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Fate of disinfection by-products during aquifer storage and recovery

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ABSTRACT: Data from the literature and from the Bolivar ASR site were assessed to determine the attenuation of disinfection by-products (DBPs), in particular trihalomethanes (THMs) and haloacetic acids (HAAs), by chemical, microbial and adsorptive processes during ASR. HAAs are readily degraded under both aerobic and anaerobic conditions. Highly reducing conditions are required for effective degradation of all THMs; chloroform is the most recalcitrant with bromoform the most readily degraded. Under less highly reducing conditions, e.g., nitrification, brominated THMs can be degraded. Degradation rates under all reducing conditions increase with the degree of bromine substitution. Under aerobic conditions, THMs are not degraded. Attenuation of both THMs and HAAs by adsorption or chemical hydrolysis appears to be minimal. DBP attenuation at the ASR site reflected what was expected from the literature and demonstrates that different redox zones in the aquifer have a significant effect on THM attenuation rates.

1 INTRODUCTION

Aquifer storage and recovery (ASR) is becoming increasingly important as a means of storing excess water for recovery and use in times when water from other sources is scarce. ASR projects frequently utilise potable water for recharge with a view to recovering the water for drinking. Recharge water is often chlorinated to avoid problems such as biological fouling of the borehole by microbial growth.

Chlorine is widely used for disinfection of drinking water as it is both cheap and effective. However, it can react with the naturally occurring organic matter (NOM) in water derived from the decay of plant and animal matter in catchments, to produce a range of halogenated DBPs of which the trihalomethanes (THMs) and haloacetic acids (HAAs) predominate (Krasner et al. 1989). Brominated DBPs arise from the oxidation of bromide which is a natural constituent of water to hypobromous acid by the chlorine used for disinfection. The hypobromous acid reacts with the NOM in competition with the chlorine, thereby leading to incorporation of bromine into the DBPs formed. DBPs in water used for drinking are of concern because of their possible deleterious health effects and acceptable levels are covered by various guidelines and standards.

Chlorinated potable or reclaimed water used as a recharge source will therefore contain DBPs. Thus there is a possibility that recovered water may also contain DBPs. Consequently the ability to predict the fate of these compounds during ASR is important in relation to the subsequent use of this water.

The THMs normally encountered in chlorinated waters are chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (BF). In many waters, CF predominates but in more saline waters BF can be the predominant THM. The salinity of the water also determines to a large extent the distribution of HAAs. The HAAs encountered range from monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA) through mixed halogenated species through to brominated acetic acids such as dibromoacetic acid (Krasner *et al.* 1989).

2 ATTENUATION PROCESSES

During storage, concentrations of contaminant chemicals such as the DBPs can be reduced via a number of processes such as dilution/dispersion, chemical and microbial degradation and adsorption (McCarty *et al.* 1981). The focus of this paper is on degradation and adsorption, and dilution and dispersion which relate to site-specific hydrodynamics are not considered.

2.1 *Attenuation by chemical means (hydrolysis)*

THMs and HAAs can potentially be degraded by chemical hydrolysis by attack of hydroxide ion at the carbon bearing the halogen substituent. However extremely long hydrolysis half-lives of 140 (bromodichloromethane) to 3500 years (chloroform) have been reported (cited in Buszka *et al.* 1994). Rapid hydrolysis under highly alkaline conditions (pH ~14) has been reported (Shams El Din *et al.* 1998) but this is unrepresentative of natural environments.

Data on HAAs are limited. Castro *et al.* (1996) in their studies of biodehalogenation of HAAs found that for MCAA in control experiments, i.e. under abiotic conditions, no hydrolysis occurred over 2 weeks at pH 7.4. Landmeyer *et al.* (2000) also found MCAA to be stable in sterile controls over 46 days (pH not measured). Thus, although no specific hydrolysis data for HAAs are available, it would appear that rates are very slow. Thus chemical hydrolysis is not considered to be important in the degradation of DBPs such as THMs and HAAs.

