An edited version of this paper was published by AGU. Copyright (2019) American Geophysical Union.

Depth-resolved groundwater chemistry by longitudinal sampling of ambient and pumped flows within long-screened and open borehole wells

David L. Poulsen\textsuperscript{1,2}, Peter G. Cook\textsuperscript{1,2}, Craig T. Simmons\textsuperscript{1,2}, D. Kip Solomon\textsuperscript{3}, Shawan Dogramaci\textsuperscript{2,4}

\textsuperscript{1}College of Science and Engineering, Flinders University, Adelaide, Australia
\textsuperscript{2}National Centre for Groundwater Research and Training, Flinders University, Adelaide, Australia
\textsuperscript{3}Department of Geology and Geophysics, University of Utah, Salt Lake City, USA
\textsuperscript{4}Rio Tinto Iron Ore, Perth, Australia

Key Points:

• Sampling ambient vertical flows can provide more insightful data than sampling pumped flows
• Ambient flows can be sampled without purging or pumping the well
• In-well samples are either from a discrete source or the mixture can be deconvolved

Accepted in Water Resources Research 28 October 2019
DOI: 10.1029/2019WR025713

Corresponding author: D.L. Poulsen, david.poulsen@flinders.edu.au
Abstract
Depth-resolved chemistry samples are critical to a wide range of groundwater investigations. If a well intersects zones of variable concentrations, a pumped sample is a composite of the inflows, which mix in the well. Where discrete concentrations are required, excessive mixing makes samples less useful and potentially misleading. However, installations for depth-discrete sampling are expensive, particularly for regional studies, so sometimes there is incentive to use existing infrastructure designed for other purposes (e.g. supply wells). This paper shows how the resolution of groundwater chemistry derived from long-screened and open borehole wells can be improved by measuring and sampling the in-well vertical flow regimes in ambient (un-pumped) and/or pumped conditions. The ambient flow regime, driven by a natural vertical head gradient, is shown to be particularly useful to sample groundwater native to defined inflow zones (head in the zone > head in the well), and avoid zones impacted by the invasion of intraborehole flow (head in the zone < head in the well). Depth-specific samples are interpreted either as native groundwater from a discrete source, subject only to analytical error, or a mixture from multiple sources that can be deconvolved, incorporating error in both flow and concentration measurement. Depth-resolved age tracers (CFCs, $^{14}$C and He) in groundwater from three supply wells are verified with samples from a multi-depth nest of piezometers. Results show old groundwater at all depths and the simultaneous occurrence of young water at shallower depths in undisturbed dual-porosity fractured aquifers in the Pilbara region of Western Australia.

1 Introduction
Groundwater chemistry sampled from wells is used to define contaminant plumes (e.g. Einarson, 2006), determine sources of nutrient pollution (e.g. Kendall & Aravena, 2000; Widory et al., 2005) and to assess the timescales of groundwater flow and solute transport using environmental tracers (e.g. Cartwright et al., 2017; Cook & Herczeg, 2000), among many other types of investigation. If the screened or open interval of a well intersects different concentrations, a pumped sample will give some mixture of them. The chemical composition of a sample is affected by the position and length of the well screen with respect to the intersected distribution of hydraulic conductivity and head (Einarson, 2006; Brassington, 1992), the pumping rate at which the sample was obtained (McMillan et al., 2014; Poulsen et al., 2018), and the history of ambient vertical flow through the well prior to sampling if it has been left un-pumped (Elçi et al., 2001; Mayo, 2010; McDonald & Smith, 2009; McIlvride & Rector, 1988; Poulsen et al., 2018; Reilly et al., 1989; Silliman & Higgins, 1990; Shapiro, 2002). These factors could cause a constituent of interest to be overestimated, underestimated or missed entirely if the composite sample is not correctly interpreted.

The representativeness of a sample depends on the aims and scale of investigation (Claasen, 1982; Neilsen & Neilsen, 2007). High-resolution contaminant monitoring requires samples from very discrete depth intervals (e.g. < 1 m), whereas regional scale environmental tracer studies can use data from somewhat larger intervals. Although groundwater usually contains a range of ages at any depth simply due to the tortuosity of flow paths through porous media (e.g. McCallum et al., 2015), the value of age tracers is diminished by excessive mixing in wells (Cook et al., 2017; McCallum et al., 2014; Müller et al., 2016), and bias caused by recovery of ambient flows (Poulsen et al., 2018; Zinn & Konikow, 2007).

