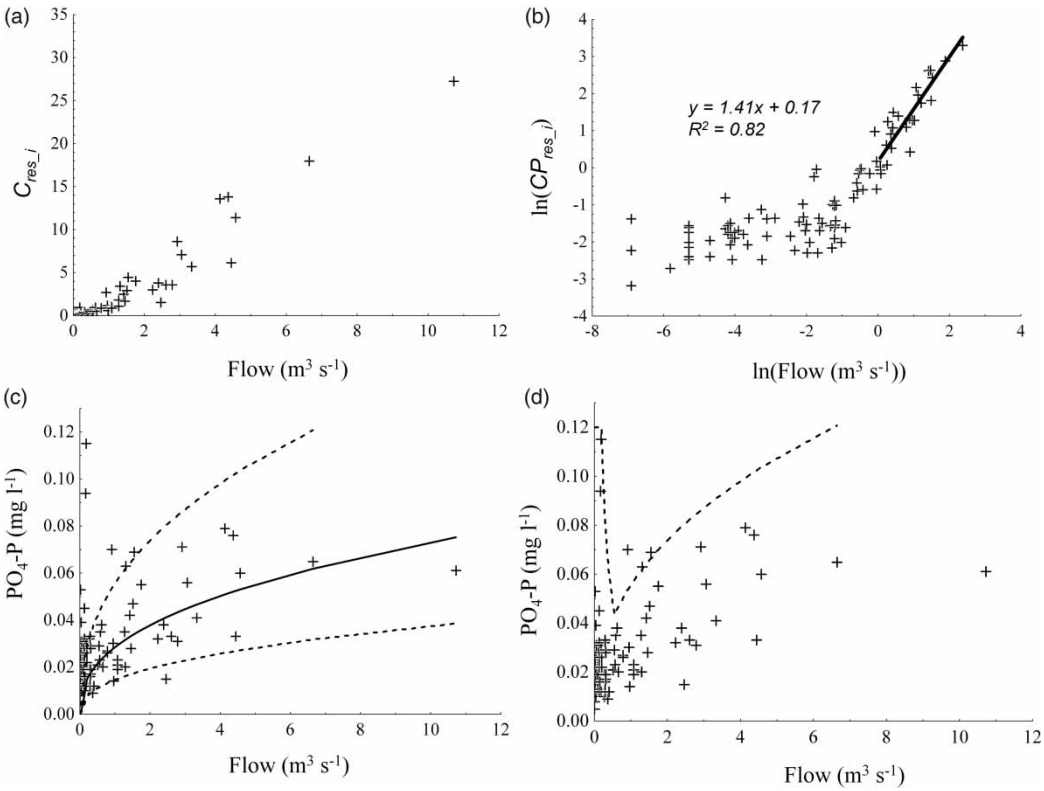

Figure 2 | Separating the point and diffuse source nutrient signatures for B3H021. (a), (b) The relationship between flow and the residual ratios using original and ln transformed data. (c) Illustration of the final diffuse source model with prediction limits. (d) The final uncertainty envelope curve for the combined point and diffuse sources.

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are used to define the linear regression relationship between the natural log transformed values of Q_i and C_{res_i} and generate predicted residual ratios (CP_{res_i}):

$$\ln(CP_{res_i}) = m \times \ln(Q_i) + c \quad (6)$$

or in the non-linear form using untransformed values:

$$CP_{res_i} = \exp(c) \times Q_i^m \quad (7)$$

where c and m are the parameters of the regression relationship.

In this example (B3H021), the points selected for inclusion were limited to flow (Q_i) values of $>1\ m^3\ s^{-1}$, ($\ln(Q_i) > 0$), given the assumption that diffuse sources of nutrients will only start significantly influencing in-stream nutrient concentrations at flows $>1\ m^3\ s^{-1}$. The linear regression equation for the natural log transformed values, the parameters m and c and the R^2 value (0.82) are given in Figure 2(b). The 90% prediction limits around the relationship between C_{res_i} and Q_i are also computed. The simulated diffuse source concentrations (C_{diff_i}) are calculated by back transforming the predicted values of the residual ratios as well as the upper and lower 90% prediction limits (Figure 2(c)):

$$C_{diff_i} = C_{pmaxsim_i} \times CP_{res_i} \quad (8)$$

The diffuse source envelope $C_{diff_maxsim_i}$ is defined by using the upper 90% prediction limits within Equation (8) and can be combined with the point source envelope defined by values of $C_{pmaxsim_i}$ calculated in Equation (4) to obtain an overall envelope of maximum phosphate concentration due to both point and diffuse sources shown for B3H021 in Figure 2(d).

In summary, the model assumes that the point source envelope curve can be used to differentiate between the point and diffuse sources signatures in the observed concentration data (C_{obs_i}). Residual ratios with relatively high values (C_{obs_i}/C_{maxsim_i}) with respect to the point source effect envelope curve are further assumed to represent the contributions of the diffuse sources. The 'statistical' component of the model therefore involves fitting a regression equation to the residual ratios and estimating 90% prediction limits to represent the uncertainty in the diffuse source part of the model.

