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Calculating pesticide half-lives in reservoirs for model parameterisation

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Abstract: Estimation of pesticide half-lives in streams and reservoirs is important for evaluating ecological and health impacts and for the parameterisation of water quality catchment models. Limited data are available in Australia on pesticide half-lives in freshwater systems, with northern hemisphere data often unsuitable for southern hemisphere application.

A 20-year water quality data set initially established to monitor nutrient and pesticide trends in reservoirs in the Condamine Balonne Catchment, Queensland, Australia, was reviewed to determine whether half-lives could be estimated from historic monitoring data in reservoirs.

Sampling was conducted from four reservoirs within the Condamine/Balonne with the reservoir capacities ranging from 260 to 10,000 ML. Data was examined to identify periods of no inflows to the reservoirs to determine a true half-life not affected by inflows. Half-life and rate constants were estimated using a simple first order exponential decay function. Median half-life estimates for several of the more frequently detected chemicals, namely atrazine, metolachlor, diuron and endosulfan, were 347, 101, 78 and 23 days respectively. Atrazine half-life in the summer months was half the median of the remainder of the year.

This analysis provides further insights into pesticide behavior in reservoirs. The derivation of pesticide half-lives in freshwater for several of the more frequently detected chemicals in eastern Australia will improve estimates of pesticide loads in catchment models.

Keywords: *Pesticides, half-life, reservoirs*

1. INTRODUCTION

The contamination of waterways and reservoirs via runoff from agricultural areas has been widely reported (Wauchope et al (2001), Pereira & Hostettler (1993), Buser (1990), CBWC (2001), Lewis et al (2009)). Concerns over the occurrence of pesticides and nutrients in surface waters is largely driven by their potential impacts on human and ecosystem health. The concern in larger streams and reservoirs focuses more on human health because they more commonly serve as sources of drinking water (Capel et al 2001). Water quality is heavily scrutinized where agriculture and urban centers coexist.

Long term water quality monitoring of streams and reservoirs is therefore important for assessing trends, for tracking water-quality response to changes in fertiliser and pesticide use and for water quality model parameterisation and validation. Ambient water quality monitoring in reservoirs provides an ideal opportunity to investigate nutrient and pesticide behavior and their fate. The rationale for using reservoirs are that they are generally a permanent source of water which enables routine monitoring at the same location in a repeatable manner. In addition, the volume balance and water quality are often monitored on a regular basis by local authorities or water managers.

Modelling offers an alternative option for assessing trends in pesticide and nutrient loads in receiving water bodies and examining responses to change in management. However, to have confidence in modelled outputs, it is imperative that models are parameterised with appropriate local data sets. Pesticide rate constants/half-life in water bodies is a variable required to better model and estimate end of river concentrations and loads.

Reported half-life data for pesticides is highly variable. For example, one of the most frequently studied herbicides, atrazine, has reported half lives in reservoirs from 13 days to 10 years, but generally in the order of weeks or months. Gangstad (1982) also found that rate constants were highly variable with the three most significant factors affecting 2-4 D decay rate being: the time of year, reservoir volume and initial concentration.

Consequently, decay rates based on local data sets for Australian conditions are required to improve our confidence in modelled predictions of pollutant loads entering receiving waters. This paper provides a summary of pesticide half-life estimates from four reservoirs in the Condamine Balonne Catchment, Queensland, Australia derived from 20 years of monitoring data.

1.1. Catchment description

The Condamine, Balonne catchment in Queensland and makes up the headwaters of the Murray–Darling Basin. It drains 96,720 km^2 west of the Great Dividing Range. The catchment has a summer dominant rainfall pattern with mean annual rainfall ranging from 1000 mm in the east to less than 400 mm to the west. Most of the Condamine, Balonne streams are ephemeral. Land use is dominated by grazing (71%), dryland cropping (14%), state forest (8%) and irrigated cropping (3%) with the remainder made up of urban, rural residential and industrial areas. Several reservoirs have been constructed along the main stream network to supply water to local townships. Figure 1 and Table 1 show the location and capacity of the drinking water reservoirs along the Condamine Balonne Stream network and the spatial distribution of cropping areas.