The ideal approach for reliable depth-resolved sampling is to use a multi-depth nest of piezometers or an engineered multi-port system. These installations are necessary for contaminated sites (usually shallow depths) and detailed investigations, to ensure accuracy of samples and avoid aquifer cross-contamination. However, their cost escalates for more regional scale studies, particularly when a large vertical interval of an aquifer sys-
tem needs to be investigated. There is therefore a financial and practical incentive to make the most of existing infrastructure, including supply or dewatering wells that have long-screened or open intervals. The challenge with such wells is to identify the depth interval and chemistry of specific inflows. Although straddle packers can be used in some situations, they are compromised where flow can bypass the packer through the gravel pack around the well screen, between a packer and a rough borehole wall or even in the formation adjacent to the packer (Nilsson et al., 1995; Taylor et al., 1990). A range of alternative methods to identify the composition of inflows have been reported. Baffle systems and separation pumping (Harte, 2013; Lerner & Teutsch, 1995) are complicated, equipment- and labour-intensive, and uncertain. An approach that has found more widespread practical application uses the flow regime in the well while it is being pumped. Depth-specific samples and measurements of vertical flow rate before and after inflowing zones are combined in a mass balance to identify the concentration of inflowing groundwater. Collar and Mock (1997) appear to be the first to report this method, but it was subsequently adopted by the US Geological Survey (Izbicki et al., 1999; Izbicki, 2004) and used to identify water quality issues (arsenic and salinity) in operational supply wells (Goldrath et al., 2015; Halford et al., 2010; Izbicki et al., 2008, 2010, 2006, 2005; Jurgens et al., 2014; Landon et al., 2010; O’Leary et al., 2012, 2015; Smith, 2005). Because these wells were always pumped at a high rate, ambient flows did not occur and it could be assumed that all inflows were groundwater native to the source interval. However, where such wells are left un-pumped, the vertical flow regime, driven by a natural vertical head gradient, is highly relevant, presenting both a problem and an opportunity.

Ambient flow is very common in un-pumped wells (Elçi et al., 2003), and over time a plume develops in the aquifer zone(s) with lower head, displacing the native groundwater. The problem is that a pumped sample is then biased towards the chemistry of the zone with higher head until such time as the plume is removed, which is often prohibitively large (e.g. Mayo, 2010; Poulsen et al., 2018, 10^3 well volumes). The opportunity offered by an ambient flow regime is that the higher head zone(s), constantly producing native groundwater, can be directly sampled without purging or pumping. This was suggested in discussion by Shapiro (2002), and by Paillet (2004) with reference to one field application (Paillet & Thomas, 1996), but the concept does not appear to have been explicitly presented in the literature.

To this end, in this paper we comprehensively show how the groundwater chemistry of discrete intervals within a long-screened well can be determined from depth-specific sampling in the ambient and/or pumped flow regimes. A key point of difference from previous studies is the focus on the ambient flow regime, which can actually provide better sampling conditions than while pumping. We verify the approach with discrete samples from a nest of piezometers, and in doing so provide insight into the range of ages present in an undisturbed groundwater system in the Pilbara region of Western Australia.

2 Theory

Figure 1 shows a conceptual diagram of a groundwater system including three aquifers separated by aquitard material. An ideal sampling installation provides representative samples from short screens isolated in each aquifer (Figure 1a). In contrast, a long-screened well connects these aquifers and provides some mixture of the inflows, which mix in the well when it is pumped (Figure 1b). If the well is left un-pumped, intraborehole flow redistributes water between aquifers (Figure 1c). Aquifer-well fluxes depend on the hydraulic head in the well (h_{av}) relative to head (and transmissivity) in the intersected aquifer intervals (h_1, h_2, h_3 ... h_z). Figure 1a shows the head in each of the three hypothetical aquifers, indicating a downward vertical gradient. When pumped, drawdown in a well may or may not be sufficient to create inflow at all depths (McMillan et al., 2014; Poulsen et al., 2018). In Figure 1b the pumping water level in the well is below the head in all three aquifers, so all are inflowing. But, when the well is not being pumped (Figure 1c)
its water level is some average of the three aquifers, according to the intersected hydraulic conductivity and head distribution (sometimes referred to as the blended water level (e.g. Quinn et al., 2015)). In this example, water inflowing from the first two aquifers (A1 and A2) moves vertically downwards in the well and outflows into the third aquifer (A3), displacing the native groundwater. A subsequent pumped sample would be biased towards the chemistries of the first two aquifers, and the third aquifer is not sampled until the intraborehole flow plume is purged. Purge volumes can be excessively large because plume volumes are large (ambient flow rate multiplied by length of un-pumped period), only a fraction of pumped discharge is sourced from the affected zone (unless packers are used), and matrix diffusive processes may delay recovery of some invading water.