Applications of the model

A point source dominated monitoring point

The Buffalo River is situated in the Eastern Cape Province of South Africa. R2H010 is a monitoring point on the Buffalo River approximately 15 km downstream of King Williams Town (Figure 3). This stretch of river is affected by two WWTW at King Williams Town and Zwelitsha, which are approximately 12 km and 4 km upstream of R2H010, respectively. The Zwelitsha WWTW can be expected to have a major effect on the water quality measured at R2H010, while the King Williams Town WWTW probably has less of an effect, as it is further upstream from R2H010, and it has been shown that phosphate is removed relatively rapidly as the Buffalo River is phosphate limited (Department of Water Affairs and Forestry 1998). The DWA has some historical monitoring data on the concentrations of phosphate that are released from the Zwelitsha WWTW (monitoring from 23 January 2002 to 3 March 2009 with 69 data values; mean = 1.52 mg l^{-1}; minimum = 0.03 mg l^{-1}; max = 4.61 mg l^{-1} standard deviation = 1.34). Unfortunately, the DWA monitoring data do not include measures of effluent flow. The addition of effluent into this stretch of the Buffalo River can however be approximated using observed flow monitoring data. DWA monitoring gauge R2H005 occurs upstream on the outskirts of King Williams Town, R2H009 and R2H016 occur on tributaries to this section of river, and R2H010 occurs immediately downstream (Figure 3).

During low-flow conditions, most of the extra flow entering this section of the Buffalo River would be from the King Williams Town and Zwelitsha WWTW. Observed flow measures from the four gauges were obtained from the DWA for days when measures of phosphate from the Zwelitsha WWTW are available. The assumption was made that most of the extra flow and phosphate load at R2H010 would have originated from the Zwelitsha WWTW, as flow and phosphate load from the King Williams Town WWTW would have been lost through evaporation and in-stream processes, respectively. Flow

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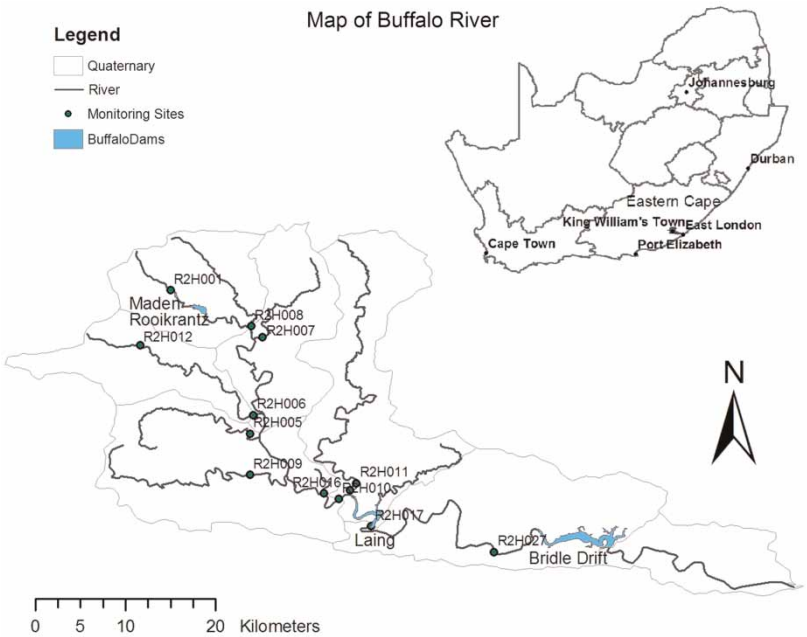

Figure 3 | Map of the Buffalo River catchment showing the study area and monitoring gauges used in analysis sources.

readings from R2H005, R2H009 and R2H016 were summed, and subtracted from the corresponding flow measures at R2H010, with the assumption that the resulting flow is the likely effluent input from the Zwelitsha WWTW. The resulting flow was plotted against the corresponding phosphate concentrations measured at the Zwelitsha WWTW (Figure 4).

From Figure 4 it can be seen that the maximum effluent flow calculated in this analysis is approximately 0.4 $m^3 s^{-1}$, while the maximum phosphate concentration is approximately 4.5 $mg\,l^{-1}$. Importantly, Figure 4 shows an apparent random relationship between phosphate concentration in WWTW effluent and effluent flow rate, which lends support to the model assumption that effluent nutrient concentrations and effluent flow rates from WWTW vary independently.

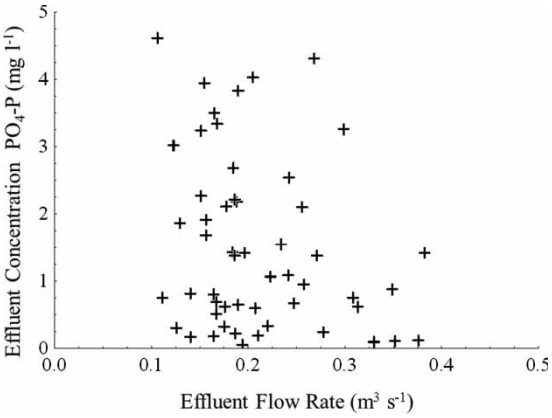

Figure 4 | Graph showing calculated effluent flow rates affecting the monitoring point R2H010, as well as corresponding concentrations of phosphate from the Zelitsha WWTW.

