# Use of rhodamine WT with XAD-7 resin for determining groundwater flow paths

**Murray E. Close · Greg J. Stanton · Liping Pang**

**Abstract** A passive sampling system for use with rhodamine WT (RWT) in groundwater tracing experiments was developed to assist in the characterisation of groundwater flow paths. Amberlite XAD-7 resin was found to be suitable for adsorption of RWT, which can then be extracted using an ethanol/water mix and analysed fluorometrically. Batch and column experiments showed that XAD-7 resin has a high RWT capacity. The adsorption was slightly dependent on pH, but was always above 75% under batch conditions. The resin had a high percentage mass recovery at flow velocities around 1.5 m/day, but this decreased with increasing flow velocities. Desorption of RWT off the resin in water is dependent on the flow velocity of water and the time after the peak RWT has passed. The mass of RWT extracted from the resin bags correlated very well with both the RWT mass flux in the water and the peak concentrations observed in the monitoring wells in a field experiment. The results of resin bags were reproducible in the field with a mean coefficient of variation equal to 16%. This method has been successfully applied to two field situations with different flow velocities to indicate groundwater flow paths.

**Résumé** Un dispositif d'échantillonnage passif destiné à la rhodamine WT (RWT) dans les expériences de traçage des eaux souterraines a été développé pour contribuer à la caractérisation des directions d'écoulement souterrain. On a trouvé que la résine Amberlite XAD-7 convenait pour adsorber la RWT, qui peut ensuite être extraite au moyen d'un mélange d'éthanol et d'eau pour être analysée en fluorimétrie. Des expériences en réacteur fermé et sur colonne montrent que la résine XAD-7 possède une forte capacité de RWT. L'adsorption dépendait en partie du pH, mais était toujours de plus de 75% dans les conditions en réacteur fermé. La résine offrait un taux élevé de restitution pour des vitesses autour de 1,5 m/j, mais ce taux a décru avec l'accroissement des vitesses. La désorption de la RWT de la résine dans l'eau dépend de la vitesse d'écoulement de l'eau et du temps après le passage du pic de RWT. La quantité de RWT extraite des sacs de résine est très bien corrélée à la fois avec le flux massique de RWT dans l'eau et avec les concentrations au pic observées dans les puits de contrôle lors d'une expérience sur le terrain. Les résultats fournis par les sacs de résine ont été reproductibles sur le terrain avec un coefficient de variation moyen égal à 16%. Cette méthode a été utilisée avec succès dans deux dispositifs de terrain soumis à des vitesses d'écoulement différentes, dans le but de déterminer les directions d'écoulement souterrain.

**Resumen** Se ha desarrollado un sistema pasivo de muestreo para su utilización con rodamina WT (RWT) en experimentos de trazadores de aguas subterráneas. El objetivo es ayudar en la caracterización de las vías de flujo de las aguas subterráneas. Se concluye que la resina de amberlita XAD-7 es adecuada para la adsorción de RWT, la cual puede ser extraída por medio de una mezcla de agua y etanol, y ser analizada después por fluorometría. Los experimentos por lotes y en columnas demuestran que la resina XAD-7 tiene una elevada capacidad para (adsorber) la RWT. Su adsorción depende ligeramente del pH, pero ha dado siempre valores superiores al 75% en ensayos por lotes. La resina tiene un alto porcentaje de recuperación de masa para velocidades de flujo en torno a 1,5 m/d, pero disminuye con valores crecientes de la velocidad. La desorción en agua de la RWT retenida en la resina depende de la velocidad de flujo del agua y del tiempo transcurrido desde la llegada del pico. La masa de RWT extraída de bolsas de resina está muy bien correlacionada con el flujo másico de RWT en el agua y con los picos de concentración detectados en los pozos de observación durante un ensayo de campo. Los resultados de las bolsas de resina han podido ser reproducidos en el campo con un coeficiente medio de variación del 16%. Este método se ha aplicado con éxito a dos emplazamientos con diferentes velocidades de flujo para indicar las vías de flujo de las aguas subterráneas.

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## Introduction

Determination of flow paths is essential in the hydrogeological characterisation at any site. In alluvial gravel groundwater systems flow-path directions on a local scale can deviate from regional piezometric contours by up to 45° (Thorpe et al. 1982; Pang et al. 1998). In karst and fractured rock aquifers there can be even more uncertainty regarding water and contaminant flow paths, with many possible outlets for water from a particular input point. Well to well, or well to spring tracer experiments, involving intensive water sampling, can be used to give accurate information. Fluorescent dyes, such as rhodamine WT (RWT), are commonly used as tracers for this purpose (Smart and Laidlaw 1977; Trudgill 1987; Sabatini and Austin 1991) because of their ease of fluorometric detection down to very low concentrations (about 0.1 µg/l), visibility at higher concentrations, and low ecotoxicity (Field et al. 1995). However, in the absence of information concerning flow direction and approximate velocity, which would indicate where, when and how often to sample, such dye tracer tests can be very time-consuming, expensive and inefficient.

