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Algal availability of phosphorus discharged from different catchment sources

Project number: **LWMD17**

Principal Investigators

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Project Objectives:
1. Describe the chemical forms and availability to algae of phosphorus contained within the discharge from a sewage treatment plant (STP), an irrigation return drain and an agricultural catchment within the Goulburn-Broken catchment.
2. Describe changes in the quantity of algal available phosphorus, including that associated with suspended sediments, from the different sources under different conditions of supply, including different flow rates and different seasons.
3. Measure longitudinal changes in the particulate and dissolved phosphorus concentrations immediately downstream of the three input sources.
4. Determine the algal availability of phosphorus in bottom sediments of the Goulburn River downstream of the three discharges.
5. Develop and test a non-specific sediment transport model incorporating particle settling and re-suspension, and couple this to a P-speciation model describing transformations between dissolved, particulate, and bottom sediment forms of P, to predict the downstream effects of nutrient discharges to streams.

Introduction:

General:

Algal Management Strategies, Nutrient Management Strategies and Catchment Management Plans frequently have as a major focus the reduction of phosphorus loads to surface waters. The expressed intention of the nutrient control is to reduce the frequency and intensity of algal blooms, particularly blooms of toxic cyanobacteria. In many instances a direct link between the magnitude of algal blooms and phosphorus loads has not been demonstrated. However, there is appreciable information in the scientific literature reporting on eutrophication that indicates phosphorus supply is likely to exert a major control on the intensity of algal blooms (Hecky and Kilham 1988). Certainly continued reduction in supply, if possible, will eventually restrict algal growth (Sas 1989).

The few detailed studies on rivers in the Murray Darling Basin have indicated that algal growth can become limited by phosphorus in these waters, but that nitrogen limitation is also common (Wood and Oliver 1995). The occurrence of nitrogen limitation when environmental conditions are suitable for the formation of a cyanobacterial bloom, accounts for the frequent appearance of nitrogen fixing species such as *Anabaena* in these river systems. The nitrogen fixing species circumvent nitrogen limitation, but their continued nutrient accrual as the population grows can subsequently result in phosphorus limitation. As a result of these interactions, reductions in phosphorus supply may reduce the occurrence of nitrogen fixing cyanobacteria, either by reducing their final biomass, or if the phosphorus is reduced to a level that leaves nitrogen present in excess, then by decreasing the likelihood of nitrogen limitation that provides them with an advantage.

Accepting the premise that phosphorus supply can be reduced sufficiently to curtail the occurrence of algal blooms, nutrient management strategies need to identify the major inflows supplying phosphorus to aquatic systems. In practice, phosphorus loads to receiving waters are calculated from the discharge volume and the total phosphorus concentration in each inflow. The measurement of total phosphorus includes all forms of phosphorus and consequently the total load calculation provides an estimate of the maximum phosphorus contribution from each source. A comparison of the total phosphorus loads across the sources is then used as a basis for targeting nutrient management strategies. Although other factors are considered in this decision, including the ease with which the phosphorus content or volume of inflows can be modified, the total phosphorus load is a key consideration.

Phosphorus occurs in many forms in aquatic systems and not all are readily accessible to algae (Bostrom et al. 1988; Oliver 1993). For example, phosphorus can be locked up within suspended sediments and colloids, incorporated into organic compounds, or stored within other organisms. As algae can only assimilate dissolved orthophosphate, less available varieties of phosphorus have to be converted into this form before they can be utilized. Transformations of the different compounds occur at different rates and some forms of phosphorus become available so slowly that they are unlikely to play a major role in supporting blooms. For example the phosphorus contained within the mineral matrix of suspended inorganic particles is released very slowly. In other cases, the phosphorus can almost immediately be made available; this is the case when it is weakly adsorbed to the surfaces of particles.

Measurements of total phosphorus do not identify the proportions that are available to the algae. This makes it difficult to predict the impact that a reduction in total phosphorus load will have on algal production, especially if it is suspected that the loads from different sources contain different amounts of available phosphate (Gerdes and Kunst 1997; Cottingham et al. 1995). A comparison of the loads of immediately available forms of phosphorus could improve identification of those inflows important in supplying phosphorus for algal blooms. A primary aim of this project was to compare the loads of algal available phosphorus to the Goulburn River from three sources previously identified as major contributors on the basis of their contributions to the total phosphorus load.

To fully assess the supply of phosphorus that could potentially support algal blooms it is necessary to measure not only the immediately available phosphorus but also the various types of phosphorus that, although initially unavailable, can be readily transformed into an accessible form. These transformations are complex and result from a number of biotic and abiotic processes that occur either in the water column or after transfer of material to the bottom sediments. The mixture of processes makes assessment difficult, but if phosphorus entering from a source undergoes large alterations in form, then differences in composition should appear in a longitudinal sampling series downstream of the source. Unfortunately, longitudinal transport also means that the impact of nutrient enrichment may occur at some distance from the source. A significant loss of phosphorus to the bottom sediments should also be apparent from a longitudinal sampling regime. Phosphorus that accumulates in the river bottom can act as a source of phosphorus at a later date, potentially enhancing the phosphorus supply to algal blooms growing nearby. This further complicates the assessment of phosphorus loads, because their influence may not be immediate, but may be realized at some future date.

Computer modeling provides perhaps the only means of including the large spatial and temporal scales that influence the extent to which phosphorus loads become available to support algae blooms. A further objective of this project was to develop and test models to describe the downstream transport of material, the transformations of phosphorus, and the vertical transfer of phosphorus to and from the bottom sediments. Numerical modeling provides a means of encapsulating and predicting the outcomes of these complex

interactions and has the potential to provide a major tool for understanding and managing phosphorus loads and fluxes.

The concept of nutrient load to a river:

Nutrient delivery to aquatic systems is generally assessed from the nutrient load contributed by each inflow. The nutrient load is calculated as the product of the nutrient concentration and the water discharge volume of inflows, which are measured at intervals and summed over time to give units of weight (eg. tonnes) per time (eg. year). The term "load" implies that the nutrient supplied by the source is retained within the receiving system, and that the nutrient quantity is increasing over time. However, care needs to be taken when interpreting the importance of a source load simply from its relative size compared to other sources.

A simple example of this approach is when nutrient loadings are calculated for a filling lake, where the load from different rivers, or even a single river, changes over time. The load calculation enables an estimate of the total quantity of nutrient delivered to the lake and the relative contribution of particular inflows. However, the simple load calculation does not tell the whole story because it is also important to know the final concentration of the nutrient in the lake as well as the total quantity. For example, the same nutrient load to a large lake will result in a lower nutrient concentration than in a small lake, simply because one contains more water than the other. Algae are usually restricted to obtaining nutrients from near-surface layers, especially during summer when temperature stratification occurs, so a lower concentration in the upper layers translates into a lower quantity of nutrient for the algae to access and consequently a lower maximum algal concentration. The total load would only be relevant if algae could access all of the nutrients in the water column. Lake nutrient loading models that estimate potential algal growth do not simply use the load but calculate the mean nutrient concentration from the total nutrient load and the volume of the lake.

Although the expected nutrient concentration in a lake can be estimated from the load, the direct comparison of river loadings will not necessarily reflect their role in influencing the lake nutrient concentration. An example will illustrate this point. If two rivers enter a lake and one provides twice the nutrient load of the other, this could occur because it has the same nutrient concentration but twice the discharge, or it could have the same discharge but twice the nutrient concentration. In one case there will be no change in the lake concentration while in the other case the nutrient concentration will increase. In both cases the quantity of nutrient delivered to the lake is the same but the water volume is different. If the nutrient concentration increases then a higher maximum algal biomass is expected to develop when conditions are suitable and so these equivalent loads will have different effects.

For a river receiving nutrients from tributaries or from artificial sources such as sewage treatment plants, the concept of a load is more complicated. If an amount of nutrient enters the river from a source but is moved downstream and washed out of the system, then the concept of a "load" to the river may not be appropriate. In effect, there will not be a load unless nutrient is retained within the river system or the concentration within the river water increases. The load calculation is useful for comparing the quantity of nutrient coming from each source, but the impact on the receiving water will not be obvious from the load calculation. If a source delivers a load at a higher concentration than occurs in the receiving water, then this will increase the concentration in the receiving water. This is considered an increased load as the quantity of nutrient per unit volume has increased and under suitable conditions the increased nutrient concentration will result in higher algal concentrations, provided that the nutrients are in a form that algae can access. In contrast, if a source delivers a load at the same concentration as the receiving water, then this will not alter the downstream concentration and will not influence the potential maximum algal concentration unless the nutrient is retained within the river and available forms accumulate.

Nutrient retention can occur if dissolved nutrients are taken up either by the bottom sediments or by organisms that are resident in the river, or if the nutrient enters in a particulate form that cannot be maintained in suspension. If a rapidly flowing river merges with a slower flowing river, larger particles that were suspended in the high flow will sediment out in the low flow, increasing the bottom store of nutrient in that section of the river. However, to have an impact on algal blooms, the increased quantity of nutrient must become available for use by the algae, either directly or following transformation. Consequently both the form of the supplied nutrient and its location within the river is important. If an increased load results through adsorption of dissolved nutrients onto the bottom sediments, or through sedimentation of nutrients with particles, the algae may not have direct access to these nutrient stores. The effect of the load will then depend on transformations of nutrients within the sediments and the vertical movement of bottom nutrients into the water layers where the algae grow.

The phosphorus available to support an algal bloom consists of dissolved ortho-phosphate which is immediately available for uptake by algae, plus any additional replenishment of ortho-phosphate that occurs within the time period of the bloom. It has been shown that suspended particles can be a major source of available phosphorus in turbid waters (Oliver 1993). Phosphorus that is weakly adsorbed to particles is rapidly released into solution as the algae take up the dissolved phosphorus. This exchange buffers the reduction in dissolved phosphorus concentration until the exchangeable component of the phosphorus on the particles is depleted. Similarly, phosphorus can exchange with the bottom sediments and this can augment the nutrient supply in the water when conditions are suitable. The re-supply of phosphorus from the bottom can be enhanced if the sediments are depleted of oxygen by bacterial metabolism, as this causes higher concentrations of dissolved phosphorus in the interstitial waters.

Assessing the influence of a nutrient supply on a receiving system is complicated and determined by a number of factors including: the nutrient supply (the load), the nutrient concentration, the nutrient form (availability), its transportation, and its transformations. The aim of this project was to provide a better understanding of these components as they influence phosphorus delivery to a river system, and to identify the implications for nutrient management. The study focuses on assessing changes in phosphorus supply in the context of its importance in stimulating algal growth. However, the extent to which algal growth will be enhanced also depends on the suitability of other environmental conditions that influence growth and enable the organisms to take advantage of the nutrient supply.

Location:

The project was based on the Goulburn River in North-East Victoria (Figure 1). The three major sources of phosphorus to this river were identified in previous studies from analyses of the total loads and are, irrigation return drains (contributing 47%), upland catchments with dryland farming (contributing 30%) and sewage treatment plants (contributing 14%) (Draft Goulburn Broken Catchment Water Quality Strategy 1996). The figure in brackets is the estimated percentage contribution made by each source to the total phosphorus load in the Goulburn River.

The purpose of this project was to identify the major interactions that influence the delivery, transport and transformation of phosphorus within the Goulburn River. Three field sites were selected to provide examples of each of the major phosphorus sources (Figure 1). The Acheron River drains an upland catchment of 700 km² containing improved pastures for cattle and sheep. The Shepparton sewage treatment plant (STP) operated by Goulburn Valley Water receives municipal sewage as well as fruit processing effluent. Effluent release is generally restricted to a six months period from May to October when river flows are high. Rodney Main Drain delivers return water from an irrigation area of 268 km² supporting horticulture, orchards and dairy cattle.

Each of the three sources enters the Goulburn River at locations where there is a downstream reach of at least 15 km that is largely unaffected by other inflows except during heavy rain. This allowed for longitudinal assessments of changes in phosphorus forms and concentrations downstream of each source. Nine transects were established in each experimental reach, with one transect located upstream of the source and eight located downstream at 1 to 2km intervals. The nine transects were surveyed for channel morphology and sampled for sediment characteristics. These locations were also used as longitudinal sampling positions to investigate phosphorus transformations and interactions with the bottom sediments as material moved downstream.

Figure 1. Map of the Goulburn River showing the three experimental sites (large filled circles).
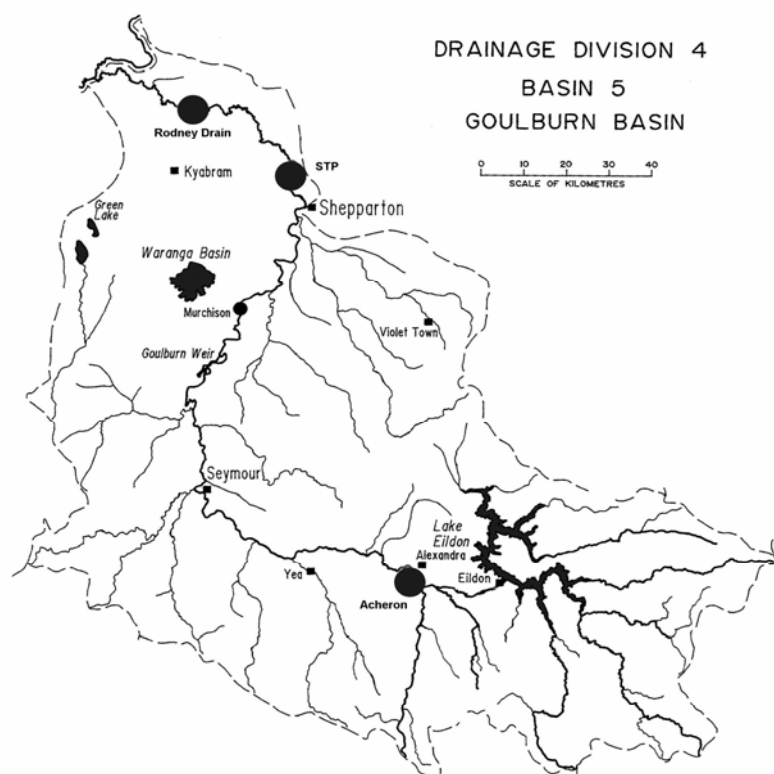
Methods:

Samples from the inflow sources were collected at fortnightly intervals and analysed for nutrient concentrations and water quality characteristics. Filtration (0.22µm) was used to partition the total phosphorus into dissolved and particulate forms, providing an estimate of the concentration of dissolved ortho-phosphate immediately available to the algae and the quantity of phosphorus associated with particles. The "algal available" phosphorus was measured using a phosphorus desorption technique developed in a previous LWRRDC project (No. 88/74) and involves the addition of iron oxy-hydroxide coated strips of filter paper to water samples. The iron strongly adsorbs dissolved phosphorus and rapidly depletes its concentration causing exchangeable phosphorus to move off the suspended particles into solution where it too adsorbs to the iron strips. This desorption technique provides a measure of the dissolved plus exchangeable phosphorus concentration and estimates the amount of algal available phosphorus in the sample. On occasions, samples were size fractionated using continuous flow centrifugation and tangential flow ultra-filtration to investigate the association of phosphorus with particles of different sizes. These

techniques were also used during selected field trips to measure changes in concentration and forms of phosphorus at intervals downstream from the sources. During these field trips adsorption isotherm experiments were used to assess the phosphorus adsorption characteristics of suspended particles and bottom sediments.