The historical DWA data for R2H010 show a strong decreasing concentration with increasing flow for both phosphates (Figure 5(a)), and nitrites + nitrates (Figure 5(b)), with no indications of increasing concentration with increases in flow, suggesting that diffuse sources of nutrients do not play a major role in this section of the Buffalo River.

The model estimated parameters for the phosphates model are:

$Q_{pmax} = 0.4\ m^3\ s^{-1}$; $Q_{pmin} = 0.016\ m^3\ s^{-1}$;
$C_{pmax} = 5.36\ mg\ l^{-1}$; $C_{pmin} = 0.003\ mg\ l^{-1}$

The model estimated parameters for the nitrites + nitrates model are:

$Q_{pmax} = 0.4\ m^3\ s^{-1}$; $Q_{pmin} = 0.016\ m^3\ s^{-1}$;
$C_{pmax} = 22.5\ mg\ l^{-1}$; $C_{pmin} = 0.02\ mg\ l^{-1}$

In both the phosphate and nitrite + nitrate models, 100% of the validation data points fall within the envelope curve

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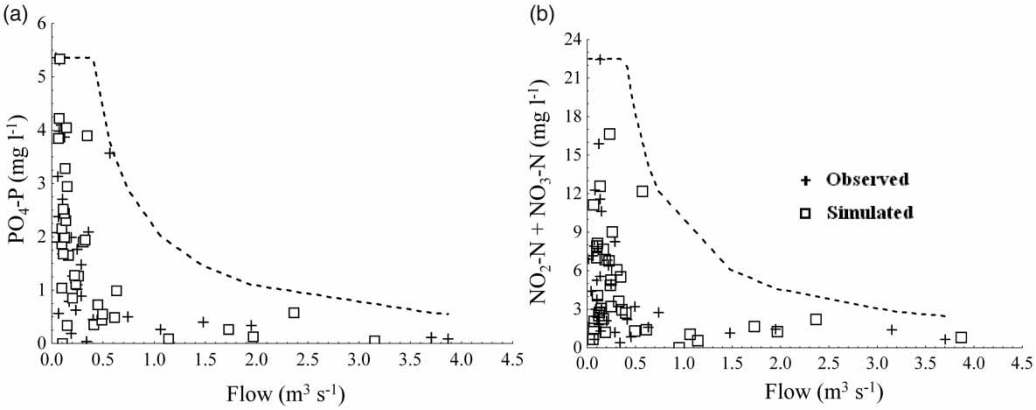

Figure 5 | Observed flow versus PO_4-P (a) and NO_3-N + NO_2-N (b) for the gauging site R2H010 for the data sets used in model calibration and validation. The dashed lines represent the envelope curves for the phosphates (a) and nitrites + nitrates model (b).

(Figure 5). Figure 5 also indicates that there are no residuals in the observed nutrient concentration data with respect to the point source envelope curves. The conclusion is therefore that the diffuse source models are not required for this site.

The values of Q_{pmax} for both the phosphate and nitrite + nitrate models are similar to maximum effluent flow calculated using historical flow monitoring data (Figure 4). In addition, the C_{pmax} of 5.36 mg l^{-1} calculated for phosphate is similar to the maximum effluent phosphate concentration within the historical monitoring data for the Zwelitsha WWTW. The fact that both models generated the same Q_{pmax} is encouraging and suggests that the same point sources are influencing concentrations of both phosphate and nitrite + nitrate, as might be expected from WWTW.

A diffuse source dominated monitoring point

The DWA monitoring point X3H006 is located on the Sabie River. The catchment area is dominated by forest plantation (61%), undegraded bush (16%), degraded natural areas (11%) and cultivated permanent commercial irrigation (7%). Some diffuse nitrogen inputs would be expected from forest plantations, associated with the high concentration of leaf litter. Some natural sources of nitrogen may arise from the undegraded bush land cover, and the cultivated land cover may also contribute some diffuse nitrogen as fertiliser is often applied to cultivated land. The observed DWA historical monitoring data for the monitoring point X3H006 (Figure 6) show an overwhelming trend of increasing nitrite + nitrate concentration with increasing flow and possibly a very weak point source signal.