A passive method for adsorbing tracers at a particular well or spring location would indicate the spatial distribution of the tracer transport, and hence groundwater flow direction. This would result in better design of a detailed tracer experiment if this was required, with a greatly reduced, better targeted number of sampling locations and analyses, with the consequent reduction in the time and expense required. A passive method using cotton for adsorbing fluorescent whitening agents or optical brightners was developed and tested by Smart (1976) and Thrailkill et al. (1983). Smart reported some limited success in quantitative evaluation of surgical cotton detectors using a filter fluorometer. However, Thrailkill et al. encountered many problems including cotton decomposition and silting of detectors. Their final conclusion was that the technique showed potential, but required further investigation and testing especially with respect to the materials used, and the equilibration conditions used in the experiment such as agitation and temperature.

In this paper, a cost- and time-effective method for determining groundwater flow directions using RWT tracer is presented. This technique involves placing bags of XAD-7 resin in many well/spring locations that can adsorb RWT during tracing experiments. The sorbed RWT can then be extracted and fluorometrically analysed to give accurate dye mass flux information and, hence, information regarding the spatial distribution of tracer. The studies quoted in the previous paragraph have shown the need for a permeable, yet robust tracer collector, and the need for reproducible adsorption and desorption results. The first part of this paper describes such a collector and presents laboratory experiments that assess the adsorption of RWT from water under both static and flowing conditions. Desorption of the RWT from the resin using various solvents is described and results presented from laboratory experiments to demonstrate the quantification of

the tracer mass, together with the implied limitations of this technique. The second part of the paper describes the application of the method to two field situations. The usefulness and applicability of the technique are discussed.

## Materials

Amberlite XAD-7 resin is a non-ionic aliphatic acrylic polymer available from Rohm and Haas Company. It has a macroreticular structure, high surface area and an aliphatic surface nature, which results in adsorption of non-polar and slightly polar compounds from aqueous systems (Table 1). RWT is a bright fluorescent red dye developed especially for water tracing. It can be detected fluorometrically down to about 0.1 µg/l and visually down to about 25 µg/l. It has an excitation wavelength of 556 nm and an emission wavelength of 580 nm. The chemical structures of XAD-7 resin and RWT are shown in Fig. 1.

The XAD-7 resin was prepared by hot solvent washing the beads (20–60 mesh) in acetone and methanol for 2 h each, using a Soxhlet extractor, followed by thorough washing with Milli-Q water. After drying, the resin was contained in small permeable nylon (75 mesh) bags that permitted easy passage of water while retaining the resin beads. Each resin bag contained 0.4 g of resin and had a cross sectional area of about 1 cm². The water chemistry used in the batch and column tests, as well as the groundwater chemistry for both field sites, is summarised in Table 2.

**Table 1** XAD-7 resin physical properties

| XAD-7 resin properties | |
| --- | --- |
| Appearance | Hard white translucent beads; odourless; pH neutral |
| Matrix | Macroreticular aliphatic cross linked polymer |
| Density | 655 g/l |
| Specific gravity | 1.06–1.08 |
| Surface area | $\geq$380 m²/g |
| Porosity | $\geq$0.50 ml/ml |
| Average pore diameter | 8 nm |
| Specific pore volume | 1.08 cm³/g |

**Table 2** Water chemistry for the laboratory tests and field experiments

| Parameter | Units | Laboratory tap water | Burnham groundwater | Hamilton groundwater |
| --- | --- | --- | --- | --- |
| pH | | 7.2 | 6.9 | 6.8 |
| Conductivity | mS/m | 12.0 | 10.4 | 27.0 |
| $HCO_3$ | mg/l | 65.0 | 38.0 | 46.0 |
| Cl | mg/l | 4.9 | 5.6 | 9.5 |
| $NO_3$–N | mg/l | 0.9 | 1.7 | 16.0 |
| $SO_4$ | mg/l | 5.6 | 5.4 | 13.0 |
| Na | mg/l | 7.4 | 7.7 | 10.0 |
| K | mg/l | 0.8 | 0.9 | 6.6 |
| Ca | mg/l | 13.7 | 11.3 | 19.0 |
| Mg | mg/l | 1.9 | 3.7 | 9.6 |

(a)
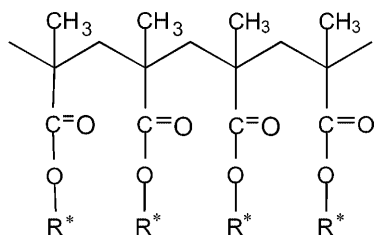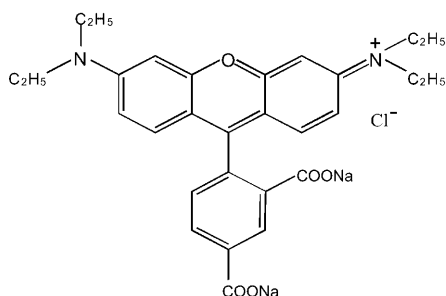


R* = Polyfunctional Aliphatic Residue.