2.2 *Attenuation by adsorption*

The adsorption of organic chemicals from water onto particulate matter is described by K_{oc} which is the partition coefficient for the chemical between the water and the organic component of the particulate matter. Only the organic component of the particulate matter is considered as it is generally assumed that adsorption occurs solely with this material. K_{oc} is not available for many compounds but can be calculated from K_{ow}, the octanol/water partition coefficient which is a measure of hydrophobicity and which is more readily available. Karickhoff *et al.* (1979) determined that $K_{oc} = 0.63K_{ow}$, although other relationships have been proposed.

During recharge as water moves through the aquifer, compounds will be adsorbed until equilibrium, as determined by K_{oc}, is reached. . The overall effect of adsorption on movement of recharge water away from the ASR well will be the retardation of components relative to the movement of conservative components such as chloride, i.e. the apparent velocity through the aquifer will be reduced relative to the conservative tracer. The retardation factor can be calculated from the breakthrough curve at an observation well. Retardation is also proportional to K_{oc}.

Table 1 lists the DBPs for which K_{ow} has been determined, K_{oc} which is calculated from the relationship given above, and the calculated retardation factors assuming linear adsorption isotherms. These data indicate that in aquifers with low organic content, retardation and hence adsorption of THMs and HAAs will be minimal.

Table 1: K_{ow}, calculated K_{oc} and retardation factors of DBPs, assuming a bulk density of aquifer solids of 2.65 g/cm^3, a porosity of 0.3 and an organic carbon content of 0.1%.

DBP	K_{ow}	K_{oc}	Retardation factor
CF*	93	59	1.4
BDCM*	76	48	1.3
DBCM*	123	77	1.5
BF*	240	151	1.9
DCAA**	8.3	5.2	1.0
TCAA**	50	32	1.2

* – cited Buszka *et al.* 1994; ** - International Labour Organisation, International Chemical Safety Cards (Internet)

2.3 *Microbial degradation*

2.3.1 *Trihalomethanes*

THMs and in particular CF have been the focus of a number of studies on microbial degradation under anaerobic conditions. Under denitrifying conditions all THMs apart from CF were biotransformed with the more highly brominated THMs being more readily removed. Under the more highly reducing conditions of sulphate reduction, THMs apart from CF were again biotransformed with the more highly brominated compounds being more readily removed. Under the highly reducing conditions of methanogenesis, all THMs including CF were biotransformed with the more highly brominated compounds again being more readily removed (Bouwer & Wright, 1988). In contrast, Gupta et al. (1996a) reported CF to be transformed under sulphate reducing conditions. The data are summarised in Table 2 (adapted from Bouwer & Wright, 1988).

Table 2. Relative reactivities of THMs under anoxic conditions

THM	Conditions required for significant transformation	Relative reactivity
CF	Methanogenesis Sulphate Reduction?	+
BDCM	Denitrification Sulphate Reduction Methanogenesis	++
DBCM	Denitrification Sulphate Reduction Methanogenesis	+++
BF	Denitrification Sulphate Reduction Methanogenesis	++++

From their experiments Bouwer & Wright (1988) generated rate data for THM transformations in anoxic biofilm columns. From these data half lives can be calculated under the different reducing conditions which gives an indication of the relative rates of transformations under anoxic conditions (Table 3).

Table 3: Half lives for biotransformations of THMs under various reducing conditions. Concentration of biomass is 0.01 mg/L which is cited as a reasonable value.

THM	Half life (days)		
	Denitrification	Sulphate Reducing	Methanogenesis
CF	-	-	330
BDCM	1700	990	63
DBCM	ND*	ND*	ND*
BF	300	98	35

*- ND = not determined

Thus BF is biotransformed approximately 10 times faster than CF under methanogenic conditions. In addition, changing the conditions from denitrifying to methanogenic also increases the rate of BF transformation by a factor of approximately 10.

