Sorption and degradation of selected five endocrine disrupting chemicals in aquifer material

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Abstract

Sorption and degradation of the five selected endocrine disrupting chemicals (EDCs) including bisphenol A (BPA), 17β-estradiol (E2), 17α-ethynylestradiol (EE2), 4-*tert*-octylphenol (4-*t*-OP) and 4-*n*-nonylphenol (4-*n*-NP) have been investigated in the laboratory using sediment and groundwater from an aquifer in Bolivar, South Australia. The sorption coefficients measured on the sediment were in the following order: 4-*n*-NP > 4-*t*-OP > EE2 > E2 > BPA. The sorption coefficients (K_f values) for the five EDCs were 3.89, 21.8, 24.2, 90.9 and 195, respectively. The alkylphenols 4-*t*-OP and 4-*n*-NP had strong binding on the sediment while BPA had a weak affinity. Degradation experiments of the five EDCs showed that E2 and 4-*n*-NP degraded quickly under aerobic conditions with a half-life of 2 and 7 days, respectively. EE2 degraded slowly with an estimated half-life of 81 days in the aquifer material under aerobic conditions while the other two chemicals (BPA and 4-*t*-OP) remained almost unchanged. Little or no degradation of the five EDCs except slow degradation for E2 was observed within 70 days under anaerobic conditions in native groundwater.
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1. Introduction

Aquifer storage and recovery (ASR) has been used as a management tool for the conjunctive use of surface and groundwater in Australia as well as in other countries [1]. The introduction of sewage treatment plant effluents into aquifers creates the potential for groundwater contamination due to the existence of various classes of contaminants in the effluents. Endocrine disrupting chemicals (EDCs) are compounds that may be present in such effluents and there is an emerging interest in their fate in the environment and on their possible effects on natural ecosystems as well as on human health [2]. Therefore, it is necessary to understand the behavior and fate of these EDCs in aquifers.

Five representative EDCs were chosen in this study: natural estrogenic steroid 17β-estradiol (E2), synthetic steroid 17α-ethynylestradiol (EE2), industrial chemical bisphenol A (BPA), and surfactant degradation products 4-*tert*-octylphenol (*4-t*-OP) and 4-*n*-nonylphenol (4-*n*-NP). These five chemicals have been found in sewage effluents at concentrations ranging from ng/L to μg/L [3–9]. The fate of the five EDCs in the environment has been reviewed by Staples et al. [10], and Ying et al. [8,9]. However, little information is available about their behavior and fate in the aquifer. Thus, this study will investigate the sorption and degradation of these five EDCs in aquifer material. The study focuses on the degradation in native groundwater rather than in nutrient-enriched reclaimed water, due to the need to establish the worst-case scenario for the persistence of EDCs in aquifer.

2. Materials and methods

2.1. Chemicals

Hormone steroids including 17β-estradiol (E2) and 17α-ethynylestradiol (EE2) were obtained from Aldrich,

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while 4-t-OP was obtained from Chem Service, and bisphenol A (BPA) and 4-n-NP were purchased from Fluka (Riedel-de Haën). The physiochemical properties of these chemicals were given in Table 1. HPLC grade methanol and acetonitrile were obtained from BDH (England). Stock solutions (100 mg/L) of each standard as well as mixtures were prepared in methanol.

2.2. Aquifer materials

The aquifer materials (sediment and groundwater) used in this study were collected from the ASR well at Bolivar in South Australia, corresponding to a relatively permeable horizon. Limestone sediment samples were from a depth of 153–154 m while groundwater was from the well 300 m from the injection well. This is representative of native groundwater at this site [15]. Groundwater was collected in a 2.5 L brown glass bottle, transported in a cooler to the laboratory and stored in a fridge at 4°C. The physiochemical properties of aquifer materials were analyzed and are presented in Table 2.

