A review of sediment and nutrient concentration data from Australia for use in catchment water quality models

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Review and summary of constituent concentration data from Australia for use in catchment water quality models

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Executive Summary

Land use change is seen as the primary factor responsible for changes in sediment and nutrient delivery to water bodies. Understanding how sediment and nutrient (or constituent) concentrations vary with land use is critical to understanding the current and future impact of land use change on aquatic ecosystems. Due to the large size of many catchments, and the cost of water quality measurements, our understanding of the sources and rates of constituent generation is largely dependent on the use of models. The subsequent confidence in these models is reliant on access to quality input data.

This study collated runoff, concentration and constituent load data for Australian catchments from published papers, reports and in some cases unpublished documents. We collated water quality data from runoff events with a focus on areas that have a single or majority of the contributing area under one land use. Based on a review of the literature there are 5 broad methods used to calculate a mean event constituent concentration and a discussion of the strengths and weaknesses of the various approaches is given.

Data were collated for total suspended sediments (TSS), total nitrogen (TN) and total phosphorus (TP). Where possible, information on the dissolved forms of nutrients were also collated. For each data point, information was included on the site location, land use type and condition, contributing catchment area, runoff hydrology, lab analysis methods, number of samples collected over the hydrograph and the constituent concentration calculation method. The data were recorded in an excel data base and can also be viewed using Google Earth.

A total of ~750 entries were recorded in the data base from 514 different geographical sites covering 13 different land uses. Analysis of the data found that there was little difference between data collected using "grab" sampling (over the hydrograph) versus auto-sampling (although the data set for this analysis was small). Analysis also showed that there wasn’t a statistically significant difference (p<0.05) between data collected at plot and catchment scales for the same land use. This is most likely due to differences in land condition over-shadowing the effects of spatial scale. There was, however, a significant difference in the concentration value for constituent samples collected from sites where >90% of the catchment was represented by a single land use, compared to sites with <90% of the upstream area represented by a single land use. This highlights the need for more single land use constituent concentration and load data, preferably over a range of spatial scales. Based on these analyses the final synthesis data is presented using the whole data set, as well as for sites where a single land use is represented in >90% of the contributing catchment area.

Overall, the land uses with the highest median TSS concentrations were Mining (~50,000 mg/l), Horticulture (~3000 mg/l), Cotton (~600 mg/l), Grazing on native pastures (~300 mg/l), and Bananas (~200 mg/l). The highest concentrations of TN are from Horticulture (~32,000 ug/l), Cotton (~6,500 ug/l), Bananas (~2,700 ug/l), Grazing on modified pastures (~2,200 ug/l) and Sugar (~1,700 ug/l). For TP it is from Forestry (~5,800 ug/l), Horticulture (~1,500 ug/l), Bananas (~1,400 ug/l), Grazing on modified pastures (~400 ug/l) and Grazing on native pastures (~300 ug/l). For the dissolved nutrient fractions, the Sugar land use has the highest concentrations of dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP), and the Urban land use had the highest concentrations of dissolved inorganic phosphorus (DIP).

This report also demonstrates that all water quality data is extremely variable, even if collected using the same methods, from the same land use in a similar region. There are a range of factors that produce a constituent value (such as soil type, land condition, rainfall pattern etc), and modellers need to be aware of these issues before applying the data. This document discusses some of the options and issues associated with using water quality data in catchment models, and modellers may want to use different data for different tasks. The data base developed in this study may be used as a portal to access publications with water quality data that may be suitable for a range of modelling applications.
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2 Introduction

Understanding the generation and movement of excess sediments and nutrients through catchments, and their subsequent impact on downstream aquatic ecosystems, is the ‘holy grail’ for a large number of research agencies around the world. It is well documented that phosphorus, when in excess, can limit the biological productivity of freshwater ecosystems (e.g. Davis and Koop, 2006; Heathwaite, 2003) and that excess nitrogen, in particular nitrate, appears to be detrimental for marine systems (e.g. Fabricius, 2005; Fabricius et al., 2005; Smith et al., 2006). Excessive erosion and delivery of fine and coarse sediment to rivers and coastal systems is problematic in many parts of the world, and the processes and impacts are well documented (e.g. Meade, 1988; Prosser et al., 2001b; Rutherfurd, 2000; Walling, 2006). Constituent (e.g. sediment, nitrogen and phosphorus) generation, cycling, movement and storage processes are complex and vary with watershed conditions such as land use, rainfall and geology (Young et al., 1996). Land use change, however, is seen as the key factor responsible for changes in sediment and nutrient delivery to downstream water bodies (Harris, 2001). Therefore, understanding how constituent concentration varies with land use is critical to understanding the current and future impact of land use change on downstream water bodies.

Due to the large size of many catchments, and the cost of water quality measurements, our understanding of the sources and rates of constituent generation at the catchment scale is largely reliant on the use of models. Most models require data to help formulate the initial conceptual structure, calibrate the model and test the model outputs (Bloschl and Sivapalan, 1995). In Australia, the most recent modelling platform for evaluating catchment scale constituent losses is Source Catchments (formerly known as WaterCAST). This is a lumped, semi-distributed, conceptual catchment modelling framework that operates on daily time step. It allows for the construction of models by selecting and linking component models from a range of options (Argent et al., 2008). Source Catchments conceptualises a range of catchment processes using sub-catchments which are composed of Functional Units (FUs). Each FU is characterized by similar pollutant generation processes, which are typically determined using an event mean concentration (EMC), and/or dry weather concentration (DWC) approach (e.g. Chiew and Scanlan, 2002). Concentration data are separated into EMC and DWC values because concentrations can vary considerably between event and baseflow conditions. Data representing the mean concentrations of sediment, nitrogen and phosphorus are also required by other models used in Australia (e.g. MUSIC, see Fletcher et al., 2004; and SedNet, see Wilkinson et al., 2004).

The new generation of catchment models (e.g. Source Catchments) incorporate their own rainfall/runoff routines to simulate flows, yet to calculate constituent loads, estimates of constituent concentrations are required. At present there is no single, peer reviewed document that provides a summary of constituent concentration data for the whole of Australia. As a result, models that are applied in areas that are relatively data poor end up using data from elsewhere. This data can sometimes be well outside their geographic and climatic region. Having knowledge of data collected from a range of sites and land uses around Australia will provide model builders with a more robust data set from which to parameterise their models. “Models are our attempt to encapsulate our understanding of the real world. They are not the real world, and without data they are simply imagination and computer games” (Silberstein, 2006). Hence, this report will provide a summary of suitable water quality data for use in catchment models.

The reason that it is difficult to find suitable water quality data for use in catchment models is that water quality data is also expensive to collect. Water quality monitoring is the systematic collection and analysis of samples with the aim of providing information and knowledge
about a body of water and the factors affecting it. Monitoring of water quality (both surface and sub-surface) is undertaken for a range of reasons including protecting public health and aquatic ecosystems, environmental reporting, licence compliance and research. Water quality monitoring is carried out by a wide range of organisations from local, state and federal government as well as the private sector and community groups. It has been estimated that Australia spends $142 - $168 m each year on water quality monitoring (http://www.anra.gov.au/topics/water/pubs/national/water_quality.html). Water quality monitoring is largely funded by public money, and therefore these data should be shared where-ever possible. A lot of the water quality data collected is available on-line via the State Government water quality web sites (see Appendix A). Some local councils also provide data and reports on their web sites (for example, see http://www.hornsby.nsw.gov.au/environment/index.cfm?NavigationID=1040), and in some states there are regional groups that monitor water quality, for example the South East Queensland Ecosystem Health Monitoring Program (EHMP), Melbourne Water and the Fitzroy Basin Association. At a federal level, the Australian Water Data Infrastructure Project (AWDIP) was established under the national component of the Natural Heritage Trust to facilitate national assessments of Australia’s water resources (http://www.daff.gov.au/brs/water-sciences/ground-surface/awdi-project). The framework will enable on-line access to data sets via a network of distributed jurisdictional databases. This technology will be available to emerging water information systems as they become operational (for example the Australian Water Resources Information System proposed by the National Water Commission and being implemented by the Bureau of Meteorology). A description of the different federal water data management projects can be found at http://www.daff.gov.au/__data/assets/pdf_file/0005/382523/WRON_AWDIrelationship.pdf.

The data housed in government data centres provide important baseline information regarding the health of our streams, rivers and in some cases groundwater. They also provide a good spatial representation of water quality in many areas, and are often used to check whether different regions are meeting the ANZECC water quality guidelines (e.g. Moss et al., 2005). Unfortunately, however, the majority of these data are collected during dry weather under base flow conditions without associated flow data. At present there is no central accessible data base documenting data that has been collected in ‘event’ conditions. The majority of water quality studies fall into two broad categories:

1. Base flow data collection which is used for routine monitoring and compliance checks and sometimes for ecological research; or
2. Event based sampling which is used for estimating soil and nutrient erosion rates and constituent load exports.