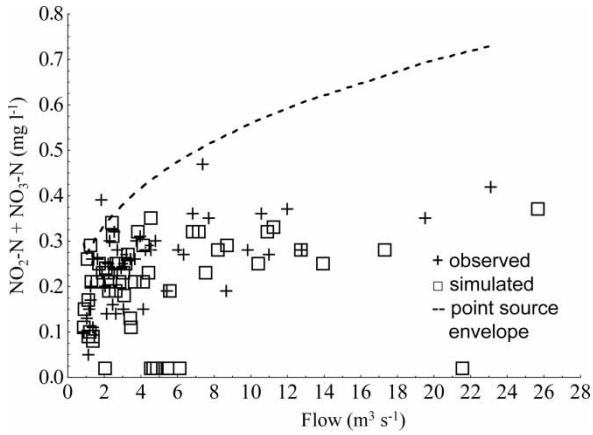

Figure 6 | Observed flow and nitrite + nitrate data together with the upper simulated prediction limits generated by the model for the gauging site X3H006.

The following model parameters fitted the observed data for the point source signature:

$$Q_{pmax} = 0.3 \text{ m}^3 \text{ s}^{-1}; Q_{pmin} = 0.001 \text{ m}^3 \text{ s}^{-1};$$
$$C_{pmax} = 0.30 \text{ mg l}^{-1}; C_{pmin} = 0.02 \text{ mg l}^{-1}$$

The regression equation (with an $R^2 = 0.91$) for the residual ratio values (from which the diffuse source predictions are derived using Equation (9)) is:

$$\ln(CP_{res_i}) = 1.32 \times \ln(Q_i) - 0.51 \quad (9)$$

Figure 6 shows the final envelope curve, dominated by the upper prediction limit of the diffuse source model.

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While the validation data points all fall within the limits of the envelope, values at high flows substantially over-estimate the maximum observed concentrations.

Using the monitoring point X3H006 as an example, it can be demonstrated that it is unlikely that effluent released from a WWTW would cause high in-stream concentrations of nutrients at high flow, even during localised flooding events when the capacity of a WWTW would be overloaded leading to untreated sewage being released into a river. Applying standard flood estimation methods (Alexander 1990) to the town of Sabie above X3H006, a high intensity rainfall event is unlikely to produce an effluent release rate from a WWTW of above 0.3 $m^3 s^{-1}$, as not all storm-water runoff from the town will be routed through the WWTW. For an effluent flow of 0.3 $m^3 s^{-1}$ to produce high in-stream concentrations of nitrite + nitrate within the Sabie River at high flows of approximately 25 $m^3 s^{-1}$ (see Figure 6), effluent concentrations of nitrite + nitrite would have to be in the region of 33 mg l^{-1}, which is unlikely, especially as storm-water runoff would dilute the untreated sewage that is released into a river. In the case of the Sabie River, it is much more likely that the extensive irrigation in the valley bottom areas above X3H006 is responsible for high nitrite + nitrate concentrations at high flows.

Results of the models applied to all data

The model was applied to data from other gauging stations (Figures 7 and 8). The parameter values obtained for the models are given in Table 2.

The monitoring points A7H001 (Figure 7(a)), C5H035 (Figure 7(b)) and T5H002 (Figure 7(d)) show relatively minor phosphate point sources linked to relatively small diffuse source phosphate inputs. K3H001 (Figure 7(c)) appears to have quite similar point and diffuse source inputs, although the diffuse source is defined by a relatively small number of data points. Both W5H026 (Figure 7(e)) and X2H015 (Figure 7(f)) have substantial point source inputs and no discernable diffuse source signatures. All of the examples illustrate that there are always a relatively small number of data points that can be used to identify the parameters of the diffuse source model. While the percentage number of validation points that lie within the model prediction limits is always high (Table 2), this is partly a result of the quite large prediction limit bounds of the diffuse source model.

The results for the nitrite + nitrate data (Figure 8) are quite similar to the phosphate model results, however, there are no situations that clearly show a combination of both point and diffuse source signatures. A2H106, S7H001 and W2H009 (Figure 8(a), (d), (f)) show clear point source signatures only (with some isolated moderately high nutrient values at high flows), while for sites A9H001, K1H004 and T5H002 (Figure 8(b), (c), (e)) the diffuse source signature dominates. The comments made in the previous paragraph about the phosphate model prediction limits, and the number of validation points that are included within them, are also applicable to the nitrite + nitrate model.

As the diffuse source model is based on residual ratios from the maximum point source envelope, it is clearly always necessary to include a point source component even when there is little evidence of its existence (Figures 7(d) and 8(e)). In these situations, a nominal point source effect is included and this can affect the quantification of the diffuse source parameters (e.g. T5H002 in Table 2 and Figure 8(e)). While this does not affect the final result of the model for individual sites (the simulated residual ratios are back-transformed using the same diffuse source parameters) it does largely preclude comparisons being made between the diffuse source parameters for different sites and establishing links between the parameters and causative factors.

