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Characterisation of Chemical Hazards in Stormwater

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Australian Government
Department of Industry, Innovation and Science
Business Cooperative Research Centres Programme

Characterisation of Chemical Hazards in Stormwater
Cities as Water Supply Catchments - Risk and Health: Understanding Stormwater Quality Hazards (Project C1.2)
1-2017

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Date of publication: January 2017

An appropriate citation for this document is:

Gernjak, W., Lampard, J. and Tang, J.Y.M (2017) Characterisation of chemical hazards in stormwater. Melbourne, Australia: Cooperative Research Centre for Water Sensitive Cities

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Acknowledgements

The authors acknowledge the significant support and assistance provided by industry partners in conducting the monitoring program for this research. In particular we would like to thank the following collaborating councils and government agencies, and their respective employees for much valued assistance with sample collection and logistics: David Beharrel and Paul Fredericksen (Hornsby Shire Council, NSW), Jay Jonasson and Sophia Findlay (Ku-ring-gai Council, NSW), Nicole Reid and Emma Britten (Orange City Council, NSW), and Emma Christie, Steve Fisher, Antonietta Torre, and Belinda Quinton (Department of Water, WA). The authors also acknowledge the support of the Commonwealth of Australia through the Cooperative Research Centre Programme.

The authors also acknowledge their collaborators within the project: Rupak Aryal, Jeffrey Black, and Jurg Keller (AWMC, The University of Queensland); Eva Glenn and Beate Escher (Entox, The University of Queensland); Ana Deletic, David McCarthy, and Peter Kolotelo (Monash University); Jatinder Sidhu, Warish Ahmed, Simon Toze, and Andrew Palmer (CSIRO); Heather Chapman (Griffith University); and Eloise Larsen for editing assistance (AWMC, The University of Queensland).

Overview

The current report summarises the findings of a two phase investigation into the presence of chemicals in Australian stormwater (urban runoff). The data was produced within project *C1.2 Cities as Water Supply Catchments – Risk and Health: Understanding Stormwater Quality Hazards* within the scope of the CRC for Water Sensitive Cities. Water quality data presented are predominantly event mean concentrations from samples (n=94) collected during urban run-off events (2011-2014) from a total of ten different catchments across four states of Australia, i.e. New South Wales (n=21), Queensland (n=41), Victoria (n=26) and Western Australia (n=6, these samples were collected as grab samples during rain events).

This document follows the Urban Water Security Research Alliance Technical Report No. 102 *Health Risk Assessment of Urban Stormwater* (Sidhu *et al* 2012) which presented findings for phase one samples obtained during the preliminary scoping study for the project. Phase one samples were collected from eight catchments across New South Wales, Queensland and Victoria. An overview of these catchments can be found in Tang *et al* (2013). Samples were collected from an additional two sites in Western Australia during Phase Two. These sites consisted of an urban drain in the central area of Perth, and the inlet of the drainage system of a new urban development in the outer suburbs of Perth. The catchments in Queensland, New South Wales, Victoria and Western Australia are a combination of commercial, industrial, and residential land uses in temperate, sub-tropical and Mediterranean style climates. Samples were collected from within stormwater drains, from waters that receive stormwater, and from the inlets to wetland treatment systems in order to be representative of the broad range of capture locations that may be utilised for stormwater reuse schemes.

The study focused on several groups of contaminants, predominantly those present in the dissolved phase such as metals, nutrients, and hydrophilic trace organic contaminants such as pharmaceuticals, pesticides and endocrine-disrupting chemicals. Biological effects of the trace organic contaminants were measured by in vitro tests. Other bulk water quality properties, such as the presence of ions e.g. chloride and sulphate, electrical conductivity (EC), pH, total suspended solids (TSS), and ultraviolet absorbance were also measured. Phase one sampling investigated the presence of chemicals identified as potentially present in urban stormwater during a review of international, peer-reviewed and grey literature pertaining to the water quality characteristics of urban stormwater runoff. Analyses for phase two samples focused on those chemicals detected during phase one sampling. Methodological procedures for chemical and bioassay analyses conducted in this project are described in Sidhu et al. (2012) and Tang et al. (2013).