Most event data is collected over short duration and has not (until more recently) been considered as part of routine monitoring program. Event monitoring has historically been carried out by research groups within various agencies, and the associated data is written into journal papers and reports.

This study focused on collating runoff, concentration and constituent load data for Australian catchments. Data was taken primarily from published papers, but some data was taken from reports and unpublished documents. This document builds on the work of Marston et al., (1995), Young et al., (1996), Fletcher et al., (2004) and Brodie and Mitchell, (2005). The aim of this study was to collate water quality data that was collected under event conditions with a focus on data collected from areas that have a single or majority of the contributing area under one land use. Data from event conditions is considered important as the large events contribute the majority of the sediment or nutrient load to downstream water bodies (Furnas, 2003). Dry weather or base flow concentration data were generally only reported when it was measured at the same site as the event data. Data measured to describe the processing of nutrients were not included in this study if they were only collected during base flow over a short time period (i.e. a few days) (e.g. Hadwen et al., 2009). Similarly, data were
not included if they integrated a range of land uses or if they were largely measured in estuarine rather than freshwater conditions (e.g. Eyre and Balls, 1999). Salinity, herbicides and pesticides were not included in this review. Although a thorough review of the literature was undertaken, it is acknowledged that there is likely to be additional data housed in government and company reports that was not captured in this data base. Therefore this data base should not be considered as the only resource for people looking for water quality data.

The purpose of this document is not necessarily to provide a ‘final’ generic look up table of values for modellers to apply to studies around Australia, although a summary table is provided in Section 5.3. The main purpose of this report is to let the Australian hydrological modelling community know that the data base exists, and should be used as a portal to access publications with water quality data that may be suitable for a range of modelling applications. There are a range of factors that produce a constituent value, and modellers need to be aware of these issues before applying the data. It is also important to point out that the spatial scale that constituent data is applied (i.e. the classification method for defining a functional unit, FU) will vary depending on the specific model set up. Hence, modellers may want to use different data for different tasks. The aim of this document is to:

- Summarise the water quality data collated for the dominant Australian land uses;
- Demonstrate that water quality data can be highly variable even if collected using the same methods, from the same land use in similar region; and to
- Discuss the options and issues associated with using water quality data in catchment models.

This report starts by outlining the different approaches used for measuring mean constituent concentration (Section 3) and then outlines the methods used to classify and analyse the collated data (Section 4). Section 5.1 provides an inventory of the data collated, and then Section 5.2 provides a justification for the interpretation of water quality data according to the different data collection methods, spatial scales and proportion of the catchment under a single land use. This is then followed by a summary of the data in Sections 5.3 and 5.4. Section 6 discusses some of the issues that need to be taken into consideration when using water quality data in models. These include issues such as uncertainty, and the range of constituent values possible due to the variability in land and flow condition. Section 7 provides a summary of the report and outlines the areas for further research.

### 3 Defining mean concentration

Defining what represents an event or quick flow verses base or slow flow can be conducted using a range of methods including hydrological analysis (e.g. Grayson et al., 1996; Nathan and McMahon, 1990) through to field observation. In this section we are not dealing directly with how a hydrological event is defined, as this is dealt with within in the Source Catchments model directly (see eWater-CRC, 2010). This section discusses how a mean concentration is defined for an event flow.

A number of different uses of the term EMC have evolved over the last few decades and the terms EMC and mean event concentration are often used interchangeably despite being derived differently. The event mean concentration (EMC) is a flow-weighted average of constituent concentration and is reported in units of mg/L (Charbeneau and Barrett, 1998). Formally, EMC is defined as total constituent mass, M, discharged during an event divided by total volume (V) of discharge during an event (Huber, 1993) (Equation 1).

\[
EMC = \frac{\int C(t)Q(t)\,dt}{\int Q(t)\,dt}
\]  

Equation 1
The term EMC appeared to originate in urban and road stormwater runoff research, however, it is now widely used for land use specific modelling of water quality for a range of land use types (e.g. Chiew and Scanlan, 2002; Collins and Anthony, 2008; Kim et al., 2004). Although EMC is often used in association with the Source Catchments model, there are 5 methods (found in the literature) used to calculate a mean event concentration. The methods include:

1. Dividing constituent load (t) by flow volume (ML) (according to Equation 1) where the constituent load may be calculated using a range of methods (see Johnes, 2007; Letcher et al., 1999; Marsh and Waters, 2009b for a discussion of different approaches). **All subsequent uses of the term EMC in this report refer to this method.**

2. Using flow duration curves to differentiate between ‘event’ and ‘dry’ whether conditions for which the concentration data samples were collected. For example, Chiew and Scanlan (2002) defined ‘event’ samples as those collected during flow events that are exceeded 5% of the time, and base flow or dry weather samples are exceeded less than 20% of the time.

3. Using runoff data to identify flow events, but it is not directly reporting the flow values. In such cases, average measured concentrations are presented (e.g. Nelson et al., 2006). This approach appears to be more common in studies with a focus on eutrophication or ecological processes.

4. Collecting concentration data during events without information on the specific flow conditions at the time of sampling. This approach is often used in areas with poor gauging and/or when gauges are not located at sites with a single land use (e.g. Bainbridge et al., 2009).

5. Converting unit area yield data (e.g. kg/ha/yr) to a concentration (mg/l) using associated published flow data (e.g. Marston et al., 1995). Information on the sample hydrograph is often not explicitly provided, and therefore it is difficult to ascertain if the result is representative of ‘event’ or ‘base’ flow. Therefore the results are considered as an integrated concentration.

To summarise, method (1) is considered as an event mean concentration (EMC) value, whereas methods (2) to (5) are mean event concentrations (MEC) that directly use measured concentration data. The data base developed, and the subsequent results presented in this document, have utilised data collected and analysed using each of the methods outlined above. Where ever possible, a description of the various techniques and methods were provided in the data base. When concentration data is reported, some studies report arithmetic ‘mean’ values and other studies report ‘median’ values. Median rather than mean values are often used to reduce the influence of large outliers in the data. For the purpose of this study the mean and median values are lumped to represent the ‘average’ water quality concentration coming from a given land use. The variations in water quality observed at the National scale are considered to be larger than the variation resulting from different statistical approaches.

### 4 Methods: data base fields and classifying the data

This section describes what data were collected and what considerations were made when collating and cataloguing the data. In some cases the raw data was available, but in most cases the interpreted data published in tables and figures within the relevant documents were used to derive the water quality data for each site.
4.1 Location information

For each water quality entry, information on the following site characteristics were collected:

- Basin name (e.g. Torrens River)
- Basin ID using the Australian Water Resources Council basin numbers (e.g. 504) as represented in the NLWRA (2000)
- State or Territory
- Gauge Number where applicable (e.g. A5040583)
- Latitude and Longitude

4.2 Land use type and condition

Application of mean concentration values generally requires ‘single-land-use’ data due to the high variability in constituent concentrations demonstrated for sites under different land uses and conditions (Young et al., 1996). The breakdown and number of land use categories used varies depending on the study, and ranges from 3 broad land use categories in the study by Bramley and Roth (2002) to 11 categories in the study by Fletcher et al (2004). The use of ~5 land use categories is typical for the majority of regional or catchment studies (e.g. Bainbridge et al., 2009; Chiew and Scanlan, 2002; Cogle et al., 2000; Rohde et al., 2008) and these increasingly match with the State or Federal mapping categories. This study collated data for the whole of Australia and therefore the data were classified into 13 categories using the ALUM (Australian Land Use Mapping) classifications given in Table 1. It is important to note that some land uses can fall into a number of categories. For example, Dairy may be considered as 3.2.0 (Grazing modified pasture) or 4.2.0 (irrigated modified pasture) or as 5.2.1 (Intensive animal production, dairy).