An important feature of these microbial processes is the products formed. Under denitrifying conditions BF was converted stoichiometrically to dibromomethane while under more strongly reducing conditions, less dibromomethane was determined (Bouwer & Wright, 1988). With CF, dichloromethane (DCM) and carbon dioxide are the products most commonly reported. DCM has been reported as not being further degraded (Yu & Smith, 1997) or degraded but at a slower rate (Gupta *et al.* 1996a,b). Freedman & Gossett (1991) reported that DCM can be utilised as a growth substrate under methanogenic conditions so under the right conditions, DCM formation from CF would not be an issue. The variable fate of DCM appears to depend on the microorganisms present (a number of studies have employed mixed cultures of anaerobic microorganisms), the presence of other substrates, the reducing status of the environment and the time frame of the experiments.

THMs have been reported to be non-degradable under aerobic conditions (Bouwer *et al.* 1981). However more recent work has shown chloroform can be cometabolised by methanotrophic and other oxidising bacteria. Cometabolism involves the oxidation of the chemical of interest by a microorganism which is at the same time utilising a primary substrate, generally methane, as a source of energy for growth (Alvarez-Cohen *et al.* 1992). As this is an oxidation process, the products of the reaction are carbon dioxide and chloride, i.e. mineralisation occurs. However, the coexistence of the microorganism, a primary substrate such as methane and the chemical of interest, e.g. CF, may not always be present in nature. At this stage, the importance of this process as an attenuation mechanism for THMs is unclear.

2.3.2 Haloacetic acids

Microbial degradation of HAAs appears to occur relatively easily under aerobic conditions as evidenced by the attenuation of these compounds with increasing residence time in water supply distribution systems (Chen & Weisel, 1998). Various aerobic bacteria have been shown to effect degradation with some being specific in terms of the HAAs which they can degrade (Yu & Welander, 1995). HAAs can also be degraded under anaerobic conditions (de Wever *et al.* 2000, Egli *et al.* 1989). Thus the ability to degrade HAAs both aerobically and anaerobically makes them susceptible to ready removal as this can occur in any environment. This is reflected in ASR studies where HAAs disappeared very quickly in comparison with THMs (Singer *et al.* 1993, Thomas *et al.* 2000).

Under both aerobic and anaerobic conditions, the major product from MCAA is carbon dioxide. TCAA can be more recalcitrant with some microorganisms only degrading DCAA and MCAA (Williams *et al.* 1995) or if they degrade TCAA, MCAA and DCAA are unaffected (Yu & Welander, 1995). Under aerobic conditions the products are the 2-hydroxy acids (Table 4). These are probably the precursors to the final product of carbon dioxide. The relative rates of reaction of the 3 chlorinated acetic acids and 1 brominated acetic acid together with the products of the reaction are shown in Table 4. These data are specific for the enzyme isolated by Motosugi *et al.* (1982). Other microorganisms and hence possibly different enzymes, and mixed cultures will produce different rates and may have different specificities. Under anaerobic conditions, MCAA has been shown to produce glycolic acid which further produces methane and carbon dioxide (Egli *et al.* 1989). De Wever *et al.* (2000) found TCAA to produce only DCAA under anaerobic conditions with one particular microorganism.

Table 4: Products and relative reactivities of HAAs with the enzyme D,L-2-haloacid dehalogenase isolated from *Pseudomonas* sp. strain 113 (Motosugi *et al.* 1982)

HAA	Reaction product	Relative reactivity
MCAA	Glycolic acid	1.0
MBAA	Glycolic acid	8.5
DCAA	Glyoxylic acid	0.12
TCAA	Oxalic acid	0.03

3 CASE STUDY (BOLIVAR)

An ASR research project that has been underway since 1999 in South Australia involves the use of reclaimed water from the Bolivar Sewage Treatment Works near Adelaide for aquifer recharge. ASR is made possible through further treatment of the effluent by a dissolved air flotation and filtration (DAFF) process to remove algae prior to chlorination and recharge. The injectant displaces brackish ambient groundwater and is withdrawn during the dry summer months for irrigation of crops north of the city.

