

## **Monitoring solvents in the Birmingham aquifer (UK): 1987, 1998 and on to the next millennium**

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**Abstract** Chlorinated solvents are exceedingly common groundwater contaminants in aquifers that underlie urban areas. A case study is presented of the Birmingham aquifer (UK) using data from two surveys of solvent occurrence conducted a decade apart (1987 and 1998). Active abstraction boreholes (mainly industrial-use) were used to obtain groundwater samples. The suitability of such boreholes to observe relevant contaminant hydrogeological processes and provide long-term monitoring is illustrated. Although the Birmingham data set is relatively sparse, interpretations may nevertheless be offered on solvent occurrence, persistence of solvent source zones, effects of changing groundwater abstraction, solvent attenuation in the aquifer and trends in solvent mass removal by groundwater abstraction. It is concluded that active abstraction boreholes may provide useful data on urban groundwater quality trends and their use in the next millennium should not be overlooked.

### **INTRODUCTION**

Since the early 1980s it has become apparent that chlorinated solvents are exceedingly common contaminants in aquifers that underlie urban-industrial areas. Such solvents include TCE (trichloroethene) and PCE (perchloroethene) that have been ubiquitously used for metal degreasing and textile dry-cleaning. Pankow & Cherry (1996) indicate extensive research continues into the fate of solvents in aquifers and development of remediation technologies. Key solvent attributes that cause persistent and widespread occurrence in groundwaters include: (a) their DNAPL (dense non-aqueous phase liquid) nature allowing solvent “residuals” and “pools” to form deep below the groundwater table that slowly dissolve; and (b) their weak “natural attenuation” behaviour—sorption and (bio)degradation may often be limited.

Although specifically installed monitoring wells may often be the preferred approach to characterize solvent plumes in groundwater, experience at many USA “Superfund” sites has indicated that millions of dollars may need to be spent to characterize a plume (Jackson, 1998). Such expensive monitoring is often not viable for many countries, or perhaps warranted for some aquifer conditions and existing observation wells or boreholes (used for water level measurement or abstraction), may need to be used to provide aquifer quality data. Although such monitoring is often regarded as “second-best”, we aim to illustrate through a case study of the Birmingham aquifer involving two surveys a decade apart (1987 and

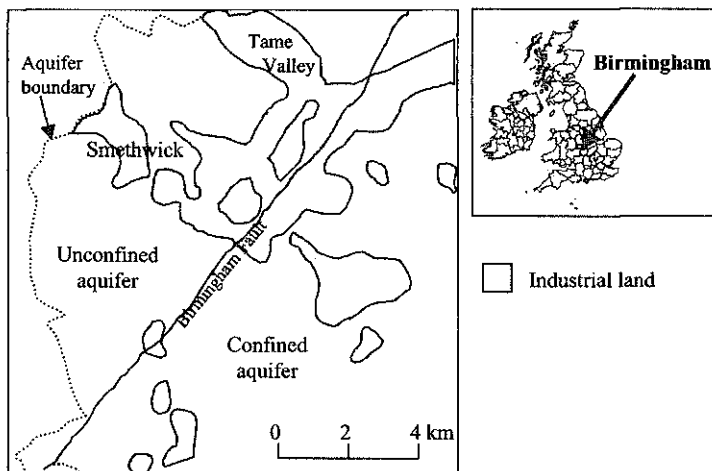
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1998), that monitoring of solvent groundwater quality using existing deep, active abstraction boreholes can provide valuable data on solvent-aquifer processes and trends.

## LAND USE AND HYDROGEOLOGY

The Triassic sandstone aquifer underlying Birmingham, the UK's second largest city, has mainly been used as a water supply to serve its resident industry, specific industries having a licence to abstract a defined volume of groundwater for a declared use. Most abstracted groundwater has been used for industrial processes such as cooling, cleaning and product manufacture. Public supply from the aquifer has been very limited as Birmingham imports its water supply from the Elan Valley in Wales. Solvents have been widely used in the industrial areas, particularly TCE in metals-related industries that have dominated industrial land use.