Table 1: Summary of land uses and the number of sites included in the data base

<table>
<thead>
<tr>
<th>Land use</th>
<th>ALUM classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bananas</td>
<td>3.4.0</td>
</tr>
<tr>
<td>Cotton</td>
<td>3.3.6</td>
</tr>
<tr>
<td>Dryland Cropping</td>
<td>3.3.0</td>
</tr>
<tr>
<td>Forest</td>
<td>1.1.0</td>
</tr>
<tr>
<td>Forestry</td>
<td>2.2.0</td>
</tr>
<tr>
<td>Grazing Modified Pastures (including dairy)</td>
<td>3.20, 4.2.0 or 5.2.1</td>
</tr>
<tr>
<td>Grazing Native Pastures</td>
<td>2.1.0</td>
</tr>
<tr>
<td>Horticulture</td>
<td>4.4.0</td>
</tr>
<tr>
<td>Military</td>
<td>1.3.1</td>
</tr>
<tr>
<td>Mining</td>
<td>5.8.3</td>
</tr>
<tr>
<td>Mixed</td>
<td></td>
</tr>
<tr>
<td>Sugar Cane</td>
<td>3.3.5</td>
</tr>
<tr>
<td>Urban / Industry</td>
<td>5.4.2</td>
</tr>
</tbody>
</table>

For each data entry the following information were recorded when available:

- Primary land use (name and number) using the classification methods derived by the Bureau of Rural Sciences (BRS, 2006). Note that no distinction was made between irrigated and non-irrigated sugar cane;
- Secondary land use and % coverage;
- Vegetation type;
- Land condition;
- Soil type;
- Contributing catchment area.
Data from plot or hillslope scale studies were also included in the data base as these were often the only data available for some land uses. Vegetation and soil types were given generic descriptions based on the information provided in the references. Where precise information was available that allowed classification according to accepted standards (e.g. the Australian Soils Classification system), this information was recorded. No attempt was made to go beyond the descriptions provided.

It is also important to note that some studies have identified sources or processes responsible for constituent generation ‘within’ a given land use. For example, Fletcher et al., (2004) and Duncan (1999) have divided the urban landscape up into roads, roofs etc. Similarly, Visser et al (2007) determined that headlands and drains were the dominant source of sediment within sugar cane landscapes and Bartley et al., (2007b) identified channels as the major source of sediment from grazed systems. In this study, however, no attempt has been made to differentiate between generation processes occurring within a landuse.

4.2.1 Comparison of the same land use in different condition

It is acknowledged that both land use, and land condition, can influence the quality of water coming off a given site. The same land use type can yield very different constituent concentrations when in poor condition, compared when it is good condition (Bartley et al., 2010a; see Figure 1 and 2). This is due to differences in rainfall, runoff, vegetation, soil type, slope and management practices. These factors collectively create different land condition. To demonstrate how variable land condition can be in both space and time, data collected at a range of scales from a 14 km² grazed catchment in the Burdekin basin is presented in Figure 2. These data demonstrate how the annual catchment total suspended sediment (TSS) EMC value (derived from sediment load and runoff data) can vary by more than 100% when the ground cover changes by an average of just 1% (see Figure 2A). This difference is due to large differences in the amount and intensity of rainfall between years with similar cover. On the other hand, it is also possible to obtain quite different TSS EMC values at a site when the ground-cover changes significantly (by ~20%) through time on a given hillslope (Figure 2B). Based on this analysis, knowledge of the soil and vegetation condition were considered to have an important influence on the constituent water quality values measured, and were captured in the data base where-ever available. Knowledge of the rainfall pattern and intensity contributing to a given constituent concentration is also important but was not explicitly recorded in this study.

Figure 1: Example of Grazing (on native pastures) for a site with low cover in poor condition (left) and the same site 6 years later with high cover in good condition (right) (Source: Bartley et al., 2010a).
4.3 Constituents measured

In this study, the three constituents of interest were suspended sediment, nitrogen and phosphorus. Sediment concentration data were recorded as mg/l and nitrogen and phosphorus ug/l. The total suspended sediment (TSS) data were assumed to represent sediment <63um. Bedload was not explicitly recorded in the data base. Where data were provided as kg/ha/yr, these data were converted to mg/l when flow and catchment area information were provided.

As different forms of nutrients (e.g. dissolved versus particulate or inorganic versus organic) are known to have different effects on food webs and freshwater and marine ecology (Fabricius, 2005; Murray and Parslow, 1999), information on the form of nitrogen and phosphorus was recorded where possible. The forms of N and P recorded were Dissolved Inorganic Nitrogen (DIN), Dissolved Organic Nitrogen (DON), Dissolved Inorganic Phosphorus (DIP) and Dissolved Organic Phosphorus (DOP). For some studies, only TN and one form of dissolved nutrient data were provided, and in these cases the dissolved concentrations were calculated by difference.

4.4 Sample collection methods

A monitoring program, whether for routine condition reporting, or for a research project, needs to follow accepted standards where possible. In Australia, there are water quality standards (AS/NZS 5667) and QA/QC guidelines that are outlined in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000), and the Australian Guidelines for Water Quality Monitoring and Reporting (ANZECC and ARMCANZ, 2000b). In this study, it is assumed that all field sample collection, handling, storage and processing has met established protocols. Preservation and storage requirements were not explicitly recorded, although quality assurance and quality control (QA/QC) issues and procedures were assumed to have occurred.

It is acknowledged that the methods and approaches for collecting water quality samples (e.g. pump sampler versus manual collection) can result in significantly different values for constituent concentration (Facchi et al., 2007). Hence, when information on the data collection method was provided, this information was recorded in the data base. This included information on whether the sample was collected from:

- a pumping sampler, and the location of that sampler (e.g. edge or stream centre)
• grab samples and the location of the sample collection (e.g. bridge, stream edge etc)
• a boat
• or other device

In this study it was not possible to do a thorough investigation into the sources of variability or error introduced at each stage of the water quality data collection process (as done in Harmel et al., 2006b). There was, however, an opportunity to evaluate if the sample collection method, and more specifically if knowledge of the flow or hydrograph at the time of sample collection, influenced the event mean water quality. This was considered important to evaluate as often areas that are suitable for obtaining single land use water quality data are not located adjacent to hydrological gauging stations.

A simple comparison of three data sets from the same land use (forest) in similar geographic and climatic region (wet tropics of North Queensland) is presented. In this comparison the first study from the Tully catchment, data were collected manually (i.e. not using an automatic sampler) when the rivers were in ‘event’ mode. No hydrograph data were presented with the concentration data (Bainbridge et al., 2009). Data from the second catchment were also collected manually, however, information about the hydrograph and more importantly, where these samples were collected on the hydrograph (rising or falling stages) were provided (Rohde et al., 2008). In the third catchment, 173 samples were collected using an ISCO automatic sampler and stage recorder. Turbidity was also recorded continuously and used to predict continuous TSS, TN and TP loads (McJannet et al., 2005).

4.5 Lab analysis procedure
It is acknowledged that the lab analysis method used can have profound implications on the results of water quality analysis and thus impact on the analysis of historical water quality trends. Therefore, where information regarding the lab methods used were available (e.g. whether nitrogen is analysed using Kjeldahl digestion or persulfate autoclave digestion), this information was recorded in the data base. It was also recorded, where possible, if the lab was accredited with the National Association of Testing Authorities (NATA). There are standard analytical methods for analysing samples from the water column, sediments and biota and many of these have been cited in the NWQMS monitoring guidelines (http://www.environment.gov.au/water/policy-programs/nwqms/). The primary reference for methods of determining the concentrations of the various forms of nitrogen is the *Standard Methods for the Examination of Water and Wastewater 20th edition* (APHA, 1998).

4.6 Constituent concentration calculation methods
There are five approaches used in literature to calculate and report mean event concentration. These were described in more detail in Section 3, and are summarised below:
1. Dividing constituent load divided by the flow period;
2. Using flow duration curves to identify a consistent flow value to represent ‘event’ and ‘dry’ (or base) flow conditions;
3. Using flow equipment to define an event, but not reporting flow values;
4. Collecting concentration data without knowledge of the specific flow conditions at the time of sample collection;
5. Converting unit area losses to concentrations by dividing by flow.

It is important note that mean event concentration (MEC), which is the average constituent value measured during an event (represented by methods 2,3,4 and 5 above), is not the same as event mean concentration (EMC), which is the concentration derived when dividing total load by flow. Method 1 is the only method that formally calculates an EMC.
Each of the entries in the data base were given one of these classification values. This approach meant that it was possible to include more data from around Australia, whilst providing users with the opportunity to exclude data if they have reason to believe a given approach distorts the final mean values.

4.7 **Number of samples and location on the hydrograph**

The number and location of samples collected during an event hydrograph can influence the calculated load and thus the mean concentration calculated (e.g. Leecaster et al., 2002). Load estimation using sample sizes less than 8 rarely predict a load within 50% of the true mean (at 95% confidence level), and the best performing sampling methods are those with samples on both the rise and fall of the event (Marsh and Waters, 2009b). Observational errors associated with nutrient load estimates based on poor data can lead to a high degree of uncertainty in modelling and nutrient budgeting studies (Johnes, 2007). It is also acknowledged that the relationship between stream-flow and concentration can follow a variety of non-linear forms which have important process implications (Nistor and Church, 2005; Sansalone and Cristina, 2004) and as a result, the large events may carry the highest loads, but may not have the highest concentrations. Hence, it is important in any sampling campaign that the whole hydrograph, including the first or initial events in the rainy season, are collected to adequately represent average concentrations from a given area.