Effluent quality with regard to ammonia from Bolivar is very variable. The lagoon from which the recharge water is taken has relatively high ammonia levels in winter but during summer nitrification occurs resulting in low ammonia levels. For example in 2000/2001, ammonia levels declined from 29 mg/L in August (the end of winter) to 0.06 mg/l in early March (the end of summer) (Vanderzalm *et al.* 2002). Thus, during winter, most of the chlorine added prior to recharge was consumed by the ammonia and THM levels were very low (10 – 20 µg/L). During summer THM levels were much higher (140 – 150 µg/L) and afforded an ideal opportunity for studying the attenuation of these compounds during the storage phase.

THM and chloride data for a recent storage period (autumn 2001) are shown in Table 5 for the ASR well and in Table 6 for the observation well 4 metres away. The consistency of the chloride data over this period indicates that mixing with the ambient groundwater, i.e. dilution, was not a factor in attenuation of the THMs. The chloride concentration of the ambient groundwater was 940 mg/L.

Table 5: THM and chloride data for the recharge well during a storage period. Day 0 represents the recharge water THMs on the last day of recharge.

Day	THM Concentration (µg/L)					Chloride Conc.
	CF	BDCM	DBCM	BF	Total	(mg/L)
0	33	8	46	58	145	415
7	71	20	10	<1	101	382
12	46	6	3	<1	55	360
28	12	2	3	<1	15	358
69	4	<1	<1	<1	4	387
82	2	<1	<1	<1	2	363
109	<1	<1	<1	<1	<4	370

Table 6: THM and chloride data for the 4 metre observation well during a storage period. Day 0 represents data at the well on the last day of recharge. Travel time between the recharge and observation well is approximately 1 day.

Day	THM Concentration (µg/L)					Chloride Conc.
	CF	BDCM	DBCM	BF	Total	(mg/L)
0	41	56	40	6	143	394
7	47	57	38	5	147	370
12	35	41	26	3	105	360
28	33	27	12	1	73	381
69	-	-	-	-	-	-
82	19	9	5	1	34	379
109	14	2	<1	<1	16	357

The results indicate a phenomenon reported in other studies, i.e. the initial increase in the concentration of the more refractory THMs as residual chlorine continues to react with the organic matter either in the recharge water or perhaps the microbial material in the immediate vicinity of the recharge well. However during this initial period the more labile THMs, although probably still being formed as a result of chlorination of the injectant at the wellhead, are being degraded at a faster rate resulting in all the BF being removed in the first week of storage. The other two bromine containing THMs are removed by day 69 and CF by day 109. The removal of CF suggests a methanogenic environment at the recharge well with the ease of removal of the various THMs following the trend determined experimentally (Bouwer and Wright, 1988). The methanogenic environment at the recharge well was supported by the finding of significant production of methane and carbon dioxide at this site (unpublished data).

Removal of THMs at the observation well proceeds at a slower rate. Again there is evidence of initial increases in THM levels, removal by degradation and possible adsorption but it is not possible to isolate the various processes. The travel time for recharge water to reach the observation well had been shown to be approximately 1 day. As the THM levels in the recharge water in the few weeks before recharge ceased were relatively constant, the water at the observation well would have had initial THM levels much the same as recharge water at day zero. Therefore THM levels at the observation well reflect changes due to an approximately 1 day transport from the recharge well. There is a smaller increase in the CF level compared with the recharge well which suggests the higher levels at the recharge well during the initial period of storage is a localised effect due to a higher level of biomass acting as a precursor. BF is highly attenuated during transport suggesting that degradation near the recharge well is quite rapid. The possibility also exists that some adsorption may also be occurring. BF and DBCM are attenuated more slowly at the observation well compared with the recharge well suggesting either less anoxic conditions or less biomass effecting degradation. As CF is attenuated at the observation well and this only occurs under methanogenic conditions, the results suggest that the observation well environment is methanogenic with the reduced rate being due to a lower biomass. This was supported by the finding of methane at this site but at much lower levels than at the ASR well (unpublished data).