The potential phosphorus supply from the river bottom was estimated from vertical concentration gradients of phosphorus within the interstitial water of the sediments. Vertical profiles of interstitial phosphorus concentrations along with ammonia, iron and dissolved organic carbon concentrations were measured at selected sites using *in situ* pore water "peepers". The peepers are comprised of a vertical series of 6mm x 60mm, water-filled chambers, positioned at 1 cm intervals in a perspex plate and covered on each face with 0.22μm membranes. These devices were pushed into the sediment and left for periods of two weeks. Dissolved compounds in the interstitial water equilibrate across the membranes enabling the concentrations of dissolved species at different depths below the sediment surface to be measured. An attempt was made to identify the major processes generating the profiles and to estimate the potential phosphorus exchange rates by matching the shape of the concentration profiles with those generated by a digenesis model (SNAPP) devised by Dr. Mike Harper as part of NEMP Project UM036.

Sediment cores were taken from sites near to the peepers and frozen before being sliced into segments of few centimeters length to provide data on the depth distribution of total nutrients and total organic carbon.

To integrate the variety of processes influencing the movement and transformation of phosphorus within the river, a coupled sediment transport, phosphorus speciation model was derived and fitted to the field data.

Results against objectives:

Objective 1: The algal available component of the total phosphorus load from each of the three sources varied with conditions, especially changes in rainfall and flow (Figure 2). To provide an average estimate of the distribution of the total phosphorus between dissolved, exchangeable and particulate forms the cumulative load of each of these was calculated for the two-year sampling period (Figure 2). The total cumulative phosphorus loads for the two-year study period were 16, 11 and 34 tonnes respectively for the Acheron River, Rodney Drain and Shepparton STP. The average percentage contribution of the algal available phosphorus to the total phosphorus load was 32% in the Acheron River, 53% in Rodney Drain and 18% in the STP effluent. Consequently, the immediately available phosphorus supplied by each source was 5, 6 and 6 tonnes respectively. So despite significant differences in the total loads, each site supplied a similar quantity of immediately available phosphorus to the river. Consequently, transformations and re-distributions of phosphorus will be critical in assessing the relative impact of each of these sources. For example, it might be expected that the particulate phosphorus from the STP will be more readily transformed into an available form because of its organic composition, but its accessibility to algae will also depend on the location of this transformation and on nutrient redistribution within the water column.

The average percentage of algal available phosphorus associated with particle surfaces but rapidly exchangeable (measured using the iron-strip desorption technique) was 25%, 23% and 29% respectively for the three sites. The similarity of these percentages is surprising, as the particles from the STP are largely organic in composition and quite different from the more inorganic particles in catchment discharges. The value of the exchangeable phosphorus as a nutrient supply to algae will depend on the phosphorus adsorption characteristics of the particles and whether the particles are retained in suspension or settle to the bottom. However, it is apparent that in these systems most of the available phosphorus (ca. 75%) is delivered as 0.22 μm filterable reactive phosphorus. This has important catchment

management implications because strategies to minimise the release of dissolved phosphorus are far more difficult to implement than strategies to capture particle-bound nutrients.

Cumulative, total nitrogen loads over the same two-year period were 225, 37 and 139 tonnes respectively for the Acheron River, Rodney Drain and the STP. Ratios of TN:TP (14, 3, and 4 wt:wt respectively) indicate that the Acheron discharge is nitrogen rich relative to the needs of algae (7 wt:wt), while the other two sites are nitrogen poor. As nitrogen poor conditions enhance the likelihood of nitrogen fixing cyanobacteria occurring, the dynamics of nitrogen within the receiving water is of importance. Only preliminary information could be gathered on nitrogen within the resources of this project, and there is little information on the inorganic forms contributing to the total nitrogen load.

Cumulative Phosphorus Loads and Discharge in Rodney Drain

Legend: Discharge (ML/d) — FRP cumul (kg) — Fe-P cumul (kg) — TP cumul (kg)
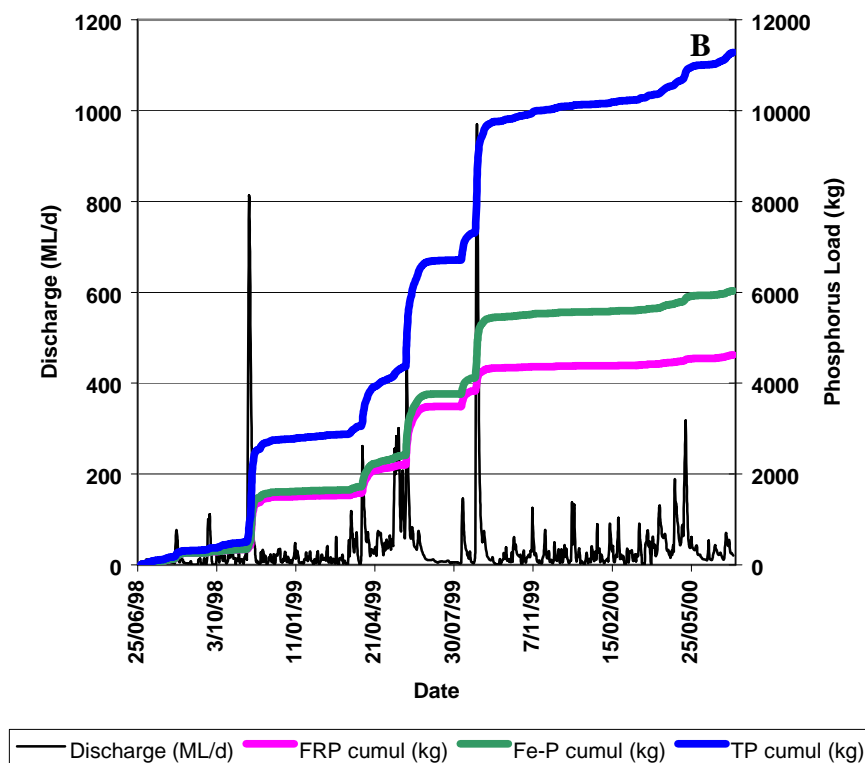
Cumulative Phosphorus Loads and Discharge in the Acheron
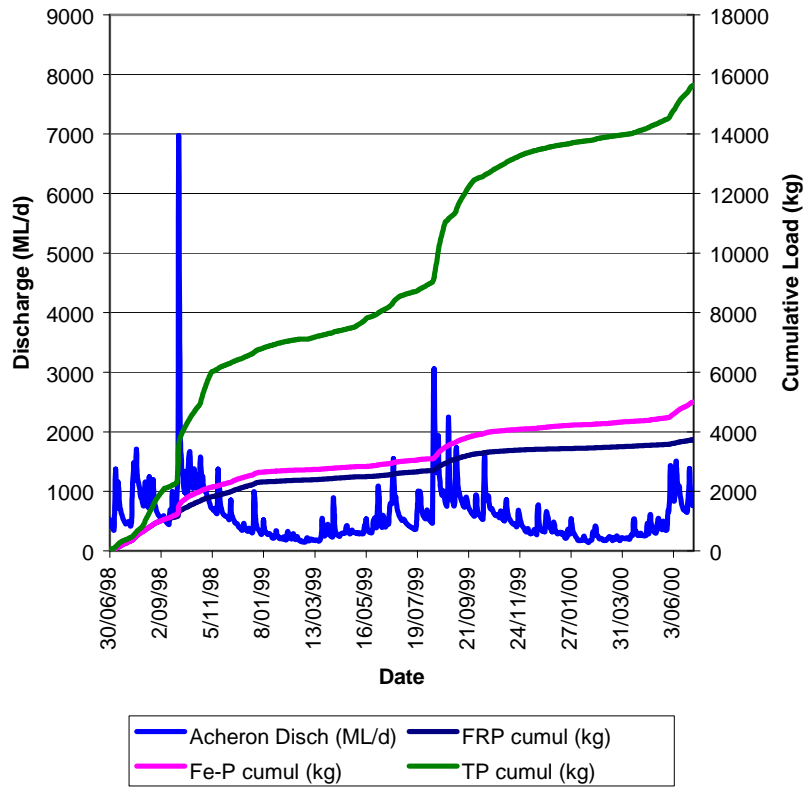
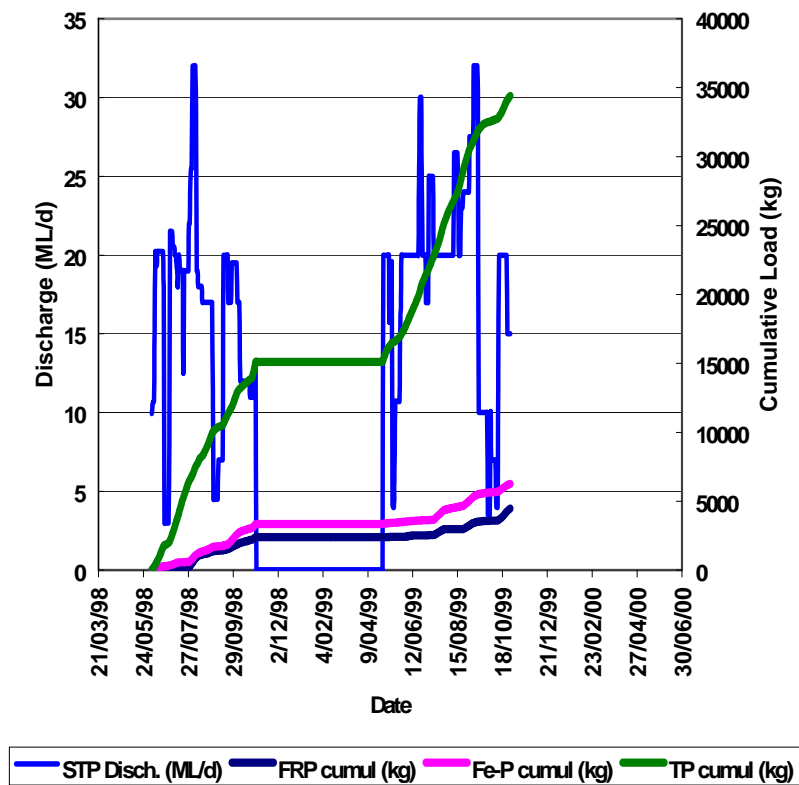## Cumulative Phosphorus Loads & Discharge from the Shepparton STP

Figure 2. Cumulative loads of total phosphorus, bio-available phosphorus (Fe-P) and filtered reactive phosphorus (FRP 0.22 µm) along with daily discharge for the period of the project.

Objective 2: In the Acheron catchment, large increases in cumulative phosphorus loads were associated with large increases in discharge (> ca. 1,500 ML/d), although not all flow events increased phosphorus loads to the same extent (Figure 2A). A similar pattern was observed in Rodney Drain, with larger loads being associated with increased discharge, although the discharge ranges are substantially less (max.950 ML/d) than in the Acheron River. Discharge levels of 150 ML/d were sufficient to increase phosphorus loads in Rodney Drain (Figure 2B). As expected, the phosphorus load from the STP is determined by the release rate, which is matched to dilution flows within the river.

The flow related increases of load in the Acheron River and Rodney Drain were partially due to the greater water volume being delivered, but are further accentuated by increased nutrient concentrations in the higher discharges, with very large increases obvious in the irrigation drain (Figure 3). In the Acheron River higher concentrations were mainly due to increases in non-exchangeable particle bound phosphorus, forms that are not immediately available to algae (Figure 3). The increased particle load was associated with increased discharge rather than with major local rainfall events, suggesting it results from re-suspension of bottom sediments or from upper-catchment sources. High flows in the Acheron occurred between August and October in both years.

In contrast, rapid increases in discharge and cumulative phosphorus loads in Rodney Drain were closely associated with rainfall events. Higher phosphorus concentrations were due to increases in the concentrations of both available phosphorus and particle phosphorus forms (Figure 3). It is suspected that increased phosphorus concentrations in the drain are the result of rainfall run-off from the surrounding irrigated catchment, especially in the first year of the record. In the second year rainfall did not always appear to cause increased discharge and in these cases phosphorus loads were not greatly affected. Because of these complex interactions large increases in loads were less predictable than in the Acheron River and occurred throughout the year. It is suspected that changes in drain management during the second year may have influenced loads.

Objective 3: Different longitudinal patterns in phosphorus concentration were observed in the Goulburn River downstream of each source. Despite carefully choosing sampling occasions to try and maximise differences in phosphorus concentration between the sources and the Goulburn River, the upstream and downstream concentrations were generally very similar due to the large dilution of the inflow. As expected, the greatest differences were observed from the influence of the STP and this site provided the best opportunity to examine changes in the river due to an increased phosphorus load.

The concentration of material measured immediately downstream of each source was usually the concentration expected from volumetric mixing of the inflow with the Goulburn River. Downstream changes were then compared with this expected starting concentration. Surprisingly, the concentrations of TP and FRP remained constant in the river reaches downstream of the sites. Even when inflows from the STP resulted in substantial increases (>30 µgP/L) in the concentrations of FRP and bioavailable phosphorus the concentrations remained constant to 26km downstream, which was the furthest measured point.