For a well affected by intraborehole flow, we contend that a clearly defined ambient flow regime actually provides better sampling conditions than the pumped regime (potentially making the latter unnecessary). This is because the in-well chemistry at all depths is the product of an established flow regime, and inflows are exclusively from zones that produce native groundwater. In contrast, pumping alters the pre-existing flows and a certain time is required for the chemistry at all depths in the well to be representative of the new flow regime. Although a hydraulically steady flow regime occurs as soon as drawdown stabilises, a chemically steady regime is not reached until the inflow located furthest from the pump reaches the pump (Reilly & LeBlanc, 1998; Martin-Hayden, 2000; Martin-Hayden et al., 2014) and inflow compositions stabilise (e.g. following purging of an intraborehole flow plume). This travel time is a function of the inflow distribution.
to the well, and in particular it is inversely related to the fraction sourced from the inflowing zone most distant from the pump.

In a clearly defined and chemically steady flow regime, the chemistry at any depth in a well is a mixture of all upstream inflows (indicated by the grab samples in Figure 1b and 1c). If concentration and flow rate are measured before and after an inflow zone, then the concentration of the inflow is given by (Collar & Mock, 1997):

\[ C_i = \frac{Q_a C_a - Q_b C_b}{Q_a - Q_b} \] (1)

where the concentration \( C \) from a given aquifer interval \( i \) is calculated to explain the observed concentration change in the well at the measured flow rates \( Q \) before \( b \) and after \( a \) the producing interval. This assumes all significant inflows are accurately identified, complete mixing of inflow with flow already in the well, no loss of flow between the samples and that chemical alterations within the well are negligible. The resulting concentration is averaged either over a unique inflowing interval identified in the flow profile, or simply the spacing between the depth-specific samples. This approach is similar in many ways to using longitudinal sampling in a river to estimate the chemistry of groundwater inflows to the river (Batlle-Aguilar et al., 2014). As such, there is a minimum distance required for mixing of inflows with flow already in the well, which is much greater in laminar flows than turbulent flows. In either case the cross-sectional area of a well is usually small enough that the sampling process itself, even with low-rate pumping, will likely introduce convergent flow at the pump intake depth, thereby effectively sampling all flow lines in the well, even in an otherwise laminar flow regime.

3 Site Description

We applied this sampling approach in three inactive supply wells in the Pilbara iron ore mining region of Western Australia (Figure 2, Table 1). The wells are in the southeastern Hamersley Basin situated on relatively wide plains, which are surrounded by hills of banded iron formation and intersected by dykes and faults. Further information on the physiography, climate, geology and general hydrogeology of the area is available in existing publications (Cook et al., 2017; Dogramaci et al., 2012; Dogramaci & Skrzypek, 2015; Rojas et al., 2018). This paper mainly demonstrates the sampling concept and method, so we focus on the immediate borehole environment more than the broader hydrogeological context that would inform a particular avenue of investigation.

Lithological logs for the wells (Figure 3) indicate that the regional aquifer is mainly the Paraburdoo Member of the Wittenoom Formation, which is part of the Hamersley Group. This was logged as dolomite, but it is more widely known to include interbedded shale, dolomite, sandstone and mudstone. Groundwater flows mainly in weathered and fractured zones within this variably competent formation. The overlying Tertiary Detritals also variably form aquifers or aquitards depending on the amount of silt and clay matrix filling pore space in the sand and gravel. WB11AH001 intersected material logged as fault gouge, indicating a geological complexity at this location, which has deformed and smeared different formations together.