(b)



**Fig. 1** Chemical structures of **a** XAD-7 resin and **b** RWT

## Desorption of RWT from the Resin

The resin bags were removed from the sample solution, rinsed with water, and then excess water was removed with a tissue to minimise unadsorbed RWT carry-over or dilution with rinsate. The RWT was desorbed from the XAD-7 resin using solvent extraction. Various solvents were tested for this purpose including methanol, ethanol, dichloromethane and acetone. All these solvents extracted the RWT dye sufficiently well. However, in order to measure the extracted RWT concentration spectrofluorometrically a solvent/water mix was required. Therefore, only ethanol, methanol and acetone were suitable. Etha-

nol was selected as the preferred solvent because of its low toxicity and relative non-volatility. The RWT was desorbed by placing the resin bag in a 20-ml solution of 50/50 ethanol/water mix and stirring for 10 min. Once stirring was complete, the bag was drained and squeezed with tweezers to ensure no desorbed RWT was discarded. The ethanol/water mix was measured directly using a fluorometer provided the RWT concentration was within the fluorometer range. If dilution was required, the 50/50 ethanol/water-mix ratio was maintained. Fluorometric analysis was conducted using a Shimadzu RF-1501 spectrofluorometer. Excitation and emission wavelengths for the ethanol/water mix were 535 and 545 nm, respectively, with a detection limit for RWT of 0.2 µg/l.

## Batch Adsorption Tests

Batch tests investigating RWT adsorption processes were carried out under static conditions. Three sets of experiments were carried out to determine equilibration times, resin adsorption capacity and the effect of pH and RWT concentration on RWT adsorption. Resin adsorption of RWT over time was investigated by adding 0.4 g of resin to 5-l duplicate solutions for RWT concentrations of 100 and 1,000 µg/l. These solutions were mixed continuously. Small aliquots of these solutions were removed for RWT concentration analysis at regular intervals over an 8-day period.

The RWT adsorption capacity of the resin and the influence of initial RWT concentration on adsorption was measured by adding 0.4 g of resin to RWT solutions with concentrations ranging from 20–45,000 µg/l. The solutions were continuously stirred and, once an equilibrium state was reached, the resin was removed and the final solution concentrations were measured to indicate the amount of RWT adsorbed. This procedure was repeated using a constant initial RWT concentration (500 µg/l) and with varying the solution pH between 4–11, in order to investigate the effect of pH on the adsorption process.

Figure 2 shows that the adsorption of RWT by the resin was rapid in the first 24 h, particularly in the first 3 h, followed by a slow sorption until about 96 h, after

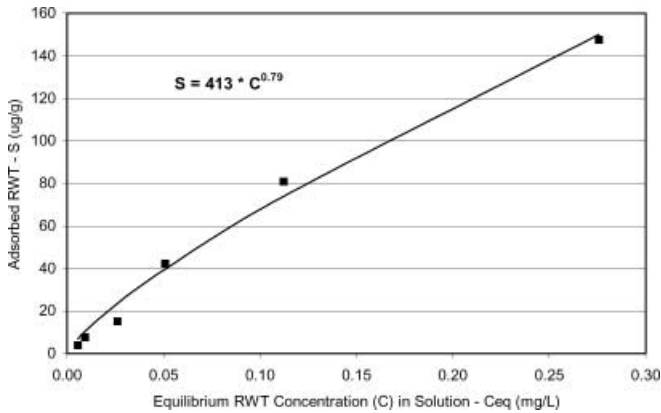**Fig. 2** Adsorption of RWT by XAD-7 resin with time
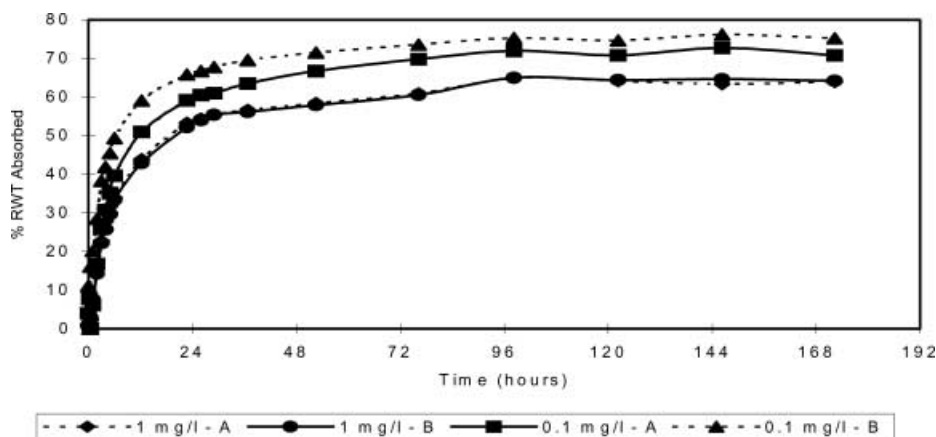
**Fig. 3** Freundlich isotherm for XAD-7 resin adsorption of RWT (for initial RWT concentrations <1 mg/l)



**Fig. 4** The effect of pH on XAD-7 resin sorption of RWT

which it appears to be at equilibrium. About 75 and 65% of RWT was adsorbed for initial solutions of 100 and 1,000 μg/l, respectively. The adsorption capacity of the resin is calculated to be more than 5 mg/g of resin from these results. In a practical sense, this is a very high RWT capacity and would seldom, if ever, be exceeded in a field situation.