General parameters

The electrical conductivity (EC) of stormwater samples was generally low, and comparable to many drinking water sources, with the median being 183 µS/cm across the whole dataset. The EC of six samples taken from two drains in Western Australia ranged from 670 to 900 uS/cm, and were likely more saline than the surface-only stormwater drainage collected in the other states due to groundwater-surface water interactions. These findings suggest that in general, stormwater is suitable for land application and also drinking water applications without any further salinity adjustments. In contrast, the EC of secondary wastewater effluent typically ranges from 500 to 2,000 µS/cm, but can also be higher depending on the presence of industrial discharges to sewers, and seawater tidal ingress in coastal sewage treatment plants.

The dissolved organic carbon concentration in stormwater averaged 3.7 mg/L, which again, is comparable to many drinking water sources and slightly below typical secondary wastewater effluent. The high average specific ultraviolet absorption (SUVA) of the stormwater would suggest that substantial amounts of the dissolved organic matter would be amenable to elimination by coagulation treatment. Turbidity measurements ranged from 4 to 114 NTU with a median of 29 NTU and average of 34 NTU. These turbidity values are well within the ranges of surface water used for drinking water production prior to treatment by conventional coagulation and flocculation. These values also suggest that effective disinfection should be possible with ultraviolet irradiation or chemical additives such as sodium hypochlorite. The intermittent nature of supply and variability in water quality must be taken into account when considering the cost effectiveness of stormwater treatment.

In summary, the bulk water quality properties of untreated stormwater make it amenable to conventional treatment and in principle, a suitable water source for a range of applications. However, water quality risks potentially arise from contamination due to pathogenic microorganisms, and inorganic and organic pollution at trace levels. Whereas contamination by pathogens is described in Sidhu et al. (2012) and a separate CRCWSC report, the following sections summarise the findings of our campaign sampling several groups of inorganic and organic trace contaminants.

Metals

Individual metals were measured between 48 and 92 times in stormwater from 10 catchments. For the complete dataset please refer to the CRCWSC Stormwater Quality Database. It is generally accepted that metal contamination can occur in stormwater due to diverse sources. With reference to the Australian Drinking Water Guidelines (NHMRC & NRMMC 2011), there are some metals that are not of public health concern but may lead to aesthetic and other bulk parameter issues such as increased colour or turbidity, e.g. iron and aluminium. Other metals such as zinc and copper may be moderately toxic in high concentration. Consequently, these metals also have moderately high guideline values in the Australian Drinking Water Guidelines, ranging from 200 to 3,000 µg/L. Secondly, there are a number of metals recognised for their considerable toxicity with consequently lower guideline values ranging from 1 µg/L (mercury) to 50 µg/L (chromium, molybdenum). A select group of metals were not measured because the analytical method could not ensure accuracy below 10µg/L.

Figure 1 gives an overview of the metal concentrations found in Australian stormwaters. As can be seen, taking the Australian Drinking Water Guidelines (NHMRC & NRMMC 2011) as reference, several metals such as nickel or lead typically occur at concentrations close to- or above their respective guideline value. Very few obvious trends can be discerned, and variability is high, even within individual catchments.

In general, the median values for aluminium (Al) and iron (Fe), respectively, in NSW are about double the median for those in the wider dataset. This is consistent with the increased colour of the waters in those particular NSW catchments. Interestingly, in WA vanadium (V) is approximately 10 times higher, and zinc (Zn) ten times lower than in the other catchments, suggesting that geology can play an important role in water quality. Zinc contamination in stormwater has been associated with run-off from roofs. The median zinc values in WA, NSW, QLD, and VIC are 26, 81, 88, and 147 µg/L, respectively (90% percentiles for NSW, QLD, and VIC were 494, 195, and 964 µg/L, respectively), suggesting that real differences exist among states and climates, albeit the variability within a single site may be sizeable. In practical terms, this implies that depending on the intended uses of stormwater, treatment to decrease the heavy metal concentration may be necessary. In particular, for potable reuse, potential contamination with toxic heavy metals will need to be well managed.