The interesting result is the large increase in the level of BDCM compared with the recharge well. This must be due to further reaction of residual chlorine with precursors, either in the recharge water or in the aquifer, but why this is not reflected in large increases in CF concentrations as well is not clear. It may be possible that the nature of the precursors are different at the recharge well compared with the observation well leading to the different distribution of THMs.

As discussed earlier, the fate of CF under methanogenic conditions appears to vary, depending on the microorganisms present. DCM is a product commonly reported but in this case it was not possi-

ble to analyse for DCM with sufficient sensitivity to determine if it were formed.

HAA data collected to date has been less detailed. Recharge water had a range of HAAs present with a relatively high proportion of brominated compounds (Table 7). Only dichloroacetic acid at a concentration of 1 µg/L was detected at the observation well on the day that recharge ceased confirming the ready removal of these compounds (Landmeyer *et al.* 2000; Thomas *et al.* 2000; Singer *et al.* 1993) as they are effectively removed during the approximately 1 day that recharge water takes to reach the observation well.

Table 7: HAA levels in recharge water and the 4 metre observation well at the end of the recharge period.

HAA	Concentration (µg/L)	
	Recharge water	4 metre observation well
Monochloroacetic acid	<5	<5
Dichloroacetic acid	3	1
Trichloroacetic acid	18	<1
Bromoacetic acid	<1	<1
Dibromoacetic acid	<1	<1
Bromochloroacetic acid	2	<1
Bromodichloroacetic acid	35	Not determined

4 SUMMARY AND CONCLUSIONS

Disinfection by-products can be an important component of chlorinated potable water and treated effluent used for aquifer recharge, especially when ammonia levels are low. Attenuation processes in aquifers include adsorption, chemical and microbial degradation. The literature indicates that the main process leading to reduced concentrations of trihalomethanes and haloacetic acids is microbial degradation, with degradation under methanogenic conditions being the most effective removal mechanism.

Preliminary data for the Bolivar ASR site indicated extremely rapid removal of HAAs. Brominated THMs were also rapidly removed with chloroform being the most persistent. However chloroform was completely removed during a 109 day storage period suggesting the environment at the ASR well to be methanogenic. Removal at the 4 metre observation well was not complete during this period although approximately two thirds of the chloroform was removed during this period. This suggests that the environment at this site was methanogenic but the biomass of microorganisms capable of degrading chloroform was insufficient. Dichloromethane was a likely product of chloroform degradation but analytical procedures for its determination at sufficiently low concentrations were not available.

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REFERENCES

Alvarez-Cohen, L., McCarty, P.L., Boulygina, E., Hanson, R.S., Brusseau, G.A. & Tsien, H.C. 1992. Characterization of a methane-utilizing bacterium from a bacterial consortium that rapidly degrades trichloroethylene and chloroform. Appl. Environ. Microbiol. 58: 1886-1893.

Bouwer, E.J., Rittmann, B.E. & McCarty, P.L. 1981. Anaerobic degradation of halogenated 1- and 2-carbon organic compounds. Environ. Sci. Technol. 15: 596-599.

Bouwer, E.J. & Wright, J.P. 1988. Transformations of trace halogenated aliphatics in anoxic biofilm columns. J. Contam. Hydrol. 2: 155-169.

Buszka, P.M., Brock, R.D. & Hooper, R.P. 1994. Hydrogeology and Selected Water-Quality Aspects of the Hueco Bolson Aquifer at the Hueco Bolson Recharge Project Area, El Paso, Texas. US Geological Survey, Water-Resources Investigations Report 94-4092.

Castro, C.E., O'Shea, S.K., Wang, W. & Bartnicki, E.W. 1996. Biodehalogenation: Oxidative and hydrolytic pathways in the transformations of acetonitrile, chloroacetonitrile, chloroacetic acid and chloroacetamide by Methylosinus trichosporium OB-3b. Environ. Sci. Technol. 30: 1180-1184.