The percentage adsorption of RWT for solutions with initial concentrations from 20–1,000 μg/l ranged between 68–77%. For initial concentrations of 4.5 and 8.9 mg/l RWT the percentage sorption was around 65%, and for an initial concentration of 45 mg/l RWT the percentage sorption was 44%. As the adsorption was non-linear a Freundlich isotherm was fitted to the data.

$$S = K_f C^N$$

where $S$ is the mass adsorbed per mass of resin, $C$ is the equilibrium aqueous concentration, $K_f$ is the Freundlich sorption coefficient and $N$ is the Freundlich exponent. The Freundlich isotherm for the solutions with initial RWT concentrations under 1,000 μg/l is shown in Fig. 3. $K_f$ was estimated as 413 (mg/g)/(mg/l)$^N$, indicating that the XAD-7 resin is an excellent sorbant of RWT. The Freundlich exponent, $N$, which gives a measure of non-linearity of the adsorbance with concentration, was calculated to be 0.79, indicating a slight decrease in sorbancy as RWT concentrations increase. Freundlich isotherms have been used to describe RWT adsorption to natural sand alluvium by Sabatini and Austin (1991). The observed $K_f$ values were much lower for the natural sand alluvium (six orders of magnitude) compared with the resin, as would be expected.

There was some effect of pH on the XAD-7 resin sorption of RWT. Figure 4 indicates that the resin adsorbs more than 75% of the RWT at all pH levels between 4–11 with adsorption increasing to around 90% in both acidic and alkaline conditions. This is a result of the interaction between the chemical structures of XAD-7 resin and RWT. XAD-7 resin is a macroreticular aliphatic polymer resin that absorbs large hydrophobic (non-polar) compounds from polar solvents such as water.
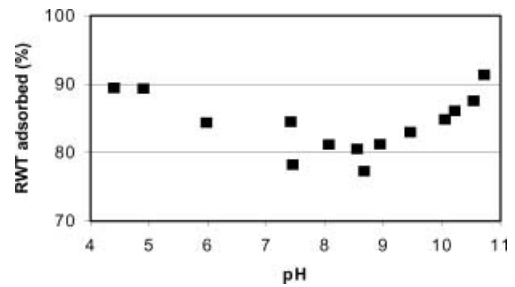
RWT is a large aromatic compound with two carboxylic acid groups and two dimethyl amide groups attached (Fig. 1). Protonation of the carboxylic acid group occurs at low pH, which decreases the charge associated with the RWT, thus increasing the hydrophobicity and absorption by the resin. However, above pH 9 deprotonation of the amide groups occurs, also resulting in decreased hydrophobicity and increased absorption. Although adsorption is least between pH 6–9 (pH found in most natural waters) it is still sufficiently high for the required purpose.

In summary, the batch adsorption tests indicated that the adsorption of RWT was reasonably rapid and was largely complete in the first 24 h, although some further adsorption did occur up to 96 h. The adsorption capacity of the XAD-7 resin was high and unlikely to be exceeded in a field tracing situation, there was a slight effect of pH on adsorption but sorption was greater than 75% for all pH values, and the sorption was slightly non-linear and fitted a Freundlich isotherm.

## Laboratory Column Tests

Small plastic columns with chambers (φ=12 mm, L=16 mm) were constructed to house one resin bag and ensure all flow passed directly through the bag. Peristaltic pumps were used to pass a known constant flow though the resin bags. The cumulative flow was also measured independently for each chamber system.

Column experiments were carried out to investigate both the RWT adsorption process, and the potential desorption of the dye back into the water after the RWT peak has passed. The first set of column experiments examined the effect of flow velocity, RWT concentration and time on RWT adsorption. Flow velocities of 1.5, 10, 25 and 300 m/day were used. At each flow velocity, RWT solutions of 5, 50, 200 and 1,000 μg/l were injected through the resin bag chambers for 1 h, with resin bags being removed in triplicate and extracted after 30 min and 1 h. The effects of initial RWT concentration, flow velocity and time on the percentage mass recovery were assessed using multiple regression analysis. A second set of column experiments were carried out to investigate the potential desorption of the dye back into the water after the RWT peak has passed. The experi-
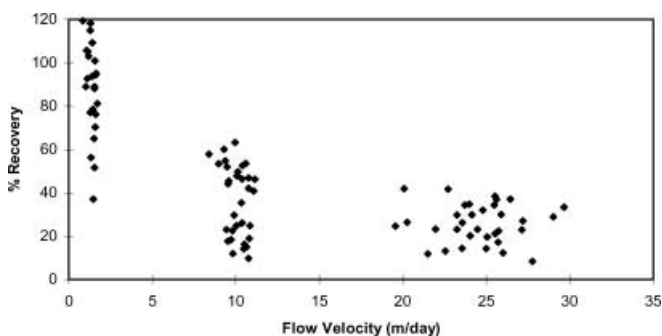
**Fig. 5** The effect of flow velocity on mass recovery of RWT from the resin for flow velocities <30 m/day