Therefore, where possible, data were classified according to the following:

1. More than 8 samples were collected evenly over the event hydrograph;
2. More than 8 samples were collected on rising or falling limbs of the event hydrograph;
3. Less than 8 samples were collected, although they were measured evenly across the event hydrograph, and/or at least the peak of the event was captured;
4. More than 8 samples were collected, however, this was dominated by low flow conditions, and did not adequately capture the event hydrograph;
5. Less than 8 samples were collected and did not capture the whole hydrograph;
6. No hydrograph information was supplied with the concentration or load data;
7. Continuous turbidity was used as a surrogate for suspended sediment. Although the TSS-turbidity relationship may change within and between events for a given site (Sun et al., 2001), this is considered as the most accurate way of calculating the 'true' load (Walling and Webb, 1981).

It is also important to have information on the size of the event with respect to the long term flow record (i.e. flow duration curves and/or exceedence probabilities). Therefore, where possible, information was recorded on whether:

1. Flow data is provided and the location of the sampled event with respect to the long term flow record is given;
2. Flow data provided, but no historical context given;
3. No flow data were provided.

4.8 **Determining if there are differences in constituent concentration for different plot sizes and proportions of a contributing land use**

In the Source Catchments model, it is common to configure and characterise the Functional Units (FU’s) within a model according to land use (e.g. Searle and Ellis, 2009). The model set up is very flexible and therefore the FU size can vary from the size of plot (≈< 1 km²) to sub-catchment (1-100 km²) or larger, depending on the quality and size of the initial data inputs (e.g. Digital Elevation Model). Due to the variable sizes of the FU’s it was important to evaluate:
(1) If there is a difference between water quality data measured at plot and catchment scales; and
(2) What the minimum % catchment area a particular land use should occupy before the water quality data can be considered to be dominated by the activities of that land use.

It is well-established that sediment loss from small (i.e. 1 m²) plots will yield more sediment than at the hillslope scale (e.g. 100 m²) due to sediment storage within the hillslope catena (Ludwig et al., 2007; Parsons et al., 2006). Phosphorus concentrations also decrease with increased plot scale (Sharpley and Kleinman, 2003) although there is less evidence for a similar decline with nitrogen due to the pathways (i.e. surface and sub-surface) for dissolved nitrogen loss on the hillslope. It is generally agreed that erosion rates from plot scale studies should not be extrapolated beyond this scale (Parsons et al., 2006), however, for a number of land uses in Australia (e.g. bananas), plot data is often all that is available. Therefore it is important to find out if these data are suitable for application in catchment models, or whether only catchment scale data should be used. To do this, data from the Forest and Grazing (on native pastures) land uses were analysed to test if there was a difference in the constituent values at different spatial scales. These were the only land use types where >90% of the catchment was represented by a single land use at different scales. The scale classes used were plot to small catchment (which is <1 km² for grazing and < 10km² for forest due to limited data), medium catchment (1-100 km²) and large catchment scales (> 100 km²). Note that for the grazing land use the plot data were generally from sites less than 0.01 km², but a 1 km² threshold was used to accommodate the few studies that were larger than 0.01 km². There was no statistical difference between TSS concentrations for plots that were <0.01 km² and plots between 0.01 and 1 km² (p=0.9, data not shown).

Knowledge of the minimum % contribution of a single land use has not been defined in the literature. The land use percentages reported vary from as low as 5% for intensive high fertiliser land uses (e.g. bananas) that rarely occupy whole sub-catchments (e.g. Bainbridge et al., 2009), to 100% contribution for less intensive land uses such as forestry (e.g. Hunter and Walton, 2008). As an example, Rohde et al., (2008) have classed some land uses as ‘sugar’ as the ‘major’ land use category, however, it only represents 25% of the catchment, and no mention of the other land uses in this catchment are given. So although this catchment has been classed as sugar, as this is the land use that dominates the water quality signal (e.g. nitrate), the majority of the catchment is under forest.

This is important for applying these data in modelling situations. For example, if users of the Source Catchments model are characterising the functional units (FU’s) in a model according to land use, then it is important to be representing each specific land use appropriately. This also implies having an understanding of the condition of the land use. In the majority of studies, the water quality measured at a sub-catchment is a conglomerate of the range of land uses upstream (e.g. 25% sugar, 50% forest, 25% grazing) and just because one of the land uses may be more intensive (e.g. sugar) it does not necessarily mean that the water quality downstream is representative of that land use on its own. In other international studies, researchers have undertaken a land use specific compilation of data for plot scale data alone (see Harmel et al., 2006a), however, the Source Catchments model generally operates at a sub-catchment scale and therefore processes other than just hillslope or sheet erosion need to be taken into consideration (e.g. gully erosion, groundwater input etc). To test if there are differences in the constituent concentration values for different proportions of a given land use, data from the Forest and Grazing (on un-modified pastures) land uses were analysed as these land uses had the most data. They were grouped according to the proportion of area with a single land use (i.e. >90%, 70-90%, 50-70% and <50%). A Kruskal-Wallis One Way Analysis of Variance on Ranks was performed to identify if there was a % threshold that gave a statistically different result for TSS, TN and TP.
4.9  *Linking the data base to Google Earth*

The water quality database was developed using Microsoft Excel. An Excel macro was created to convert the data into a Keyhole Markup Language (KML) file. This KML file can be viewed using Google Earth TM, a spatial mapping program.
5 Results

5.1 Summary of data sets used in data base

A total of 757 entries were put into the data base from 514 different geographical sites covering 13 different land uses (Table 2). A list of references used to create the data base are given in Appendix B. A total of 44 entries (~6%) had data that could be used to calculate both event concentrations (EMC) and dry weather or base-flow (DWC) concentrations at the same site, and only 41% of sites had data for all three constituents: TSS, TN and TP. For the total data base, ~70% of sites provided sufficient information to describe the sample collection methods, ~85% provided information about the method used to calculate the mean constituent concentration and ~26% described the number of samples collected over the hydrograph. Only 17% of entries provided information on the laboratory analytical methods used and <5% described the condition of the land use upstream of the sample collection point in terms of vegetation cover or management practices.

Figure 3 presents a geographical summary of the location of the 514 sites in the data base. It shows that there is a heavy bias to data from Queensland. This may reflect the amount of research conducted in Queensland due to the link between catchment condition, water quality runoff and the health of the Great Barrier Reef (GBR) or, to some extent, it may reflect the author’s ability to access event data collected in this State. A copy of the KML file used to generate the Google Earth Map of water quality sites is available from the eWater CRC (http://www.ewater.com.au/).

Table 2: Summary of land uses and the number of sites included in the data base (including plot/hillslope studies)

<table>
<thead>
<tr>
<th>Land use</th>
<th>Number of sites in data base (primary land use)</th>
<th>Number of sites &gt;90% land use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bananas</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Cotton</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Dryland Cropping</td>
<td>27</td>
<td>0</td>
</tr>
<tr>
<td>Forest</td>
<td>121</td>
<td>&lt;17</td>
</tr>
<tr>
<td>Forestry</td>
<td>27</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Grazing Modified Pastures (includes dairy)</td>
<td>70</td>
<td>&lt;17</td>
</tr>
<tr>
<td>Grazing Native Pastures (includes savannah / woodland grazing)</td>
<td>269</td>
<td>&lt;58</td>
</tr>
<tr>
<td>Horticulture</td>
<td>23</td>
<td>13</td>
</tr>
<tr>
<td>Military</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>Mining</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Mixed or unknown</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Sugar Cane</td>
<td>35</td>
<td>14</td>
</tr>
<tr>
<td>Urban / Industry</td>
<td>85</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 3: Location of water quality data sites reported and entered into the data base are indicated by the red markers.

Figure 4: An example of the data available for the the Bowen River catchment in Queensland for 2004.
5.2 Preliminary analysis to determine data for inclusion in final results

Initial analysis of the data was undertaken to determine if some samples should be excluded from the final summary results due to:

(a) sub-optimal sampling protocols (e.g. collecting water quality samples at a site without specific hydrographic data) (Section 5.2.1)

(b) variations in the spatial scale at which the samples were collected (Section 5.2.2); or

(c) the proportion of the land use area upstream of a water quality collection point not being representative of a single land use (Section 5.2.3)

A number of box and whisker plots are presented in this report and Figure 5 describes the statistical data represented in the figures.