2.3. Sorption tests

Sorption of five endocrine disruptors (BPA, E2, EE2, OP and NP) was measured at room temperature (about 25°C) by a batch equilibration method. Preliminary tests showed sorption of all five EDCs reached equilibrium within an hour, which is consistent with those sorption kinetics reported by Lai et al. [12] and Düring et al. [16]. The test was separated into two groups, one for BPA, E2 and EE2 and the other for 4-t-OP and 4-n-NP. In the sorption test of BPA, E2 and EE2, 10 g of sediment was weighed into each 250 mL glass bottle, 100 mL of groundwater was added into each bottle. Five concentrations were used in the sorption test: 2.5, 5, 10, 15, and 20 μg/L. The sediment solutions were equilibrated by shaking in a mechanical shaker for 16 h. After equilibration, the bottles were centrifuged at 3000 rpm for 30 min.

In the sorption test of 4-n-NP and 4-t-OP, 2 g sediment was used due to their high sorption on sediment. The concentrations used were as follows: 40,

60, 80 and 100 μg/L for 4-n-NP and 5, 10, 20 and 40 μg/L for 4-t-OP. The solutions containing 4-n-NP were only shaken for 2 h to minimize the losses of this compound which were observed during control experiments. Other conditions were the same as those for BPA, E2 and EE2. After centrifugation, the supernatants were further filtered through Whatman glass fiber filters (GF/C). The filtrates were then analyzed by a Varian HPLC with a fluorescence detector. All tests were done in duplicate or triplicate.

Controls without sediment but with different concentrations of each chemical were prepared at the same time during the sorption test. No significant loss (<3%) was found in the controls for BPA, E2, EE2 and 4-t-OP during the sorption process, but some loss was found for 4-n-NP after overnight shaking. Therefore, in the sorption test of 4-n-NP, a short equilibration time (2 h) was used. Controls with different concentrations of 4-n-NP as well as the other four chemicals (BPA, E2, EE2 and 4-t-OP) in groundwater were prepared during the sorption and analysis processes as quantitation controls.

Sorption of a chemical from solution to a solid phase can be described by using the Freundlich equation, which defines a nonlinear relationship between the amount adsorbed and the equilibrium solution concentration

$$S = K_f C^{1/n}, \tag{1}$$

where S is the concentration of a chemical adsorbed by the soil (mg/kg); K_f is the Freundlich sorption coefficient; C is the equilibrium solution concentration (mg/L) and $1/n$ is a power function related to the sorption mechanism. When the value of n is unity, we have the simple linear isotherm

$$S = K_d C, \tag{2}$$

where K_d is the sorption coefficient (L/kg).

Many studies show that in the absence of strong ionic interactions the sorption of chemicals closely depends on the organic content in the soil/sediment. By normalizing sorption from a total soil basis to an organic carbon basis, the organic carbon sorption is defined

Table 1
Physiochemical properties of five EDCs

Chemical name	Molecular weight	Water solubility (mg/L at 20°C)	log K_{ow}[a]
Bisphenol A (BPA)	228.0	120 [11]	3.32 [11]
17β-Estradiol (E2)	272.4	13 [12]	3.94 [12]
17α-Ethynylestradiol (EE2)	296.4	4.8 [12]	4.15 [12]
4-t-Octylphenol (4-t-OP)	206.0	12.6 [13]	4.12 [14]
4-n-Nonylphenol (4-n-NP)	220.0	5.43 [13]	4.48 [14]

[a] Octanol–water partition coefficient.

Table 2
Physiochemical properties of aquifer materials[a]

	pH	NO$_3$–N (mg/L)	PO$_4$–P (mg/L)	TC (mg/L)	IC (mg/L)	DOC (mg/L)	SO$_4$ (mg/L)
Groundwater	7.9	0.02	0.02	56	49	7	250

	pH	TC (%)	OC (%)	CEC(NH$_4$) cmol(+)/kg	CO$_3$ as CaCO$_3$ (%)	Clay (%)	Silt (%)	Sand (%)
Aquifer material	8.9	1.9	0.5	2.4	12	3.1	1.1	83