DISCUSSION

Due to the way in which the point source component is constructed, the model cannot be assessed against observed data in the conventional way using objective functions. Models are typically calibrated against one data set and verified against an independent data set. The use of a random generator to quantify the point source influence within the model means that no attempt is made to accurately simulate individual observed data values. This is justified by the assumption that much of the scatter in the observed data is related to the random nature of the point source output, in terms of both quantity of effluent flow, and nutrient concentrations. Although the model cannot be tested in the

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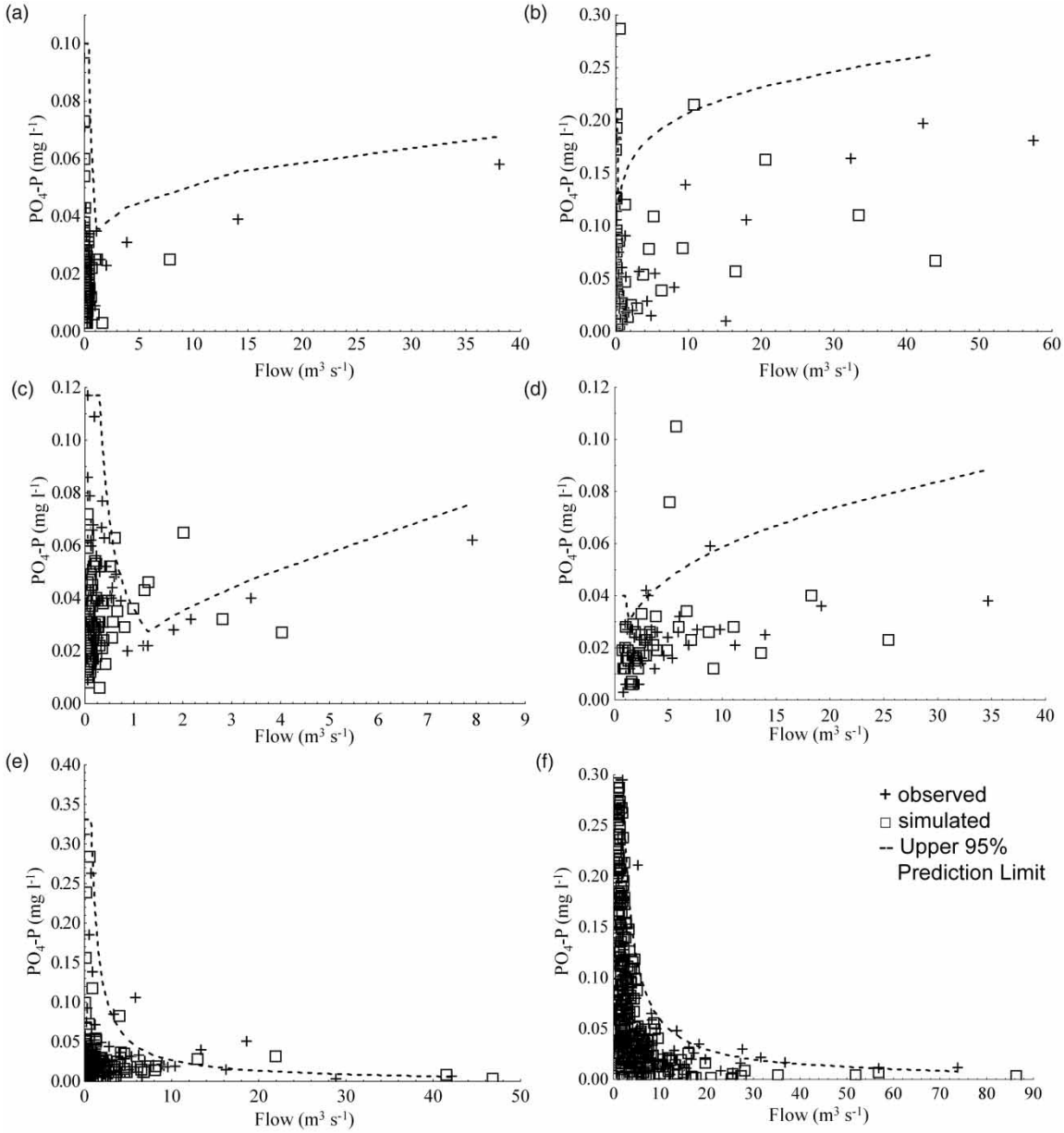

Figure 7 | Examples the model applied to phosphate historical monitoring data from DWA monitoring sites: A7H001 (a); C5H035 (b); K3H001 (c); T5H002 (d); W5H026 (e); and X2H015 (f).

conventional sense, the model parameters can be compared to measured point source data if available. In this study the validation of the model has been based on an upper prediction limit envelope curve using a calibration data set and assessing how many of the validation data set points fall within the envelope curve.