The phosphorus transport model (described later) provided an explanation for the unexpected constancy of the FRP and bioavailable phosphorus concentrations downstream of each source even when inflows causing substantial increases in phosphorus concentrations. In each case longitudinal measurements were made sometime after inflows

from the sources had commenced and within this period a new dynamic equilibrium had been established with the bed for an extensive distance along the river.
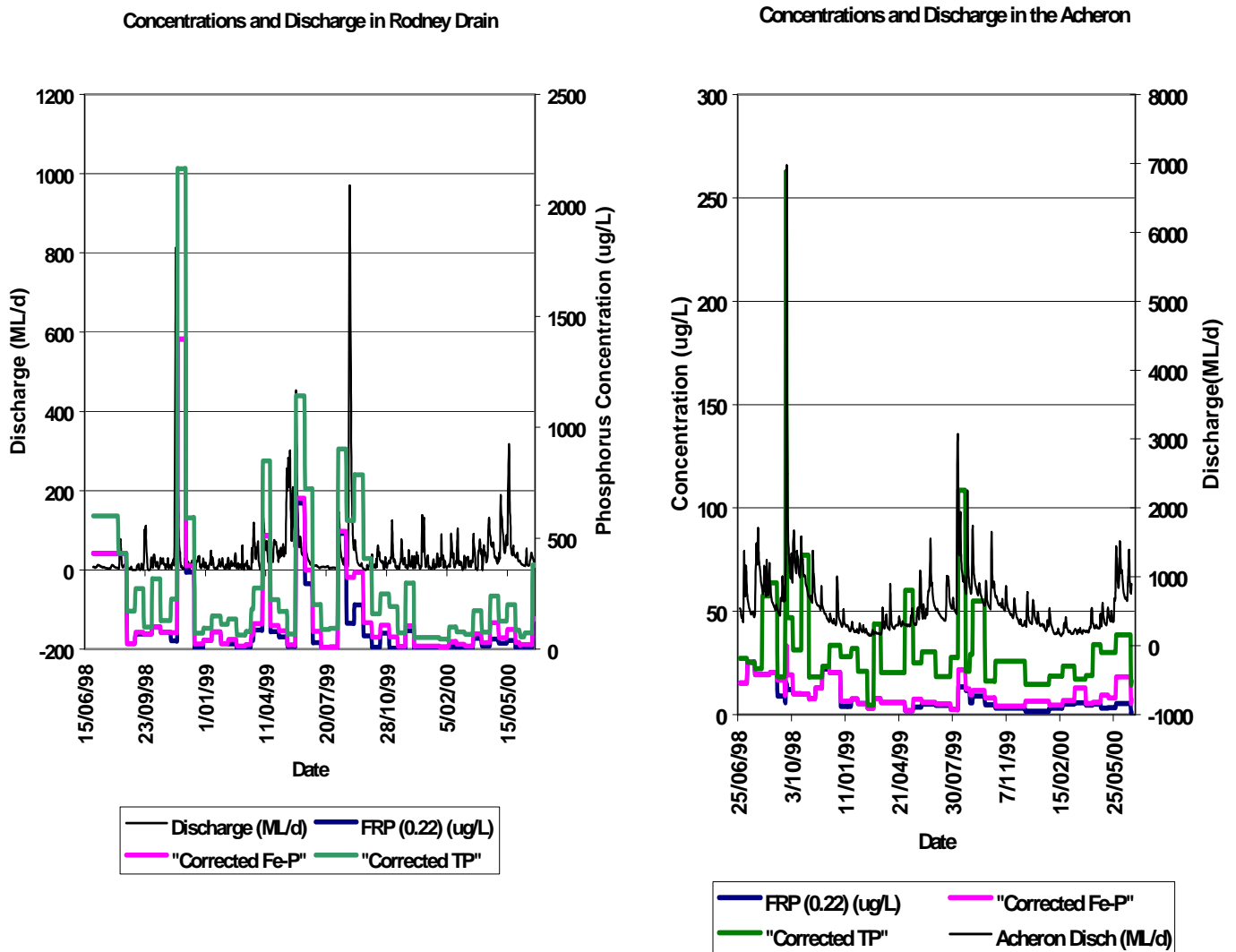
Concentrations and Discharge in Rodney Drain

Concentrations and Discharge in the Acheron

Figure 3. Discharge and concentrations of phosphorus in Rodney Drain and the Acheron River.

Objective 4: The exchange of nutrients between the bottom sediments and the overlying water is dependent on the dissolved nutrient concentration within the pore water of the sediment compared to that in the river water. If interstitial concentrations are high then nutrients will move into the water column at a rate determined by diffusion in the sediment and across the sediment-water interface. Two types of processes control the dissolved nutrient concentration in the bottom sediments; abiotic adsorption-desorption interactions between dissolved orthophosphate and particles; and the mixed biotic/abiotic processes that result from biologically mediated breakdown of organic material. The adsorption-desorption component is assessed in the section below dealing with the particle transport model (Webster et al. 2001).

Oxygen is utilised in the microbial breakdown of organic material and when the rate of breakdown exceeds the oxygen supply rate then oxygen concentration falls. Once the concentration is reduced to low levels the decomposers use other compounds in place of oxygen, first nitrate, and then iron oxyhydoxides, and finally carbon dioxide and sulphate can be utilised. Iron oxyhydroxides become soluble as a result of their transformation, and as the exchangeable phosphorus on particles is largely associated with iron, it too is released into solution. Anoxic conditions can therefore lead to large increases in the interstitial phosphorus concentration and potentially enhance its flux into the overlying water. Directly measuring the processes influencing sediment digenesis is difficult, especially when the bottom sediments show significant spatial variability and when environmental conditions change with time. Instead, the approach used here was to measure the interstitial concentrations of dissolved compounds that are important products of digenesis, including phosphorus, ammonia, iron, nitrate and dissolved organic carbon. Vertical profiles of interstitial concentrations were obtained from the deployment of peepers at each site to cover a range of sediment types. A digenesis model (SNAPP) developed by Harper (2001) as part of a NEMP Project (Final Report of NEMP Project: UMO36, "Nutrient release from river sediments: Phase II-Validation and application of sediment-release model") was used to help interpret the vertical concentration profiles and to estimate flux rates. This is a complex model and its application proved difficult, so the information presented here is of a preliminary nature. In essence, the variables of the model where estimated from measurements where possible, but in many cases general values from the literature had to be used. Further analyses on samples collected and stored during the project will continue and should improve the estimates of these variables and increase confidence in the interpretation of the model.

ACHERON PEEPER FRP
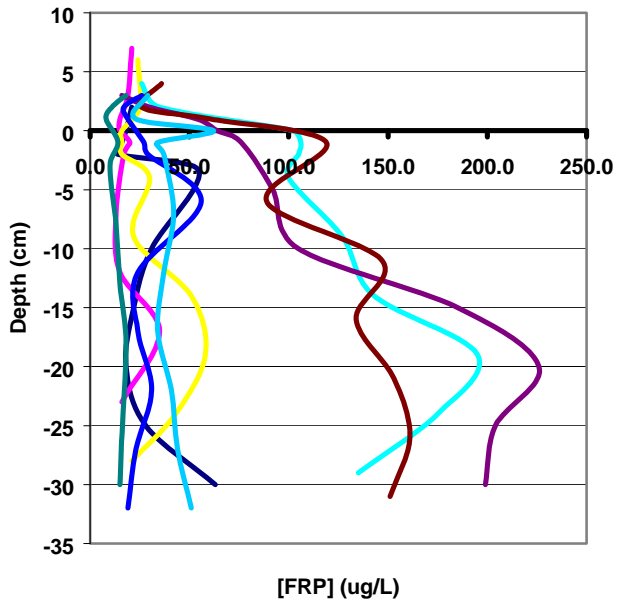
RODNEY PEEPERS FRP
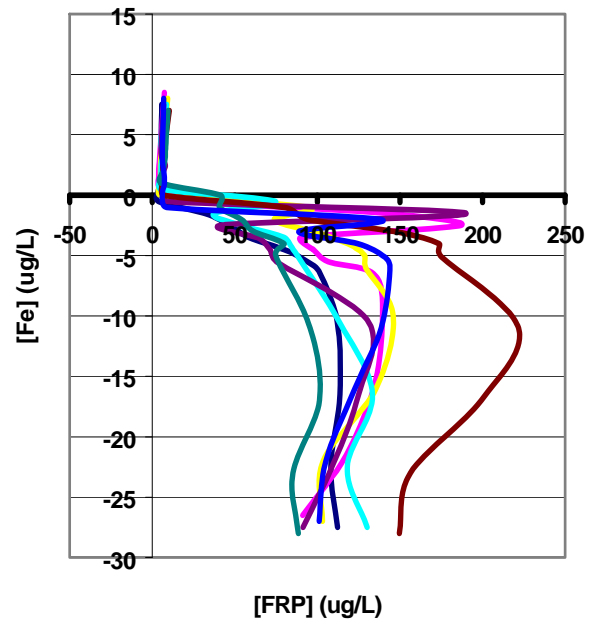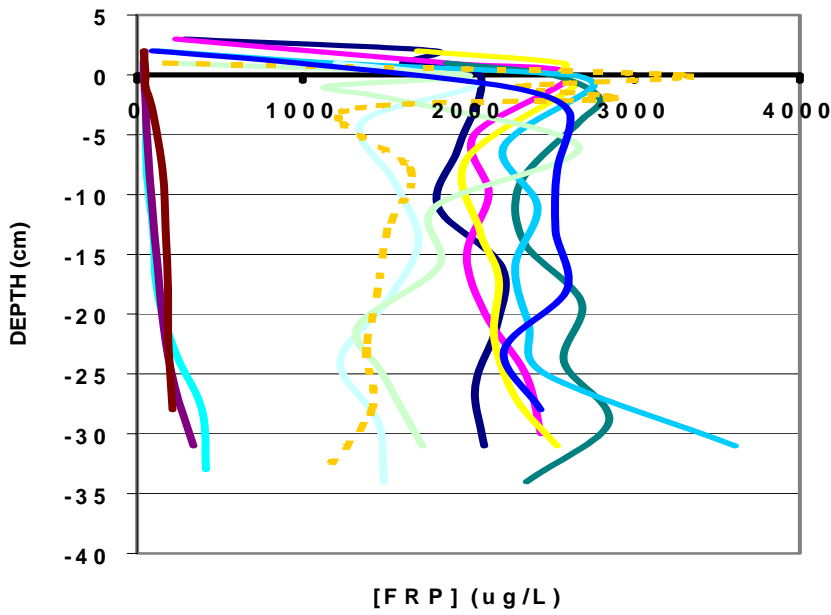
S T P   P E E P E R S   F R P

Figure 4. Vertical profiles of the dissolved phosphorus concentration in sediment pore water measured using peepers.

At each of the sites the peeper data grouped into only one or two sets even though an effort was made to cover a range of sediment types. Vertical profiles of pore-water reactive phosphorus concentrations determined from the peepers are shown in Figure 4. It is evident that high dissolved phosphorus concentrations occur in the sediments downstream of the STP and these are 10-20 times greater than concentrations measured at the Acheron site and the Rodney Drain site. Through a trial and error approach the SNAPP model was adjusted to approximate the FRP data and simultaneously match the profiles for iron and ammonium at each of the sites. At the STP site the maximum flux of phosphorus to the overlying water estimated by the model was 0.25 mmol/m²/d and occurred just prior to the reduction in the simulated organic load from the STP (Figure 5). Four weeks later, during the period when peepers were again installed, the estimated flux was 0.13 mmol/m²/d. If the average water depth is 1m and a parcel of water takes one day to traverse the 20km experimental reach, then the flux from the sediments increases the concentration in the water by 3.5 µgP/L.

At the Acheron River site the maximum flux was estimated at 0.025 mmol/m²/d, ten times less than that for the STP. Assuming the same estimates of travel time and water depth this flux would increase river concentrations by ca. 1 µgP/L (Figure 5).
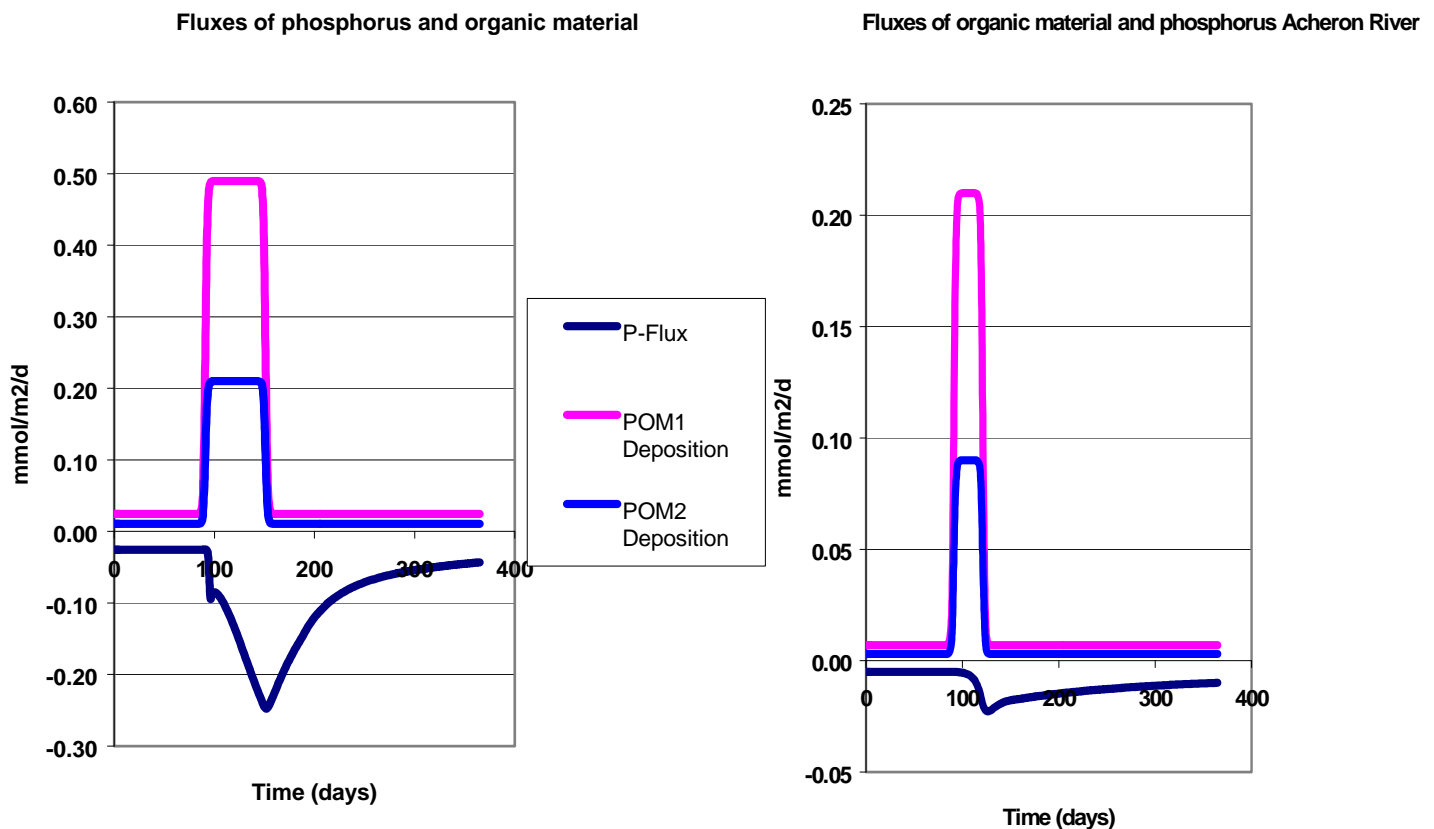

Figure 5: Deposition of particulate organic matter in two forms and the estimated phosphorus flux rate from the sediment to the overlying water modelled for two sites, (A) STP (B) Acheron River.