[a] TC = total carbon, IC = inorganic carbon, DOC = dissolved organic carbon, OC = organic carbon, CEC = cation exchange capacity

as following:

$$K_{oc} = K_d\% \; \text{Organic carbon}. \qquad (3)$$

2.4. Degradation experiments

Biodegradation of 5 EDCs (E2, EE2, 4-*n*-NP, BPA, 4-*t*-OP) in an aquifer material was undertaken under aerobic and anaerobic conditions. In these experiments, 5 g of the same aquifer material (153–154 m deep) and 5 mL of groundwater (300 m well) from Bolivar, South Australia were used during all experiments. The concentration applied for each chemical was 1 μg/g in aquifer material (sediment) by adding into each tube 50 μL of stock solution. All five compounds were present in each microcosm and interaction effects on degradation rates were assumed to be negligible. The incubation temperature used in the studies was 20°C. The concentrations of the five compounds were monitored on days 0, 1, 3, 7, then weekly until 70 days. All experiments were performed in duplicate, and duplicate sterile controls were monitored at the same times.

Aerobic study: Aquifer materials (sediment and groundwater) were weighed into 100 mL Schott bottles. Half of the bottles were sterilized by autoclaving at 120°C under 300 kPa chamber pressure for 30 min for three times within three days, and used as controls. Chemicals were spiked at the required concentration (1 μg/g). All bottles were incubated in a temperature-controlled chamber. The small volume of the aquifer media in the large bottle ensured aerobic conditions. Those bottles were shaken for 1 min at each sampling time.

Anaerobic study: Aquifer materials (sediment and groundwater) were weighed into Hungate anaerobic culture tubes (16 × 125 mm^2). Half of them were sterilized by autoclaving and used as controls. These Hungate tubes were placed into an anaerobic incubation chamber filled with nitrogen gas. The lids of these tubes were loosened to facilitate gas exchange. Resazurin was added at a concentration of 0.0002% into two tubes as a redox indicator. Reducing conditions within tubes were indicated by the disappearance of the red resazurin color. All tubes were left in the anaerobic incubation chamber for nearly a month until the tubes containing the redox indicator resazurin turned colorless. Sulfate (SO^{2-}) was the dominant electron acceptor, confirmed by the formation of dark sulfide mineral on the surface of sediment. Chemicals were spiked into each tube at a required concentration and the lids of all tubes were tightened after spiking. All operations were performed inside the anaerobic incubation chamber. Then all the tubes were incubated in the same chamber as in the aerobic study.

2.5. Extraction and analysis

Each entire sample was extracted twice with 20 mL of ethyl acetate by shaking for 2 h each time. The extracts were dried under a gentle nitrogen stream and redissolved in methanol. The recoveries were 97±2.6%, 96±1.2%, 96±0.6%, 105±2% and 91±3% for BPA, E2, EE2, 4-*t*-OP and 4-*n*-NP, respectively. Controls of only sediment and groundwater without the EDCs were extracted and no interfering compounds were found in HPLC analysis. Water samples were directly analyzed by online solid phase extraction and HPLC [17]. A Varian high performance liquid chromatographic system was used in this study, which consisted of an autosampler (Model 9100), a solvent delivery system (Model 9012 pump), a fluorescence detector (Model 9070) and an on-line sample preparator (Prospekt, Model 9200). The instrument was equipped with a reversed phase column (Adsorbosphere C18, 5 μ, 250 × 4 mm^2) from Alltech. For compounds of interest, the fluorescence detector settings were 230 nm excitation and 290 nm emission. The mobile phase for gradient elution were Milli-Q water and acetonitrile (ACN) delivered at a constant flow rate of 1 mL/min. The gradient program of the mobile phase was as follows: 30% ACN and 70% water at 0 min, 40% ACN and 60% water at 5 min, 60% ACN and 40% water at 10 min, 80% ACN and 20% water at 20 min and isocratic purge until 30 min, and increasing to 100% ACN and 0% water at 35 min. The total run time for an HPLC analysis was 35 min. The injection volume of standards

and samples was $50 \mu L$ for injection using autosampler and 50 mL of water for on-line sample preparator. The extracts were quantified by calibration curves of the external standards. The detection limit of the on-line solid extraction HPLC was 10 ng/L for E2, EE2 and BPA and 30 ng/L for OP and NP; whereas the detection limit of the HPLC method with normal autosampler injection was $10 \mu g/L$ for E2, EE2 and BPA and $30 \mu g/L$ for OP and NP.

