Research on metals in stormwater for aquifer storage and recovery in alluvial aquifers in Melbourne, Australia

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Abstract

Aquifer storage and recovery (ASR) can provide efficient temporary storage of stormwater for recycling and reduce evaporation losses. The injection of stormwater introduces oxygen, nutrients, suspended solids, organic carbon and other pollutants like heavy metals into an aquifer. This may change the hydrogeochemical equilibrium in the subsurface and influence the behaviour of heavy metals. Stormwater samples from Melbourne had Cr, Cu, Pb and Zn concentrations that exceeded Australian guidelines for freshwater aquatic ecosystems. Of special concern are Zn and Cu as they are found predominantly in the soluble fraction and are attached to the finer suspended solids that are difficult to remove. The overall objective of this recently commenced study is to evaluate the behaviour and fate of heavy metals during ASR. This will require characterisation of metals in stormwater, identifying their association with particulates, correlating their concentrations with surrogate variables, exploring spatial and temporal changes in near-well geochemical composition at a demonstration ASR site, using batch and column tests under laboratory conditions to evaluate factors affecting behaviour of metals and developing models to predict their long-term fate and identify the need for any corrective actions to ensure sustainability of stormwater ASR operations.

Keywords

Stormwater quality; heavy metals; aquifer storage and recovery; geochemical interactions.

INTRODUCTION

Melbourne is a city with growing population, increasing water demand and limited freshwater supply from surrounding catchments. It overlies a range of productive aquifers, but beneficial use of groundwater is often limited by salinity levels (Leonard, 1992). On the other hand the city produces a large volume of stormwater runoff during the winter months from the impervious areas and discards this water into rivers and Port Phillip Bay, impairing its water quality. This situation can be improved and one measure is the recycling of stormwater (DSE, 2004). As most of the rain falls in winter, but is needed mostly in summer the key issue for harnessing it is storage. Aquifer storage and recovery (ASR) seems a potential option to limit surface storage space, evaporation losses and to protect water quality (Pyne, 1995). Stormwater includes a range of pollutants that may affect the groundwater quality and aquifer geochemistry, so a long-term risk assessment regarding groundwater pollution is warranted. Stormwater constituents include oxygen, organic carbon, total suspended solids (TSS) and electron donating substances like nitrate. These may change the geochemical conditions in the aquifer significantly (Stuyfzand et al., 2002) and influence the mobility and speciation of other pollutants like heavy metals.

Heavy metals are often present in urban runoff in concentrations exceeding Australian guidelines for freshwater aquatic ecosystems and are priority pollutants due to their phyto- and cytotoxicity (Makepiece et al., 1995). They undergo various biogeochemical processes during ASR that are mostly reversible. The main attenuation process, sorption, is controlled by the aquifer material, while metal speciation, metal concentration and binding forces are influenced by pH, Eh, ionic strength, co-sorbents etc. (Appelo and Postma, 1999; Bradl, 2004). Nevertheless ASR schemes are usually based on technical feasibility, meaning they are implemented in transmissive aquifers with limited clay content and therefore limited sorptive capacity. In addition previous ASR studies showed that geogenic heavy metals have been released due to the induced changes of the redox state, with arsenic often being of special concern due to limited adsorption (Stuyfzand, 1998).

In one stormwater ASR study (Herczeg et al., 2004) conducted in South Australia, mass balances were determined for particulate matter. Although the mass of particulates recovered was similar to the mass injected, the recovered mass was largely composed of aquifer material (Dillon and Pavelic, 1996). A major proportion of the metals injected are retained within the aquifer. Metals of stormwater origin may potentially be remobilised if exposed to further redox or pH changes, as with geogenic metals. Most redox reactions produce protons (Appelo and Postma, 1999) and depending on the buffering capacity of the aquifer this might reduce pH, and increase the solubility of heavy metals. In a reclaimed water ASR study Vanderzalm (2004) found that dissolved organic carbon (DOC) decreased in recovered water. This suggests that organic complexation of metals within the aquifer may be possible and could further increase solubility of heavy metals. Geochemical reactions that occur when recharged water interacts with the ambient groundwater and aquifer matrix are expected to be site-specific. Such information for Melbourne aquifer systems is unknown and aquifer geochemical properties are poorly defined. This paper presents the first part of our study focusing on the hydrogeology of Melbourne and specific aspects of stormwater quality in Melbourne relating to metals, while outlining the future research programme.