Well LHRP4 was installed in 2006 and is located on Pebble Mouse Creek, a tributary to Welli Wolli Creek (Aquaterra, 2007). Although relatively close to mining (~2 km, Figure 2b), it is unaffected by dewatering induced drawdown because an intervening dolerite dyke forms a hydraulic barrier (Figure 2c). Upstream of the dyke a modest hydraulic gradient (0.00015 m/m) prevailed, while across the dyke there was a 40 m drop in groundwater level. Records show that a water level drop across the dyke was present before mine dewatering commenced, but it was about half as much. Wells WB11AH001 and WB11HD6001 were installed in 2011 and they are remote from mining or notable surface water features (Aquaterra, 2011). Drilling was completed with mud rotary (LHRP4)
or air percussion (WB11AH001 and WB11HD6001) methods. The wells are constructed of machine slotted (1 mm aperture) PVC pipe with a nominal 0.2 m internal diameter, packed with graded (3.2 - 6.4mm) clean gravel, and completed at the surface with a concrete pad and cover (Figure 3). In LHRP4, telescoping borehole diameters were used (0.45, 0.32 and 0.27 m), while for WB11HD6001 and WB11AH001 the holes were consistently 0.3 m, giving a nominal gravel pack thickness of 50 mm. The gravel pack has much higher conductivity than the native geology (e.g. gravel: \(\sim 250\) m/d, dolomite: \(\sim 0.5\) m/d, Freeze and Cherry (1979)), except perhaps in the most productive aquifer zones, and as such it could act as a conduit for vertical flow outside the well casing. In LHRP4 the gravel pack above the screen may enable water from shallower depths to contribute to inflow at the top of the screen.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LHRP4</th>
<th>WB11HD6001</th>
<th>WB11AH001</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elevation, m AHD</td>
<td>621</td>
<td>669</td>
<td>665</td>
</tr>
<tr>
<td>Easting, m MGA Zone 50</td>
<td>715628</td>
<td>738339</td>
<td>741389</td>
</tr>
<tr>
<td>Northing, m MGA Zone 50</td>
<td>7452508</td>
<td>7442083</td>
<td>744794</td>
</tr>
<tr>
<td>Screen interval, m ToC</td>
<td>65.9-141.8</td>
<td>35.2-143</td>
<td>34.5-155</td>
</tr>
<tr>
<td>Diameter, m</td>
<td>0.195</td>
<td>0.203</td>
<td>0.203</td>
</tr>
<tr>
<td>Transmissivity, m²/d</td>
<td>2.91²</td>
<td>2.90-6³6⁰²</td>
<td>20³⁰²</td>
</tr>
<tr>
<td>Intraborehole flow, l/min</td>
<td>-6</td>
<td>-5 and +4</td>
<td>+1</td>
</tr>
<tr>
<td>Blended water level, m ToC</td>
<td>27.54</td>
<td>27.20</td>
<td>22.60</td>
</tr>
<tr>
<td>Drawdown @ 40 l/min, m</td>
<td>&lt;0.05</td>
<td>&lt;0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Well vol. (water filled casing/screen), litre</td>
<td>3420</td>
<td>3748</td>
<td>4285</td>
</tr>
<tr>
<td>Purged (start-end sampling), well vol.</td>
<td>4.6-6.5</td>
<td>3.0-5.0</td>
<td>2.8-4.1</td>
</tr>
</tbody>
</table>

\(^a\)Top of Casing (ToC) \(\sim 0.5\) m above ground level; \(^b\)(Aquterra 2007); \(^c\)(Aquterra 2011)

### 4 Methods

#### 4.1 Environmental Tracers

Environmental tracers that indicate groundwater age are used in this paper to demonstrate the utility of the sampling approach. Cook et al. (2017) describe the use of chlorofluorocarbons (CFCs) and radiocarbon \(^{14}\)C to characterise young and old groundwater respectively, in the context of this study area. In summary, CFCs are an event marker whose concentrations have increased from zero over the last 60 years due to anthropogenic release. The maximum expected concentration is approximately 180 pg/kg for CFC-12 in water that was recharged in the years 2003-2004. \(^{14}\)C activity in groundwater decreases with time by radioactive decay at a known rate (half-life of 5730 yrs) and this can be related to the time since recharge, in the age range of 200-30000 yrs. Here we consider the reported percent modern carbon (pmC) as an indicator of groundwater age, without applying any corrections for rock-water interactions. We also measured noble gases (He, Ne, Ar, Kr and Xe) and specifically looked at helium because its concentration in groundwater is known to increase with time due to radiogenic release from aquifer materials, among other sources (Solomon, 2000). Prior to recharge, precipitation in equilibrium with the atmosphere at this site will contain about 4.07×10⁻⁸ cubic centimetres of He per gram of water at standard temperature and pressure (ccSTP/g). A measurable increase of He in groundwater is expected after a residence time on the order of 10³ years for typical regional aquifers (Solomon, 2000).