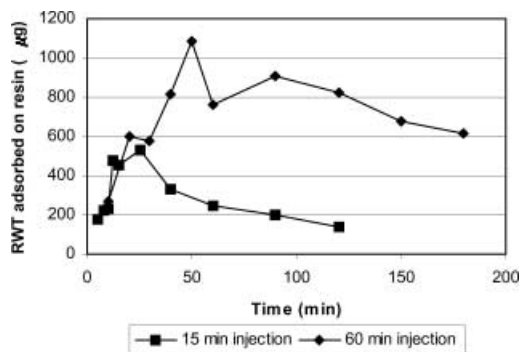**Fig. 6** The sorption pattern of RWT onto XAD-7 resin at a flow velocity of 300 m/day for injection times of 15 and 60 min

ments used input RWT concentrations of around 200 µg/l and a flow velocity of 300 m/day, with ten resin bag chambers being set up in parallel. The RWT solution was injected for either 15 or 60 min and then the injection solution was switched to water for the following 2 h. During the RWT injection period, resin bags were removed and extracted every 2–3 and 10 min for the 15- and 60-min injections, respectively, and resin bags were removed and extracted every 30 min during the water-flushing period.

In the first set of column experiments there was a strong linear relationship between the initial RWT concentration and the RWT mass recovered off the resin at a constant flow velocity ($r^2$=0.93, $n$=9 for experiments at 1.5 m/day), consistent with the batch test findings. There was no relationship between the injection time and the percentage RWT sorbed to the resin ($r^2$=0.02, $n$=93), indicating that the mass flux is the important parameter. The percentage mass recovery decreases with increasing flow velocity (Fig. 5), with the average mass recovery for a velocity of 300 m/day (not shown on the graph) of 4%. There is some scatter in the data, probably because of differences in the input concentrations combined with the non-linear adsorption isotherm. The decrease is non-linear with flow velocity and is probably a residence time effect. As the flow velocity increases, the residence time decreases and there is a decreasing percentage of the RWT coming into contact with the resin for sufficient time to be adsorbed onto the XAD-7 resin sites. The multiple regression analysis of the first set of column experiments (Table 3) demonstrates the effect of injection concentration, injection time and flow velocity

on the per cent mass recovery of RWT. The flow velocity was a very significant effect whereas the injection concentration was less significant and the injection time was not significant at all.

The second set of column experiments examined the adsorption characteristics of RWT onto the resin under flowing conditions as well as the desorption of the RWT from the resin after the RWT concentration peak has passed through and the resin bag was being flushed with fresh water (Fig. 6). The flow velocities used were extremely high (300 m/day) and desorption was expected to be greatest in this situation. There is a fairly linear adsorption pattern with the amount of RWT adsorbed increasing with time and mass flux during the injection stage. However, during the flushing stage, significant desorption occurred at this flow velocity (Fig. 6). The desorption increased with increasing flow velocity, as would be expected, and other column experiments carried out for flow velocities under 15 m/day indicate that desorption is much more limited (<10% in 2 days and 25% in 5 days).

The column experiments showed that there was constant adsorption of RWT with increasing time and RWT concentration, consistent with the batch results, but that the mass recovery decreased with increasing flow velocity. If the resin bags were left in the water after the RWT peak had passed then some RWT would desorb, with the rate of desorption increasing with increasing flow velocity. At low to moderate flow velocities (<15 m/day) desorption should not be a problem, but it could be a concern at higher flow velocities.

## Field Tracer Experiments

### Burnham Field Site

The first field experiment was conducted on a site located at Burnham, Canterbury, New Zealand. The geological formation consists of well-sorted, little weathered fluvioglacial outwash gravels with varying proportions of sand, silt and clay, and is part of the Central Plains Aquifer system. The groundwater level varies annually between 9 to 14 m below ground level (b.g.l.). The

**Table 3** Multiple regression analysis for the first set of column experiments

Dependent variable: percentage mass recovery of RWT

| Effect | Coefficient | $t$ | $p$ (2-tail) | $n$ |
|---|---|---|---|---|
| Constant | 51 | 5.08 | <0.0005 | 90 |
| Injection concentration | –0.018 | –2.34 | 0.022 | 90 |
| Injection time | 6.2 | 0.53 | 0.597 | 90 |
| Flow rate | –0.25 | –3.69 | <0.0005 | 90 |