3. Results and discussion

3.1. Sorption on an aquifer material

Sorption of the five EDCs on the aquifer material from Bolivar has been tested using a batch method with a concentration of each EDC at $\mu g/L$ levels. Controls gave recoveries exceeding 97% for all chemicals except 4-n-NP (only 62%) when shaken for 16 h. For 4-n-NP, shaking time was reduced to 2 h giving a recovery of 89%. The sorption isotherms of the five EDCs are given in Fig. 1.

The experimental data were subjected to regression analysis using a Freundlich model ($\log S = \log K_f + 1/n \log C$). The values of sorption coefficients (K_f) and the Freundlich exponents ($1/n$), as well as correlation coefficients (R^2) are given in Table 3. Bisphenol A (BPA) had the lowest K_f value (3.89) while 4-n-NP had the highest K_f value (195). This is consistent with their elution order on the reverse phased high performance liquid chromatogram we obtained during analysis. The sorption coefficient of a chemical depends on the physiochemical properties of the chemical and the sorbent (Tables 1 and 2). Less polar compounds tend to have higher adsorption on sediments. Due to the low organic carbon content of this aquifer material, the K_f values measured on the sediment for the five compounds were relatively low.

The sorption of the three EDCs (E2, EE2 and 4-t-OP) was nonlinear because the sorption exponents ($1/n$) deviated significantly from 1. Therefore, K_{oc} values could not be defined from Eq. (3). However the measured K_f values of these compounds were substituted to estimate the corresponding K_{oc} values at the measured concentration ranges.

The organic carbon normalized K_{oc} values for the five EDCs varied widely from 778 for BPA to 38,900 for NP, which are comparable to the reported values [11,12, 18–20]. For BPA, no measured sorption constant K_{oc} values have been reported so far. But Howard [11] calculated K_{oc} values of 314–1524, corresponding to BPA using an aqueous solubility of 120 and a $\log K_{ow}$ of 3.32. The sorption data suggested a modest sorption of BPA on soil or sediment. Lai et al. [12] measured sorption coefficients of E2 and EE2 and MeEE2
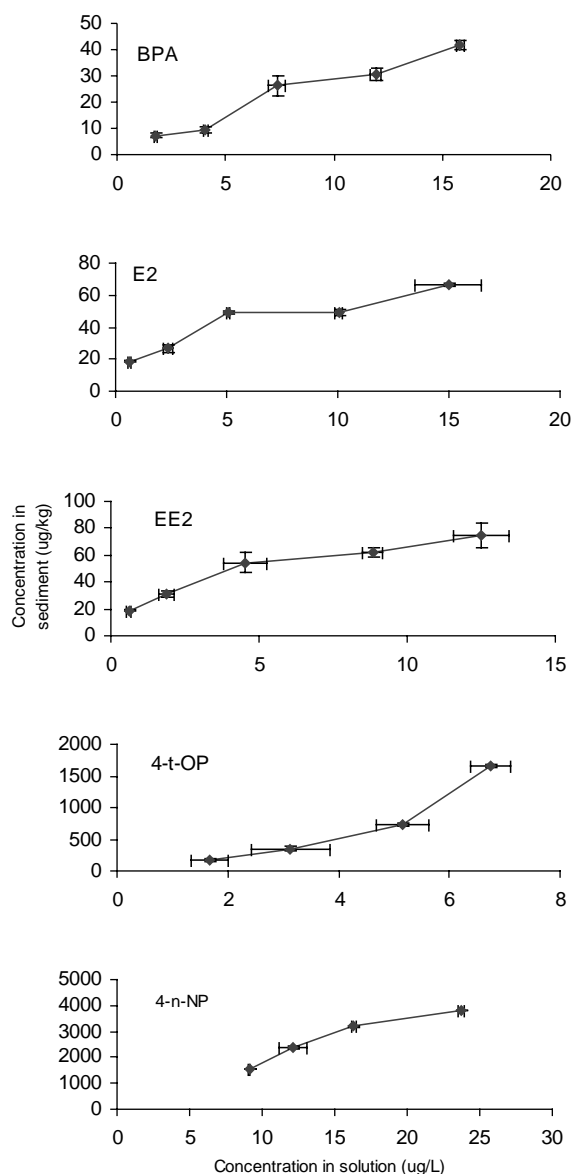

Fig. 1. Sorption isotherms for the five EDCs on an aquifer material.