Chen, W.J. & Weisel, C.P. 1998. Halogenated DBP concentrations in a distribution system. J. Am. Water Works Assoc. 90(4): 151-163.

de Wever, H., Cole, J.R., Fettig, M.R., Hogan, D.A. & Tiedje, J.M. 2000. Reductive dehalogenation of trichloroacetic acid by Trichlorobacter thiogenes gen. nov., sp. nov. Appl. Environ. Microbiol. 66: 2297-2301.

Egli, C., Thuer, M., Suter, D., Cook, A. & Leisinger, T. 1989. Monochloro- and dichloroacetic acids as carbon and energy sources for a stable methanogenic mixed culture. Arch. Microbiol. 152: 218-223.

Freedman, D.L. & Gossett, J.M. 1991. Biodegradation of dichloromethane and its utilization as a growth substrate under methanogenic conditions. Appl. Environ. Microbiol. 57: 2487-2857.

Gupta, M., Gupta, A., Suidan, M.T. & Sayles, G.D. 1996a. Biotransformation rates of chloroform under anaerobic conditions -II. Sulfate reduction. Water Res. 30: 1387-1394.

Gupta, M., Sharma, D., Suidan, M.T. & Sayles, G.D. 1996b. Biotransformation rates of chloroform under anaerobic conditions -I. Methanogenesis. Water Res. **30**, 1377-1385.

Karickhoff, S.W., Brown, D.S. & Scott, T.A. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13: 241-248.

Krasner, S.W., McGuire, M.J., Jacangelo, J.G., Patania, N.L., Reagan, K.M. & Aieta, E.M. 1989. The occurrence of disinfection by-products in US drinking water. J. Am. Water Works Assoc. 81(8): 41-53.

Landmeyer, J.E., Bradley, P.M. & Thomas, J.M. 2000. Biodegradation of disinfection byproducts as a potential removal process during aquifer storage recovery. J. Am. Water Resour. Assoc. 36: 861-867.

McCarty, P.L., Reinhard, M. & Rittmann, B.E. 1981. Trace organics in groundwater. Environ. Sci. Technol. 15: 40-52.

Motosugi, K., Esaki, N. & Soda, K. 1982. Purification and properties of a new enzyme, DL-2-haloacid dehalogenase, from Pseudomonas sp. J. Bacteriol. 150: 522-527.

Shams el Din, A.M., Arain, R.A. & Hammoud, A.A. 1998. Kinetics of hydrolysis of chloroform and bromoform in aqueous solutions. Desalination 120: 41-51.

Singer, P.C., Pyne, R.D.G., Mallikarjun, A.V.S., Miller, C.T. & Mojonnier, C. 1993. Examining the impact of aquifer storage and recovery on DBPs. J. Am. Water Works Assoc. 85(11): 85-94.

Thomas, J.M., McKay, W.A., Cole, E., Landmeyer, J.E. & Bradley, P.M. 2000. The fate of haloacetic acids and trihalomethanes in an aquifer storage and recovery program, Las Vegas, Nevada. Ground Water 38: 605-614.

Vanderzalm, J.L., Le Gal La Salle, C., Hutson, J.L. and Dillon, P.J. (2002) Water quality changes during aquifer storage and recovery at Bolivar, South Australia. This volume.

Williams, S.L., Williams, R.L. & Gordon, A.S. 1995. Degradation of haloacetic acids (HAA) at maximum residence time locations (MRTLs). Proc. Am. Water Works Assoc., Water Quality Technology Conference, New Orleans, LA Part II, 1357-1366.

Wilson, J.T., Enfield, C.G., Dunlap, W.J., Cosby, R.L., Foster, D.A., & Baskin, L.B. 1981. Transport and fate of selected organic pollutants in a sandy soil. J. Environ. Qual. 10: 501-506.

Yu, Z. & Smith, G.B. 1997. Chloroform dechlorination by a wastewater methanogenic consortium and cell extracts of Methanosarcina barkeri. Water Res. 31: 1879-1886.

Yu, P. & Welander, T. 1995. Growth of an aerobic bacterium with trichloroacetic acid as the sole source of energy and carbon. Appl. Microbiol. Biotechnol. 42: 769-774.