Table 1. Storage capacity and catchment area draining each of the reservoirs

Reservoir name	Maximum volume (ML)	Maximum depth (m)	Catchment area (km^2)
Yarramalong	390	3	6,347
Lemontree	265	2	6,948
Loudoun	588	5	11,843
Chinchilla	9,780	8	18,906

2. METHOD

In 1991, the not-for-profit community group the Condamine Balonne Water Committee (CBWC), representing 16 local councils and seven water user groups established a water quality monitoring program. The aim of the program was to monitor spatial and temporal changes in pesticides in the seven major reservoirs used for town water supply and irrigation in the Condamine Balonne catchment in Southwest Queensland, Australia. Monitoring has continued over this period through various funding sources with monitoring expanded to include both filtered and unfiltered nutrients and basic water chemistry analysis from 2005 onwards. The results presented in this paper has been derived from the CBWC database.

2.1. Sampling locations

Of the seven reservoirs monitored the four discussed in this paper (Figure 1 and Table 1) had the most comprehensive historical set of data and were the sites where pesticides were frequently detected due to their proximity to cropping areas. Note that three of the four reservoirs are less than 600 ML, with Chinchilla reservoir having a significantly larger storage volume at 10,000 ML. Aggregated data is reported from both the small and large reservoirs.

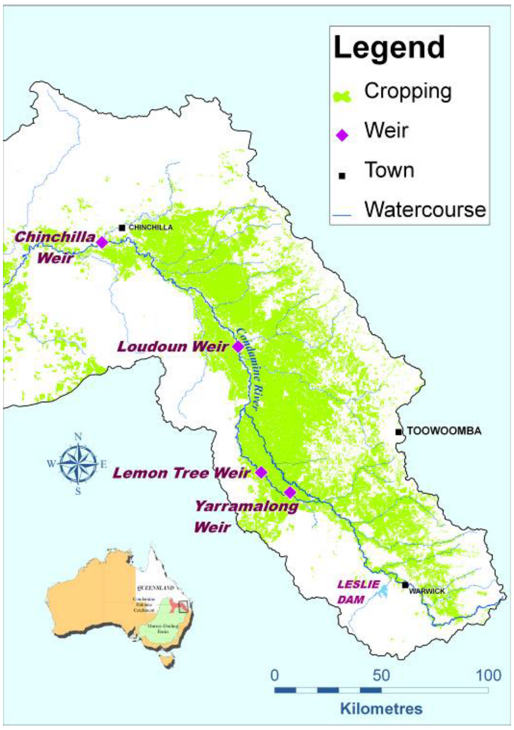

Figure 1. Condamine Balonne catchment showing location of town water supply reservoirs (weirs) sampled and cropping areas.

2.2. Sampling procedure and analysis

Sampling frequency varied from year to year depending on funding. Between 1991 and 1996 sampling was conducted on a two monthly basis, from 1998 to 2011 a minimum of three samples were collected per year. The aim was to sample at the beginning (September), middle (December) and end (March) of the summer cropping period when the probability of runoff from cropping areas entering the reservoirs was at its highest. Whilst the monitoring program was not designed to track pesticide decay, the data offered the potential to provide in situ estimates of pesticide decay.

Sample collection was undertaken during both ambient and storm runoff periods depending on weather conditions on the allocated sampling days. Water quality samples were collected from the reservoirs at the same location each time. Pesticide and nutrient samples were collected as per the State Government protocols (DERM 2009). Laboratory analysis included a broad scan for over 100 pesticides and speciated nutrients. It is acknowledged that stratification may occur in these reservoirs at times. The assumption is that the reservoirs were well mixed given the shallow depth of storage. Further work is required to explore this issue.

2.3. Data analysis

Volume, surface area and depth relationship data were available for Lemontree, Loudoun and Chinchilla reservoir with Yarramalong reservoir characteristics approximated from Loudoun reservoir data. Daily water level data were available for each reservoir which enabled a daily volume to be calculated. Pesticide concentration data was assumed to represent the average concentration on a given day. Pesticide half-lives were calculated from data collected during periods of no inflow to the reservoirs with sampling occurring over periods from 50 to 500 days. Figure 2 shows two examples in 1997 and 2000 where samples were taken during such periods. Reduction in water volume in the reservoirs were due to extraction for town water supply and irrigation, evaporation and infiltration losses.