#### 4.2 In-Well Flow Measurement

The in-well flow regimes were measured with an electromagnetic (EM) borehole flowmeter (Century Geophysical LLC, model 9721, response range 0.05–40 ±0.021/min). Measurements were made with the instrument held stationary at regular depths, and with
Figure 2. (a) Location of the study area in the Hamersley Basin, Western Australia; (b) location of the sampled wells in the study area, showing their proximity to the Hope Downs 1 (HD1) and Hope Downs 4 (HD4) mines; (c) locality of LHRP4 showing topographic elevation contours relative to the Australian Height Datum (m AHD), groundwater hydraulic head contours based on the blended water levels shown next to the symbols (m AHD, taken Jun-Aug 2016) and interpreted groundwater flow direction; (d) position of the multi-depth nest of piezometers adjacent to LHRP4, showing estimated mode of spreading of the intraborehole flow (IBF) plume from LHRP4 at 130-140 m depth. Piezometer completion depths are indicated, with groundwater elevations in brackets (m AHD, taken 30 Apr 2017).

Figure 3. Lithological logs, construction details and measured standing water levels (SWL) for the long-screened wells and piezometers adjacent to LHRP4. Diagrams not to scale. Piezometers are spaced approximately 10 m apart as shown in Figure 2d.
a flow diverter (rubber gasket) in the space between the instrument body and well casing, aiming to force all flow through the sensor. While this maximises the sensitivity to low flow rates, it has been found that friction related head loss becomes increasingly significant when flow through the sensor increases above a threshold of about 101/min (Arnold & Molz, 2000). Specifically, the nozzle equation given by Arnold and Molz (2000) indicates head loss across the sensor (0.025 m inside diameter) of 0.007 m at 101/min and 0.11 m at 401/min, the maximum flow rate used in this work. In comparison, water level drawdown in the wells used in this study was <0.05 m when pumping at 401/min. Given the highly productive nature of these wells we expect resistance to flow through the meter could be greater than that for inflow from the overlying zone between the meter and the pump (Zlotnik & Zurbuchen, 2003; Ruud et al., 1999), causing the meter to underestimate borehole flow at rates above about 101/min. Flow may also bypass the meter in the gravel pack (or void) around the well screen. This zone shrinks as the meter is raised in the well, and eventually all discharge is forced through the sensor at the top of the screen. Together these effects can result in an over-estimate of the fraction of inflow sourced from near the top of the well. We have not attempted to account for this head loss related bias in the analysis, but the 101/min threshold is indicated on the borehole flow plots, and it is dealt with where relevant in the results. In addition to this systematic bias in flow measuring, practical uncertainties with measuring the flow profiles include an imperfect seal of the flow diverter, and turbulence, which can cause random noise in the measurements. We represented this uncertainty in the analysis by assigning an error of ±5%. This compares to the generally much lower manufacturer-stated error of ±0.02 l/min in ideal conditions.

The flowmeter was calibrated in the water-filled blank casing above the top of the screen in each well. A stationary zero-flow point was followed by raising the instrument at a known rate and using the well diameter to calculate flow rate through the sensor. In pumped conditions, the stationary meter was also calibrated to the known discharge rate. Assuming the well diameter remains constant, any bypass flow due to an imperfect seal of the diverter in the well is built into the calibration.