![Box and whisker plot]

Figure 5: A description of the statistics represented by the box and whisker plots in subsequent sections

5.2.1 Comparison of constituent data collected using different methods

A simple comparison of three data sets from the same land use (forest) in a similar geographic and climatic region (wet tropics of North Queensland) is presented in Table 3. Preliminary results suggest that data collected without specific hydrographic data are lower, particularly for nitrogen, than for sites where samples were collected in association with hydrographic data (Table 3). This result may be due the condition of the catchment, magnitude of the event or other environmental factors as outlined in Section 4.2.1, although it is also likely that the high concentrations that often occur at the beginning of events were missed and, on average, this resulted in lower median concentrations of constituents. Figure 6 demonstrates the higher constituent concentrations measured at the beginning of an event on the Mossman River, North Queensland. These early concentrations are much higher than for subsequent events with similar discharge. These results suggest that concentrations may be lower when samples are not collected simultaneously with flow data.

This section provided a simple demonstration of the possible ramifications of sampling without appropriate hydrographic data, however, there is insufficient data to demonstrate a statistically significant difference and thus little justification for excluding data collected without associated hydrographic data. It is important to note that this is example is relevant to event conditions. The reverse situation may also occur whereby insufficient base flow sampling is undertaken to represent nutrient concentrations in groundwater dependent systems or perennial streams.
Table 3: Comparison of measured ‘median’ constituent concentration values for sites with the same land use and similar climate, but using different sampling methods. Note: (i) these are measured concentration data and not EMC values and (ii) the use of median values results in subtle differences in nutrient balance calculations reported in the table.

| Case Study | Catchment Method of sampling | Land use type and % land use | Catchment area (km²) | No. of samples | Source of data | Median values | TSS (mg/l) | TN (ug/l) | PN (ug/l) | TFN (ug/l) | DON (ug/l) | DIN (ug/l) | TP (ug/l) | PP (ug/l) | TFP (ug/l) | DOP (ug/l) | FRP (ug/l) |
|------------|-------------------------------|-----------------------------|----------------------|----------------|---------------|---------------|------------|----------|----------|-----------|-----------|-----------|----------|---------|----------|-----------|-----------|-----------|
| 1          | Tully-Murray catchment (Davidson Creek, Fishtail) | Manual without hydrograph | Forest, 98% | 93 | 10 | Bainbridge et al (2009) | 2 | 150 | 27 | 119 | 69 | 39 | 14 | 5 | 8 | 6 | 2.2 |
| 2          | Pioneer (St. Helen’s Creek) Manual over hydrograph | Forest, 98% | 24 | 16 | Rohde et al., (2008) | 95 | 566 | 133 | 453 | 243 | 209 | 68 | 34 | 26 | 8 | 19 |
| 3          | Mossman River ISCO sampler with stage recorder | Forest, 99% | 87 | 173 | McJannet et al., (2005) | 8 | 555 | 215 | 340 | 299 | 41 | 14 | 4 | 5 | 5 | <1 |
Figure 6. Discharge against sample concentrations of total nitrogen, total phosphorus (A) and total suspended sediment (B) at Upper Mossman (Source: McJannet et al., 2005). Note nutrient data units are mg/l in this specific graph.

5.2.2 Variation of data at different spatial scales

Data from the Forest and Grazing (on native pastures) land uses were analysed to test if there was a difference in the constituent values at different spatial scales. Statistical transformation of the data was not possible, therefore a non-parametric Mann Whitney rank sum test was used to determine if there was a statistical difference in the data at different spatial scales.

For total suspended sediments (TSS) there was no statistical difference (at the p< 0.05 level) between plot (<1 km²) and medium catchment (1-100 km²) scale data for both the forest (p = 0.427) and grazing land use (p=0.097). There was a statistical difference between TSS values for Grazing between the moderate catchment (1-100 km²) and large catchment (>100 km²) sizes (p<0.001) and this may reflect the incorporation of gullies as a sediment source at the larger scale (> 100 km²), and hence higher mean TSS values for catchments greater than 100 km² when compared to catchments between 1-100 km² (Figure 8). There was insufficient data to allow further analysis of the forest land use at larger scales. It could be argued that using data from the whole of Australia contributed to the high variability within a given data set, however, there can be as much variability in the constituent concentration within the same land use of similar size as there is between different sizes (see Section 4.2.1 and Figure 7). Therefore the geographical spread of the data was not considered to strongly influence this result. There were no statistical differences between plot and catchment scale studies that justify analysing data collected at different scales separately.
Figure 7: Comparison of data from the same land use (Grazing on native pastures) in the same catchment (Burdekin River Basin) showing the variation in TSS values between plot scale studies (<1 km²) and large catchment areas (~7,000 km²). Data sourced from Hawdon et al., (2008), Bartley et al., (2010a), Bainbridge et al., (2007), and Bartley et al., (2007a).

We had insufficient data to undertake the same analysis for sugar cane at different spatial scales as fertiliser intensive land uses rarely occupy catchments greater than 100 km². Using TN values, however, there is a statistically significant decline (p < 0.05) between TN values measured at the plot or <1 km² scale compared with catchment scales (> 1 km²) (Figure 9). In this analysis the plot scale data were represented by > 95% sugar land use. For the 1-100 km² and >100 km² groups, the proportion of sugar represented was between 25-100% and 31-72% which suggests that once data from other land uses are included, the water quality concentrations or TN and TP in sugar cane are reduced. The reason why the TP values increase again at the larger scale (> 100 km²) in Figure 9B is possibly due to the increased contribution of channel erosion processes which would increase the amount of sediment attached phosphorus.

Figure 8: The difference in TSS concentration values for sites at plot, medium-catchment and large catchment scales for the (A) Forest and (B) Grazing (on native pastures) land uses. Note for both sets of data the land use occupied >90% of the catchment.
Figure 9: The difference in (A) TN concentration and (B) TP values for sites at plot (<1 km²), sub-catchment (1-100 km²) and large catchment scales (>100 km²) for the Sugar land use. Note that the proportion of the catchment represented by sugar cane in each category varies. For the <1 km² data sugar is >95%, for 1-100 km² it is between 25-100% and for the >100 km² it is between 31-72%. Note that the TSS plot for sugar has a very similar pattern as TP.

5.2.3 Does the constituent concentration vary when the proportion of upstream land use changes?

The results of the Mann-Whitney Rank sum test suggest that, in the majority of cases, there is a statistically significant difference between the constituent value measured from a site where a single land use occupies >90% of the site, compared with sites that has < 90% of the upstream catchment area dominated by one land use (see Table 4). This result appears to be stronger for low intensity land uses such as forest (Figure 11) and high fertiliser land uses such as sugar (Figure 12), than for moderate land uses such as grazing (Figure 10). A detailed discussion of some of the reasons for this difference are given in Section 6.

Table 4: Summary table showing when there was a significant difference (p<0.05) between sites that had >90% of the catchment under a single land use compared with 70-90% of the area.

<table>
<thead>
<tr>
<th></th>
<th>Grazing</th>
<th>Forest</th>
<th>Sugar*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>(p=0.025)</td>
<td>(p=0.05)</td>
<td>(p = 0.003)</td>
</tr>
<tr>
<td>TN</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>(p=0.187)</td>
<td>(p=0.03)</td>
<td>(p=0.014)</td>
</tr>
<tr>
<td>TP</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>(p=0.589)</td>
<td>(p=0.01)</td>
<td>(p=0.005)</td>
</tr>
</tbody>
</table>

*Note that sugar had different % land use contribution thresholds than grazing and forest
Figure 10: (A) TSS (B) TN and (C) TP for Grazing land use according to the % of that land use represented above the water quality sampling point

Figure 11: (A) TSS (B) TN and (C) TP for Forest land use according to the % of that land use represented above the water quality sampling point
Figure 12: (A) TSS (B) TN and (C) TP for the Sugar land use according to the % of that land use represented above the water quality sampling point. Note that the % threshold of land that was used for TSS was slightly different to that for TN and TP due to limited data, and the land use % representations are different to the grazing and forest data sets.
5.3 **Summary of water quality data for different land uses**

Based on the results presented in Sections 5.2.1, Section 5.2.2 and 5.2.3, the final data is presented in two sections:

1. The main graphs (Figure 13, Figure 14 and Figure 15) and Table 5 and Table 6 present a summary of the plot and catchment data together for all land use data based on the land use classification given in the original documents from which the data were derived. These results are presented to show the range or spread of data and allows the whole data base to be utilised in generating the summary statistics.