**Fig. 7** Layout of wells at Burnham experimental field site with maximum RWT concentrations observed in each well. RWT concentrations for wells 1, 2, 4, 6, 7 and 10 are from this experiment and those from wells with an asterisk are from a similar experiment in May 1995 (Pang et al. 1998)
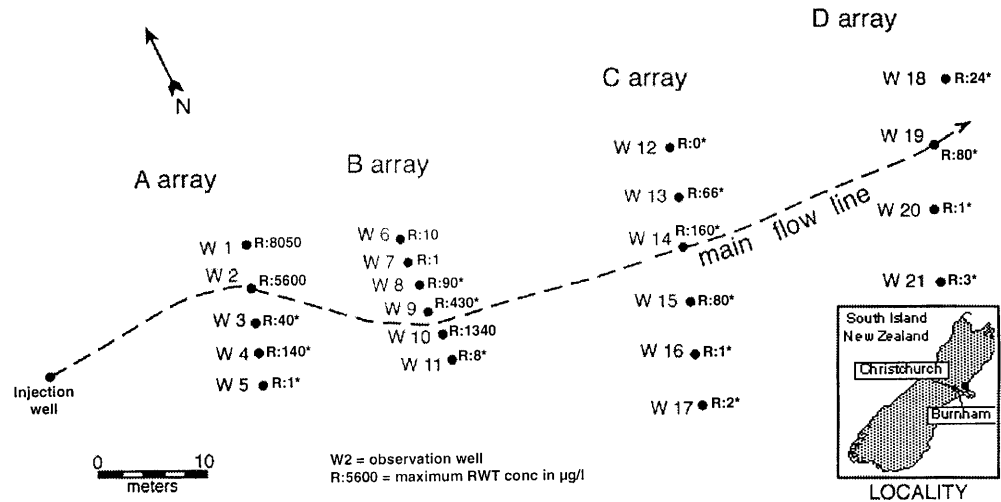
groundwater flow direction in the study site is easterly toward the ocean with an overall hydraulic gradient of about 0.0012. The pore water velocities are high with a range of 24–100 m/day and a median of 60 m/day (Pang et al. 1998). Hydraulic conductivity values measured from pump tests range from 10–5,600 m/day in the Central Plains Aquifer system close to the study site (Environment Canterbury, unpublished data), and have been measured between 5,000 and 14,000 m/day at this experimental site using well tracer tests (Pang et al. 1998). The site includes 22 wells with one injection well and 21 observation wells situated in four arrays at approximately 20, 40, 65 and 90 m down-gradient of the injection well (Fig. 7). All wells had a diameter of 100 mm and had slotted PVC screens from 12 to 18 m (screen porosity approximately 20%). Earlier site characterisation experiments had established the main flow line and groundwater dispersion characteristics at the site (Pang et al. 1998).

Forty litres of RWT (concentration =880 mg/l) was injected into the injection well between 13.5 to 15 m b.g.l. using a well packer, which was kept inflated throughout the experiment. Resin bags, which contained exactly 0.4 g of washed XAD-7 resin, were placed in triplicate at various depths in four down-gradient wells (wells 1, 4, 6 and 10). Six duplicate sets of resin bags were placed in wells 2 and 7. The injection concentration and the observation wells used were based on results from previous experiments at the site. Wells 1–4 and 6–10 were approximately 20 and 40 m down-gradient from the injection well, respectively (Fig. 7). The resin bags only occupied a small volume within the well screen, so there should be little disturbance of groundwater flow within the well because of the resin bags. Each resin bag was able to intercept the total mass of dye passing through that point, based on the mass flux of RWT, the cross sectional area and the sorption capacity of the resin. Along with the resin bags, manual sampling tubes were also placed in the well at the same depths as the resin bags. Hourly manual water samples were taken
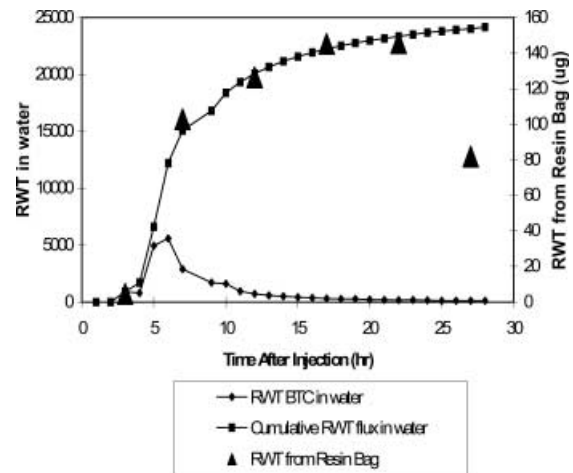


**Fig. 8** A comparison of RWT in water samples with the amount of RWT adsorbed and extracted from the resin bags in well 2. Units for RWT BTC in water =μg/l; units for cumulative RWT flux in water =μg. Note the *dual labels* for the vertical axis

to give RWT concentration breakthrough curves. The triplicate bags were collected 28 h after the injection, allowing sufficient travel time for the dye tracer to pass through the well array. Sets of duplicate resin bags were removed every 3 and 4 h from wells 2 and 7, respectively, to enable time series analysis. The mass of dye intercepted in the resin bags was then extracted and measured fluorometrically.