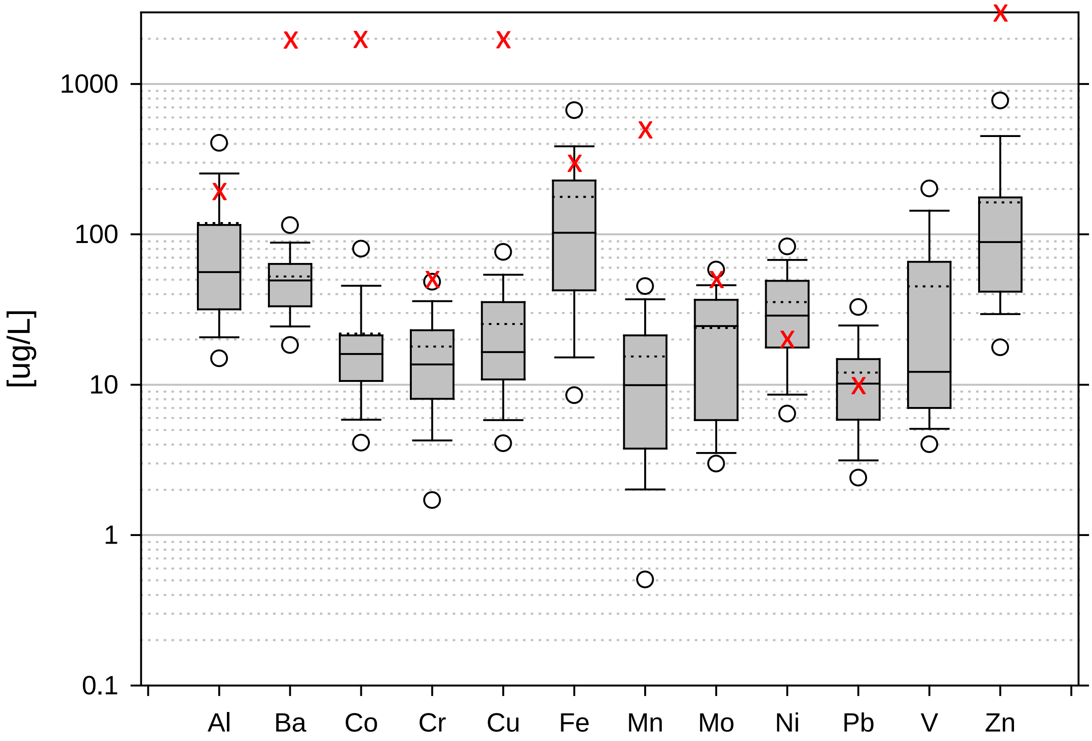

Figure 1: Summary box-plot of metal concentrations in Australian stormwater. n=48-92 from 10 catchments. The box represents the second and third quartile, with the dotted line being the mean, and the solid line, the median. The whiskers mark 10% and 90% percentile, and the open circles, 5% and 95% percentile. The cross represents the guideline value from the Australian Drinking Water Guidelines. Vanadium is not regulated in Australia, but has a notification limit of 50 µg/L in California's drinking water.

Pharmaceuticals and personal care products

A total of 58 pharmaceutical and personal care products were measured. Most of these products are described in the Australian Guidelines for Water Recycling – Augmentation of Drinking Water Supplies (AGWR-ADW, NRMMC, EPHC, & NHMRC 2008). Some unregulated substances such as the artificial sweetener acesulfame-K were also measured.

Generally, although some substances were found above the limit of quantification (LOQ) with varying frequency, caffeine was the only substance detected which exceeded the guideline values listed in the AGWR-ADW (NRMMC, EPHC, & NHMRC 2008). The guideline value for caffeine is 0.35 µg/L, which is close to the median value found (0.27 µg/L) with some measurements exceeding the guideline value considerably (maximum value, 5.2 µg/L). It could be argued that the caffeine guideline value was set conservatively, employing a generic toxicology scheme so that a lifetime exposure through consuming about 60,000 L of drinking water would lead to a cumulative caffeine exposure through this pathway of less than the amount contained in a cup of coffee.

Two other substances were measured at >10% of their respective guideline values in the AGWR-ADW (NRMMC, EPHC, & NHMRC 2008). These were triclosan (maximum 0.07 µg/L, 90% percentile 0.01 µg/L, guideline value

0.1 µg/L) and acetylsalicylic acid. However, the latter was only detected once above its LOQ. Among the comprehensive list of chemicals measured, very few compounds occurred close to their respective AGWR-ADW guideline value. This would be the expected result as even in raw untreated wastewater most of the guideline values of these pharmaceutical and personal care products would rarely be exceeded.