METHOD

A literature review was conducted on hydrogeology of Melbourne, mostly from reports of the Geological Survey of Victoria. Relevant data were also gathered from the Victorian Geoscientific Database (Department of Primary Industries), Groundwater Database (SKM), the Victorian Water Resources Data Warehouse and from personal communication with senior hydrogeologists.

Table 1. Stormwater monitoring sites in Melbourne

Site	*Primary land use*	*Area (m^2)*	*Impervious fraction*
Monash Roof (MR)	coated aluminium roof	50	1.00
Gilby Rd (GR)	commercial	28,200	0.80
Shepherds Rd (SR)	medium density residential	37,980	0.45
Richmond (RI)	high density residential	89,120	0.74

As not many comprehensive data sets for Australian urban stormwater runoff have been collected so far, the Institute for Sustainable Water Resources in conjunction with the Co-operative Research Centre (CRC) for Catchment Hydrology has been monitoring stormwater quality and quantity around Melbourne for different catchment sizes and land uses. So far only flow hydrographs, TSS, total nitrogen and total phosphorus for rainfall events have been measured. The automated samplers are triggered via increased flow and subsequent samples are taken at set times after the first trigger with high sampling frequency in the rising limb of the hydrograph and decreased sampling in the hydrograph tail. According to the hydrograph volumes composite samples for event mean concentration (EMC) measurements are made. Of these, four sites (Table 1) have been chosen for more detailed water quality measurement to enable characterization of Melbourne's stormwater for the ASR assessment. Since December 2004 incoming samples are now analysed for pH, electrical conductivity (EC) and alkalinity (Gran-plot). Composite samples are analysed for EMCs of major ions (Na, K, Mg, Ca with flame spectroscopy and Cl, SO_4 with flow injection analysis) and total/dissolved organic carbon (TOC/DOC with TOC analyser). EMCs of heavy metal

(Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) are determined for the soluble fraction (< 0.45 µm), acid-extracted size fraction 0.45–63 µm and acid-extracted size fraction > 63 µm measured with ICP-OES. To date 11 samples have been analysed and sampling is ongoing.

RESULTS AND DISCUSSION

Review of hydrogeology of Melbourne

The site selection for an ASR scheme depends on hydrogeological characteristics, availability of land to harvest the stormwater, and a localised demand. Three broad classes of aquifer system occur; confined sedimentary aquifers, fractured rock systems and unconfined alluvium. The implementation of ASR would be technically most feasible in confined sedimentary aquifers with large storage potential and very limited impact on surface features. Fractured rocks often prove to have limited recovery efficiency due to their heterogeneous characteristics. Unconfined aquifers have constraints on recharge volumes, but are cheaper to construct. The area of most interest is the central section of the sandy unconsolidated (semi-)confined Fyansford Formation-Brighton Group aquifer system with brackish groundwater in the southeast of Melbourne. The Tertiary Fyansford Formation is made up of marine coarse to fine grained sand, gravel and discontinuous sandy limestone layers about 30–50 m below the surface (Leonard, 1992). The total formation is up to 60 m thick that thins towards the north. The transmissivity of 20–30 m^2/d makes it suitable for small scale ASR schemes (AGT, 2002). Salinity levels vary greatly (~100–6,000 mg/L). Areas with salinity above 1,500 mg/L are targeted for ASR as this reduces potential impacts on beneficial use of the groundwater. The relatively low hydraulic gradient (~ 0.001) in the central section of the aquifer system is favourable for ASR schemes as this increases the recovery efficiency in brackish aquifers.

Stormwater quality

Table 2 shows a wide range of values for each parameter between events and between sites. This is due to the fact that many parameters e.g. catchment characteristics, antecedent dry-weather period, rainfall volume and intensity