RWT was detected in 8 of the 11 well/depth combinations that were monitored (Fig. 7). The groundwater flow direction, which was variable over the site and reflected the fluvial deposition pattern, could be clearly seen both from the RWT peak concentrations (Fig. 7) and the amounts of RWT extracted from the resin bags. Of the two wells sampled throughout the experiment (to give a time series record of RWT sorbed to the resin), there was very little RWT detected in well 7, so only the time series record from well 2 is shown (Fig. 8). The cumulative

**Fig. 9** Comparison of cumulative RWT mass from water samples with RWT extracted from the XAD-7 resin for each well/depth for Burnham field experiment
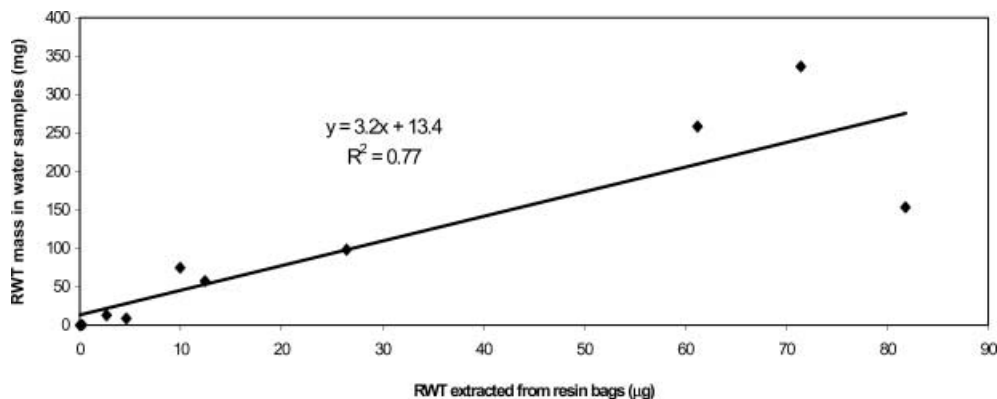


RWT mass in the water samples was calculated by averaging sequential RWT concentrations from the RWT breakthrough curve (BTC) and multiplying this with the time difference between the measurements, the flow velocity and the cross-sectional area of the resin bag. Figure 8 shows excellent agreement between the cumulative RWT mass in the water samples and the mass of RWT extracted from the resin bags. After the RWT peak concentrations passes through the well, adsorption to the resin bag slows in parallel with the cumulative curve. Adsorption continues until about 20 h when the RWT concentration in the well is such that RWT desorption becomes the dominant process. This desorption is clearly indicated by the extracted RWT concentration of the final resin bag taken at around 27 h, where the RWT concentration in the groundwater was less than 2% of peak concentrations. The desorption indicated by this last point (~40%) is likely to be the result of the high groundwater flow velocities of the site.

A comparison of total well mass flux of RWT and RWT extracted from the resin bags from all the wells monitored in the Burnham field experiment is given in Fig. 9. There is a good linear relationship between these two variables, as expected. The resin bags were all taken from the wells at the end of the experiment, 28 h after injection, and there was probably some desorption of RWT from wells 1 and 4. These were located 20 m from the injection well (Fig. 7), similar to well 2, and would probably experience similar levels of desorption as observed for well 2 (Fig. 8). There was also a very good correlation between the mass of RWT extracted from the resin bags and the peak concentrations observed in the monitoring wells ($r^2=0.88$, $n=10$). Both the peak concentration and the total mass flux are useful parameters in characterising groundwater flow and for designing more detailed groundwater tracing experiments. The amount of RWT extracted from the resin bags ranged between 0.3–3.7% of the total RWT mass estimated from the water samples. These recoveries are lower than those observed in laboratory column experiments (3.5–4.1%) for flow velocities of 300 m/day and much lower than recoveries observed at around 25 m/day (10–40%). This is probably because of the desorption of RWT noted above, and the fact that all the water was directed through the resin bags in the column experiments, whereas this was not possible in the field experiments. The per cent mass recoveries estimated for the time series in well 2 ranged from 4.3% at 3 h, 2.4–3.2% between 7 and 22 h, and 1.3% at 27 h (Fig. 8).

### Hamilton Field Site

The second field site is located near Hamilton, Waikato, New Zealand. The unconfined aquifer material consists of alluvial pumice sand derived from volcanic deposits. The overlying allophanic soils are formed from silty/sandy alluvium of volcanic origin. A 30-cm-thick silt layer occurs about 5.5 m below ground level forming an aquitard. Five 15-mm-diameter piezometers were placed in an arc covering 110°, 1.5 m from an injection well (diameter 50 mm). They were spaced 0.65 m apart with their installation depth just above the silt layer. Water column depths in the piezometers measured at the time varied from 0.23–0.7 m, indicating some variation in the depth of the aquitard. The in-situ groundwater was near neutral with a pH value of 6.8 (Table 1). The hydraulic conductivity of the aquifer material estimated from two pump tests was around 100 m/day. The tracer test described here has been analysed by Pang and Close (2001) and the derived groundwater flow velocity was 0.44 m/day. Further details concerning the field site are contained in this reference.

This site was chosen to test the resin bags as there was an ongoing pesticide leaching trial that included monitoring of the shallow groundwater and the flow direction of the shallow groundwater was uncertain at the site. An earlier tracer experiment carried out about 100 m south of the wells used in this experiment, had indicated that the flow direction was east-south-east (about 110°), which was similar to the direction derived from the piezometric contours (Hadfield et al. 1999). However, results from the groundwater monitoring of tracers and pesticides indicated that the flow direction was much more towards the south. This tracer experiment using the resin bags was used to determine the groundwater flow direction at the actual pesticide-leaching trial site.