Objective 5: The phosphate ion is a highly surface active species which is readily adsorbed to clay particles in the sediment and the water column. The adsorption process has a fast initial step reflecting surface reactions and a slower intra-particle diffusion step (Barrow 1983). The initial adsorption step is reversible and the adsorption/desorption processes coexist in a dynamic equilibrium. This abiotic process can act as a key regulator of the concentration of dissolved P in the water column. As the water column P concentration increases, additional phosphate is adsorbed to the particles in both water column and sediment, as phosphate is taken up by phytoplankton additional P is released from the particles. These uptakes and releases dampen the fluctuations in water column phosphate and constitute a "phosphate buffer mechanism" (Froelich 1988). This model underpins much of our later analysis and discussion.

Quantitative analysis of adsorption

In the following, we describe the adsorption interactions between dissolved P and that reversibly adsorbed to suspended and settled sediments. In other words, we consider the fast-reaction component of P sorption only (adsorption). Figure 6 shows the results of a series of adsorption experiments performed on suspended sediment samples from stations in the
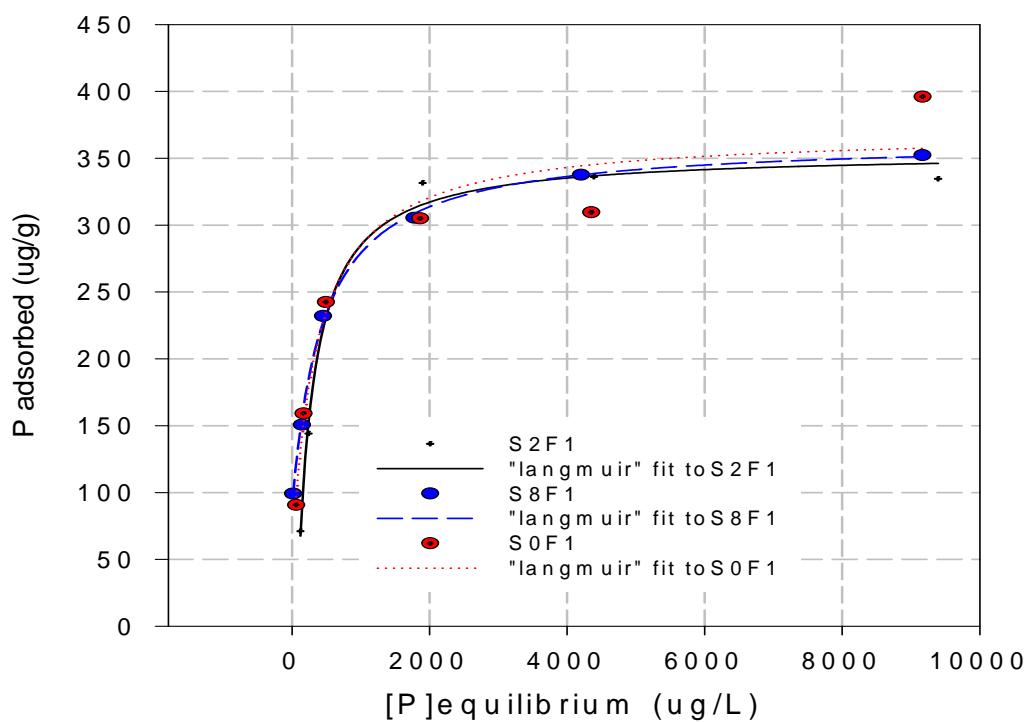

Figure 6. Adsorption experiments using suspended sediments collected downstream of the STP in the Goulburn River. Lines are Langmuir Isotherms fitted to the data.

Goulburn River downstream of the sewage treatment plant (STP) at Shepparton. The time taken for the determination was several hours so that these data could be reasonably expected to represent the fast sorption process. A mathematical expression frequently used to represent adsorption data is the Langmuir isotherm and the lines on Figure 6 show the result of fitting this expression to the data. The isotherm equation is:

$$P_S = \frac{P_{max} K_L P_D}{1 + K_L P_D} \qquad (1)$$

where P_S (kg kg^{-1}) is the concentration of P adsorbed to the sediment and P_D (kg m^{-3}) is the dissolved P concentration. Here and in the following, the dissolved concentration, P_D, will refer specifically to the inorganic phosphate that adsorbs to sediment surfaces. The equation requires the estimation of P_{max} which is the maximum adsorption capacity and K_L which is related to its slope at low concentrations (Froelich, 1988). These values were estimated by fitting the isotherm expression to the measurements. The rate of adsorption to sediments decreases as the dissolved concentration increases, but we are mainly interested in the adsorption behaviour near the natural concentration in the river. For low concentrations, the adsorption isotherm is approximately linear and can be expressed as:

$$P_S = K_D P_D. \qquad (2)$$

where $K_D = P_{max} K_L$ is the adsorption coefficient. The assumption of a linear adsorption isotherm vastly simplifies the analysis and is approximately valid provided that $K_L P_D < 1$.

Buffering capacity of suspended sediments
We consider what effect adsorption has on the availability of dissolved P in the water column for algal growth. With the simple adsorption/desorption model (Eq. 2), a change in the dissolved P concentration, ΔP_D, causes a change in the concentration of P adsorbed to the sediment, ΔP_S, according to:

$$\Delta P_S = K_D \Delta P_D \qquad (3)$$

The amount of P that has been desorbed from the suspended sediment to the dissolved form is $TSS \times \Delta P_S$, where TSS is the concentration of suspended sediment. The total amount of dissolved P sequestered by algae when the dissolved concentration is reduced by ΔP_D would be:

$$\Delta P_{Ex} = \Delta P_D + TSS \times \Delta P_S \qquad (4)$$

so that a buffering capacity for the suspended sediment, Ω, can be defined by:

$$\begin{aligned} \Omega &= \frac{\Delta P_{Ex}}{\Delta P_D} \qquad (5) \\ &= 1 + TSS \times K_D \end{aligned}$$

after substitution of Eq. 3 into Eq. 4. The buffering capacity describes the ability of the suspended sediment in a river to provide P for algal growth beyond that residing in the dissolved pool. A buffering capacity of unity means that the suspended sediment has no effect on the availability of P.

Sediment – water column exchange dynamics

We now consider the adsorption/desorption reactions between dissolved P in the water column and surficial sediments. As before for suspended sediments, we ignore biotic uptake by benthic organisms and co-precipitation with calcite. Australian lowland rivers are mainly soft and so precipitation of calcite minerals is not generally important. The Murray satisfies this criterion certainly as far downstream as the junction with the Darling (Mackay *et al.* 1988).

Suppose that the sediment and water column are initially in equilibrium with one another with respect to *P* concentrations. Even though phosphate ions cross back and forth across the sediment surface, the net flux is zero. In this situation, the (dissolved) concentration in the water column equals the pore-water concentration; that is, the dissolved concentrations in both sediments and water column are equal and $P_D = P_0$ (Fig. 7).
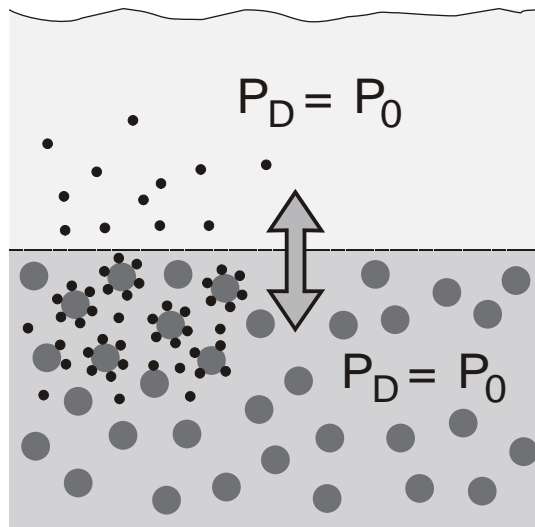

Figure 7. Schematic of P adsorption/desorption equilibrium between sediments and water column.

If we further define the bulk concentration of exchangeable P within the sediments to be P_T (kg m⁻³) and the concentration of P adsorbed to the sediments to be P_S (kg kg⁻¹), then the bulk concentration of P in the sediment is:

$$P_T = \phi P_D + (1-\phi)\sigma P_S \qquad (6)$$

where P_D is the pore-water concentration (kg m⁻³), ϕ is porosity and σ is the density of the sediment grains.

If we assume that adsorption/desorption obeys similar dynamics within the sediments as in the water column, then Eq. 2 applies and Eq. 6 reduces to:

$$P_T = (\phi + (1-\phi)K_D\sigma)P_D$$
$$= \psi P_D \qquad (7)$$

where K_D is an adsorption coefficient appropriate for settled sediment and $\psi = \phi + (1-\phi)K_D\sigma$. Comparison of Eqs. 5 and 7 shows that ψ is equivalent to a buffering capacity of the surficial sediment. If we set $K_D = 10\,\mathrm{L\,g^{-1}}$, take a nominal value for ϕ of 0.5, and use $\sigma = 2{,}650\ \mathrm{kg\,m^{-3}}$, then $\psi \sim 13{,}250$. In other words, the amount of *P* adsorbed to the sediment is many times that in the pore water. A surficial sediment layer of 1cm

thickness would contain the same store of *P* as a water column 133 m deep if the concentration in the water column equalled that in the pore water.

The diffusion of P through the sediment is described with the one-dimensional diffusion equation:

$$\frac{\partial P_T}{\partial t} = D_S \phi \frac{\partial^2 P_D}{\partial z^2} \qquad (8)$$

The term on the left hand is the rate of change of the bulk P concentration with time *t*. The term on the right is the divergence of the flux due to molecular diffusion through the interstices and so it involves gradients in the pore-water concentration only. D_S is the molecular diffusivity of P within the sediment matrix. This diffusivity is reduced from its value in free water because the diffusing ions have longer pathways due to their having to diffuse around sediment grains (Berner 1980). The sediment is assumed to have uniform physical properties and concentrations of P are assumed to vary in the vertical coordinate, *z*, only. Substitution for P_D from Eq. 7 gives

$$\frac{\partial P_T}{\partial t} = \frac{D_S \phi}{\psi} \frac{\partial^2 P_T}{\partial z^2} \qquad (9)$$

Equation 9 has the form of the normal one-dimensional diffusion equation if an effective diffusivity is defined as:

$$D' = \frac{D_S \phi}{\psi} \qquad (10)$$

Longitudinal distribution of P in the Goulburn River

We investigate the dynamics of P exchange within the Goulburn River by examining the adjustment of dissolved P concentrations downstream of the discharge of treated sewage from the Shepparton STP (sewage treatment plant). For this analysis, we apply a model of P transport in a river, which includes downstream transport in the water column by the river flow and also adsorption and diffusion through the riverbed (Fig. 8). The model considers that P which is potentially exchangeable between its adsorbed and dissolved phases. The model does not consider explicitly the fate of other forms of P such as dissolved and particulate organic P. The implications of uptake by phytoplankton are considered later.
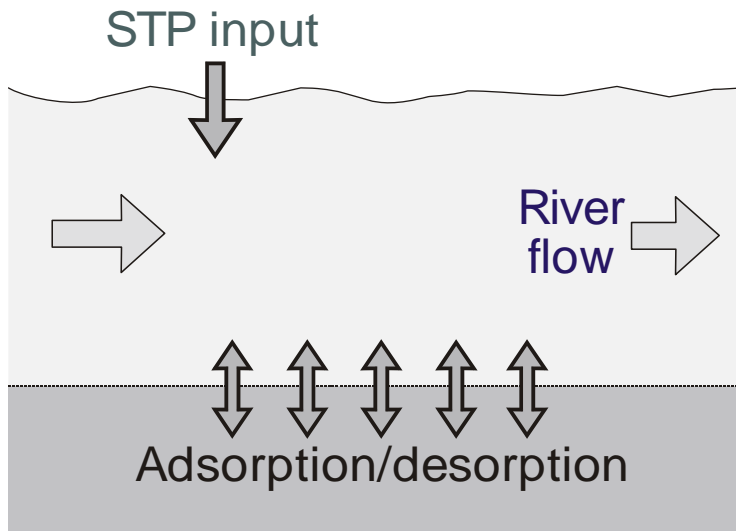
Figure 8. Schematic of modelled phosphorus transport in the Goulburn River showing downstream advection and adsorption/desorption with the riverbed.

Model description

The model assumes the river to be of uniform depth, h, and to have a uniform width, w. The origin of the model coordinate system, $(x,z)=(0,0)$, is defined to be the sediment surface at the point of discharge of the excess P into the river. The coordinate x aligns with the downstream direction; z is the vertical coordinate as before. The equation for the total (exchangeable) P concentration in the water column, P_T, is

$$\frac{\partial P_T}{\partial t} + U \frac{\partial P_T}{\partial x} = \frac{F}{h} - G \qquad (11)$$

where t is time, U is the river flow speed, F is the flux of phosphorus from the sediment into the water column, and G is a loss term due to the uptake of dissolved P by phytoplankton. The first term on the left hand side of this equation describes the time rate of change of P in the water column. The other term on the left accounts for changes in the water column concentration due to advection of P downstream. The term involving F on the right hand side is the change in the water column concentration due to adsorptive or desorptive exchange with the bed. The phytoplankton growth term will be set to zero for now. Equation 11 describes 'plug flow' in the river; longitudinal dispersion is neglected. We consider the water column to be sufficiently well mixed vertically and laterally that water properties are effectively uniform in these two dimensions so that riverine transport can be represented using a one-dimensional equation in the downstream direction.

The transport of exchangeable P within the bed is assumed to be described by Eq. 9. The modelled concentration of total P in the sediments and in the water column is obtained as the solution of the coupled equations Eqs. 9 and 11. The equation for total P in the water column (Eq. 11) is solved numerically using an upwind differencing scheme (Roache, 1982). The equation for the diffusion of P through the sediments is also solved numerically using a forward-time central-difference discretisation scheme (Roache 1982). The time and space intervals used in the schemes were checked to ensure proper convergence of the numerical solutions.

The solutions of Eqs. 9 and 11 are coupled by the flux of P across the sediment surface into the water column. The flux is limited by transport across the diffusive and turbulent boundary layers within the water column just above the surface and can be represented by expressions of the form:

$$F = \text{St} \times U \times (P_D^0 - P_D^w) \qquad (12)$$

where St is the roughness Stanton Number, a prescribed function of flow speed, surface roughness, and free-water diffusivity of *P*. We choose a formulation of St proposed by Bilger and Atkinson (1992) and assume a surface roughness of $0.01\,\text{m}$ for the Goulburn River application. In Eq. 12, P_D^0 is the concentration of P in the pore water at $z = 0$ and P_D^w is the concentration of dissolved P in the water column. Both P_D^0 and P_D^w are obtained as part of the modelled solution in the water column and sediments.