Pharmaceuticals and personal care products may also be interesting indicators of sewage contamination of stormwater, providing an alert to a potential pathogenic risk. A challenge with individual indicators may be that their origin cannot be fully ascertained. For example, detections of caffeine and the artificial sweetener acesulfame-K may occur because of sewage ingress into stormwater or alternatively because of e.g. a can of soft drink being spilled on a walkway. In addition, drawing any correlation may be made more difficult as some trace organic contaminants such as paracetamol can be very biodegradable, whereas others can be quite persistent e.g. acesulfame-K or carbamazepine. For example, in Western Australia, stormwater sampled from an urban drain with known sewage ingress showed considerable acesulfame-K and carbamazepine concentrations (2.7 and 0.045 µg/L, respectively) that would suggest a cross-contamination of 10-25% sewage when compared to published concentrations for untreated sewage. However, other bulk pharmaceuticals that are biodegradable such as paracetamol or salicylic acid were either not detected or present in very low concentrations indicating that while sewage was present it was not recent contamination.

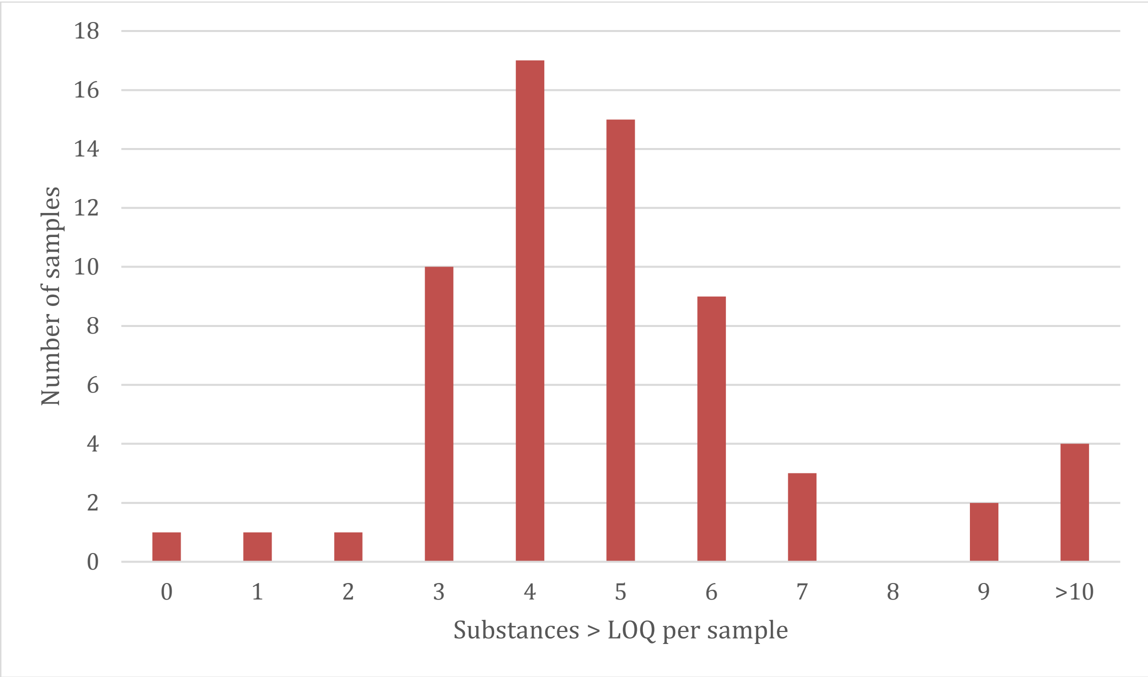

Figure 2: Histogram of occurrence of pharmaceuticals and personal care products above level of quantification (LOQ) in individual samples.

However, the simultaneous presence of a number of pharmaceuticals in a stormwater sample could be a suitable indicator for the presence of sewage contamination and a possible associated pathogenic risk. Of the 63 samples analysed, only 6 samples contained concentrations above the LOQ for ≥9 of the 58 substances analysed per sample, whereas most of the samples contained only 3 to 7 substances above the respective LOQs. Interestingly, the samples that contained a high number of pharmaceuticals represented both big and small storm events, and consequently gave an indication of both sewer overflows and permanent ingress.

In summary, measuring pharmaceuticals and personal care products in stormwater is a promising method for detecting contamination from sewage. However, the current state-of-knowledge does not allow us to apply chemical analysis data as a quantitative indicator of sewage contamination in stormwater.