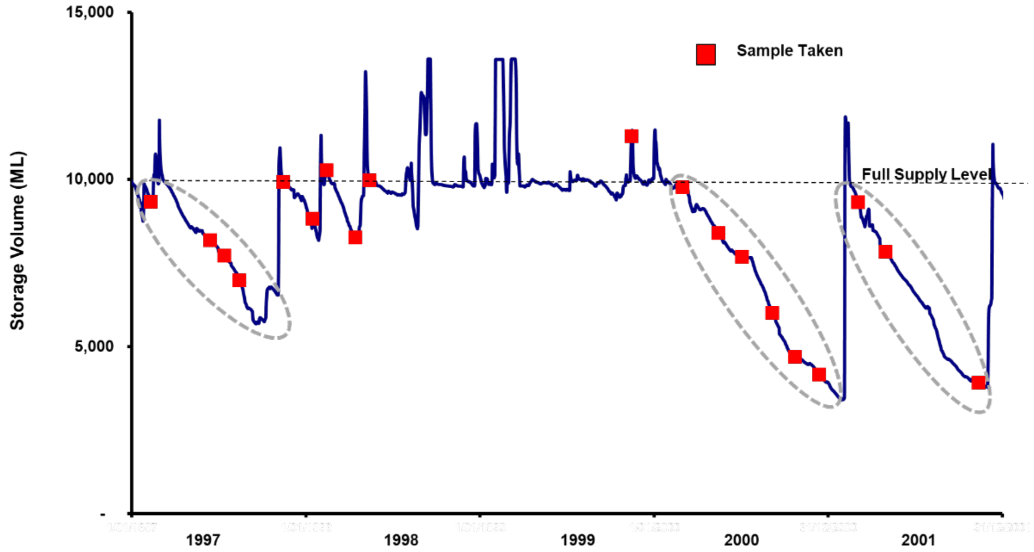

Figure 2. Chinchilla reservoir volume changes over 5 years. Pesticide samples that had been collected during no inflow or cease to flow periods provided the data used to calculate half-lives (grey dashed ellipses)

2.4. Half-life calculation

Pesticide half-life T (days), or the time required to reduce the concentration by 50%, is calculated as a function of the rate constant k (days^{-1}) where:

$$T = \ln(2)/k \tag{1}$$

The rate constant k, is typically derived by plotting the pesticide concentration over time and fitting a first order decay function where:

$$C(t_2) = C(t_1)*\exp\,[-k(t_2-t_1)] \tag{2}$$

Where $C(t_1)$ is the initial concentration and $C(t_2)$ the concentrations at time t_2.

It is noted that evaporation of the water, while leaving the mass of solute behind, may result in an increase in the concentration, while extractions reduce both water volume and solute mass in concert. If the loss of water from evaporation (McJannet et al. 2012) or the volume of extractions and other loses is known, then concentration or load can be corrected, and the true half-life calculated. This data was not available at the time of writing, hence the results presented provide an approximation of median and ranges of in-situ values of T under typical reservoir conditions.

3. RESULTS

Half-life calculations were made for a number of the more frequently detected pesticides of interest. Figure 3 provides examples of changes in atrazine concentrations through time in Chinchilla reservoir.

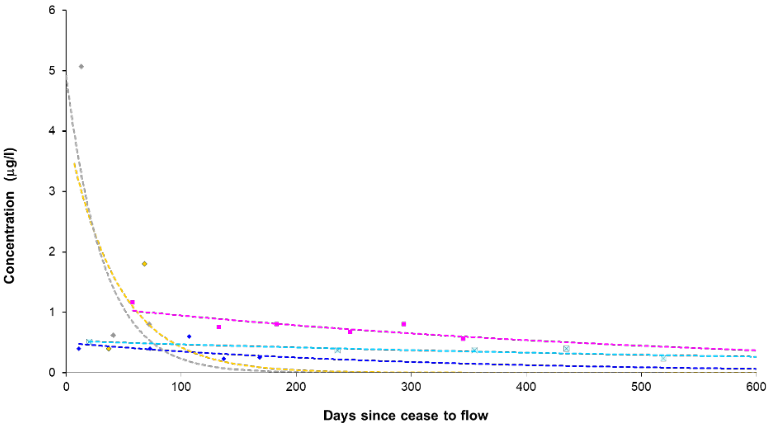

Figure 3. Atrazine decay in Chinchilla Reservoir for five different no-flow periods

Table 2 provides a summary of the median half-life and 25th and 75th percentile values for the respective average half-life calculations for the seven most frequently detected pesticides.