4.3 Sampling and Analysis

Depth-specific samples were obtained from the ambient and pumped flow regimes in each of the three wells in late April 2018 with an air operated submersible piston pump (Bennett Sample Pumps, Inc., model 1400-6 ¾ inch). A low flow rate (0.5–11/min) was used so that the prevailing in-well flow regime was altered as little as possible. We had a priori knowledge of the ambient flow regime to inform the choice of sampling depths, so sampling was done on arrival at each well, at progressively increasing depths, prior to any other disturbance. After sampling, the ambient flow regime was measured to establish the conditions prevailing at the time of sampling. Then a pumped flow regime (401/min) was created with a submersible pump (Grundfos, model SQEN3) placed above the screen. Sampling commenced after between 3 and 6.5 well volumes had been purged, which occurred while the pumped flow profile was being measured. In the pumped flow regime the procedure started with a sample from just above the screen, followed by progressively increasing depths, and ending with another sample from above the screen. The samples from above the screen represent the composite of all inflows to the well, and the difference between these samples indicates the degree to which the chemistry of inflows was stable during the sampling procedure. At each depth, for both ambient and pumped sampling, the sampling line was purged of its volume (15 litres) and field parameters (electrical conductivity, pH, and reduction-oxidation potential) were observed to be stable before to sampling. In total about 30 litres of water was removed during sampling at each depth, which is approximately the same as the volume of water contained in 1 m of well casing, so the sample can be attributed to the intended depth even in a weak in-well flow regime.
Samples were collected for $^{14}$C, CFCs, noble gases and major/minor ion chemistry in new and unused containers, rinsed with sample prior to filling. Samples for $^{14}$C were collected in 500 ml High Density Polyethylene (HDPE) bottles and analysed at the GNS Science Rafter Radiocarbon Laboratory (New Zealand). Results are given as percent modern carbon (pMC) according to the convention described in Stuiver and Polach (1977), with a one standard deviation (1σ) analytical precision of between 0.3 and 0.4 pMC. Samples for CFC analysis were collected (bottom filled, zero headspace) in 125 ml clear glass bottles with metal lined screw lids and analysed for CFC-11, CFC-12 and CFC-113 concentrations at GNS Water Dating Laboratory (New Zealand). Only the CFC-12 values are included in this paper, as measured. The analytical precision (1σ) of these analyses was between 1.2 and 3.6 pg/kg for CFC-12, and the detection limit is approximately 5 pg/kg. However, sampling was done through nylon tubing, and this may introduce contamination of up to 5 pg/kg for CFC-12 (Cook et al., 1995). Together these errors mean that reported CFC-12 concentrations below about 10 pg/kg are generally indistinguishable from zero. We consider precision of the results by comparing duplicate samples, because this better represents variability due to common sampling issues with dissolved gases, as described by Cook et al. (2017). The difference between duplicate results was within 20% of the mean value for 75% of samples for CFC-12, suggesting that actual precision (2σ) is in the vicinity of ±20% for this range of measured concentrations. Samples for noble gases were collected in clamped copper tubes and analysed by the Noble Gas Lab at the University of Utah (United States). The total helium concentrations included in this paper have an analytical precision of about ±1%, but the absolute accuracy is ±5% because the high helium concentrations required splitting prior to inlet into the mass spectrometer. Major and minor chemical constituents were collected in 500 ml HDPE bottles and analysed at Australian Laboratory Services (ALS) in Perth. This paper also includes results of composite samples obtained from these wells in June 2016 using the same methods and laboratories. On that occasion, the wells were pumped from above the screen at 180 l/min, with a longer duration of purging (8-10 well volumes) prior to sample acquisition.

4.4 Interpretation

The depth-specific samples are interpreted in the context of the flow regime from which they were taken. In each flow regime, the most upstream sample is representative of the average inflow concentration from a single interval, and is subject only to the analytical error, reported here as the 95% confidence interval (2σ). Downstream samples are deconvoluted using Eq. (1), and the estimated inflow concentration is subject to errors in both the concentrations and flows measured in the well (as given above). A Monte Carlo approach was used to include the error associated with each parameter in the mass balance. The 95% confidence interval from 10000 iterations of a normally distributed variation of each parameter about the measured value is reported.

The profiles of measured in-well flow rates are interpreted to identify inflowing zones, and the increase of flow rate between each pair of depth-specific samples. The minimum significant inflow is relative to the magnitude of flow already in the well, and the concentration difference between inflows. A physical constraint on the combined interpretation of inflow rates and solute concentration is that concentrations cannot be negative, nor should they be unrealistically high. The practitioner must be alert to either of these situations, which indicate that either the flow profile is in error or that aquifer-well fluxes are more complex than conceived in this paper. We cover the difficulties with flow measurement and potential error in Section 4.2 and in the discussion (Section 6).