Endocrine-disrupting chemicals and industrial chemicals

In this project stormwater samples were analysed between 25 and 56 times for a number of known endocrine-disrupting chemicals. Among the steroidal hormones neither 17α-estradiol, 17-α-ethinylestradiol, 17-β-estradiol, estriol, nor estrone were detected above the LOQ in any of the 56 samples quantified. Another active ingredient in contraceptive pills, mestranol, was quantified above the LOQ in 8 of 25 samples at concentrations of 6-32 ng/L. Mestranol was added to the analytical suite in 2013 and was only profiled for five catchments. Mestranol was detected in stormwater from three of the five catchments i.e. 5 detections from 11 samples, 2 from 3 samples, 1 from 3 samples, respectively, with the other two catchments both without detections from 4 samples, respectively. It is noteworthy that the range of concentrations encountered was above the AGWR-ADW guideline value of 2.5 ng/L (NRMMC, EPHC, & NHMRC 2008).

Other industrial compounds such as 4-t-octylphenol and 4-nonylphenol (surfactants), and bisphenol A, which is used in many applications such as polycarbonate plastics and epoxy resins are frequently detected in stormwater. Concentrations of 4-t-octylphenol and nonylphenol varied strongly with, for example, 4-t-octylphenol being detected above the LOQ (10 ng/L) in 35 out of 56 samples. The median concentration was 19 ng/L, the 90% percentile was 200 ng/L, and the maximum value found was 4,900 ng/L, i.e. approximately 250 times the median value. Similarly, nonylphenol was detected at 26 times above the LOQ (100 ng/L) in 56 measurements. Comparing 4-t-ocytylphenol and nonylphenol in a probability chart (Figure 3) it is apparent that, on average, concentrations of nonylphenol were 5 to 10 times higher than 4-octylphenol, although 4-octylphenol has several strong outliers so that the maximum concentration is higher. In comparison, bisphenol A concentrations are less diverse with the median concentration being 155 ng/L and the maximum concentration being 2,000 ng/L (Figure 3).

For 4-t-octylphenol, nonylphenol and bisphenol A, it is also interesting that their occurrence is strongly affected by the catchment properties, i.e. their sources are relatively specific (Figure 4). For example, it is clear that 4-t-octylphenol is found in high concentrations in stormwater from the Hornsby site and the industrial site, whereas nonylphenol is in high concentrations in stormwater from Makerston Street. Bisphenol A was detected across all catchments but also appears to be influenced by site specific characteristics with Ku-ring-gai and the Hornsby sites showing the highest concentrations. All values encountered for these industrial compounds were considerably below the respective guideline values of 500,000, 50,000 and 200,000 ng/L for nonylphenol, 4-t-octylphenol and bisphenol A (AGWR-ADW - NRMMC, EPHC, & NHMRC 2008). This data gives further evidence that specific catchment characteristics such as land use and point sources can influence the extent of chemical contamination in stormwater.