Application to the Goulburn River at Shepparton
For application to the Goulburn River, the model requires the specification of desorption coefficients for suspended and settled sediments, the suspended sediment concentration and dissolved P concentrations in the river upstream of the STP, and the loading of dissolved P from the STP. These are estimated as follows:

Desorption coefficients
Desorption coefficients were estimated directly in the laboratory by measuring the amount of P that is adsorbed to suspended sediment at increasing concentrations of dissolved P additions. Experiments were performed on water samples collected on October 13, 1999 at S0 upstream of the STP discharge and at S3, 1950 m downstream of the STP discharge. The adsorption coefficients, $K_D = P_{\max} K_L$, determined in this way are 54 and 99 Lg^{-1} at S0 and S3 respectively, values that seem very high compared to other values measured in Australian rivers (Oliver *et al.* 1998).
An alternative method for estimating an effective K_D is to solve Eq. 5 for K_D in terms of the other parameters in the equation; that is:

$$KD = (\frac{\Delta Pex}{\Delta PD} - 1)TSS^{-1} \qquad (13)$$

ΔP_{Ex} in this situation is estimated as the measured Fe-strip exchange concentration, ΔP_D is measured FRP, and *TSS* is our estimated concentration of total suspended solids. Table 1 shows the value of K_D

Site	Date	Method	K_D (Lg⁻¹)	pH
S0	13/10/99	Isotherm	54	7.0
S3	"	"	99	7.0
S0	12/10/99	Iron-strip	17.1	7.0
S0	13/10/99	"	8.8	7.4
S2-S8	12/10/99	"	5.7	7.4
S2-S4b	13/10/99	"	4.2	7.4

Table 1. Comparison of adsorption coefficients estimated using differing methods.

The iron-strip method yields K_D's that are an order of magnitude smaller than those estimated from the adsorption experiments. Possible explanations are that the isotherm method measures adsorption rather than desorption measured by the iron-strip method. Also, it is known that pH can have a significant effect on adsorption/desorption of P. In Table 1, the three highest K_D's were measured with the lowest pHs. Application of the Fox model of phosphate adsorption to iron oxyhydroxide (Fox, 1989) would suggest a reduction in K_D by a factor of 3.0 when the pH is increased from 7.0 to 7.4. Thus, the variation in pH could

at least partly explain the range of K_D. The iron-strip determination of K_D for S0 on the 12/10/99, when adjusted for a pH of 7.4 using the Fox model, becomes 5.7 which is more in line with the other three iron-strip determinations. For the base run in the model, we set $K_D = 10\,\mathrm{Lg}^{-1}$ and will explore the effect of significantly varying K_D from this value. The value of K_D assigned to the surficial sediment will also be assumed to be $10\,\mathrm{Lg}^{-1}$ although this may not be the case in reality. Webster *et al.* (2001) have shown that adsorption over seasonal time scales involves only the top few millimetres of sediment if transport is assumed to be diffusive. We might reasonably expect that the surficial sediments (top few millimetres) have similar properties to the suspended sediments.

Riverine suspended sediment concentration
Long-term measurements of water quality parameters including suspended solids have been made on a monthly basis at Shepparton upstream from the STP (site 405204C). Between 11/3/99 and 26/6/00, continuous measurements of turbidity were made using a Hydrolab probe at a site just upstream from the STP discharge. There is a good correlation between suspended solids and turbidity measured at the same time (Fig. 9). We calculate a continuous time series of TSS from the Hydrolab data using the best fit relationship:

$$TSS(\mathrm{mgL}^{-1}) = 1.65\,(\mathrm{mgL}^{-1}) + 1.04\,(\mathrm{mgL}^{-1}\mathrm{NTU}^{-1}) \times Turbidity \qquad (14)$$

Riverine dissolved P concentration
Dissolved P concentrations have been measured routinely at site 405204C as well as at site GR11, several kilometres further upstream of the STP. The average concentration for the period 5/5/99-9/11/99 for which there are coincident measurements is $13\,\mu\mathrm{gL}^{-1}$ at 405204C versus $70\,\mu\mathrm{gL}^{-1}$ measured at GR11 on behalf of Goulburn Valley Water (GVW). Measurements made in the river on 23/9/99, 12/10/99, and 13/10/99 by the MDFRC appear to lie between the other two sets of measurements. The significant differences between the measurements at 405204C and at site GR11 are difficult to reconcile. These sets of measurements were undertaken by different laboratories so it would appear that the treatment of samples and the laboratory techniques for their analysis may be responsible for the discrepancy. We shall adopt the measurements obtained for the GVW, not because they are necessarily correct, but because they should provide consistency with their measurements of dissolved P in the STP discharge.
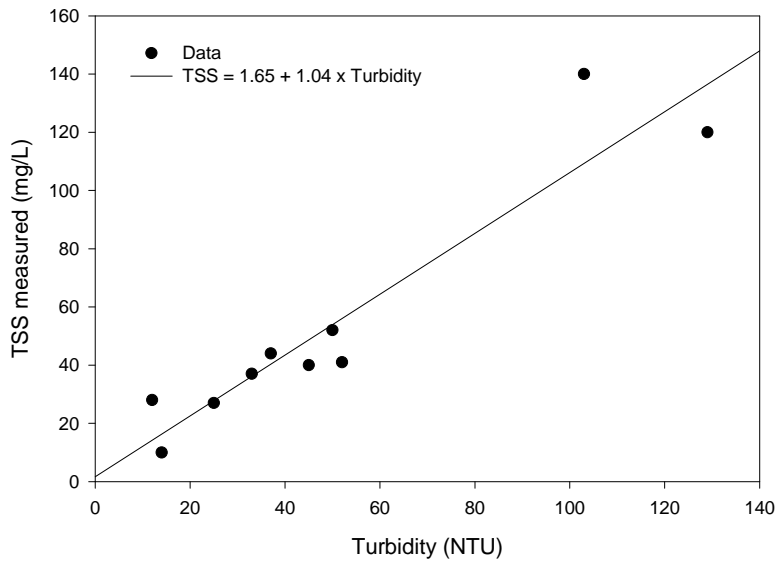
Figure 9. Plot of *TSS* measured at GR 11 versus turbidity measurements obtained with the Hydrolab.

Examination of the time series of dissolved P concentrations through 1999 suggests that they generally increased with discharge. However, dissolved P concentrations appeared to be even better related to *TSS*. Figure 10 shows the 1999 FRP concentrations measured at GR11 plotted against *TSS* inferred from the Hydrolab measurements. We fitted the measured dissolved P concentrations using the relationship:

$$P_D = 49\,\mu\text{gL}^{-1} + 0.00478\,(\mu\text{gL}^{-1}/(\text{mgL}^{-1})^2) \times TSS^2 \qquad (15)$$

Estimation of dissolved P in STP effluent
Four measurements of FRP in the STP effluent were obtained by the GVW during the period of effluent discharge. The results ranged between a low concentration of $890\,\mu\text{gL}^{-1}$ to a high of $3{,}300\,\mu\text{gL}^{-1}$ with an average of $1{,}540\,\mu\text{gL}^{-1}$. Fortnightly measurements of FRP by the MDFRC showed the concentration to be highly variable between sampling times. Concentrations varied from less than $20\,\mu\text{gL}^{-1}$ to a high of $3{,}106\,\mu\text{gL}^{-1}$. The average concentration was $948\,\mu\text{gL}^{-1}$ which is substantially less than that measured by the GVW. However, the MDFRC samples were filtered with a $0.22\,\mu\text{m}$ filter prior to analysis, whereas the GVW used a $0.45\,\mu\text{m}$ filter. The MDFRC also measured iron-strip phosphate on the samples. The average iron-strip exchangeable phosphate was measured to be $1{,}241\,\mu\text{gL}^{-1}$ with an expected error of the mean of $184\,\mu\text{gL}^{-1}$. For the model of P transport in the river, it is the total exchangeable P in the effluent that is the pertinent input to the river. The measurements of FRP in the effluent by the GVW agree with the MDFRC iron-strip determination within 20%, but for consistency with the upstream measurements of phosphate we will use the GVW measurements for effluent concentration as well. Further, we will specify the exchangeable phosphate concentration in the effluent to be a constant $(1{,}540\,\mu\text{gL}^{-1})$ despite the certainty that the true concentration underwent large deviations from this value during the period of discharge.
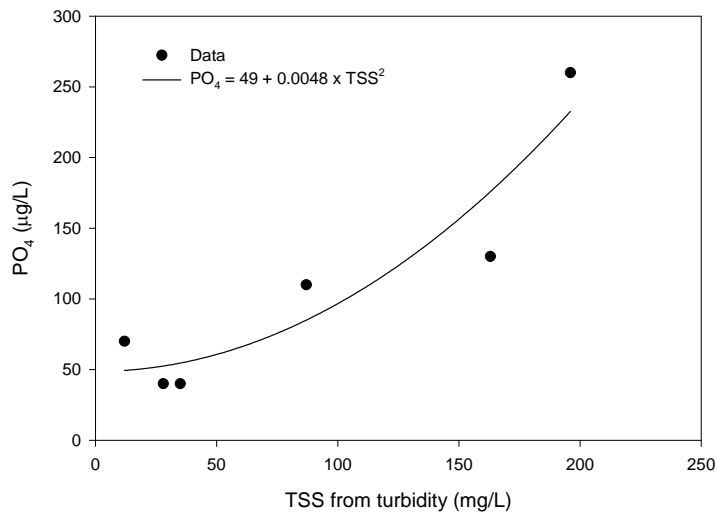
Figure 10. Plot of FRP measured at GR11 versus TSS estimated from Hydrolab probe.

Other parameters
River discharge levels required by the model were obtained from a gauged station. Daily volumes of the STP discharge were obtained from GVW. Sediment porosity was measured at three locations at each of sites S2 and S8. The porosities of the six samples varied between 0.41 and 0.71. In the model, we use the mean porosity of 0.55.

Model results
The model was run for the nine-month period 12/3/99 to 31/12/99 corresponding to Julian Day (JD) 71 to 365. The initial condition of dissolved P and suspended sediment concentration on JD 71 was set equal to the upstream (upstream of the STP) concentrations on that day. The base model run, which we present first, assumes $K_D = 10\,\mathrm{Lg}^{-1}$ and the other loading parameters as defined in the above paragraphs.

Figure 11 shows the predicted concentrations of dissolved P, P_D, at 50 km intervals along the Goulburn River starting from immediately upstream of the STP outfall. The STP discharges to the river between JD 121 and JD 301. For most of the time, the specified P_D upstream of the STP is less than $60\,\mu\mathrm{gL}^{-1}$, but during periods of elevated discharge ($> 1000\,\mathrm{MLd}^{-1}$) between Julian days 97-100, 152-177, 221-257 and on JD 313, upstream P_D exceeded this value substantially. Most of the time *TSS* is $\sim 50\,\mathrm{mgL}^{-1}$, but during the periods of elevated discharge *TSS* was measured to be considerably higher. It is our assumed relationship between *TSS* and P_D that causes the elevated concentrations of dissolved P during flow events. Even though the flow event between JD 97-100 had a maximum flow ($3{,}700\,\mathrm{MLd}^{-1}$) that was much less than that of JD 221-257 ($16{,}631\,\mathrm{MLd}^{-1}$), the maximum calculated *TSS* in the first event ($340\,\mathrm{mgL}^{-1}$) was substantially greater than that in the other event ($207\,\mathrm{mgL}^{-1}$). A different assumed relationship between *TSS* and P_D would change the time series of upstream P_D.
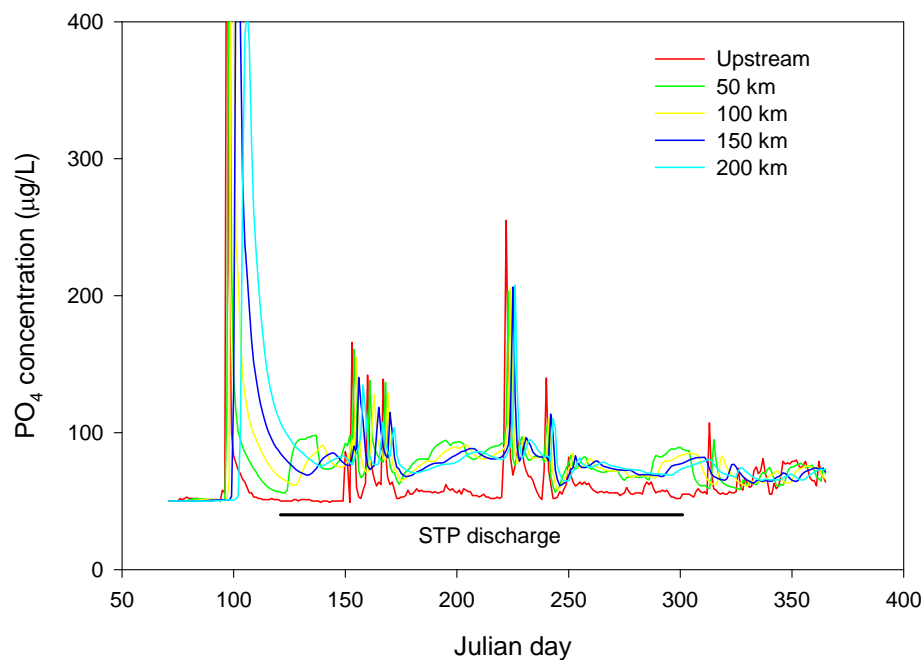
Figure 11. Modelled dissolved P concentrations at 50 km intervals along the Goulburn River.

The response of P_D along the river to event JD 97-100 illustrates important features of its response to changes in the dissolved concentration in the water column. The concentration response at stations at increasing downstream distance from the STP show increasing lags that simply reflects the time of travel of the concentration pulse. However, the duration of the concentration pulse increases markedly at the downstream stations. At the upstream site, the concentration has effectively returned to its pre-event value after about 6 days. At 200 km downstream the concentration pulse arrived on JD 104 and concentrations were still declining towards pre-event levels at JD 138 when the discharge from the STP began to be felt. The spreading of the concentration pulse is due to two effects. First, a strong flow in the river causes elevated concentrations to be spread over a considerable downstream distance. Consequently, if the flow slows before the pulse reaches a station, it takes a longer time for the pulse to pass and the pulse appears to have spread in time. The second effect is due to adsorption by the bed. As the pulse passes a particular location, the elevated concentration causes adsorption to surficial sediments. Peak concentrations are reduced. After the pulse passes the pore-water concentrations exceed those in the overlying water column and P is released.