(mestranol) on a sediment and the $\log K_f$ values were 1.71, 1.56, 1.33, 1.72 and 2.26, respectively. They found the sorption on sediments was nonlinear with sorption constants ranging from 0.57 to 0.83. These data showed estrogenic steroids had modest sorption on sediment. The sorption of estrogens correlated with the presence of organic carbon content and also increased with salinity in water [12].

Düring et al. [16] quantified sorption of 4-nonylphenol on a set of 51 soils with calculated K_{oc} value of 9300. Ferguson et al. [18] investigated the partitioning of alkylphenol ethoxylate metabolites to suspended solids

Table 3
Sorption coefficients of five EDCs on the aquifer material

Compound	K_f	$1/n$	R^2	K_{oc}
BPA	3.89	0.85	0.93	778
E2	21.8	0.40	0.95	4360
EE2	24.2	0.46	0.98	4840
4-t-OP	90.9	1.45	0.97	18,200
4-n-NP	195	0.97	0.95	38,900

in Jamaica Bay, New York. The K_{oc} values were 245,000 for NP and 151,000 for OP [18]. The Sekela et al. [19] measured similar log K_{oc} values for NP on five samples (K_{oc} 50,000–398,000). Johnson et al. [20] used laboratory batch techniques to study the sorption of OP on sediments from three English rivers of contrasting water quality. The results showed that given either sufficient time or mixing, a large proportion of the OP in solution will sorb to the bed sediments, with distribution coefficients (K_d) of 6–700 and organic carbon normalized partition coefficients (K_{oc}) 3500–18,000 (cf. current results; 18,200). The sediments that sorbed the highest quantities of OP had higher total organic carbon and a greater proportion of clay and silt particles.

The results of this study indicate that BPA has lowest sorption, two steroids (E2 and EE2) have modest sorption, and surfactant degradation products (4-t-OP and 4-n-NP) have highest sorption on the currently tested aquifer material. These observations are supported by previously published data.

To estimate the travel time of the species in the aquifer at Bolivar research site, the retardation factor, R, [21] was calculated using the lowest measured K_d from different sorption equilibrium concentrations in this study and the measured bulk density of $1.4\,g/cm^3$ and a porosity of $0.45\,cm^3/cm^3$. This represented the worst-case scenario for the potential mobility of these species in the aquifer. The retardation factors for this aquifer were found to be 8, 16, 20, 320 and 500 for BPA, E2, EE2, 4-t-OP and 4-n-NP, respectively. This indicates that sorption substantially increases residence time of 4-t-OP and 4-n-NP in aquifer.