Figure 1 depicts aspects of the Birmingham conurbation and aquifer. The Birmingham Fault divides the city: to the east the thick (20–100 m), low permeability Mercia Mudstones confine the Triassic sandstone aquifer; to the west the Triassic sandstone aquifer is unconfined and outcrops, or is covered by 0–40 m thick Recent and Pleistocene fluvial and glacial deposits (“drift deposits”). The central portion of the unconfined aquifer to the north and south of Smethwick contains the thickest drift deposits and greatest depths to groundwater. Groundwater flow in the unconfined aquifer is generally toward the Tame Valley in the north where drift protection of the aquifer is low and groundwater levels are near to surface. Rising groundwater levels have occurred over Birmingham since the early 1960s, a consequence of the steady decline in industrial use of groundwater. Sandstone hydraulic conductivity is about 1–10 m day<sup>-1</sup> and matrix groundwater velocities are calculated to be around 15 m year<sup>-1</sup>, although velocities will be greater where fractures are present.



**Fig. 1** Birmingham conurbation and hydrogeology (most of the area shown is urbanized).

## SURVEY METHODOLOGY

The first survey of organic water quality of the Birmingham aquifer was undertaken by Rivett *et al.* (1990a, 1990b, 1990c) and Lerner *et al.* (1992) during 1986–1988, the “1987 survey”. That survey revealed chlorinated solvents, particularly TCE, to be the main contaminants present. A recent survey for solvents has been conducted, the “1998 survey”, in which an attempt was made to re-sample the 1987 survey boreholes and any new boreholes that had since become available. Both surveys used active abstraction boreholes that are regularly pumped by various Birmingham industries for their private water supply. Boreholes are typically 80–150 m deep and extensively screened to allow potential withdrawal of groundwater from the full aquifer depth. Individual boreholes typically abstract 0.1–1.0  $\text{Ml day}^{-1}$ , a maximum being about 3  $\text{Ml day}^{-1}$ .

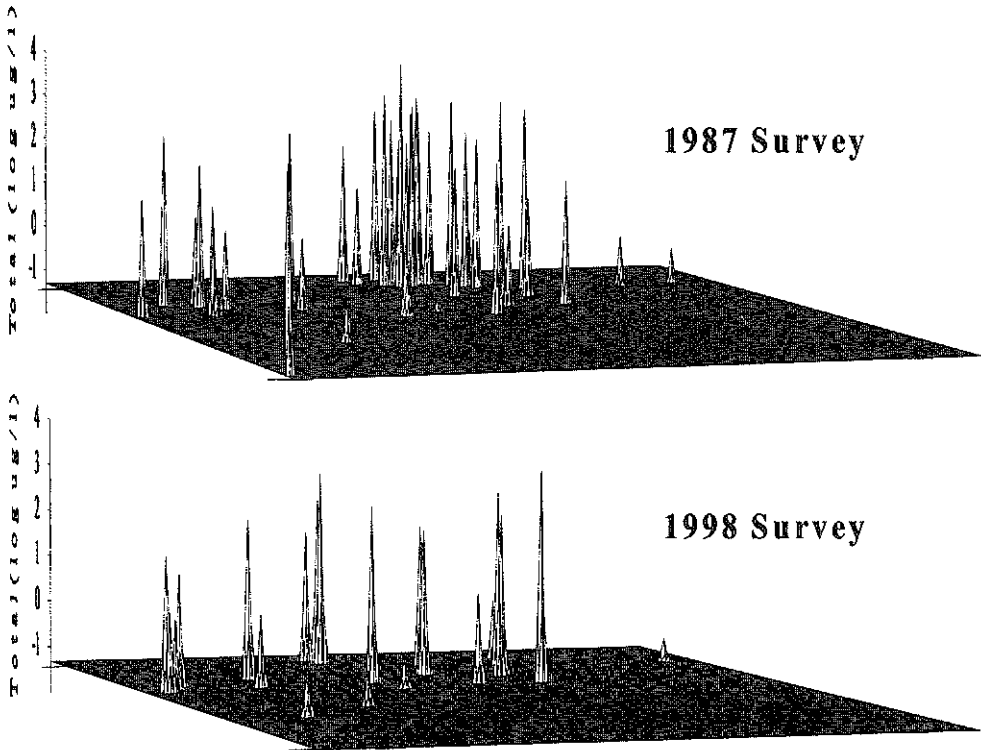
To assist data comparison, the 1998 survey adopted similar purging protocols to those used in the 1987 survey. Purging aimed to remove at least three borehole volumes and achieve conductivity stabilization, although this was not always practicable. Glass VOC sample vials were filled from sample taps located as close as possible to the wellhead. Solvent analysis was via liquid-liquid pentane extraction and GC-ECD analysis for the chlorinated solvents: TCM (trichloromethane), TCA (1,1,1-trichloroethane), CTC (carbon tetrachloride), TCE and PCE. In addition, for the 1998 survey a “headspace” sampler and GC-MS with selective ion monitoring was used to analyse for the three dichloroethene isomers (1,1-DCE, *cis*-1,2-DCE and *trans*-1,2-DCE) and vinyl chloride (VC), compounds that may be anticipated to arise from microbially mediated anaerobic biodegradation of TCE or PCE.