Table 2. Selected stormwater data sets of sampled stormwater events

	Total rainfall (mm)	*Peak rainfall intensity (mm/h)**	*Peak flow rate (L/s)*	*Duration (h)*	*ADWP (days)*	*pH*	*EC (µS/cm)*	*TOC/ DOC (mg/L)*	*TSS (mg/L)*	*Cu (total/ < 0.45µm) (µg/L)*	*Zn (total/ < 0.45µm) (µg/L)*
d.l.							1	1	0.5	0.79	3.00
MR	2	2	2.3	0.2	2	5.6	37	3/3	11	9.2/3.8	101/84.5
	3.4	1.8	1.5	1	11	5.7	29	5/4	91	27.1/4.7	343/267
	4.8	0.6	0.5	3	1	5.3	17	2/2	8	3.6/3.2	127/124
GR	2.6	1.4	340	2	11	6.5	95	17/9	138	84.5/19.4	1,456/849
	3.6	0.6	160	5	1	6.4	58	9/6	17	17.5/12.4	738/695
	4.8	1.2	450	2	5	6.9	54	6/3	54	10.7/4.7	335/221
SR	6.2	3.4	490	3	10	6.5	96	17/9	432	74.3/6.6	897/142
	144.4	4.4	470	20	4	6.7	74	6/4	220	11.2/4.5	175/136
RI	9.4	8.4	2,850	2	1	6.6	52	9/4	318	89.6/5.0	1,826/83.8
	3	1.4	185	3	12	6.4	128	12/10	196	57.3/9.7	1,395/676
	4.2	0.8	190	4	1	6.5	114	20/10	167	63.9/13.9	1,664/744

ADWP: antecedent dry weather period; d.l. detection limit; *over 10 min interval.

have a bearing on them (Wong et al., 2003). The urban stormwater pollutant concentration ranges are comparable to those found in the literature (Table 3). The samples exceed the Australian guidelines for freshwater aquatic ecosystems and for drinking water

Table 3: Comparison of guideline values and stormwater concentrations

Parameter		*Freshwater aquatic system*[1]	*Australian Drinking water guideline*[2]	*Melbourne stormwater (this study)*	*Mean storm-water* [3]	*Mean storm-water* [4]
TSS	mg/L	20	10	8–432	164	155
TOC		15		2–20	23.6	32
Al (soluble)	µg/L	55	200	153–634	900	
As (total)		24^{AsIII}/ 13^{AsV}	7	< 1.4–5.3	2	
Cd (total)		0.2	2	< 1–1.4	2	8
Cr (total)				0.3–25	70	33
Cr (VI)		1	0.05			
Cu (total)		1.4	2,000	3.6–90	80	62
Fe (total)			300	390–13,040	4,000	4,500
Pb (total)		3.4	10	1.8–243	250	140
Mn (total)		1,900	500	10.5–198		
Ni (total)		11	20	< 2 - 23.5		32
Zn (total)		8	3,000	101–1,826	910	320

Notes:
1 ANZECC and ARMCANZ, 2000: level of protection 95%;
2 NHMRC, 2004;
3 Dillon and Pavelic, 1996 (mostly Australian data);
4 Duncan, 1999 (worldwide data)

(ANZECC and ARMCANZ, 2000) for most parameters, but for the ASR scheme the environmental values (beneficial uses) of the ambient groundwater and recovered water will define the concentrations of metals and other constituents that are acceptable. These stormwater samples have lower concentrations of arsenic than have been found in Port Phillip Bay (Fabris et al., 1999). The latter data suggests that As cannot be ruled out as an issue. If pyritic material was to be present in anaerobic aquifers, sulfide oxidation caused by injection of oxygenated stormwater could lead to As mobilization (Vanderzalm et al., 2005). It can be seen that all concentrations are significantly reduced in events with a very short ADWP (Table 2), as the pollutant load is a function of build-up and wash-off. It can also be concluded that the roof catchment has generally lower pollutant concentrations compared to the other catchments. TSS concentrations are of great importance as many other toxic pollutants are associated with them, especially with the fine fraction (Liebens, 2001; Muthukaruppan et al., 2002), and is often used as an indicator of runoff pollution in general. Inverse relationships between the dissolved fraction of Zn ($R^2 = 0.77$) and Cu ($R^2 = 0.54$) with TSS could be established in agreement with findings from Sansalone & Buchberger (1997).

pH is a very important parameter influencing metal solution and soil-surface chemistry as well as complexation (Bradl, 2004). Metal solubility is also determined by the most abundant anion in the water, which can inhibit adsorption (Fic and Isenbeck-Schröter, 1989). Even though significant relationships could not be established due to the limited number of samples, nevertheless an inverse trend with salinity and pH with the dissolved fraction is apparent for most samples. The significantly lower pH and lower salinity of the roof catchment leads visibly to an increased fraction of dissolved heavy metals (Fig. 1). It was found that zinc has the highest soluble fractions with up to 98 % dissolved. Due to its high pH for the adsorption edge this was found in other studies as well (Zobrist et al., 2000). The high solubility of copper is often due to its formation of organic complexes (Van Dijk, 1971). Lead was mostly associated with the particulate matter (data not shown) in accordance with other studies (Harrison and Wilson, 1985).