3.2. Degradation in the aquifer media

Biodegradation experiments showed different behavior of the five EDCs (BPA, E2, EE2, 4-t-OP and 4-n-NP) under aerobic and anaerobic conditions (Figs. 2 and 3). Under the aerobic conditions, E2 and 4-n-NP degraded very quickly while EE2 degraded very slowly, and BPA and 4-t-OP remained unchanged over 70 days. Within 10 days, the majority of the E2 was lost, and nearly 50% of 4-n-NP was degraded in the aquifer media. Within 70 days, the EE2 concentration decreased from 1 to $0.62\,\mu g/g$ in the aquifer material (Fig. 2). The half-lives under aerobic conditions were calculated to be
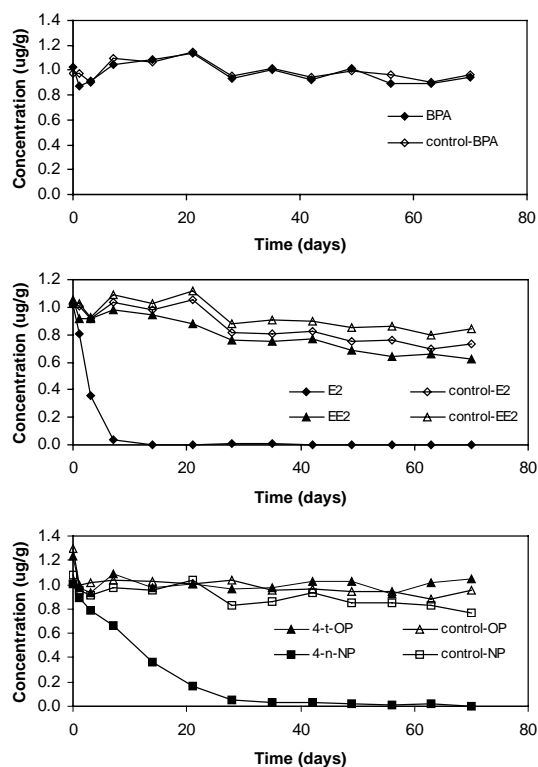

Fig. 2. Degradation of the five EDCs under aerobic conditions. Sterile samples were used as controls.

2 days for E2, 7 days for 4-n-NP and 81 days for EE2 based the first order reaction equation.

However, under anaerobic conditions, the five EDCs remained almost unchanged over 70 days although there was very slow degradation of E2 (Fig. 3). Approximately 40% of E2 was lost over 70 days with an estimated half-life of 107 days. Clearly the compounds were persistent in the anoxic aquifer material.

Biodegradation of EDCs has been reported to play a major role in the removal of these EDCs from aquatic environments. For example, rapid breakdown of BPA in natural waters has been reported. Greater than 90% degradation of BPA by Dorn et al. [22] was observed in laboratory experiments using three river waters near plastics manufacturing facilities. But Stone and Watkinson [23] reported that aerobic biodegradation of BPA was less than 1% within 28 days in OECD testing. The bacterial assemblages in the river waters near plastics factories may have developed the capability to degrade BPA in water, whereas in media without previous exposure to BPA, degradation rates are much slower [23].

Rapid biodegradation of E2 has been reported in aerobic experiments with activated sludge and biosolids [24,25], in river water and sediments [26] under aerobic conditions. However, EE2 was found more persistent
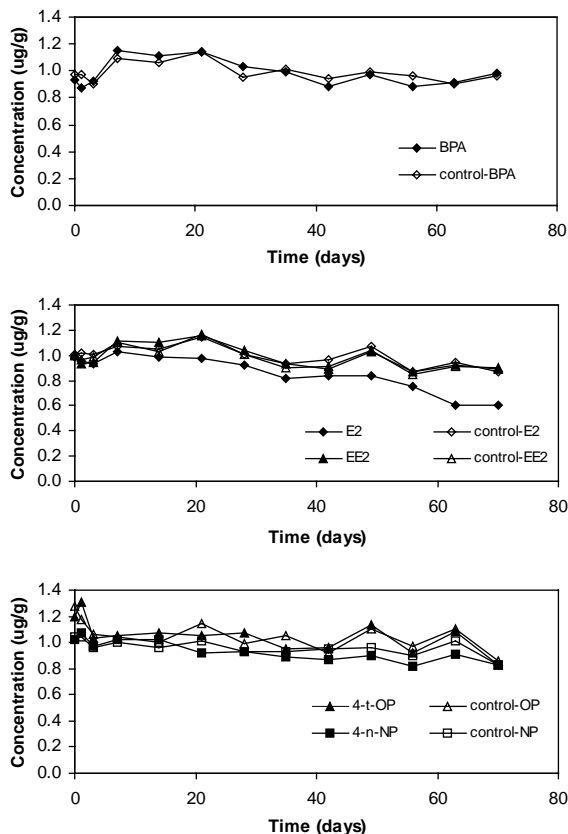
Fig. 3. Degradation of the five EDCs under anaerobic conditions. Sterile samples were used as controls.

[25,26]. The current results support those observations and also suggest that there was a very slow rate of degradation of E2 under anaerobic conditions.