4.5 Multi-Depth Nest of Piezometers

As part of this study, five piezometers were installed (November 2016) in individual boreholes adjacent to LHRP4 (Figure 2d). Each piezometer has a single 2 m screen,
the bottom of which was placed at depths ranging from 40 to 140 m. This enabled us to assess the effectiveness of the approach for identifying discrete aquifer concentrations using the long-screened well (potential interaction between LHRP4 and the piezometers is discussed in Section 6). In all cases, a similar lithology was encountered to that in LHRP4 (Figure 3) with 56–62 m of gravelly clays (Tertiary Detritals) overlying dolomite (Parabur-doo Member of the Whitenoom Formation), which included calcareous sand between 108–120 m and 132–140 m. Drilling was achieved with air percussion (0.1 m diameter bore-hole) and the 50 mm machine slotted PVC piezometers were gravel packed, except for a 2 m bentonite seal placed just above the screen and a concrete surface collar. Unfortunately, the intervals above the bentonite seals were gravel packed instead of grouted, and these may act as conduits for some vertical flow along the boreholes. We acknowledge that this may cause cross-contamination of water between depths, potentially impacting the depth-discrete nature of samples from these piezometers. Although this remains an area of uncertainty, the data presented in this paper show significant differences of tracer concentrations with depth, so any such impacts appear to be minimal. Five months after installation the piezometers were developed by pumping at least 10 casing volumes from above the screen at 101/min with a submersible pump (Grundfos, model MP1). Draw-down was small in all piezometers (<0.4 m, except 2.2 m in the 60 m piezometer), indicating productive aquifer material was intersected. Later (September 2017), each piezometer was further pumped of 10-20 casing volumes before being sampled for the same suite of tracers as the adjacent long-screened well using the same methods. With dissolved gases being sampled (CFCs, noble gases), the large purge volumes, combined with the time elapsed since drilling, were aimed at removing any drilling related modern air contamination of the aquifer.

5 Results

Laboratory analysis of samples from the three long-screened wells (Table 2) returned in-well concentrations of CFC-12 ranging between 7.9 and 70.7 pg/kg, 14C between 17.1 and 25.7 pmC, He between $9.2 \times 10^{-8}$ and $4.9 \times 10^{-6}$ ccSTP/g and TDS between 489 and 611 mg/l. CFCs showed the most evidence of stratification so we use CFC-12 to demonstrate how chemistry measured in each well can be related to the chemistry of defined depth intervals in the surrounding aquifer. We then provide depth profiles for all four of these tracers and compare the interpreted aquifer concentrations from LHRP4 with those measured in the adjacent piezometers. As a general theme, the ambient flow regimes provided good estimates of aquifer concentrations from defined inflowing zones, while the pumped regimes were complicated by returning intraborehole flow.

5.1 LHRP4

The ambient flow profile from LHRP4 shows a downwards vertical flow regime (Figure 4a). Figure 4b illustrates this, with inflow of native groundwater from two main zones, one at the top (66–70 m, 3.51/min) and the other near the bottom (123–130 m, 1.51/min), and smaller contributions from the intervening interval (11/min), all of which outflowed back into the aquifer at the bottom of the well (130–140 m, 61/min). This shows a downward vertical head gradient in the aquifer system, which was confirmed by head measurements from the nested piezometers, with a decrease of 0.08 m between 40 and 140 m depth (Figure 2d). The sample taken at 70 m depth in the ambient regime is representative of native groundwater from the upper inflowing zone (which may include a contribution from the interval above the screen, flowing in the gravel pack), with 70.7 ±14 pg/kg of CFC-12 (Figure 4a). Below this there were considerable decreases in CFC-12 concentration but little increase in measured flow rate. This caused the mass balance to give negative concentration values for inflowing groundwater, which is impossible. However, zero CFC-12 (reasonable for low permeability material) is given by slightly increasing the proportion of inflow from this intermediate interval (70–115 m), bringing its con-
Table 2. All data derived from the long-screened wells, indicating inflow concentrations in the ambient and pumped flow regimes, either from a single sample or calculated using the flow rates and tracer concentration measured in the well before and after an inflow in Eq. (1). Samples are an average of all upstream inflows. Inflow concentrations are averaged over the interpreted source depth interval. Black coloured font indicates inflows that are considered representative (also shown in Figures 4-6 for CFC-12).