The impact of bed adsorption/desorption on the dissolved P concentrations in the water column can be illustrated by setting the bed flux to zero; that is, $F = 0$. The resulting predicted concentrations with and without a bottom flux are compared in Fig. 12 at a downstream distance of 200 km. It is clear that the major effect of the sediment flux is to smooth concentrations in the water column. The arrival of the extra dissolved P from the STP on JT 138 causes a jump in P_D to over $100\,\mu gL^{-1}$ from a 'background' concentration of about $50\,\mu gL^{-1}$. By contrast, in the case of $F \neq 0$, P_D starts to increase only gradually from

a level of $\sim 75\,\mu gL^{-1}$, a concentration already elevated above 'background' due to the passage of the concentration pulse some weeks earlier.
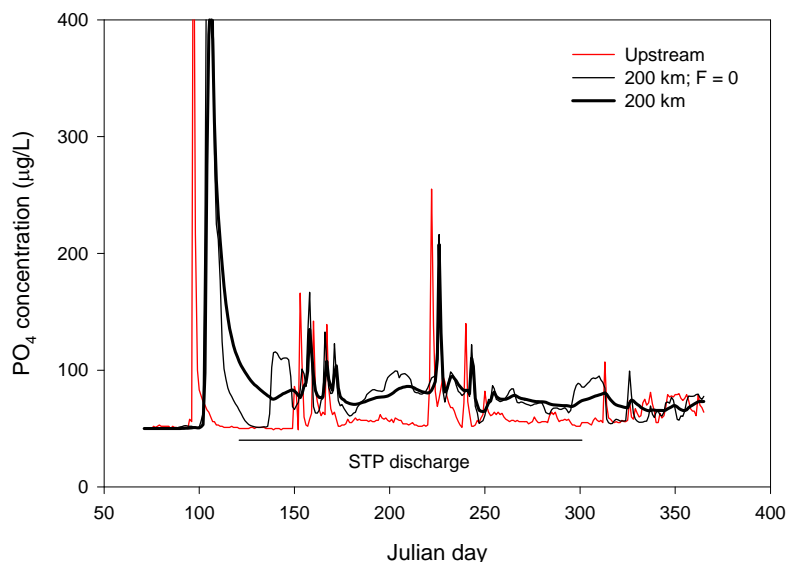

Figure 12. Comparison of modelled dissolved P concentrations at $x = 200\,\mathrm{km}$ with and without adsorption to benthic sediments.

Impact of STP discharge on P concentrations
The immediate effect of the STP discharge is to increase the riverine dissolved P concentration immediately downstream. This impact was investigated along a 20 km section of river that started just upstream of the STP. Samples were taken at a number of locations along this river section on 23/9/99, 12/10/99 and on 13/10/99. These measurements are shown in Fig. 13 and are compared to the model predictions for the same days. The first thing to note is that the measured upstream values of FRP are substantially lower than those predicted by the model. Measured upstream FRP's were 45.3, 14.1, and 15.0 μgL^{-1} on the three sampling days versus model assumed values of 56, 64, and 62 μgL^{-1} on the same three days. We suspect that the difference may be due to some invalidity in the assumptions we have used to estimate dissolved P concentrations upstream of the STP discharge, but it may also be partly due to differences in analytical techniques that we have already mentioned.

Downstream of the discharge the dissolved P concentration jumps due to the addition of more concentrated dissolved P from the outfall. The model predicts concentration jumps (downstream – upstream concentrations) of 15, 17.8, and 25.9 μgL^{-1} on 23/9/99, 12/10/99 and on 13/10/99. Measured jumps are 21.1, 34.3, and 36.6 μgL^{-1} on the same days, which are an average of 60% higher than modelled. In the model, part of the extra dissolved P added by the STP is adsorbed to suspended solids transported from upstream; *TSS* in the discharge is assumed to be zero. The predicted jump in modelled dissolved P concentration is almost all due to the effect of added load from the STP and ought to well describe using a straight dilution equation that is modified by adsorption to suspended solids – adsorption to the bed in the vicinity of the outfall has a proportionally small effect. Some of the difference between model and measurement is almost certainly due to errors to the assumed STP discharge and discharge concentration. The relative size of the STP discharge to the river discharge can be estimated from an analysis involving the change in conductivity. Nominal

STP discharges used in the model were 10, 12, and 20 MLd^{-1}, but the conductivity analysis suggested that the discharges were 12, 16, and 18 MLd^{-1} on these days assuming that the river discharges were accurate. Dissolved P concentrations in the discharge were measured by the MDFRC on the dates of the sampling to be 1.37, 1.80, and 1.80 mgL^{-1}, which are somewhat different from the constant value of 1.54 mgL^{-1} that we have assumed for the model. With our 'corrected' STP discharge volumes and concentrations, we calculate jumps of 16.2, 29.5 and 28.9 μgL^{-1} which are now 24% less than measured and a significant improvement. This calculation includes adsorption as described in the following paragraph.

For the three sampling days, we assumed *TSS* concentrations upstream of the STP of 39, 55, and 52 mgL^{-1} which are within 20% of those measured. With our assumed K_D of $10\,Lg^{-1}$, we calculate buffering capacities of Ω = 1.39, 1.55, and 1.52 for these days which means that about a third of the added dissolved P is immediately adsorbed to the suspended sediments. An error in K_D would affect the calculation of the jump. A reduction in K_D to $5\,Lg^{-1}$ would reduce the amount adsorbed by half and increase the size of the jump in dissolved P by about a sixth.
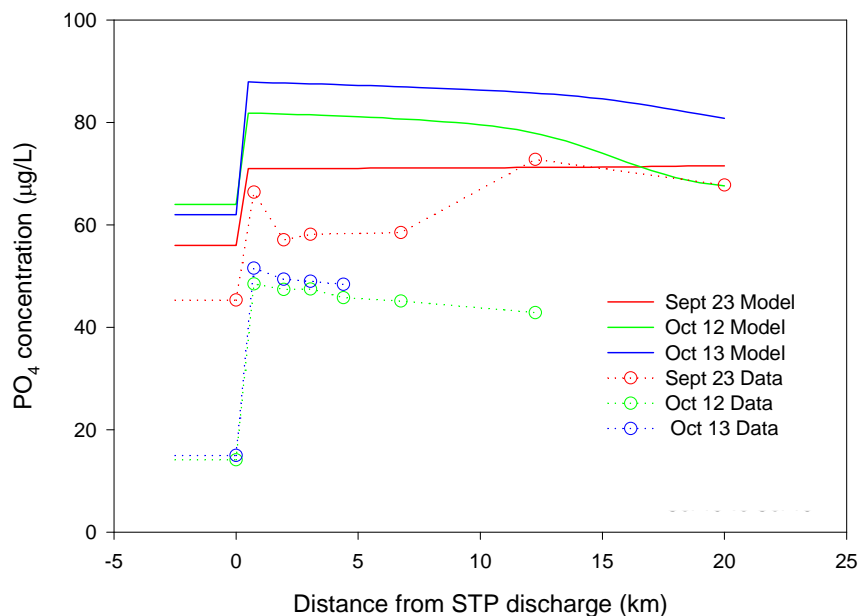

Figure 13. Comparison of measured and modelled dissolved P concentrations downstream from the STP discharge on 23/9/99, 12/10/99, and 13/10/99.

The model and measurements do agree in one major respect; that is, neither predicted nor modelled dissolved P concentrations decline rapidly downstream from the discharge. The model simulations show a modest decline in dissolved P concentration through the 20 km section of river shown. However, this decline can be attributed primarily to changes in the relative size of the STP discharge to the river discharge and to changes in upstream dissolved P and *TSS* concentrations during the time it takes the flow to travel the 20 km length of the section (~ 1 day). In effect, the concentration flowing past the STP changes with time which causes variation in concentration with distance downstream. The measured changes in dissolved P could very well be attributed to the same cause.

The relative invariance of dissolved P concentrations within 20 km downstream of the Shepparton STP stands in stark contrast to measurements made on three occasions in the Namoi River downstream from the Narrabri STP (Webster *et al.* 2001). Total Phosphorus (TP) levels in the Namoi increased sharply due to the discharge of the STP as do FRP concentrations in the Goulburn, but in the Namoi concentrations had declined significantly towards upstream levels by about 10-20 km downstream of the STP (Fig. 14). In the Namoi, most of the TP in the river was FRP. Webster *et al.* hypothesised that biological uptake by organisms living on the bed was responsible for the rapid decline. Further, it was suggested that TP concentrations did not decline quite to upstream concentrations in July 1994 because dissolved nitrogen levels had diminished to zero which limited further uptake of P. We suggest that the benthic biota were not so important in the Goulburn for sequestering of P primarily because of the river's higher turbidity. Namoi River turgidities were 10-20 NTU during the three surveys, whereas Goulburn River turgidities were about 35 NTU for the survey of 23/9/99 and were around 50 NTU for the two later surveys. It is likely that in the Goulburn biological uptake by photosynthesising organisms could occur in the shallow regions along the river edges, but how fast this process occurs and its net impact on P transport and cycling are not known.
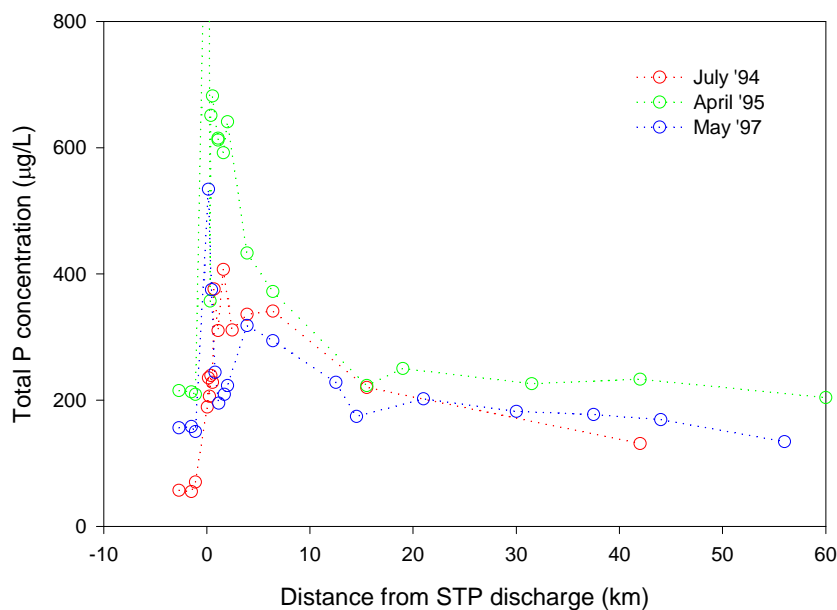
Namoi River downstream from Narrabri

Figure 14. Measured Total P concentrations in the Namoi River downstream from the discharge from the Narrabri STP in July 1994, April 1995, and May 1997 (data from Hancock unpub.).

The model assumes that uptake is strictly abiotic adsorption. Although the presence of concentration pulses associated with flow events confounds the picture somewhat, the simulation results shown in Fig. 11 suggest that dissolved P concentrations in the river will be significantly elevated by the STP discharge all the way downstream to at least 200 km. During times other than the flow events, it seems that the STP discharge elevates dissolved P concentrations by $\sim 20\,\mu\mathrm{g}\mathrm{L}^{-1}$. Dissolved P concentrations throughout the 200 km reach approach their values upstream of the STP after about JT 325; that is, about 30 days after the end of the discharge. This is the time it takes for a parcel of water to flow the length of the reach under low flow conditions.

The effect of the STP discharge upon downstream dissolved P concentrations is better illustrated using an idealised simulation in which river discharge, upstream TSS concentrations, and upstream dissolved P concentrations are all held constant. The discharge is set to $588\,\mathrm{MLd^{-1}}$, the upstream TSS concentration to $40.6\,\mathrm{mgL^{-1}}$ and the upstream dissolved P concentration to $58.0\,\mathrm{\mu gL^{-1}}$. These are the averages obtained for the low flow period of the record $Q < 1000\,\mathrm{MLd^{-1}}$ used to run the simulations already described. In like fashion, the STP discharge (when it occurred) was set equal to its average during the low flow period. At the beginning of the simulation, the STP discharge was set to zero for 10 days. After 10 days, this discharge was set to $15.85\,\mathrm{MLd^{-1}}$ for the next 180 days, and then set to zero for the remaining 30 days of the simulation. The period of non-zero STP discharge is the same as that used in the simulations already described.

Figure 15 shows the results of the simulation. The simulation at 1 km downstream from the STP represents concentrations immediately downstream from the discharge; that is, it represents the dilution of the effluent in the river and its adsorption to the suspended sediments. The effect of adsorption to the bed sediments is minimal at this distance. The time delay from the start of the STP discharge at which the dissolved P concentration increases above the upstream concentration increases with distance downstream reflecting the increasing time taken for the river to flow from the STP to the particular location. At increasing distance also, it is apparent that the approach of the concentration to its value at $x = 1\,\mathrm{km}$ slows. In effect, the bed sediments upstream continue to adsorb P, reduce the water column concentrations, and slow the approach to equilibration. At equilibrium, all P concentrations in the river downstream of the STP would equal those immediately downstream. Even after 180 days of discharge, the 'excess' concentration at 200 km (the increased concentration due to the STP discharge) has reached only 85% of its equilibrium value. After the STP stops discharging, dissolved P concentrations start to decline when the river water which passed the STP at the termination of discharge arrives at a particular location. Just as dissolved P concentrations rose most rapidly at locations closer to the STP so the drop in concentration was most rapid at upstream stations.
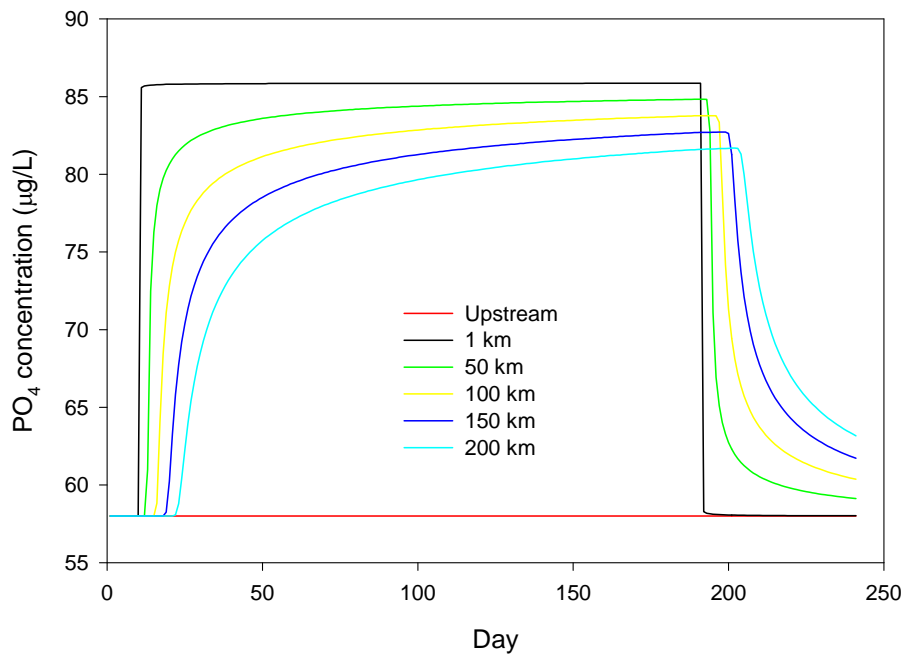
$K_D = 10 \, Lg^{-1}$

Figure 15. Dissolved P concentration at a series of distances downstream from the STP discharge obtained for idealised river and STP flows and P concentrations. In this simulation, the STP discharges between days 10 and 190.