The nutrient concentrations of effluent emitted are very seldom monitored for many WWTW in South Africa. The DWA has made accessible the results of routine monitoring of WWTW effluent. However, the data are sparse and temporally infrequent, do not cover all the operating WWTW, in most cases only measure PO_4-P, and do not measure effluent flow. While some data may be collected for specific WWTW by local municipalities, these data are not usually available in the public domain. This model makes the assumption that the high variability of nutrient

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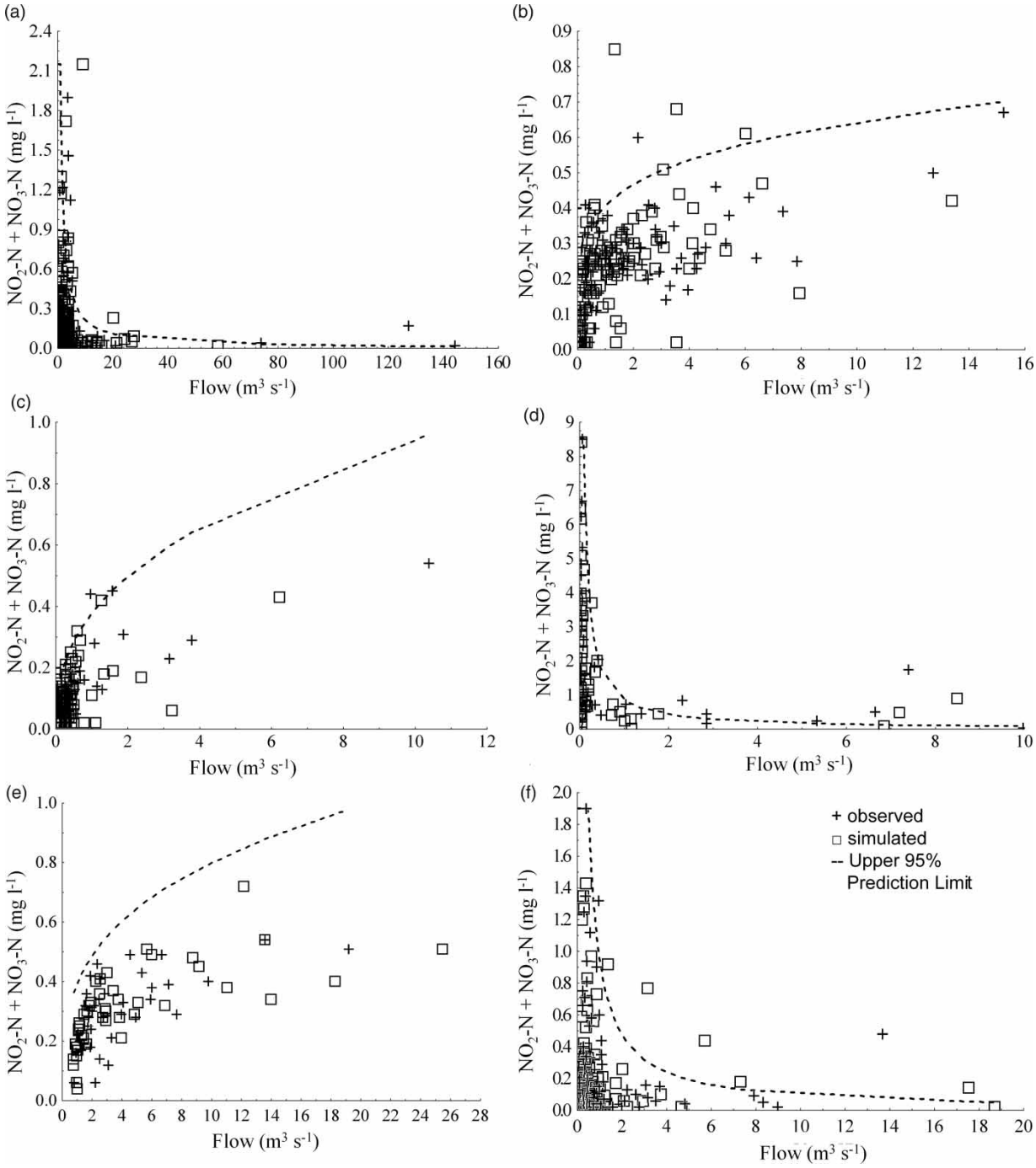

Figure 8 | Examples the model applied to nitrite + nitrate historical monitoring data from DWA monitoring sites: A2H106 (a); A9H001 (b); K1H004 (c); S7H001 (d); T5H002 (e); and W2H009 (f).

concentrations at low flow within the DWA historical monitoring data is due to point sources, such as WWTW, releasing effluent with a high variability in flow magnitude and nutrient concentration. While there are a lack of effluent nutrient concentration and flow data to confirm this assumption, Figure 4 illustrates that effluent flow and phosphate concentrations vary quite dramatically and independently for the Zwelitsha WWTW in the Eastern

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Table 2 | Parameter values obtained for a simple nutrient model applied to all Department of Water Affairs and Forestry (DWAF) gauging stations used in the study