Table 2. Median half-life for all reservoirs for the most frequently detected pesticides

Parameter	No. events	Median half-life (days)	25th/75th percentile half-life (days)
Atrazine (all data)	18	347	121/693
Atrazine (summer only)	9	173	58/693
Metolachlor (all data)	16	101	56/188
Metolachlor (summer only)	6	92	61/202
Endosulfan	7	23	18/64
Diuron	6	78	50/108
Fluometuron	4	89	89
Tebuthiuron	1	231	231
Prometryn	1	50	50

4. DISCUSSION

Pesticide half-lives were calculated from the long-term monitoring data. Figure 3 highlights the variability in the rate of decay for pesticides. The decay rate was highly dependent on the antecedent conditions in the catchment. Larger areas of cropping occur during wetter seasons resulting in increased pesticide application for weed control increasing the risk of higher pesticide concentrations into the reservoirs. Two curves of note in Figure 3 show a rapid rate of decay over the first 50 days then follow a similar trend to the remaining curves. The initial samples for both data sets were taken during the middle of the summer cropping season when the risk of runoff from cropping areas entering reservoirs are at their highest. Beyond 50 days the rate constant is similar to the remaining curves. The rapid rate of decay in pesticide concentrations, particularly for atrazine in the early period after new rainfall runoff water enters the storage could be attributed to multiple factors.

Significant mixing and dilution can occur initially with the older reservoir water and new highly turbid, organic rich runoff water contributing to changes in reservoir concentrations following rainfall runoff. The Pesticide Properties Database (PPDB), suggest that, under laboratory conditions, atrazine degraded through photolysis rapidly (half-life 2 days), as well as being adsorbed to sediments (particularly organic rich sediment) (80 days) and chemical hydrolysis (86 days). APVMA (2008) state that the primary breakdown route of atrazine is via chemical hydrolysis followed by degradation by soil microorganisms (http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/43.htm). In a study by Rose et al., (2007) looking at water samples collected from cotton farm dams in Northern NSW, enhanced degradation of prometryn, diuron and fluometuron was observed when light was introduced to samples. The major process causing the increased dissipation was unknown although high numbers of degrader microorganisms in the water was suggested as a possible reason. Other chemicals tested, showed little change with the introduction of light. Therefore, further studies that closely align to field conditions, as opposed to laboratory experiments, are warranted to better quantify the key processes that are important to enhancing the breakdown of chemicals in reservoirs.

The herbicide atrazine was highly persistent with a median half-life of approximately 350 days for all events with a shorter half-life (173 days) during summer (Figure 4). Hanson et al., (2020) reported that when exposed to sunlight, Atrazine had a half-life of 168 days and under low oxygen conditions, in excess of 500 days similar to the findings in this study. Metolachlor had a shorter median half-life at 101 days. US EPA (1987) reported a similar half-life for Metolachlor of 97 days at 20 °C in neutral Ph waters. Both herbicides were detected in the majority of samples collected and are commonly applied for weed control in sorghum, one of the most frequently grown crops upstream of the reservoirs.

Endosulfan, an insecticide applied extensively in cotton in the 1990's appears to have a relatively short half-life (23 days) and is no longer detected in reservoirs due to its limited use today. Tebuthiuron, a chemical used to control timber regrowth, has increased in its frequency of detection in recent years and has little information reported in the literature on its half-life in water. The preliminary data suggests it may be persistent in reservoirs.

Fluometuron and Prometryn were regularly detected during sampling and these herbicides were used regularly by the cotton industry for weed control. The estimated half-lives for these two chemicals was 89 and 50 days respectively although there is lower confidence in these results given the small number events available to calculate half-lives.

Future work will target no flow periods for more frequent sampling in the initial stages of no flow (<50 days) and examine the impact of seasonal variability on half-life estimates.