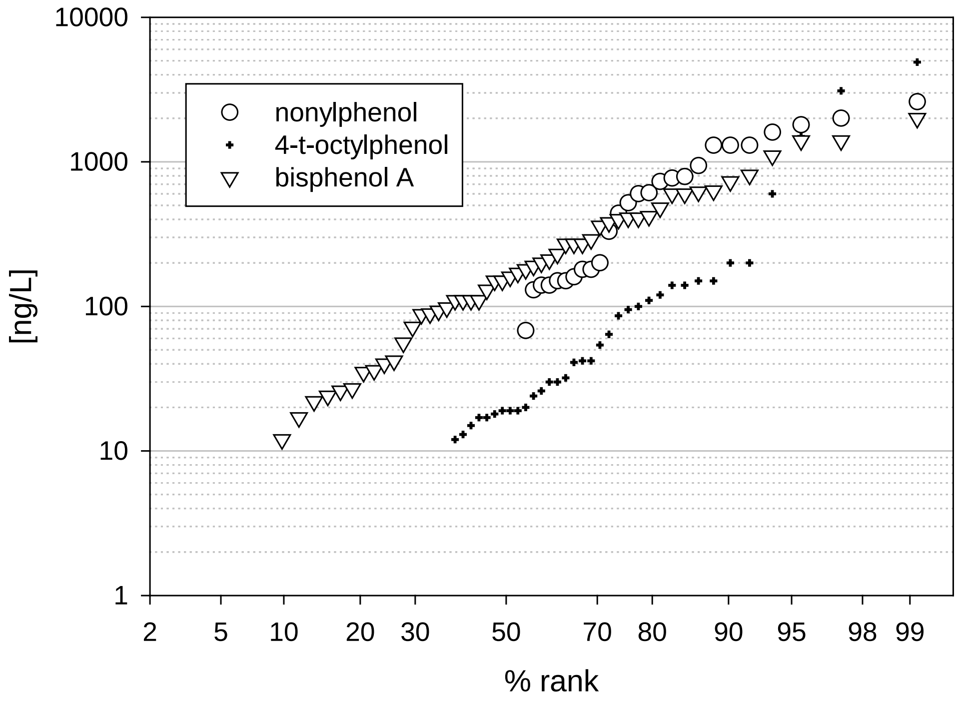

Figure 3: Probability chart of the concentrations of nonylphenol, 4-t-octylphenol and bisphenol A evidencing the log normal distribution of all concentrations.

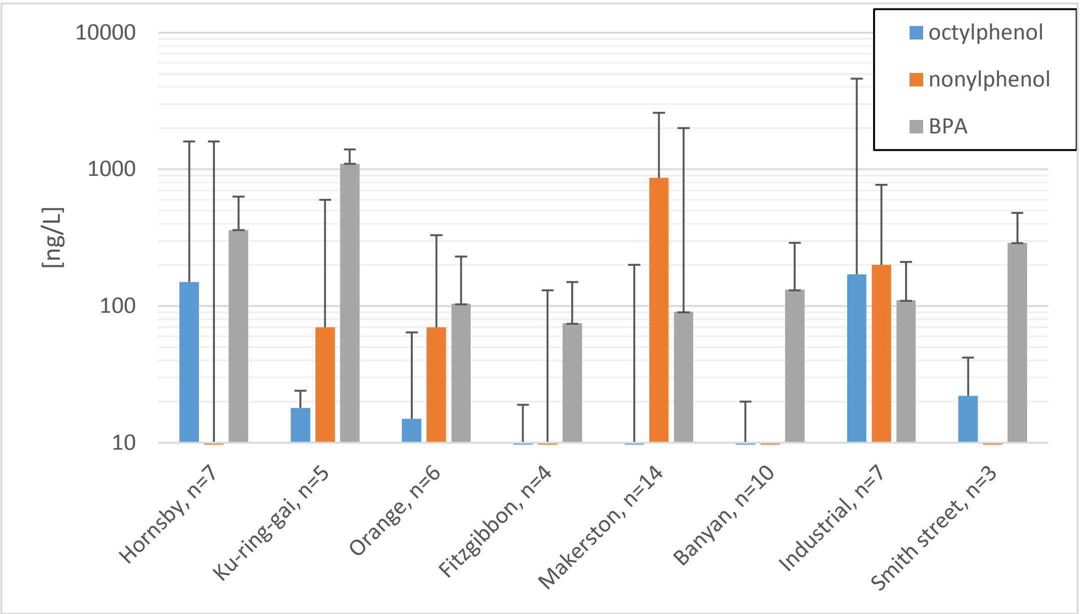

Figure 4: Bar represents median, end of whisker, the maximum value of each contaminant in each catchment. Sample numbers within each catchment are stated in the x axis.

Pesticides

It is well-known that pesticides can occur in urban run-off. Because of their known toxicity they are also strongly regulated and guideline values exist for many active ingredients. Stormwater samples were analysed for 35 pesticides, however, many were either not detected or rarely found above the LOQ (0.01 ug/L for most substances). Fifteen pesticides were found at least 10 times, with 60 to 70 samples analysed for most pesticides. The maximum values of the following substances were at least 1% of their respective AGWR-ADW guideline (maximum concentration detected followed by guideline value in brackets): MCPA: 4.4 (2) ug/L, 2,4-D: 23 (30) ug/L, mecoprop: 1.3 (10) ug/L, triclopyr: 0.88 (10) ug/L, atrazine: 2.3 (40) ug/L, bromoxynil: 1.7 (30) ug/L, diuron: 1.7 (30) ug/L, simazine: 0.51 (20) ug/L, 3,4-dichloroaniline: 0.01 (0.35) ug/L, dicamba: 1.5 (100) ug/L.