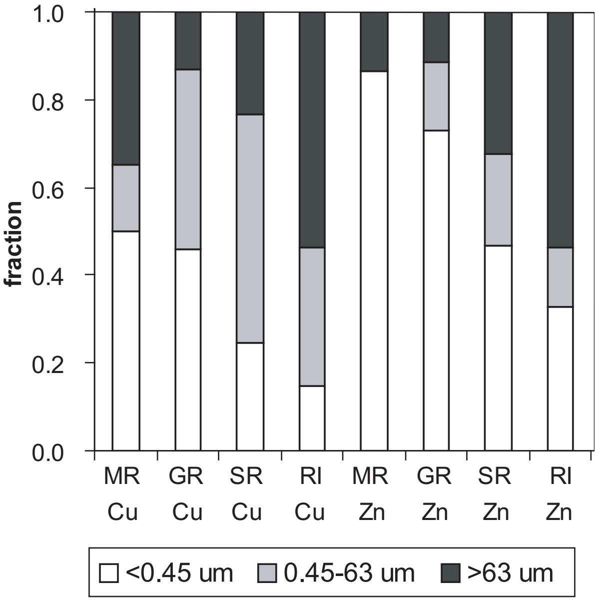

Figure 1. Copper and Zinc mean fractionation at the different sites

With regard to stormwater ASR this means that it is likely that most of the heavy metals in dissolved form and attached to the small size fraction will be introduced to the aquifer. Even deposited solids in detention ponds cannot be regarded as permanent pollution sinks, as the majority of contaminants that are particulate-associated can be transferred to the water phase especially if the physico-chemical conditions change (Pitt, 1996). The attenuation of heavy metals is a combination of different processes which are conservative and mostly reversible especially if there are significant changes in redox and pH conditions during the ASR cycle. They may accumulate adsorbed in the aquifer, be transported away as organic complexes or adsorbed to colloidal matter or be pumped back out in particulate or soluble form.

CONCLUSIONS AND FUTURE RESEARCH

From the limited set of stormwater samples analysed so far it can already be seen that stormwater quality is highly variable in time and space. This great variability poses the main challenge regarding characterisation. It was shown that heavy metals like Zn, Pb, Cu, Cr, and Ni are rather abundant in Melbourne's urban stormwater in particulate and dissolved form. Although behaviour of heavy metals at stormwater ASR sites has not been an issue under geochemical conditions experienced in Adelaide's carbonate aquifers, a precautionary approach suggests this should also be evaluated under the different geochemical conditions prevailing in Melbourne, to assess any potential for long-term variations in the quality of groundwater and recovered water, and allow management strategies to be devised if any problems are predicted.

Aquifers are important assets in a holistic urban water cycle and impacts that would impair their role must be prevented. Therefore an understanding and assessment of possible risks is warranted as a precautionary measure. Consequently the proposed activities within this research project are to:

- identify concentrations and associations with particulates of heavy metals in Melbourne stormwater;
- identify mineralogy and geochemical condition of an aquifer in Melbourne prior to ASR at a demonstration project site;
- identify mechanisms of attenuation and remobilization of these metals during ASR, making use of column and batch studies under a specified range of laboratory conditions with collected aquifer material and groundwater and using synthetic stormwater;
- quantify mass fluxes of metals into and out of the well and measure water quality in monitoring wells to determine fate of metals, and the geochemical changes that may affect metals within the ASR system;
- demonstrate the relevance of the laboratory experiments to field observations and develop a conceptual model that characterises the observed short-term behaviour of metals;

- apply an existing coupled flow and transport and geochemical model (e.g. PHT3D, Prommer et al., 2003) to simulate the observed parameters and subsequently to predict the long-term geochemical behaviour of metals at stormwater ASR sites for various scenarios, with a view to establishing any factors that may affect sustainability of operations.

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