2. Then Table 7 presents the constituent results for sites where the land use upstream is dominated by (>90%) a single land use. This data could be considered more robust when modellers are looking to represent land use specific concentrations, however, it is important to be mindful that this smaller data set is biased towards smaller plot sizes for the intensive land uses (e.g. sugar cane).

The land uses with the highest median TSS concentrations are Mining (~50,000 mg/l), Horticulture (~3000 mg/l), Cotton (~600 mg/l), Grazing on native pastures (~300 mg/l), and Bananas (~200 mg/l) (Figure 13A). The highest median TN concentrations are from Horticulture (~32,000 ug/l), Cotton (~6,500 ug/l), Bananas (~2,700 ug/l), Grazing on modified pastures (~2,200 ug/l) and Sugar (~1,700 ug/l) (Figure 13B). For TP it is Forestry (~5,800 ug/l), Horticulture (~1,500 ug/l), Bananas (~1,400 ug/l), Grazing on modified pastures (~400 ug/l) and Grazing on native pastures (~300 ug/l) (Figure 13C). A summary of the results is presented in Table 5. For the dissolved nutrient fractions, Sugar has the highest concentrations of DIN, DON and DOP, and the Urban land use has the highest concentrations of DIP (Figure 14 and Table 6).
Figure 13: Constituent concentrations for (A) Event TSS (mg/l) (B) Event TN (ug/l) and (C) Event TP (ug/l) for land uses where n>3. Note the log (natural) y axis and Dairy has been presented with Grazing on modified pastures
Figure 14: Event (A) DIN (B) DON (C) DIP and (D) DOP (μg/l) concentrations for land uses (where n > 3). Note that Bananas and cotton have been combined with Horticulture.
Table 5: Summary of data for TSS, TN and TP for the 10 major land uses identified in this study. Note that n represents a data point from a single geographical site and in some cases this represents individual event data, in other cases it represents annual or multi event averages. Data were only presented when n ≥ 3

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Table 6: Summary of data for DIN, DON, DIP and DOP for the 10 major land uses identified in this study for event (EMC) conditions only. There was insufficient data to present baseflow (DWC) values. Note that n represents a data point from a single geographical site and in some cases this represents individual event data, in other cases it represents annual or multi event averages. Data were only presented when n ≥ 3

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Table 7: Summary data for TSS, TN and TP for the 10 major land uses identified in this study where the land use upstream of the sampling point is >90% under a single land use. Data is for event (EMC) conditions only. There was insufficient data to present baseflow (DWC) values. Note that n represents a data point and in some cases this represents individual event data, in other cases it represents annual or multi event averages.

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32
5.4 **Comparison of event and base flow data for the dominant land uses**

There were sufficient data to compare event (EMC) and base flow or dry weather (DWC) TSS and TN concentrations for three land uses, and four land uses for TP (Figure 15). The TSS values recorded for event flows were all statistically higher (p< 0.05) than for base flow conditions for all land uses. For the TN data, there was no significant difference between event and base flow concentrations for forests, but the grazing land use had significantly lower DWC values than EMC values. Interestingly, the DWC TN values for the Urban land use were significantly higher (p<0.05) than the EMC values. This appeared to be skewed by data collected during baseflow conditions in the Melbourne city catchments (Mitchell et al., 1998), and suggests that there may be a source of nitrogen in the urban environment (e.g. garden fertilisers, dog manure and reticulated water leakage) that is reaching waterways under baseflow conditions. For TP, Forest, Forestry and Grazing all had statistically higher EMC concentrations than DWC (p<0.05), but there was no statistical difference between the EMC and DWC values for the Urban land use.
Figure 15: Comparison of event (EMC) and base flow (DWC) concentrations for (A) TSS (mg/l) for Forest, Grazing (on native pastures) and Urban land uses, (B) TN (ug/l) for Forest, Forestry, Grazing (on native pastures) and Urban land uses and (C) TP (ug/l) concentrations for Forest, Forestry, Grazing (on native pastures) and Urban land uses
6 Discussion

6.1 Summary of findings from this study

The overwhelming outcome from this study is that there is a high variability in water quality both within and between sites. The reasons for collecting water quality data vary considerably, and so to do the field, lab and data analysis methods. Water quality data is expensive to collect, and therefore very few studies appear to have measured all of the constituents, and collated all of the required data (including information on land condition) at a range of scales, under the most robust sampling and analysis conditions. Acknowledging that there was considerable variability in the data, a number of analyses were undertaken to determine if and when this variability affects the statistical result for a given constituent representing a given land use.

An analysis of data collected from the same land use using different field collection and data analysis procedures suggested that concentration data that is not collected simultaneously with flow data, is likely to be lower in value than when data is collected using hydrographic data (Table 3). Facchi et al., (2007) concluded that grab sampling is a relatively inefficient methodology for capturing mean concentrations for rivers subjected to highly variable loads, especially when it is restricted to office hours. Based on the analysis presented here it could be argued that grab sampling is a suitable method for estimating concentration as long as the water stage and location of the sample on the hydrograph can be determined. It is recommended that flow data be captured (or at a minimum estimated) for each site where constituent data is obtained. Sansalone et al., (2005) found that some constituents such as suspended solids are driven by the hydrology of the event, as particulate matter is reliant on the energy or stream power of an event to move the material. Dissolved constituents, on the other hand, followed an exponential type decline during the rising limb of the hydrograph. It is important therefore to collect hydrographic data at the same time as constituent data is collected so that a robust understanding of constituent generation and movement pathways can be calculated.

Based on the data sets available in this study, it was found that there wasn’t a statistical difference between the median TSS concentration values at different spatial scales (Figure 8). It is important to note that sample sizes in this study were not large (n between 3 and 33), nonetheless, this result was surprising given that other studies have advocated that it is not suitable to extrapolate results from small scale plot studies to larger catchments scales (Parsons et al., 2006). However, recent studies have shown that unit area sediment yields decline with increasing plot length for undisturbed and moderately disturbed sites, but actually increase for the highly disturbed sites (Moreno-de las Heras et al., 2010). Similarly, Wilcox et al., (2003) concluded that site condition is likely to have as much or bigger influence on the constituent concentration than the scale of study, and many studies have shown that the type of vegetation on a plot can dramatically influence constituent concentrations at a site (e.g. Michaelides et al., 2009). In addition, areas that have well developed rill erosion, the sediment concentrations are likely to increase with increasing area producing values that are similar to plot scale studies.

The results differed for the nutrient data which showed that plot scale concentrations were higher than concentrations derived from catchment studies. These results were, however, confounded by the proportion of land use represented in each of the size classes. Mitchell et al., (2009) found a near perfect linear relationship between stream nitrate concentrations and the proportion of land use upstream that used fertiliser, and similar results have been shown in other studies (e.g. Feng et al., 2010). These results appeared to be independent of catchment size and suggest that the proportion of land use upstream of the sampling point that uses fertiliser is more important that the size of the contributing area upstream. It is
important to keep in mind that there may be considerable variability between plot and catchment scale studies in certain situations. For example, a number of studies have shown that concentrations of nutrients in sub-surface and deep drainage water can be as high or higher than for surface runoff (e.g. Ridley et al., 2003) and in these cases nutrient concentrations may increase at larger spatial scales when ground water and sub-surface nutrient concentrations are incorporated.

The results presented in this study suggest that when you have <90% of a given land use, you are potentially introducing contamination or influence from other land uses into the water quality signal, and therefore data from sites with <90% are not necessarily representative of that land use when used in a modelling context (e.g. Figure 10, Figure 11 and Figure 12). Using data only from sites with >90% a single land use, although potentially more appropriate for land use based modelling, does introduce a number of problems. The primary issue is that it dramatically reduced the number of data points available for analysis in this study from 757 to ~130. It also reduces the range of plot sizes incorporated into the final analysis, particularly for the more intensive land uses (e.g. sugar cane) that rarely occupy large parts of a catchment, and are rarely in steep headwater areas. Also processes such as denitrification may have been taken into account in larger scale studies, but not plot scale studies.

It is important to note that the number of data points in each land use category is different, and this may have biased some of the results. For example, the TN values for Horticulture are dominated by a single study (where they grew lettuce, spinach, capsicum) which was based on 13 events with very high soil and nutrient loss rates (Hollinger et al., 2001). It is not certain if this study is ‘typical’ of horticulture, and these results highlight where further data collection is needed.

6.2 Issues to be aware of when using data in catchment models

This section describes some of the issues that modellers need to be aware of when using and applying average water quality data within a catchment scale modelling framework.