Nutrient	Monitoring point	Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	Diffuse model parameters (c & m in Equation (6)) and R^2 of the regression equation	% validation
NO_2-N + NO_3-N	A2H106	1.500	0.002	2.150	0.020	N/A	99.6
PO_4-P	A7H001	0.500	0.003	0.095	0.003	c = −0.47; m = 1.20; R^2 = 0.99	100.0
NO_2-N + NO_3-N	A9H001	0.600	0.001	0.400	0.020	c = −0.03; m = 1.20; R^2 = 0.87	97.1
PO_4-P	C5H035	0.200	0.002	0.210	0.003	c = −0.55; m = 3.38; R^2 = 0.88	100.0
NO_2-N + NO_3-N	K1H004	0.500	0.001	0.220	0.020	c = 2.28; m = 1.40; R^2 = 0.88	100.0
PO_4-P	K3H001	0.300	0.029	0.117	0.006	c = −0.57; m = 1.56; R^2 = 0.99	96.8
NO_2-N + NO_3-N	R2H010	0.300	0.016	22.50	0.020	N/A	100.0
PO_4-P	R2H010	0.300	0.016	5.360	0.003	N/A	100.0
NO_2-N + NO_3-N	S7H001	0.100	0.007	8.520	0.020	N/A	95.7
NO_2-N + NO_3-N	T5H002	0.001	0.001	0.001	0.001	c = 12.2; m = 1.31; R^2 = 0.85	100.0
PO_4-P	T5H002	1.000	0.100	0.040	0.003	c = −1.10; m = 1.33; R^2 0.87	95.2
NO_2-N + NO_3-N	W2H009	0.500	0.034	1.900	0.020	N/A	96.8
PO_4-P	W5H026	0.800	0.006	0.331	0.003	N/A	98.9
PO_4-P	X2H015	2.000	0.575	0.295	0.003	N/A	99.7
NO_2-N + NO_3-N	X3H006	0.880	0.001	0.300	0.020	c = −0.51; m = 1.32; R^2 = 0.91	100.0

The units for Q_{pmax} and Q_{pmin} are $m^3 s^{-1}$ and for C_{pmax} and C_{pmin} are $mg l^{-1}$.

Cape. The case study of the model applied to data collected at the point source dominated R2H010, shows that the parameters Q_{pmax}, and C_{pmax}, estimated in the model, are reasonably representative when compared to measured data. The land cover within the catchment upstream of X3H006 supports the model indication of a strong diffuse source. The land cover is dominated by forest plantations and some irrigated permanently cultivated land, which are both land cover types that are associated with diffuse sources of nutrients into rivers.

Investigating the land use (using Google Earth) in the vicinity of the other sites where significant point sources have been simulated by the model reveals that in all cases there is evidence of nearby upstream land uses that would be expected to generate a point source signature. The most dramatic effects are at X2H015 (Figure 7(f)) located about 15 km downstream of large pulp and paper mill and at S7H001 (Figure 8(d)) located within the centre of a major town (Butterworth) in the Eastern Cape Province. Performing the same model credibility checks for the diffuse source component of the model is far more difficult as it is less straightforward to identify the land uses that result in diffuse source inputs of nutrients. However, sites T5H002 (Figure 8(e)) and A9H001 (Figure 8(b)) are both within densely populated rural areas where strong diffuse signatures might be expected (intensive agriculture is also evident upstream of A9H001), while C5H035 (Figure 7(b)) is downstream of a substantial area of irrigated agriculture.

The proposed model is advantageous in that the model requires relatively few data. The model requires historical monitoring flow and nutrient concentration data, to give some measure of the diffuse and point source contribution of nutrients impacting a particular river reach. The model proposed by Bowes *et al.* (2008) requires similar data, however, their model was found to be not appropriate to conditions in South Africa. Hilton *et al.* (2002) proposed a model to estimate the relative contributions of point and diffuse source phosphorus to in-stream concentrations. Their model utilised land cover information, export coefficients and routine historical monitoring flow and nutrient concentration data. While the simple nutrient model proposed in this paper requires few data, other sources of data are valuable in confirming the model results, such as observed effluent flow and nutrient concentration data from WWTW.

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While the model attempts to simulate the variability of in-stream nutrient concentrations due to point source inputs, the data also show considerable scatter in the perceived diffuse source signature at many monitoring points (Figures 7(b), (d) and 8(b), (e)). The calculation of the upper 90% prediction limit for the diffuse signature regression equation represents an approach to incorporate a rudimentary estimate of uncertainty into the diffuse source signature component of the model. The use of the upper prediction limit reflects the fact that the main water quality management issues would be associated with excessive nutrient concentrations. There are various reasons why the diffuse source signature should show variability. However, no mechanistic understanding of this variability was built into the model because of a lack of information available to define the parameters of what would then be a more complex model. For example, diffuse source concentrations might be expected to vary with antecedent runoff conditions related to the build-up of nutrients during dry periods and potentially low levels of nutrient availability following wet periods. This antecedent effect could be due to complex input–storage–outflow relationships. The effects of antecedent conditions may be one reason why some monitoring point data show quite a wide scatter of nutrient concentrations at moderate to high flows. Antecedent conditions could be included in a somewhat more mechanistic model of the diffuse source input making use of some type of storage-outflow function to quantify nutrient availability, or by using a measure of antecedent flow in a multiple regression equation in place of simply the present day flow. A previous attempt was made to account for antecedent conditions, but it was found to be difficult to identify an appropriate antecedent period that was generally applicable to a wide range of sites (Slaughter 2011). The historical monitoring flow measures from DWA gauges are daily means, while corresponding nutrient measures are grab samples. In-stream nutrient concentrations may change within the period of a day. It has been demonstrated that effluent from WWTW show a high degree of temporal variance in both effluent flow and nutrient concentration. Diffuse sources of nutrients may also cause a high degree of variance in in-stream nutrient concentrations within a period of a day. High intensity rainfall events may occur over a period of minutes or hours. This mismatch in temporal representation between historical DWA flow and nutrient concentrations may be a shortcoming of the model represented here. However, these are the best data available with which to construct the model. For reasons that were explained earlier, it is unlikely that point source inputs would result in high nutrient concentrations at high flow. If this were the case, even catchments dominated by point sources with little or no diffuse sources would show higher nutrient concentrations at high flows.