Laboratory and field experiments all demonstrated that alkylphenols could be degraded under aerobic conditions but were persistent under anaerobic conditions [8, references therein]. The present study also showed that 4-n-NP is more rapidly degraded than 4-t-OP in the aquifer under aerobic conditions. Aerobic conditions were more favorable for the degradation of E2, 4-n-NP and EE2 in this aquifer material than under anaerobic conditions. During the course of the 70-day degradation study, BPA and OP appeared to be conservative under aerobic and anaerobic conditions, and EE2 and 4-n-NP were not degraded under anaerobic conditions. In a related unpublished study by Ying, aerobic degradation was observed for all these EDCs in a marine sediment. This indicates that degradation may depend on the microorganism communities present in the sediments.

It would appear that in the anaerobic natural environment for the Bolivar aquifer material tested, single-well ASR is unlikely to remove these five EDCs to

any significant degree. In aquifer adjacent to the point of injection, EDCs concentrations may be enriched due to sorption on sediments and organic matter that accumulate in the well during the injection phase. Consequently, on initial recovery the concentrations in the recovered water may be higher and decrease progressively with subsequent recovery. However, for dual well operations, where there is sufficient organic material in the aquifer, there is a relatively large capacity to adsorb these compounds in passage through the aquifer in relation to their potential loads in injectant. However without biodegradation, breakthrough at the recovery well would be expected ultimately, unless there is adaptation of bacterial assemblages capable of degrading EDCs. It is possible that in dual well operations significant removal of EDCs may occur due to the retention of EDCs and other injected organics over a period of time, sufficiently long to allow degradation. Further experiments are needed to assess biodegradation in aquifer materials associated with reclaimed water injection, as the reclaimed water may contain higher nutrient levels.

4. Conclusion

Among the five selected EDCs, 4-n-NP had highest sorption and BPA had lowest sorption on the aquifer material while the two steroids E2 and EE2 had modest sorption on the aquifer material. The estimated retardation factors indicate that sorption is likely to substantially increase the residence time of 4-n-NP and 4-t-OP, in particular between the injection and extraction wells. Aerobic conditions were found to be more favorable for the EDCs to degrade in the aquifer than anaerobic conditions. E2, EE2 and 4-n-NP were degraded in the aquifer under aerobic conditions while BPA and 4-t-OP persisted. In contrast, under anaerobic conditions, only E2 showed some degradation but at a very slow rate.

Further laboratory studies of biodegradation are planned using blends of reclaimed water and native groundwater to determine the influence on the fate of the five EDCs under aerobic and reducing conditions.

References

[1] Dillon P, Toze S, Pavelic P, Ragusa S, Wright M, Peter P, Martin R, Gerges N, Rinck-Pfeiffer S. Storing recycled water in an aquifer at Bolivar: benefits and risks. AWA J Water 1999;26(5):21–9.

[2] Ying GG, Kookana RS. Endocrine disruption: an Australian perspective. AWA J Water 2002;29(9):53–7.

[3] Nasu M, Goto M, Kato H, Oshima Y, Tanaka H. Study on endocrine disrupting chemicals in wastewater treatment plants. Water Sci Technol 2001;43(2):101–8.

[4] Rudel RA, Melly SJ, Geno PW, Sun G, Brody JG. Identification of alkylphenols and other estrogenic phenolic compounds in wastewater, septage, and groundwater on Cape Cod, Massachusetts. Environ Sci Technol 1998;32:861–9.

[5] Tabata A, Kashiwa S, Ohnishi Y, Ishikawa H, Miyamoto N, Itoh M, Magara Y. Estrogenic influence of estradiol-17β, p-nonylphenol and bisphenol A on Japanese Medaka (*Oryzias Iatipes*) at detected environmental concentrations. Water Sci Technol 2001;43(2):109–16.

[6] Kuch HM, Ballschmitter K. Determination of endocrine-disrupting phenolic compounds and estrogens in surface and drinking water by HRGC-(NCI)-MS in the picoram per liter range. Environ Sci Technol 2001;35:3201–6.