4.1. Implications for modelling

Catchment modelling of pesticides requires appropriate parameterisation of instream and storage decay models. The Queensland Government are undertaking a major water quality modelling program across the Great Barrier Reef (GBR) catchments specifically to estimate sediment nutrient and pesticide loads delivered to the GBR (McCloskey et al., 2021). In the absence of measured local data, these models are often parameterised with literature values obtain from other parts of the world. Previous studies on pesticides suggests that rate constants of pesticides can be highly variable. For example, if a rate constant of 0.008 (86 day half-life) was applied to a storage model to estimate daily atrazine concentrations, as opposed to 0.017 (41 day half-life), this would result in a 100% overestimation of the load transported from the reservoir. Therefore, it is imperative that locally relevant rate constant data is used to parameterise local models if we are to have confidence in modelled outputs. These findings may also have important implications when modelling pesticide transport processes. In particular, in northern Australia, where large flows tend to transport the majority of pollutants annually from the source to receiving water with summer dominant rainfall runoff. Travel times for runoff in large catchments are in the order of days to weeks with the findings from this work suggesting that pesticide half-lives may be in the order of weeks to months. Hence in-stream decay during major runoff events may have minimal impact on pesticide budgets.

5. CONCLUSIONS

Long-term historical data sets are becoming increasingly rare although they are essential for assessing temporal and spatial changes in water quality. The 20-year water quality data set used in this paper highlights the value of citizen science and provides baseline rate constant and half-lives for a range of commonly detected pesticides. Further field-based studies on pesticide decay in freshwater would improve modelled estimates of pesticide transport processes and subsequent fate.

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REFERENCES

APVMA (2021). Atrazine – Final Review Report and Regulatory Discussion. Australian Pesticides and Veterinary Medicines Authority, Kingston, Australian Capital Territory, Australia, 49pp. Accessed: September, 2017. Available from: https://apvma.gov.au/sites/default/files/publication/14361-atrazine-final-review-report.pdf.

Buser, H. (1990) atrazine and other s- Triazine Herbicides in Lakes and in Rain in Switzerland. Environ. Sci. Technol. 24 pp 1049 – 1058.

Capel, P. and Larson S. (2001) Effect of scale on the behavior of atrazine in Surface Waters. Environ. Sci Technol. Vol 35 NO. 4: pp 648 657.

CBWC (2002) Fate of Nutrients and Minimising Pesticides in the Riverine Environment. – Final Report. Condamine Balonne Water Committee Inc., Dalby Queensland.

Department of Environment and Resource Management (DERM) (2009) Monitoring and Sampling Manual 2009, Version 2. ISBN 978-0-9806986-1-9.

Gangstad, E (1982) Dissipation of 2,4-D Residues in Large Reservoirs. J. Aquat. Plant Management. Vol20: pp13-16.

Hanson, W.; Strid, A.; Gervais, J.; Cross, A.; Jenkins, J. 2020 Atrazine Fact Sheet; National Pesticide InformationCenter, Oregon State University Extension Services. npic.orst.edu/factsheets/atrazine.html.

Lewis, S.E., Brodie, J.E., Bainbridge, Z.T., Rohde, K., Davis, A.M., Masters, B., Maughan, M., Devlin, M.J., Mueller, J. & Schaffelke, B. (2009). Herbicides: a new threat to the Great Barrier Reef. Environmental Pollution 157:2470-2484.

McCloskey, G. L., Baheerathan, R., Dougall, C., Ellis, R., Bennett, F. R., Waters, D., Darr, S., Fentie, B., Hateley, L., & Askildsen, M. (2021). Modelled estimates of fine sediment and particulate nutrients delivered from the Great Barrier Reef catchments. Marine Pollution Bulletin, 165. https://doi.org/https://doi.org/10.1016/j.marpolbul.2021.112163.

McJannet, D., Webster, I.T., Cook, F.J. (2012). An area-dependent wind function for estimating open water evaporation using land-based meteorological data. Environmental Modelling and Software 31:76-83.

Pereira, W., Hostettler. (1993) Nonpoint Source Contaminating of the Mississippi River and Its Tributaries by Herbicides. Environ. Sci. Technol. 27 pp 1542 – 1552.

Rose MT, Crossan AN, Kennedy IR (2007) Dissipation of cotton pesticides from runoff water in glasshouse columns. Water, Air, and Soil Pollution 182, 207–218.

U.S. Environmental Protection Agency. Health Advisory Draft Report: Metolachlor. Office of Drinking Water, Washington, DC, 1987.10-102.

Wauchope, D., Estes, T, Allen R, Baker J, Hornsby, G, Jones R, Richards P, Gustafson D. (2001) Predicted impact of transgenic, herbicide tolerant corn on drinking water quality in vulnerable watersheds of the mid-western USA. Pest Management Science 58: 146-160, DOI: 10.1002/ps.433.