6.2.1 Uncertainty in data collection, handling, processing and analysis

No attempt was made to estimate the uncertainty for data collected in this study, however, it is acknowledged that understanding the level of uncertainty, and where it is introduced in the data collection process, may be important for deciding what data is used in a modelling project. The results presented in Harmel at el., (2006b) provide some estimate of the cumulative uncertainty in water quality data for the purpose of providing defensible estimates of data uncertainty to support water resource management. In summary, they determined that:

‘Averaged across all constituents, the calculated cumulative probable uncertainty (\(\pm\%\)) contributed under typical scenarios ranged from 6% to 19% for streamflow measurement, from 4% to 48% for sample collection, from 2% to 16% for sample preservation/storage, and from 5% to 21% for laboratory analysis. Under typical conditions, errors in storm loads ranged from 8% to 104% for dissolved nutrients, from 8% to 110% for total N and P, and from 7% to 53% for TSS.’

With respect to constituents, the study by Harmel at el., (2006b) showed that there is more uncertainty related to measuring dissolved forms of N and P than for TN, TP or TSS, and the study highlighted the importance of good QA/QC when collecting data. It is also important to note that errors can be introduced during the data analysis process, particularly when estimating constituent loads (see Kuhnert et al., 2009; Schwartz and Naiman, 1999).
6.2.2 Using ‘event mean concentration’ (EMC) versus ‘mean event concentration’ (MEC)

As described in Section 3 there are a number of different approaches for estimating average event concentration for a site. There are advantages and disadvantages with each of these methods, and it is important to highlight that use of each approach is dependent on samples being adequately collected across the hydrograph (as discussed in Section 4.7 and 5.2.1).

The EMC approach (load divided by flow) is often considered one of the more accurate techniques as it is a true flow weighted concentration, however, the amount of runoff can have a large influence on the EMC value at a given site. Even when you have two sites in a similar condition, a lower EMC value will be obtained in a year with high flow than in a year with low flow due to the dilution of constituent loads. This can be demonstrated using the data from two hillslope flume sites in the Burdekin catchment. Table 8 shows that in 2008 and 2009, the mean measured concentration from Flume 1 was similar at 88 and 98 mg/l, respectively. However, due to the higher runoff in 2008, the total load in 2008 was much higher than in 2009 and thus the TSS EMC value for 2008 (calculated as load divided by flow) was ~1/3 of that calculated for 2009. It is also interesting to note that the calculated EMC values are ~1.2 and 3.1 times higher than the average measured concentration values for Flumes 1 and 2, respectively (Figure 16). This overestimation is largely due to the load calculation (averaging) method used in this study. The load calculation method, and associated uncertainty, can vary enormously between studies (Marsh and Waters, 2009a), and this will influence the value of an EMC, but not the MEC. In some cases it may actually be more appropriate to use MEC than EMC values if the load calculation method is considered to bias the result.

Defining the mean concentration in an event by using flow duration curves (e.g. Chiew and Scanlan, 2002) has many benefits as it provides a consistent method for selecting concentrations at the same point on the hydrograph between sites and years. A limitation of this approach is that it does not distinguish between different concentrations observed in different parts of the event due to hysteresis (see Inamdar et al., 2006; Nistor and Church, 2005; Sansalone and Cristina, 2004), however, it is possible to adapt this approach to calculate mean event concentrations at different points on the hydrograph that represent the important constituent generating processes (see Section 6.2.4).

Figure 16: Comparison of mean measured annual TSS concentrations and annual TSS EMC values for Flume 1 and 2
Table 8: Annual median and mean measured TSS concentrations and the unit area sediment load and annual EMC values for 6 years of monitoring data at two hillslope flume sites in the Burdekin catchment (Source of data, Bartley et al., 2010a)

<table>
<thead>
<tr>
<th>Year</th>
<th>Flume 1</th>
<th></th>
<th></th>
<th>Flume 2</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Annual Rain (mm)</td>
<td>Runoff (mm)</td>
<td>Median of all TSS samples collected during flow events in that year (mg/l)</td>
<td>Mean of all TSS samples collected during flow events in that year (mg/l)</td>
<td>EMC (mg/l) = Total annual load divided by flow</td>
<td>Sediment loss (t/ha)</td>
</tr>
<tr>
<td>2002</td>
<td>304</td>
<td>16</td>
<td>845</td>
<td>865</td>
<td>1185</td>
<td>0.27</td>
</tr>
<tr>
<td>2003</td>
<td>245</td>
<td>32</td>
<td>439</td>
<td>460</td>
<td>551</td>
<td>0.25</td>
</tr>
<tr>
<td>2004</td>
<td>368</td>
<td>33</td>
<td>288</td>
<td>299</td>
<td>203</td>
<td>0.09</td>
</tr>
<tr>
<td>2005</td>
<td>431</td>
<td>30</td>
<td>240</td>
<td>258</td>
<td>197</td>
<td>0.08</td>
</tr>
<tr>
<td>2006</td>
<td>698</td>
<td>82</td>
<td>88</td>
<td>118</td>
<td>93</td>
<td>0.11</td>
</tr>
<tr>
<td>2007</td>
<td>771</td>
<td>147</td>
<td>62</td>
<td>60</td>
<td>44</td>
<td>0.09</td>
</tr>
<tr>
<td>2008</td>
<td>1308</td>
<td>309</td>
<td>67</td>
<td>98</td>
<td>31</td>
<td>0.14</td>
</tr>
<tr>
<td>2009</td>
<td>630</td>
<td>55</td>
<td>81</td>
<td>88</td>
<td>66</td>
<td>0.07</td>
</tr>
</tbody>
</table>

*Logger failure during wet season
6.2.3 Selecting appropriate mean concentration values for load calculations

Given that there is considerable variability in the water quality data for any given land use, there are a range of approaches available for selecting a constituent value. Young et al., (1996) summarised the three general options that modellers and catchment managers have when selecting an approach for data use and application in catchment models, (i) use a ‘best estimate’ value, (ii) use local experimental data that matches the situation or (iii) make a subjective adjustment to the available figures to account for differences in management and environmental attributes. Obviously (i) is a last resort and (ii) would be ideal, but in the majority of cases, local data with the same attributes as the modelled catchment will not be available, and therefore using a combination of (ii) and (iii) would be most appropriate.

To demonstrate the impact of using different concentration values on the end of catchment loads, data collected at the outlet of a 14 km$^2$ catchment in the Burdekin in 2001/02 wet season was used (see Bartley et al., 2010b for description of sites and methods). The 2001/02 wet season had only two events that were well sampled for TSS and continuous turbidity (see Figure 17). Walling and Webb (1981) viewed the load derived from the continuous TSS-turbidity relationship is the most accurate representation of the ‘true’ sediment load against which to assess the accuracy of estimates produced by other indirect load calculation procedures. The load calculated for the 2001/02 wet season was therefore considered as the accurate load for the site (Table 9). The mean annual sediment load for the site was then calculated using the same runoff and four different methods for estimating the mean concentration for the site. The methods included:

- Option 1: using the average sediment concentration for grazing lands in the Burdekin derived from the water quality data base developed for this project (~948 mg/l);
- Option 2: using the 90$^{th}$ percentile sediment concentration for grazing lands in the Burdekin (derived from the water quality data base) (~2925 mg/l). This site was considered to have contributed disproportionately high sediment yields based on previous modelling applications (Prosser et al., 2001a), therefore an upper bound estimate was considered appropriate;
- Applying the average concentration measured at the gauge for that year (~2395 mg/l);
- Applying the median concentration measured at the gauge for that year (1930 mg/l).