[7] Furhacker M, Scharf S, Weber H. Bisphenol A: emissions from point sources. Chemosphere 2000;41:751–6.

[8] Ying GG, Williams B, Kookana R. Environmental fate of alkylphenols and alkylphenol ethoxylates—a review. Environ Int 2002;28:215–26.

[9] Ying GG, Kookana RS, Ru YJ. Occurrence and fate of hormone steroids in the environment. Environ Int 2002;28:545–51.

[10] Staples CA, Dorn PB, Klecka GM, O'Block ST, Harris LR. A review of the environmental fate, effects, and exposures of bisphenol A. Chemosphere 1998;36(10):2149–73.

[11] Howard PH. Handbook of environmental fate and exposure data, vol. 1. Chelsea, MI: Lewis Publishers, 1989.

[12] Lai KM, Johnson KL, Scrimshaw MD, Lester JN. Binding of waterborne steroid estrogens to solid phases in river and estuarine systems. Environ Sci Technol 2000;34:3890–4.

[13] Ahel M, Giger W. Aqueous solubility of alkylphenols and alkylphenol polyethoxylates. Chemosphere 1993;26:1461–70.

[14] Ahel M, Giger W. Partitioning of alkylphenols and alkylphenol polyethoxylates between water and organic solvents. Chemosphere 1993;26:1471–8.

[15] Vanderzalm JL, Le Gal La Salle C, Hutson JL, Dillon PJ. Water quality changes during aquifer storage and recovery at Bolivar, South Australia. In: Dillon P, editor. Management of Aquifer Recharge for Sustainability. Lisse: Swets & Zeitlinger B.V.; 2002. p. 83–8.

[16] Düring RA, Krahe S, Gäth S. Sorption behaviour of nonylphenol in terrestrial soils. Environ Sci Technol 2002;36:4052–7.

[17] Ying GG, Kookana RS, Chen Z. On-line solid-phase extraction and fluorescence detection of selected endocrine disrupting chemicals in water by high-performance liquid chromatography. J Environ Sci Health 2002;B37(3):225–34.

[18] Ferguson PL, Iden CR, Brownwell BJ. Distribution and fate of neutral alkylphenol ethoxylate metabolites in a sewage-impacted urban estuary. Environ Sci Technol 2001;35:2428–35.

[19] Sekela M, Brewer R, Moyle G, Tuominen T. Occurrence of an environmental estrogen (4-nonylphenol) in sewage treatment plant effluent and the aquatic receiving environment. Water Sci Technol 1999;39(10-11):217–20.

[20] Johnson AC, White C, Besien TJ, Jurgens MD. The sorption of octylphenol, a xenobiotic oestrogen, to suspended and bed-sediments collected from industrial and rural reaches of three English rivers. Sci Total Environ 1998;210(211):271–82.

[21] Miller R, Correll R, Dillon P, Kookana R. ASRRI: a predictive model of contaminant attenuation during aquifer storage and recovery. In: Dillon P, editor. Management of Aquifer Recharge for Sustainability. Lisse: Swets & Zeitlinger BV; 2002. p. 69–74.

[22] Dorn PB, Chou CS, Gentempo JJ. Degradation of bisphenol A in natural waters. Chemosphere 1987;16(7):1501–7.

[23] Stone CM, Watkinson RJ. Diphenyl propane; an assessment of ready biodegradability. sittingbourne research center (SBRC). Sittingbourne, UK: Shell Research Limited; 1983.

[24] Ternes TA, Kreckel P, Mueller J. Behaviour and occurrence of estrogens in municipal sewage treatment plants—II. Aerobic batch experiments with activated sludge. Sci Total Environ 1999;225:91–9.

[25] Layton AC, Gregory BW, Seward JR, Schultz TW, Sayler GS. Mineralization of steroidal hormones by biosolids in wastewater treatment systems in Tennessee USA. Environ Sci Technol 2000;34:3925–31.

[26] Jürgens MD, Holthaus KIE, Johnson AC, Smith JJL. The potential for estradiol and ethynylestradiol degradation in English rivers. Environ Toxicol Chem 2002;21:480–8.