Figure 16 demonstrates the effect of changing the adsorption coefficient, K_D on the equilibration process. The first item to note is that the jump in dissolved P concentration associated with the STP discharge, ΔP_D, decreases in magnitude as K_D is increased. For K_D = 1, 10, and $100 \, Lg^{-1}$, ΔP_D = 37.3, 27.3 and $6.6 \, \mu gL^{-1}$, respectively. In effect, a larger value of K_D causes a greater fraction of the dissolved P introduced by the STP discharge to be adsorbed to the suspended sediments immediately downstream of the outfall. The buffering capacities associated with the three K_D's are calculated to be Ω = 1.04, 1.40, and 4.95 downstream of the STP discharge. At all downstream locations, the total exchangeable P is simply the product of the buffering capacity and the dissolved concentration; that is, $P_T = \Omega P_D$.
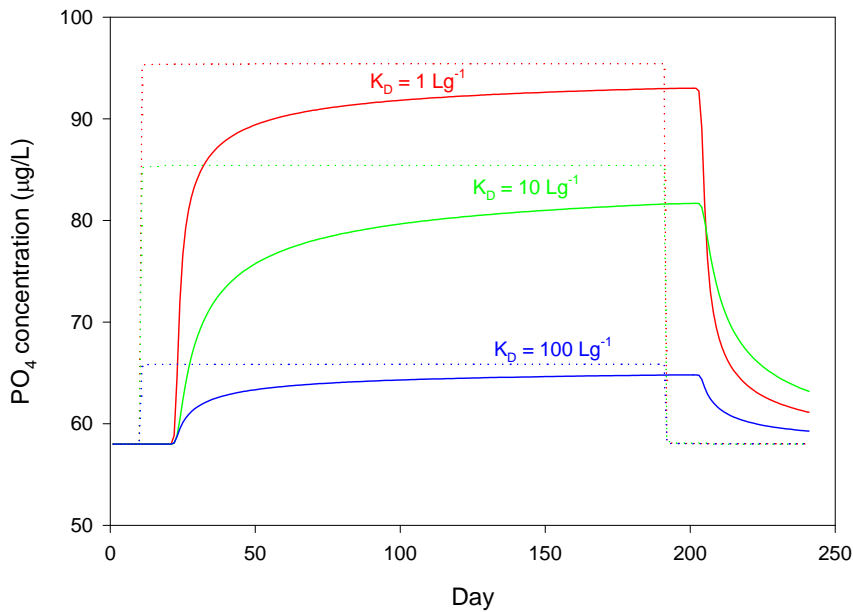
Figure 16. Simulated dissolved P concentrations 200 km downstream from the STP discharge (solid lines) as they are affected by varying the adsorption coefficient K_D. The dotted lines are concentrations 1 km downstream from the discharge. In these simulations, the STP discharges between days 10 and 190.

Although in the simulations represented in Figure 16, the amount of dissolved P introduced by the STP is the same the value of K_D does affect the amount of P that reaches $x = 200\,\text{km}$. We can define a relative concentration excess as:

$$\Delta P_D^{'} = \frac{P_D - P_D^U}{P_D^0 - P_D^U} \qquad (16)$$

where P_D^0 is the dissolved P concentration immediately downstream from the STP discharge when it is flowing and P_D^U is the upstream concentration corrected for the dilution by the STP discharge volume. Thus, when $\Delta P_D^{'} = 0$, the discharge has no effect on local concentration and when $\Delta P_D^{'} = 1$, local concentrations are the same as those immediately downstream from the discharge. In the latter case, adsorption between the observing location and the STP is zero. Figure 17 shows the relative excess for the three adsorption coefficients at $x = 200\,\text{km}$. The discharge from the STP arrives at this location on day 22. It is apparent that for the all three cases, buffering by sediments upstream is capable of reducing dissolved P concentrations for only a relatively short time, but that this time does depend on K_D not surprisingly. For K_D = 1, 10, and 100 Lg⁻¹, it takes a further 3, 12, and 6 days after day 22, respectively, for dissolved P concentrations to reach 50% of their values that would occur if no adsorption occurred. The surprising result here is that the most highly adsorptive sediments; that is for $K_D = 100\,\text{Lg}^{-1}$, were not the most effective for adsorbing dissolved P from the water column downstream of the STP.
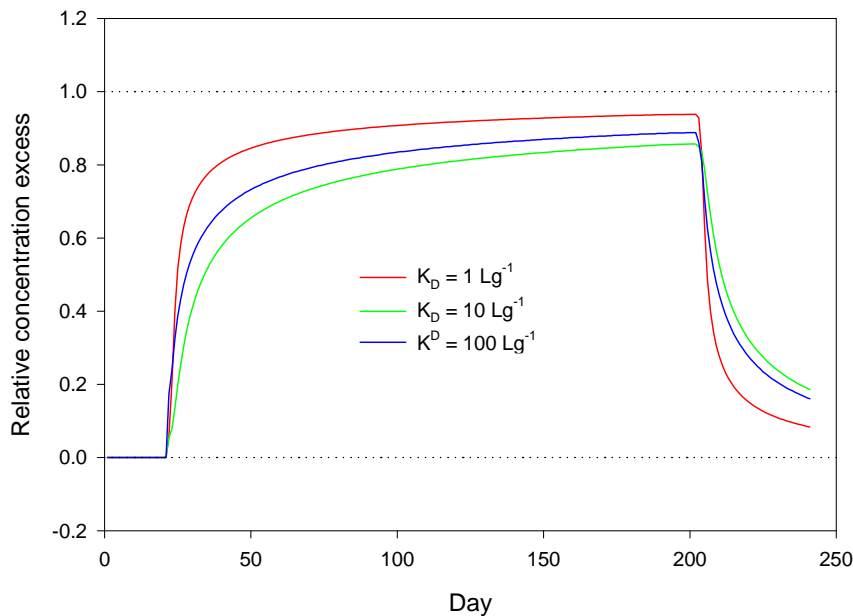
Figure 17. Simulated concentrations of dissolved P 200 km downstream from the STP discharge (solid lines) as they are affected by varying the adsorption coefficient K_D. The concentrations have been normalised by Eq.16. In these simulations, the STP discharges between days 10 and 190.

Impact of STP discharge on phytoplankton concentrations

We now consider the possible impact of the STP discharge on the concentrations of phytoplankton in the Goulburn River. The equation describing the concentration of phytoplankton in the river, *M*, is:

$$\frac{\partial M}{\partial t} + U\frac{\partial M}{\partial x} = G \qquad (17)$$

The terms on the left hand side of this equation describes the time rate of change of phytoplankton concentration in the water column and changes in the concentration due to advection of P downstream as Eq. 11 does for P_T. The *G* term on the right hand side represents the increase in concentration due to growth. In the nutrient replete situation $G = \mu M$ where μ is the specific growth rate. For our application we will set $\mu = 0.37\,\mathrm{d}^{-1}$, an *in situ* value determined for *Anabaena* in Maude weir pool on the Murrumbidgee River by Sherman *et al.* (1998). When the concentration of dissolved P has been reduced to zero, we assume that $G = F / h$ when $F > 0$; that is, the growth is sustained by P release from the bed sediments. Loss of phytoplankton due to sinking to the bed or due to other causes is neglected.

As in the previous section, we assume hypothetical discharge conditions in the river and from the STP; that is, the STP discharge commences on day 10 at a constant rate with a constant dissolved P concentration into a river having constant properties. At day 150, we suppose that a phytoplankton bloom is adverted from upstream past the STP discharge and into our 'study' section. There are many ways in which a bloom can be specified, but we shall suppose that the bloom has been growing long enough that it has depleted the

exchangeable P in the flow passing the STP to zero. In this analysis, we express phytoplankton concentrations by their P content.

Figure 18 shows the predicted phytoplankton concentrations at various downstream distances from the STP discharge for times near when the bloom is initiated and for $K_D = 10 \, \mathrm{Lg}^{-1}$.
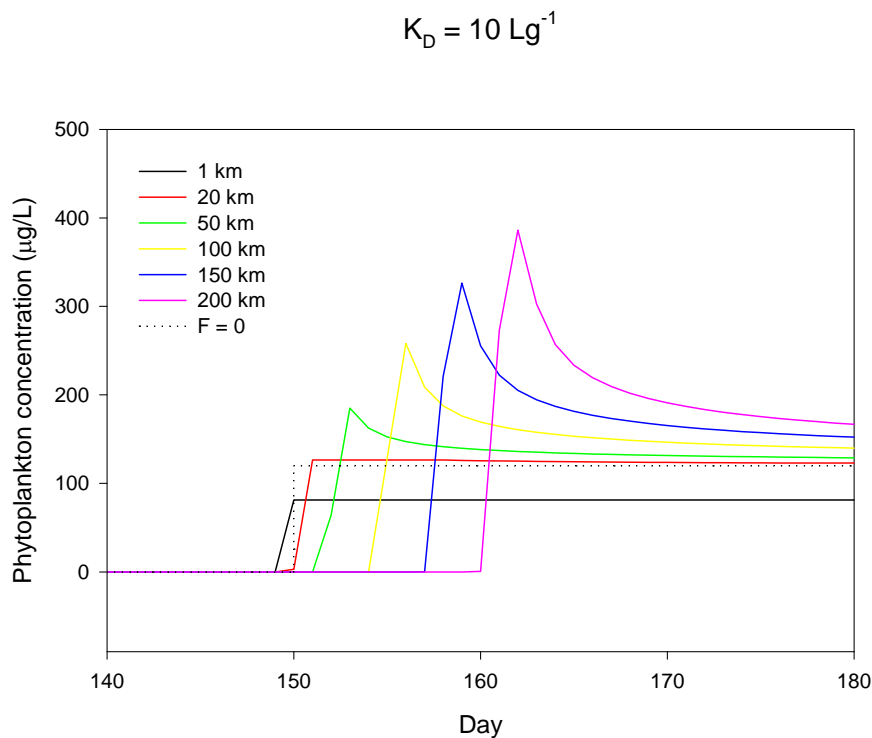
$$K_D = 10 \, \mathrm{Lg}^{-1}$$

Figure 18. Time series of predicted phytoplankton concentrations at various downstream distances for a bloom that passed the STP discharge on day 150.

Prior to day 150, the phytoplankton concentration is zero everywhere by definition, but at day 150 the concentration jumps up to equal the total P concentration that would have been experienced in the river upstream of the STP. The upstream concentration upstream is similar to that at $x = 1 \, \mathrm{km}$ (Fig. 18); concentrations immediately downstream of the discharge are reduced slightly due to the dilution effect of the STP discharge which is assumed to contain no phytoplankton. Further downstream at $x = 20 \, \mathrm{km}$, phytoplankton concentrations have increased mainly due to growth sustained by the extra dissolved P added to the river by the STP. The extra growth attributable to the addition of P by the STP is shown as the dotted line ($F = 0$). At $x = 20 \, \mathrm{km}$, the phytoplankton concentration is slightly in excess of that sustainable directly by the STP. In effect, as the phytoplankton population reduces the dissolved P concentration in the water column, additional P is desorbed from the sediments and is made available to sustain further growth.

At greater distances downstream, the time series of phytoplankton concentration shows a pronounced peak that increases in magnitude as the distance from the discharge is increased. This happens because the distance over which P can be released to sustain the phytoplankton bloom increases with distance downstream. The line, $F = 0$, is the maximum phytoplankton concentration that can be attained if there is no desorption of P from the bed. At $x = 200 \, \mathrm{km}$, desorption of P from the bed allows the maximum phytoplankton

concentration to be more than three times larger than if there were no supply of P from the bed.

Figure 19 demonstrates how the adsorption constant, K_D, affects the maximum predicted phytoplankton concentrations (expressed as their P content) at three downstream distances. Again, we use the idealised river and STP discharges and concentrations of TSS and P. The concentration of phytoplankton upstream of the STP increases linearly with K_D simply through our assumption that the upstream concentration of dissolved P is fixed implying a linear increase in exchangeable P through Eqs. 4 and 5. For the largest adsorption coefficient used in our simulations, $K_D = 100\,\mathrm{L\,g^{-1}}$, the concentration of exchangeable P is 5.1 times larger than the dissolved P concentration. Even without the STP discharge (the red curves), the concentration of phytoplankton downstream of the STP increases substantially over these upstream values due the supply of dissolved P released from the bed sediments. For the smallest K_D used in the simulations the maximum phytoplankton concentration at $x = 50\,\mathrm{km}$ is 40% larger than it would be if there were no release of P from the bed. At $x = 200\,\mathrm{km}$, the maximum phytoplankton concentration is more than double the upstream concentration. The maximum amplification factor in the concentration maximum at $x = 200\,\mathrm{km}$ over the upstream concentration is 3.6 and it occurs at $K_D \sim 16\,\mathrm{L\,g^{-1}}$. At higher values of K_D, the amplification diminishes.