Most of the pesticides listed here are herbicides. The four which had the highest ratio of maximum to guideline value are chlorinated herbicides that contain a carboxylic group. This carboxylic acid group fosters a high solubility, and consequently mobility of the pollutant with the stormwater during a rainfall event.

Taking the AGWR-ADW guidelines (NRMMC, EPHC, & NHMRC 2008) as a reference, four exceedances were observed, all for MCPA, of which three occurred in the Makerston Street catchment and one in the Ku-ring-gai City Council site. When evaluating this, recall that these guidelines refer to potable consumption, i.e. the maximum allowable exposure, and the water quality characteristics presented are for raw stormwater prior to treatment. In conclusion, with reference to the guideline values listed within AGWR-ADW, as for pharmaceuticals, the health risk arising from pesticides in stormwater should generally be very low.

Adverse biological effects in in-vitro bioassays

Chemical monitoring programs have limitations. It is not feasible to test for the myriad of registered and commercial chemicals, let alone account for incidental chemicals such as disinfection by-products or combustion by-products. The same is true for regulation which is based on a limited number of representative compounds in a given exposure scenario with an established guideline value being related to a defined endpoint such as a potential human health impact.

Instead of using a direct measure of chemical pollution, an indirect measure of adverse biological effects of a sample can be useful in detecting an unidentified or unexpected micropollutants. This can be done with bioanalytical tools that measure the in-vitro response of particular living cells or tissues to exposure to micropollutants. Using bioanalytical tools, different types of water can be compared in regards to the potential to cause an adverse health effect. For example, Macova et al. (2011) compared the application of bioanalytical tools for the evaluation of organic micropollutants during sewage treatment, water recycling, and drinking water generation. As for this study, typical assessments use a variety of bioassays to cover a range of different biological effects such as genotoxicity, estrogenicity (endocrine disruption), phytotoxicity, dioxin-like activity and non-specific cell toxicity.

In a recent scientific publication (Tang et al., 2013), we compared the water quality of stormwater from a number of catchments with previously published data from Macova et al. (2011). In summary, for most of the tests applied the toxicological burden of concern is in the range of well-treated secondary effluent. Some effects such as induced oxidative stress were generally lower in stormwater than in treated secondary effluent whereas the response in the AhR-CAFLUX bioassay was noticeably higher (factor 2-5). This bioassay is particularly responsive to polycyclic aromatic hydrocarbons (PAH) and dioxins. Since the genotoxic effects in stormwater were low, we can deduce that the effect probably stems from PAH contamination. This is an example of the aforementioned utility of bioassays to determine an effect arising from the presence of potentially multiple- or unknown chemical contaminants, where the chemical contaminant monitoring had not directly targeted PAH measurement.

Conclusion

This document has presented a summary of the chemical and toxicological qualities of untreated Australian stormwater identified during analysis of samples collected from rainfall events during the period 2011-2014. Event mean concentration data informing this summary comes from ten Australian catchments which differ by a range of factors, most notably climate and land use. Chemical analysis focused on physico-chemical characteristics such as ions (chloride, sulphate, etc.), electrical conductivity, pH, TSS, and groups of contaminants likely to be present in the dissolved phase. These included metals, nutrients, and hydrophilic trace organic contaminants such as pharmaceuticals, pesticides and endocrine disrupting chemicals. Toxicological analysis using in vitro bioassays examined six biological endpoints each targeting different modes of toxic action. These included non-specific toxicity, phytotoxicity, dioxin-like activity, estrogenicity, genotoxicity and oxidative stress.

Chemical and toxicological data from this study suggest that the quality of untreated Australian stormwater sits between the range of good quality to effectively treated secondary effluent. As a water source, stormwater is proposed to be suitable and amenable to treatment for a broad range of re-use scenarios. The level of treatment required will be influenced by the end use exposure. The *Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2) Stormwater Harvesting and Reuse* (NRMMC et al., 2009) should be followed for non-potable reuse scenarios where ingestion is unlikely such as irrigation and third pipe household use for laundry. For direct and indirect potable reuse, treatment is required to meet the *Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2) Augmentation of Drinking Water Supplies* (NRMMC et al., 2008). High variability in detections was observed between catchments and between events occurring within each catchment in this study. Site specific characterisation of stormwater quality is recommended to inform risk management strategies and the treatment barriers required to meet the relevant guidelines for the selected exposure scenario.

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