Resin bags were placed in triplicate down the five piezometers along with Teflon manual sampling tubes. Six

litres of RWT (concentration =168 mg/l) was injected into the injection well over 30 min so that groundwater mounding was avoided. Manual groundwater samples were taken daily for 24 days using a syringe and analysed for RWT. After the 24-day monitoring period, the resin bags were removed, extracted and fluorometrically analysed.

RWT was only detected in one of the five wells monitored, which indicated that the groundwater flow direction was south-south-west (about 194°). This was consistent with the general direction from the pesticide-leaching trial, but very different (about 88°) from the earlier experiment 100 m away. The difference in local flow direction of that distance probably reflects the variable permeability of the shallow alluvial sand and changes in depth of the aquitard (about 5.5 m b.g.l. at the site compared with about 9 m b.g.l. 100 m away).

The only information available for comparison with the laboratory and Burnham field experiment results was the amount of RWT extracted from the resin bags as a percentage of total RWT mass estimated from the water samples. For the Hamilton experiment, this was 3.0% compared with the 0.3–3.7% range observed at the Burnham site. A much higher recovery would be expected because of the lower groundwater velocity at the Hamilton site. The column experiments would suggest a value in the vicinity of 40–90%. The low value observed is probably a reflection of RWT desorption from the resin. This desorption had such a marked effect because the resin bags were not removed from the groundwater until 23 days after the experiment began, which was 20 days after the RWT peak had passed through the well. The delay in removal of the resin bags was because of a long tail for the RWT BTC in this well with RWT concentrations around 10% of the peak concentration 16 days after the experiment began. However, even with the observed desorption, the groundwater flow direction was clearly identified at both field sites. Analysis of the duplicates and triplicates from both field experiments indicates that the results of resin bags were reproducible with a mean coefficient of variation equal to 16%.

## Discussion

RWT combined with the resin bags clearly indicated the groundwater flow direction in both the field experiments. In both situations, the design of the intensive water sampling, which occurred alongside the resin bags to demonstrate the technique, was significantly assisted by previous experiments at the sites giving general flow direction and flow velocities. In the absence of this information groundwater tracing experiments can be very time-consuming and wasteful of resources, often with many sampling points being intensively sampled and then found to be outside the contamination plume. On a local scale, generally, water levels cannot be measured with sufficient accuracy to determine piezometric contours and, hence, flow directions on the scale of the field examples in this paper.

There has been recognition recently that commercially available RWT, such as used in this study, consists of two isomers that exhibit different adsorption properties (Shiau et al. 1993; Sutton et al. 2001). This can have implications regarding the use of RWT as a tracer in many groundwater environments. However, the adsorption of RWT onto the XAD-7 resin shown in Fig. 2 is sufficiently rapid and the determination of groundwater flow direction as presented in this paper is not compromised by the presence of two isomers in the commercial formulation of RWT.

The field applications presented here are for an alluvial gravel aquifer with high groundwater pore velocities (20–100 m/day) and for an alluvial sand aquifer with much lower groundwater velocities (~0.4 m/day). It was tested in the laboratory for flow velocities between 1.5 and 300 m/day. This technique should work adequately within this range of groundwater velocities. The earlier work on cotton detectors and optical brighteners as tracers by Smart (1976) and Thrailkill et al. (1983) was for its application in karst systems. The use of RWT combined with XAD-7 resin should have good application in karst hydrology, as well as in fractured rock systems, where it is very difficult to predict flow directions and contaminant pathways. The main limitation of this method is the necessity to have access to the groundwater so that the resin bags can be placed in possible flow paths. This is a common limitation. It is much less of an issue if springs are used or for a karst system where there is often multiple access points or discharges. If wells need to be installed then, ideally, information would be available before the expense of well installation rather than afterwards, to guide the selection of well locations. However, there are many situations where only general information is available and wells are installed in a progressive manner, and this is where this technique would be useful in determining where further monitoring wells should be installed prior to intensive groundwater characterisation or tracing experiments.

## Conclusions

Amberlite XAD-7 resin was found to be suitable for adsorption of RWT from flowing water, which can then be extracted using an ethanol/water mix and analysed fluorometrically. The adsorption of RWT onto the resin was reasonably rapid and largely complete in the first 24 h. XAD-7 resin has a high capacity for RWT, which is unlikely to be exceeded in a field tracer situation. There was a slight effect of pH on adsorption, but sorption was greater than 75% for all pH values. The resin had a high percentage mass recovery at low flow velocities (~1.5 m/day), but the per cent mass recovery decreased with increasing flow velocity. Desorption of RWT off the resin in water can occur and depends on the flow velocity of water and the time after the peak RWT has passed. The mass of RWT extracted from the resin bags correlated very well with both the RWT mass flux in the water

and the peak concentrations observed in the monitoring wells. The results of resin bags were reproducible with a mean coefficient of variation equal to 16%. This method has been successfully applied to two field situations with different groundwater pore velocities (0.4 m/day and around 60 m/day) to indicate groundwater flow paths.

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