Of the 59 boreholes sampled in the 1988 survey, only 26 boreholes were available for sampling in 1998; a further 10 new boreholes gave a total of 36 boreholes sampled in the 1998 survey. Hence, over 50% of the boreholes originally sampled in 1987 were not available for re-sampling. This is largely attributed to these boreholes no longer being actively pumped, either because the industry has closed down, or water is no longer required. A minority of 1987 boreholes (<10%) was still actively pumped, but unavailable for sampling in 1998. The majority of aquifer abstraction (and hence borehole samples) was from the unconfined aquifer.

## COMPARISON OF 1987 AND 1998 SURVEYS

### Overview of solvent occurrence

Figure 2 illustrates the occurrence of Total Chlorinated Solvents (sum of TCM, TCA, CTC, TCE, PCE) in the 1987 and 1998 surveys. Concentrations range from approximately 0.1  $\mu\text{g l}^{-1}$  up to 6000  $\mu\text{g l}^{-1}$ . TCE predominates in both surveys and has a similar distribution to Fig. 2. TCA and PCE also show significant concentrations at specific sites, although high concentrations of TCA were only found in 1987. The most significant contamination in 1987 was observed around the Tame Valley, which is mainly attributed to the area's high vulnerability to groundwater pollution, i.e. limited drift protection and shallow groundwater table. Although Fig. 2 indicates some similarities between the 1987 and 1998 occurrences, the cluster of greatest



**Fig. 2** Occurrence of total chlorinated solvents ( $\log \mu\text{g l}^{-1}$ ) in the Birmingham aquifer. Degree of solvent contamination at each borehole is indicated by “spike” heights; the “base” area coincides with the area depicted in Fig. 1.

contamination observed in 1987 is not seen in 1998. This is mainly due to the decline in sample points available in that area by 1998.

Table 1 summarises the occurrence data for TCE. All concentration intervals show a decrease in observed contamination from 1987 to 1998; for example, 76% of sites had TCE present in 1987 compared to 56% in 1998. Also, concentrations are generally lower in the 1998 survey with the UK drinking water standard of  $30 \mu\text{g l}^{-1}$  exceeded by 28% of sites compared to 40% in 1987.

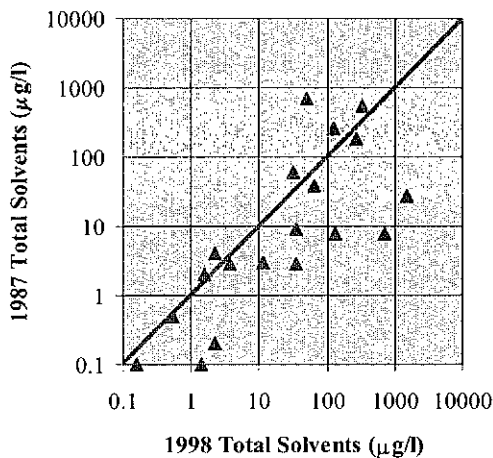
Initial inspection of Table 1 suggests that aquifer quality might have improved in 1998. However, comparison below of data from the 26 sample sites common to both surveys indicates that this conclusion is erroneous. Unfortunately, sample site availability in 1998 resulted in a bias towards sampling of boreholes that originally contained lower contamination in 1987 and partly explains the apparent improvement in quality suggested by Table 1. Of the 26 sites re-sampled in 1998, only 6 sites (23%) were previously above  $30 \mu\text{g l}^{-1}$ ; compared with the 33 sites from 1987 not re-sampled of which 18 sites (55%) were over  $30 \mu\text{g l}^{-1}$  in 1987. Hence, to evaluate solvent trend behaviour over the past decade, the preferred approach is to examine the data-set from the 26 boreholes common to both 1987 and 1998 surveys.