We determined the behaviour of the phytoplankton concentration maxima for two cases: one in which the STP had discharged for 90 days prior to the initiation of the phytoplankton bloom and the other in which the discharge had taken place for 180 days. The differences between the downstream concentrations predicted for these two scenarios were small (<2%) so we present the results for a discharge time of 90 days only in Fig. 19. As expected, the ratio of the maximum downstream concentration to upstream concentration is significantly larger when the STP is discharging. Additional P to fuel growth derives directly from the addition of dissolved P from the STP. Also, the concentration of dissolved and adsorbed P in surficial sediments downstream from the STP is greater as well when the STP is discharging which allows for enhanced fluxes into the water column when water column concentrations are reduced. For the case of a 90-day STP discharge, the concentration maximum at $x = 200\,\mathrm{km}$ increases to 4.9 times the upstream concentration versus 3.6 times for zero STP discharge and this maximum occurs at $K_D \sim 10\,\mathrm{L\,g^{-1}}$ somewhat less than the value for zero STP discharge. The addition of dissolved P from the STP as well as the release of adsorbed P from bed sediments allows for a considerable amplification of a phytoplankton bloom as it is carried downstream past the STP.
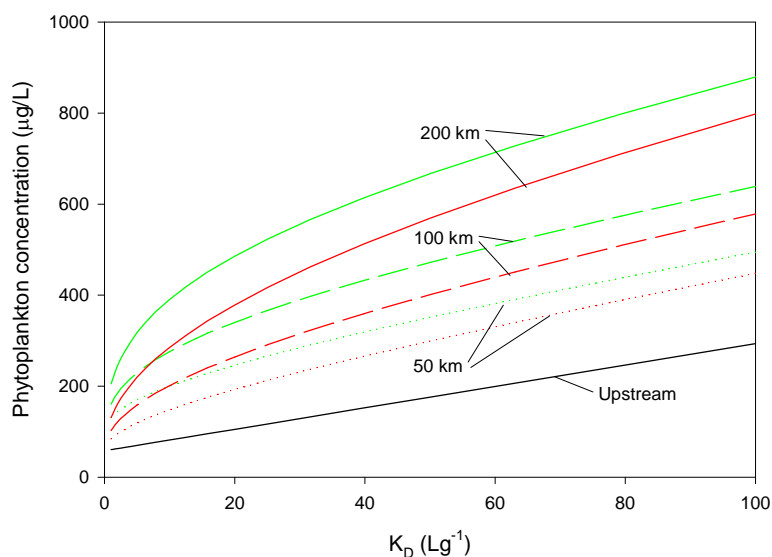
Figure 19. Maximum downstream phytoplankton concentration (expressed as P content) at three downstream distances. The red curves are the maxima attained with no STP discharge and the green curves are those attained after 90 days of STP discharge.

Summary and Discussion for Objective 5:

The adsorption and desorption of P from suspended and settled sediments has the potential to greatly increase the amount of P available in the water column for phytoplankton growth. The exchangeable P in the water column is proportional to the concentration of suspended sediments and is assumed to be proportional to an adsorption coefficient. For values of the adsorption coefficient that are conventionally measured in Australian rivers, $K_D \sim 1\,\mathrm{Lg}^{-1}$, suspended sediment concentrations would have to be very large $TSS \sim 1000\,\mathrm{mgL}^{-1}$ for the volumetric concentration of the adsorbed P to equal the dissolved concentration.

For settled sediments, the most important parameter impacting their capacity to adsorb is the adsorption coefficient. Potentially large amounts of P can be adsorbed to surficial sediments even with $K_D \sim 1\,\mathrm{Lg}^{-1}$. However, the transport of dissolved P in surficial sediments is limited by the adsorption process that constrains the way in which dissolved P can be released into the water column.

The assumption of a single adsorption coefficient to describe the adsorption/desorption process is a crude assumption. Adsorption can be 'fast' or 'slow' depending on the nature of the binding surfaces. Our modelling assumes that we consider fast adsorption/desorption only which takes place on timescales of minutes or hours which is certainly fast on the timescale of P transport in rivers or uptake by phytoplankton. Most experiments to determine adsorption/desorption properties of sediments measure fast adsorption/desorption. Slow adsorption/desorption takes place over days, weeks or possibly longer. Release of P from suspended or bed sediments through slow desorption could be large enough to significantly impact P dynamics and phytoplankton blooms in rivers.

In our analysis we have also assumed that adsorption is a linear process; that is, the amount adsorbed is directly proportional to the dissolved P concentration. It ignores the possibility

that there is a limited maximum binding capacity to sediments that may be determined by their iron content. The assumption does greatly simplify the analysis and should not fundamentally alter the conclusions that we can draw from this study.

In the Goulburn River, there is some ambiguity as to what the real binding capacity of the suspended sediments actually was. Estimation of adsorption coefficients in the laboratory yielded values that were of an order of magnitude larger than those estimated using a more field-based approach. A possible culprit here may be variation in pH which is known to have a major effect on adsorption properties. We need to know how pH impacts adsorption/desorption in Australian rivers. Potentially variations in pH causing P release could be a significant dynamic in our rivers. This is not considered in our modelling, but potentially it could be.

There is considerable discrepancy between concentrations of dissolved P measured by various laboratories on samples collected in the Goulburn River. Comparison of extended time series of measurements from the laboratories would suggest a discrepancy of about an order of magnitude. Unfortunately, samples were not collected at the same times and using the same methods so direct comparisons could not be undertaken. We have relied on measurements made on behalf of Goulburn Valley Water mainly for consistency.

Our model of P dynamics includes longitudinal transport by the river flow, adsorptive/desorptive exchange with the river bed, and uptake by phytoplankton. In our application to the Goulburn, we have estimated the suspended sediment concentration from turbidity measurements. For purposes of estimating the adsorptive capacity of the suspended sediment, this is probably a reasonable approach. The adsorptive capacity of suspended sediments is expected to be approximately proportional to the surface area of the grains as is the turbidity.
We have also needed to estimate the concentrations of dissolved P both in the river upstream of the discharge and in the discharge. From very limited data, it seems that the dissolved P concentration in the river increases as the square of the suspended sediment concentration. We conjecture that the pulses of suspended sediment that appear in the river during flow events are not primarily due to re-suspension but rather to material being washed in from the catchments. Large flows associated with releases from Lake Eildon did not cause elevated suspended sediment concentrations. It would seem that big flow events derived from precipitation are capable of mobilising large amounts of dissolved P from the landscape. We have neglected sediment settling primarily because we have insufficient data for assessing or verifying sediment settling rates. We have temporally detailed suspended sediment measurements at one location in the river via turbidity, but a second set of such measurements would be required to asses the sediment dynamics in the river.

Estimating the time series of concentrations in the STP discharge is also somewhat problematic. Measurements made of dissolved P at two-weekly intervals by the MDFRC on the effluent suggested that concentrations were highly variable from one sampling time to the next suggesting that the timescale of concentration variation was two weeks or possibly less. Measurements made on four occasions for the GVW also indicated high variability. For modelling purposes, we resort to the assumption that the concentration of dissolved P in the effluent is a constant during the period of discharge. To account properly for the impact of the STP discharge on day to day or week to week P concentrations in the river in the 100 km section of river downstream from the discharge would require monitoring of effluent concentrations more frequently than is currently undertaken.

Using estimated upstream concentrations of TSS and of dissolved P, the assumed concentrations of dissolved P in the STP discharge and the measured river and STP flows, we model the dissolved P concentrations in the river between the discharge and 200 km

further downstream. The period modelled was 294 days long within which the STP discharged into the river for 180 days. Unfortunately, we do not have the measurements necessary to support or refute the model predictions over these time and length scales. Prior to the commencement of the STP discharge, a large flow event of several days duration caused a pulse of elevated dissolved P concentration to be carried downstream past the STP discharge point. As this pulse was carried downstream by the flow, it reduced in amplitude and broadened in time. The increased time it took the pulse to pass a particular location (the broadening in time) was partly due to the slowing of the river flow speed after the pulse, but it was also due to the exchange of P with the riverbed. P was adsorbed by benthic sediments as the pulse passed and later desorbed back into the water column when concentrations fell after the passage of the pulse. The behaviour of the pulse as it was carried downstream nicely illustrates the mediating effect that the sediments have on water column concentrations of dissolved P.

Comparisons were obtained between model-predicted dissolved P concentrations and measured concentrations on three occasions along the 20 km section of the Goulburn River downstream from the STP discharge. The model-predicted concentrations just upstream from the discharge were all substantially higher than those measured as part of the three sections. This discrepancy may be partly due to the problems with consistency of measurement described in summary item 6. The upstream P concentrations are ultimately based on measurements made for the GVW, whereas the MDFRC obtained the measurements made along the river section in the detailed survey. The discrepancy may also be due to deviation in the actual dissolved P concentration from the simplified functional dependence on TSS that we have assumed.

The measured jumps in the concentration of dissolved P across the discharge location were larger than the model would suggest. This discrepancy points to errors in the prescribed STP discharge volume. Further downstream, the concentration of dissolved P largely maintains itself. This result is consistent with the model in that over a 20 km distance concentrations would be expected to be fairly constant once the STP had been discharging for more than a few days. The result is not consistent with measurements obtained in the Namoi River downstream from the Narrabri STP. In the Namoi, dissolved and total P concentrations had declined towards their upstream values at this downstream distance. The disappearance of P in the Namoi has been attributed to uptake by benthic biota. In the Goulburn, we hypothesise that the water was too turbid for benthic biota to remove significant amounts of P through photosynthetic uptake over a 20 km distance.

To better demonstrate the P dynamics in the river and how they are affected by the STP discharge, we ran the model with a series of hypothetical conditions. For these runs, the river and STP discharges and the riverine concentrations of P and TSS are all kept constant. After the commencement of the STP discharge, dissolved P concentrations in the river downstream gradually rise towards an equilibrium level. For steady river and STP discharges (as they are for these runs), this level would be the same as that achieved if there were no exchange with the bed; that is, the level would simply reflect the dilution of effluent in the river accounting for adsorption by suspended solids. The bed acts as a storage zone that slows the rise of dissolved P levels when the STP discharge starts and continues to release P back into the water column after it terminates. The effectiveness of the bed for mediating water column concentrations increases with distance downstream from the outfall and with the adsorption properties of the sediments. Immediately downstream of the discharge (1 km), concentrations are little mediated by the bed, but at 200 km downstream concentrations are still substantially less than what they would be without bed exchange even after 180 days of discharge. Conversely, the concentrations take much longer to revert to 'background' levels after the termination of the STP discharge at 200 km downstream than they do at 1 km.

The choice of the adsorption coefficient affects the mediating capability of the bed sediments in a non-obvious way. If the adsorption coefficient were zero, adsorption to bed sediments would not take place, but there would be some diffusion of dissolved P into the sediment interstices that would allow a very limited mediating capacity for bed sediments. Indeed, of the three adsorption coefficients tested, $K_D = 1, 10, 100 \, \mathrm{Lg}^{-1}$, the smallest coefficient demonstrated the least capacity to mediate water column concentrations of dissolved P. One might expect that $K_D = 100 \, \mathrm{Lg}^{-1}$ would have the largest buffering capacity, but this proved not to be the case since $K_D = 10 \, \mathrm{Lg}^{-1}$ had the best buffering capacity.

Using the model and our hypothetical discharge and concentration conditions, we investigate the impact of the release of P from benthic sediments on the growth of a phytoplankton bloom in the Goulburn River with and without a STP discharge. In our hypothetical scenario, we specify that the bloom has grown sufficiently that it has exhausted both the dissolved P in the water column and the P adsorbed to suspended sediments when it passes the location of the STP discharge. For both zero and non-zero STP discharges, the bloom grows in intensity as it is adverted downstream by the river flow. Growth is fuelled by the release into the water column of P adsorbed to benthic sediments and by dissolved P in the STP effluent if it is flowing into the river. The bloom proceeds as a pulse; that is the phytoplankton concentration at a particular location rises as the bloom approaches and falls again after it passes. At a sufficient downstream distances (>100 km), the concentrations of phytoplankton in the bloom can grow to several times its initial size even for the case of zero STP discharge. The addition of an STP discharge exacerbates the bloom both by supplying dissolved P directly into the river at the discharge point and also by raising the potential for sediments further downstream to desorb P into the water column.

Management Implications:

- The measurement of <u>total</u> phosphorus does not identify the component of the nutrient that is immediately available to support algal growth and so on its own does not provide a reliable indicator of the impact of a nutrient source. In the Goulburn system the total load from the three sources investigated was substantially different yet the load of immediately available phosphorus was similar.

- Most of the immediately available phosphorus was in dissolved form with only a small proportion attached to particles being readily accessible. This has important implications for catchment management because of the difficulty of capturing the dissolved forms.

- During high flows in Rodney Drain and the Acheron River phosphorus concentrations increased and exacerbated the increased loads associated with the flows. In the Acheron the increase was largely due to particle bound forms of phosphorus not immediately available to algae. In Rodney Drain the increase in concentration was due to both particle phosphorus and dissolved phosphorus. The significant increase in available phosphorus concentrations suggests that rainfall events that appear to drive the rapid flow increases in the drain should be captured on farm where ever possible and not discharged to the river.

- Anoxic conditions in the bottom sediments enhanced the exchange of phosphorus with the overlying water. The level of anoxia is a function of the load of organic material to the sediments and consequently downstream of the STP the phosphorus concentrations in the interstitial water of the sediments was 10-20 time s higher than at other sites. Downstream of Rodney Drain, phosphorus concentrations near

the sediment surface were on average slightly higher than those downstream of the Acheron. The delivery of organic material to the river sediments can increase the supply of phosphorus for algal growth. Reduced mixing which inhibits the re-supply of oxygen to the bottom sediments also has the potential to increase the available phosphorus. The balance between organic carbon supply and mixing conditions are poorly known for our systems making it difficult to predict the likelihood of increased supplies of nutrients from the bottom sediments.

- Even under oxygenated conditions the sediments can greatly increase the amount of phosphorus in the water column through adsorption and desorption processes. A model developed to illustrate the effect of this in the flowing river showed that substantial stores of readily available phosphorus could be adsorbed to the bottom sediments but that the quantity and its exchangeability depended on a number of conditions, one important parameter being the adsorption coefficient of the sediment. The exchangeable phosphorus on the sediments is a function of the concentration of phosphorus dissolved in the water and the adsorption coefficient which determines the partitioning between dissolved and loosely adsorbed forms. Further measurements of this characteristic are required to improve the reliability of estimates of the phosphorus immediately available to support the growth of algae.

- Phosphorus in the bottom sediments will be available to support algal growth provided that vertical movement of the nutrient into the water column is enhanced either by vertical mixing or by biological means such as vertical migration of algae. The connection between sediments and the water column require furthers assessment.

- A modelled scenario estimating the growth of an algal bloom as it moved downstream showed the cumulative effect of nutrient release from the bottom sediments. The bloom increased in size as it passed over longer lengths of river bed. One implication of this is that releasing of blooms from storages such as weir pools where they often occur may not be an appropriate option unless there is sufficient water to quickly disperse the bloom or it is known that other environmental conditions (eg. light) will become limiting under the new flow conditions.

- As expected, the condition of the bottom sediment plays an important role in mediating the impact of phosphorus loads on algal growth. There is a need for further information on the physical, chemical and biological functioning of the river bed.

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