The results show that using the average TSS concentration for this particular land use, even from the same region, resulted in sediment loads that were ~67% lower than the true load. Using the measured mean and median concentration data from the same site resulted in loads that were ~11% and 25% lower than the true load and using the 90$^{th}$ percentile EMC from the region over-estimated the true load by ~1.7%. This example has highlighted that:

(i) It is important to have an understanding of the condition and history of land use for the site being modelled compared to other sites with the same land use; and
(ii) It is important to obtain data from a site that has a similar condition to the site that is being modelled, and this may not always be in the same geographic location.
Figure 17: (A) Event 1 on 16th and 17th of December 2001 and (B) Event 2 on 15th February 2002 showing the high turbidity and sediment concentrations early in the event

Table 9: Sediment load (tonnes) calculated using the same hydrology with 4 different methods for estimating the mean concentration for the 2001/02 data set

<table>
<thead>
<tr>
<th>Option</th>
<th>Sediment load (tonnes)</th>
<th>Method</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>True load</th>
</tr>
</thead>
<tbody>
<tr>
<td>Event 1</td>
<td>True load</td>
<td>Mean concentration for the Burdekin (=778 mg/l)</td>
<td>246</td>
<td>685</td>
<td>552</td>
<td>508</td>
<td>705</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95th Percentile concentration for the Burdekin (=2925 mg/l)</td>
<td>341</td>
<td>345</td>
<td>246</td>
<td>305</td>
<td></td>
</tr>
<tr>
<td>Event 2</td>
<td>Total</td>
<td>Using average measured concentration from the field site</td>
<td>369</td>
<td>1026</td>
<td>897</td>
<td>754</td>
<td>1010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Using median measured concentration from the field site</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Using TSS-turbidity relationship</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*calculated from the data base

6.2.4 Differentiating between Event (EMC) and Base flow or dry weather (DWC) values

Models such as Source Catchments are increasingly being used to evaluate the effectiveness of best management practice for different land uses on downstream ecosystems such as the Great Barrier Reef (http://www.nrm.gov.au/funding/2008/reef-rescue.html). They are also being used to link to estuarine and marine models to track the movement of constituents from paddocks to the ocean (e.g. eReefs project). Such application of these models are likely to require a greater temporal accuracy in estimating constituent concentration than simply using average EMC or DWC values.

Figure 18 demonstrates how the concentration of sediments and nutrients can vary at different times of the wet season on the Mossman River in North Queensland, and how the event flow concentrations compare with base-flow (dry season) concentrations. It is important to note that although field data show that the EMC varies from one storm to another, use of an average EMC in multiple-event computer simulations may lead to estimates of total load that are as accurate as those obtained by more complex models (Charbeneau and Barrett, 1998). This is, however, conditional on obtaining accurate EMC or mean concentration data. If the time scale of interest is daily or hourly data, in most cases it will be necessary to compartmentalise the hydrograph into smaller units and apply concentration data that reflects the processes occurring at that point in time. Table 10 provides an example of how the total constituent load can differ when the concentration
values presented in Figure 18 are applied to the equivalent time periods on the hydrograph, versus only applying a whole of wet season mean concentration (Dec-May) and a mean baseflow concentration (Jun-Nov). These load values are then compared to the constituent load calculated using linear interpolation (Degens and Donohue, 2002; McJannet and Fitch, 2005). Using mean concentration data appears to dramatically over-estimate TP and TSS concentrations compared to the using loads calculated by linear interpolation. Dividing the runoff period into smaller time periods reduces this over estimation slightly, but in general studies that have compared modelled outputs against measured data suggest that long-term average results are better simulated than results for individual time periods (Jetten et al., 1999). This example is from a forested stream and the base flow contribution of constituents in this catchment was <3%. This suggests that in some cases, use of a single event mean concentration without a base-flow component would be appropriate, and within the bounds of load error estimates. In other cases, however, baseflow can contribute approximately two-thirds of the mean annual nitrate export as Schilling (2004) found on the Raccoon River watershed in west-central Iowa. Therefore it is important to have collated sufficient water quality data to determine the dominant flow processes and constituent concentration values prior to determining the level of hydrograph separation for calculating constituent loads.

Table 10: Difference in constituent load values for the Upper Mossman River in north Queenland using different methods for the period 1/12/03-30/06/04 (data sourced from McJannet and Fitch, 2005)

<table>
<thead>
<tr>
<th>Load (tonnes)</th>
<th>TN</th>
<th>TP</th>
<th>TSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dividing the wet season into 4 time periods (early, mid and late wet season and base-flow)</td>
<td>182</td>
<td>8</td>
<td>4858</td>
</tr>
<tr>
<td>Use event average (mean of early, mid and late wet season) and base-flow average values only</td>
<td>217.58</td>
<td>8.49</td>
<td>5200.74</td>
</tr>
<tr>
<td>Event contribution</td>
<td>211.22</td>
<td>8.23</td>
<td>5200.36</td>
</tr>
<tr>
<td>Base flow contribution</td>
<td>6.36</td>
<td>0.26</td>
<td>0.38</td>
</tr>
<tr>
<td>Load calculated using linear interpolation*</td>
<td>151</td>
<td>4</td>
<td>2902</td>
</tr>
</tbody>
</table>

*see McJannet and Fitch (2005) or Marsh and Waters (2009) for a description of this method
Figure 18. Comparison of concentrations of TN, TP, turbidity and TSS for baseflow and event conditions on the Mossman River, with event condition further divided into early (December 2003 to January 2004), mid (February to March 2004) and later (April to May 2004) stages of the wet season. Baseflow concentrations are from EPA water quality data from 34 sampling campaigns for the months May until November for the period 1994 to 1999. Baseflow data for TSS was only recorded on three occasions, each being below the detection limit (< 2mg/L) and has been recorded on the box plot as a single point at 2mg/L (Source: McJannet et al., 2005)
7 Conclusions and areas of further research

This study has presented a summary of the known and readily accessible land use based water quality data for Australian catchments and rivers. A total of 757 data points were summarised into 10 land use types. The amount and quality of the data available has increased considerably over the last 15 years since previous data collation exercises were undertaken (Young et al., 1996). Despite the size of this data base, there are still large areas of Australia for which no data exist (see Figure 3). There is also minimal or insufficient data for land uses such as Horticulture, Cotton and other high intensity crops such as bananas, particularly for large plot/catchment scales (> 1km²).

As well as presenting the summarised data collated in this study, this report provided some examples of why and how constituent concentrations vary within and between different land uses. This can be linked to processes such as the condition of the land use from where the data were collected, the data collection procedure or load calculation method. It is hoped that this study will provide modellers with an increased understanding of the processes contributing to a given constituent value, and thus the power to choose appropriate data for their modelling study. This document should be used in conjunction with other relevant publications that provide important information regarding model choice and application (e.g. Grayson et al., 1992; Jakeman et al., 2006; Jordan et al., 2010; Silberstein, 2006).

With respect to future research needs, studies have shown that information on the condition of the land can greatly improve the model results (e.g. Jetten et al., 1999). Therefore, in future studies it is critical that land use condition information is collected alongside water quality data to help differentiate between the natural changes in water quality trends, compared with changes resulting from land management (e.g. Bartley et al., 2010b; Cerdan et al., 2010). This will be critical to evaluating the impact of land use and climate change on water quantity and quality in the future.

There is also a need to improve our understanding of the amount, timing and form of constituents leaving a given land use. The use of high frequency monitoring data is likely to provide important insights into this process (Bende-Michl and Hairsine, 2010) although Beck et al., (1990) raise the possibility that more intensive monitoring may simply uncover yet greater heterogeneity and so require still more monitoring. The need, therefore, is for catchment monitoring to be at a scale that is relevant to the question of interest. At present, the high cost of water quality sample collection and analysis inhibits the broader temporal and spatial collection of data. Therefore any methods that will reduce the costs associated with collecting data, whilst simultaneously increasing our understanding of the various pathways for constituents, are most welcome. As well as improved data collection methods we will also need appropriate data analysis and statistical methods to interpret these data. Use of EMC values is reliant on accurate load estimates, which require appropriate calculation and uncertainty estimation (e.g. Kuhnert et al., 2007). If land use based modelling remains as the most suitable approach for modelling constituent loss at the catchment scale, then more land use specific data are required urgently. This finding needs to be communicated to Government agencies that are initiating event based monitoring programs around Australia.
Take home messages....

- More data is needed from high fertiliser land uses such as cotton, horticulture and bananas at both plot and catchment scales;
- More data is needed from ‘single land use’ sites at a range of scales (plot, sub-catchment and catchment);
- Land condition and management data should be collected for the land surfaces upstream of the sampling point where ever possible so that changes in water quality due land use/management change can be separated from changes to do with climate variability;
- Collection of water quality concentration data is of limited value when not collected with simultaneous flow data;
- Modellers need to be aware of the quality of the water quality data they are using. Factors such as rainfall intensity and amount, land condition, sample collection methods and load calculation methods all influence the final concentration value.
8 Acknowledgements

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9 References


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10 Appendices

10.1 Appendix A: List of Government water quality data sites

Victoria - http://www.vicwaterdata.net/vicwaterdata/home.aspx
10.2 Appendix B: references used in the water quality data base


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10.3 Appendix C: Recommendations for using the Excel data base created for this study

Harmel et al., (2006a) developed a similar data base for sites in the USA and in a subsequent document (Harmel et al., 2008) he describes the MANAGE data base and its application. In the first instance, we aim to make the Google Earth kml file available to eWater partners. Further discussion is required about the arrangements under which the data base would be made available to non eWater partners as well as how it is supported and maintained into the future.