**Table 1** Percent frequency occurrence of TCE in 1987 and 1998 Birmingham surveys.

	1987 (% of 59 sites)	1998 (% of 36 sites)
TCE >0.1 $\mu\text{g l}^{-1}$	76	56
TCE >30 $\mu\text{g l}^{-1}$	40	28
TCE >100 $\mu\text{g l}^{-1}$	30	19

### Contaminant source zone persistence

Figure 3 compares total solvent concentrations observed in 1987 with those re-sampled in 1998 and provides a better opportunity to evaluate trends in aquifer contamination over the past decade. Data points generally plot either close to the 1:1 line indicating concentrations have remained fairly similar over the decade, or to the lower right of that line indicating a concentration increase from 1987 to 1998. This is a significant result and suggests observed 1998 aquifer contamination has remained at least as poor, if not worse, than that observed in 1987, contrary to the apparent improvement suggested by Table 1.

**Fig. 3** Correlation plot of total chlorinated solvents data for 1987 and 1998 surveys.

There are two main reasons for the persistence of solvent concentrations in abstracted groundwater: (a) there has been continued spillage of solvents to the aquifer over the past decade; and, (b) DNAPL residual and pools of solvents present in the aquifer prior to 1987 are still slowly dissolving and acting as a semi-infinite source of groundwater contamination. There may well have been recent solvent spills; however, many companies have adopted improved solvent handling practices and release rates are likely less than in previous decades. Explanation (b) is preferred; the data likely illustrate the longevity of solvent (DNAPL) source zones and their long-term capacity to generate dissolved solvent plumes in groundwater. The data are consistent with findings at high-resolution monitored sites and conceptual DNAPL models that have developed (Pankow & Cherry, 1996). Figure 3 suggests that solvent contamination in the Birmingham aquifer is a long-term problem that may last decades into the next millennium.

## Groundwater abstraction influences

Major changes in the rates of groundwater abstraction at individual boreholes between 1987 and 1998 may be anticipated to have a significant impact on concentrations observed in the two surveys. The zone of influence of a borehole and hence its interaction with solvent plumes and source zones changes with abstraction rate. A greater abstraction rate may interact with more distant contaminant sources causing concentrations to increase or decrease depending on the relative proportions of clean and contaminated waters drawn in. It is proposed that major changes in concentrations observed at some sites in Fig. 3 may be ascribed to large abstraction changes that occurred between 1987 and 1998. For example, two boreholes had operated for only short periods when sampled in 1987 and both contained  $<10 \mu\text{g l}^{-1}$  solvents at that time. After continual abstraction over the decade, one borehole had risen to  $135 \mu\text{g l}^{-1}$  and the other to over  $700 \mu\text{g l}^{-1}$  by 1998. Solvent increases are attributed to contamination being drawn into the boreholes as they gradually established a steady-state flow regime and interaction with contaminant sources and plumes in the vicinity. Tracer tests elsewhere suggest that under natural gradient conditions transverse dispersion of dissolved plumes is weak and that long, thin contaminant plumes develop. It is hypothesized that the Birmingham aquifer likely contains a multitude of solvent source zones that have led to discrete long, thin contaminant plumes, rather than a "blanket" of contamination. When a new borehole is installed, it may well show zero or low level contamination as narrow plumes under natural flow conditions could easily evade the borehole unless the source is located directly up hydraulic gradient. As boreholes are pumped with time, discrete plumes are eventually drawn in and contaminant levels rise in the abstracted water. This is a reasonable explanation for solvent increases observed above and may suggest that any new boreholes installed in industrial areas of the aquifer may be prone to similar rises in contamination with time.

## Solvent plume attenuation via sorption and degradation

Dissolved solvent plumes may be retarded relative to flowing groundwater due to sorption to aquifer solids, or attenuated by abiotic (chemical) or biotic (biodegradation) reactions that transform and remove contaminant. Brief evidence for these processes is presented below.