Seasonal variations in the application of fertilisers to agricultural land may contribute to variability, although no clear seasonal variations in the nutrient signatures were identified for the sites used in this study. Nutrients are also subject to in-stream modification, such as nitrification of nitrogen species and nutrients being taken up by aquatic flora. These are likely to be highly temporally variable processes that would further contribute to variability in the relationships between flow and nutrient concentrations. For example, degradation rates of nitrogen are related to temperature, and are therefore dependant on seasonality. Variability could also be the result of high flow processes in larger rivers re-introducing nutrients derived from point or diffuse sources into the water column through scouring of the channel sediments.

Certain countries gauge the need for management intervention on estimates of annual nutrient load. It is also possible to obtain an estimate of annual nutrient load using this model, provided that daily flow observations are available. Given daily flows, the model can be used to calculate a daily nutrient load, which can be summed to estimate the annual load. In this case, the point source envelope would not be used to calculate the point source signature for a particular flow, as this represents the maximum possible in-stream nutrient concentration due to point source influence. The same uniformly distributed random number method that was described earlier could be used to estimate a daily nutrient concentration due to point sources that would fall inside of the point source envelope curve. The diffuse source signature as represented by the regression line and not the upper 90% prediction limit can be converted to load directly.

Given that the model makes no explicit attempt to simulate in-stream nutrient processes, the implication is that the

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simulation of any point source impact would have to be in close proximity to the site of interest. However, it is possible that point sources that are located far upstream of the site of interest could generate a nutrient signature downstream that is more similar to a diffuse source. The reason for this is that the point source load during low flows could be partially taken up through the different in-stream processes discussed above, including the binding of nutrients to sediment particles. Some of this load could then be re-introduced to the water column during high flows, which would contribute to a downstream diffuse-type signal (i.e. higher concentrations associated with higher flows). However, this is not necessarily a shortcoming in the model as nutrients released from the sediments effectively become a diffuse source, even though the original source of the nutrients may have been a point source. The model may therefore be able to represent the result of these effects despite not simulating the processes explicitly.

CONCLUSION

This investigation shows that it is possible to separate nutrient concentration versus flow relationships in South African rivers according to whether they originate from point or diffuse sources. The study has proposed a simple mechanistic model for the point source component combined with a statistical model to represent the diffuse component. The results of applying the model are presented using the upper prediction limits of nutrient concentrations for different flows, which is aligned with the purpose of the model to support water quality management decision making. Most management decisions would be concerned with identifying situations where nutrient levels exceed certain thresholds of concern. Based on a number of study sites, which all have different observed nutrient–flow relationships, the model performs satisfactorily in that it can represent the envelope of observed concentrations.

The point source component of the model has the advantage over a simple statistical model in that the parameters are directly associated with the variations in point source discharge and concentrations. An implication is that the values of these parameters can be modified to investigate different management scenarios. An example might be to investigate the effects of increasing effluent discharges from expanding urban areas or improving the operational management of WWTW that are currently over loaded (Department of Water Affairs 2009).

The parameters of the diffuse source statistical model are far more difficult to identify with the possible causes as there is no mechanistic understanding contained within the model. Previous attempts to relate the variations in these parameter values to upstream land use types were not very successful (Slaughter 2011). Part of the problem is related to the availability of appropriate land use data that are explicitly associated with diffuse nutrient sources. This problem could be addressed through further data collection and analysis. However, part of the problem is also related to the complexity of nutrient transport processes at catchment scales, which cannot be resolved within a simple model of this type. The results indicate that the model can be calibrated against limited observation data and in a currently un-gauged situation these data could be provided through a short-term, water quality data collection programme covering a range of flow conditions. The opportunities for using the model to better understand the impacts of upstream land use developments, or water quantity and quality management decisions, are currently limited. Further research is required to link the parameters of the diffuse source regression equation to causative effects and part of this research may include choosing an alternative to the residual ratio approach for the regression model. Some qualitative assessments of the land uses upstream of the sites used in this study certainly confirm the likely existence of causative effects (densely populated rural areas and irrigated agriculture) at those locations where the data and the model indicate strong diffuse source signatures.

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