PCE was the most hydrophobic solvent analysed and hence should be the most retarded of the monitored solvents. Based upon the empirical correlation of Piwoni & Banerjee (1989), PCE was calculated to have an aquifer retardation factor of 1.9 and TCE 1.3. There is some evidence, admittedly weak, that PCE plume development is slower than TCE in the aquifer. Of the seven sites re-sampled that displayed PCE contamination, the ratio of PCE:TCE has increased at six of these sites from 1987 to 1998 which may be indicative of retarded migration of dissolved-phase PCE due to sorption, although other explanations are also possible.

Rising trends in TCA at some boreholes monitored during 1986–1988 suggested that TCA levels may have been increasing in the aquifer relative to TCE, a possible

explanation being the later introduction of TCA into general industrial use (since 1970s) and hence TCA may have a delayed aquifer impact relative to TCE. Unfortunately none of the boreholes with elevated concentrations (up to  $800 \mu\text{g l}^{-1}$ ) of TCA encountered in 1987 were available for sampling. Data available from six boreholes that previously contained TCA at  $0.1\text{--}10 \mu\text{g l}^{-1}$  in 1987 indicated little concentration change by 1998 (all still  $<10 \mu\text{g l}^{-1}$ ), hence the anticipated concentration increase was not obvious. Although declining use of TCA in recent years due to its adverse ozone impact may be an explanation, the lack of increase is more likely attributed to TCA degradation via abiotic hydrolysis. Dilling *et al.* (1975) report an hydrolysis half-life of 6 months.

Biodegradation was not assessed during the 1987 survey. However, data on VC and DCEs, breakdown products of PCE, TCE or TCA, were obtained in 1998. Chemical analysis method development was being undertaken during this sampling event and results are regarded as being of a semi-quantitative nature in need of some confirmation. Results are likely to be negatively biased due to long sample holding times and the absence of VC contamination reported in all samples needs confirmation in particular. Cis-DCE was the primary degradation product and was detected at seven of the 36 sites. Concentrations were in the range  $5\text{--}130 \mu\text{g l}^{-1}$  and were coincident with samples containing elevated TCE and PCE, although not all such samples contained this transformation product. The preferential formation of cis-DCE is consistent with observations of others elsewhere (Barrio-Lage *et al.*, 1986). The detection of cis-DCE suggests that cometabolic anaerobic dechlorination reactions are occurring in parts of the aquifer. The key question being, are these sufficient to cause "natural attenuation" of solvents in the aquifer and form harmless products such as ethene? (Note that DCEs and VC are more toxic than their precursor solvents). The lack of any evidence of VC formation and also detection of TCE and PCE at a number of borehole sites that do not use solvents suggests it may not be sufficient. Further biodegradation research in the aquifer is required, in particular the identification of primary substrates and the role of sandstone iron and manganese in the redox reactions.

### **Solvent removal via borehole groundwater abstraction**

An estimate of solvent mass being removed from the aquifer via abstracting boreholes may be made from solvent concentrations detected in the surveys and annual borehole abstraction. For the year 1987,  $1500 \text{ kg year}^{-1}$  of TCE (five drums) were removed which compares to approximately  $160 \text{ kg year}^{-1}$  for the 1998 data, only about 10% of the previous quantity. The main reason proposed for the decline is the lack of availability of many of the boreholes that were observed to be highly contaminated in the 1987 survey. Most of these are no longer pumping, although it is possible that a few may still be operating and abstracting significant solvent quantities that could not be accounted for in the present survey. Present data suggest that an equivalent of  $1350 \text{ kg year}^{-1}$  of TCE that was being removed from the aquifer in 1987 is no longer being captured by abstracting boreholes and potentially able to further disperse into the aquifer.

## CONCLUSIONS

The Birmingham case study illustrates that valuable insight into solvent contamination of the aquifer may be obtained from a relatively sparse data-set obtained from sampling existing industrial abstraction boreholes. Interpretation of 1987 and 1998 survey data could have been considerably enhanced by regular collection of samples during the intervening period, e.g. even just bi-annual sampling, at a selection of borehole sites. Neither owner industries or regulator were able to provide such data. It is anticipated that solvent behaviour and long-term trends could usefully be observed in many urban aquifers world-wide by regular sampling of existing borehole abstractions (particular those not having a sensitive water use), and provide cost-effective insights into solvent problems that may persist far into the next millennium. Large "integrated volume" samples obtained from such boreholes provide unique and complimentary data to that obtained from any specifically installed solvent monitoring well points.

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