<table>
<thead>
<tr>
<th>Source depth interval (m)</th>
<th>Flow ratea (l/min)</th>
<th>14C (pmC)</th>
<th>CFC-12 (pg/kg)</th>
<th>He (ccSTP/g)</th>
<th>TDS (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHRP4</td>
<td>before</td>
<td>after</td>
<td>before</td>
<td>after</td>
<td>before</td>
</tr>
<tr>
<td>66-70</td>
<td>0</td>
<td>-3.57</td>
<td>25.4</td>
<td>25.4</td>
<td>70.7</td>
</tr>
<tr>
<td>70-95</td>
<td>-3.57</td>
<td>-4.17</td>
<td>25.4</td>
<td>25.7</td>
<td>70.7</td>
</tr>
<tr>
<td>95-115</td>
<td>-4.17</td>
<td>-4.35</td>
<td>25.7</td>
<td>13.6</td>
<td>51.4</td>
</tr>
<tr>
<td>115-135</td>
<td>-4.35</td>
<td>-5.96</td>
<td>25.2</td>
<td>24.2</td>
<td>-588</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source depth interval (m)</th>
<th>Flow ratea (l/min)</th>
<th>14C (pmC)</th>
<th>CFC-12 (pg/kg)</th>
<th>He (ccSTP/g)</th>
<th>TDS (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ambient flow regime (downward)</td>
<td>before</td>
<td>after</td>
<td>before</td>
<td>after</td>
<td>before</td>
</tr>
<tr>
<td>66-142b</td>
<td>0</td>
<td>180</td>
<td>24.8</td>
<td>24.8</td>
<td>9.0</td>
</tr>
<tr>
<td>66-142c</td>
<td>40</td>
<td>-25.6</td>
<td>30.2</td>
<td>30.2</td>
<td>9.0</td>
</tr>
<tr>
<td>66-142d</td>
<td>40</td>
<td>25.5</td>
<td>37.5</td>
<td>37.5</td>
<td>843</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source depth interval (m)</th>
<th>Flow ratea (l/min)</th>
<th>14C (pmC)</th>
<th>CFC-12 (pg/kg)</th>
<th>He (ccSTP/g)</th>
<th>TDS (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pumped flow regime (upward)</td>
<td>before</td>
<td>after</td>
<td>before</td>
<td>after</td>
<td>before</td>
</tr>
<tr>
<td>WB11HD6001</td>
<td>0.73</td>
<td>1.01</td>
<td>17.1</td>
<td>18.4</td>
<td>13.3</td>
</tr>
<tr>
<td>ambient flow regime (upward)</td>
<td>before</td>
<td>after</td>
<td>before</td>
<td>after</td>
<td>before</td>
</tr>
<tr>
<td>WB11AH001</td>
<td>0.35</td>
<td>1.01</td>
<td>17.7</td>
<td>16.6</td>
<td>10.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source depth interval (m)</th>
<th>Flow ratea (l/min)</th>
<th>14C (pmC)</th>
<th>CFC-12 (pg/kg)</th>
<th>He (ccSTP/g)</th>
<th>TDS (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pumped flow regime (upward)</td>
<td>before</td>
<td>after</td>
<td>before</td>
<td>after</td>
<td>before</td>
</tr>
<tr>
<td>34.5-155b</td>
<td>0</td>
<td>21.6</td>
<td>28.7</td>
<td>28.7</td>
<td>-</td>
</tr>
<tr>
<td>34.5-155c</td>
<td>40</td>
<td>20.8</td>
<td>17.5</td>
<td>17.5</td>
<td>-</td>
</tr>
<tr>
<td>34.5-155d</td>
<td>40</td>
<td>20.9</td>
<td>16.3</td>
<td>16.3</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source depth interval (m)</th>
<th>Flow ratea (l/min)</th>
<th>14C (pmC)</th>
<th>CFC-12 (pg/kg)</th>
<th>He (ccSTP/g)</th>
<th>TDS (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pumped flow regime (concurrently downward)</td>
<td>before</td>
<td>after</td>
<td>before</td>
<td>after</td>
<td>before</td>
</tr>
<tr>
<td>35-40</td>
<td>32.6</td>
<td>20.5</td>
<td>25.4</td>
<td>25.4</td>
<td>119</td>
</tr>
<tr>
<td>35-65</td>
<td>2.2</td>
<td>20.5</td>
<td>25.4</td>
<td>25.4</td>
<td>119</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source depth interval (m)</th>
<th>Flow ratea (l/min)</th>
<th>14C (pmC)</th>
<th>CFC-12 (pg/kg)</th>
<th>He (ccSTP/g)</th>
<th>TDS (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pumped flow regime (concurrently downward)</td>
<td>before</td>
<td>after</td>
<td>before</td>
<td>after</td>
<td>before</td>
</tr>
<tr>
<td>40-65</td>
<td>2.2</td>
<td>21.1</td>
<td>7.9</td>
<td>7.9</td>
<td>1.09e-7</td>
</tr>
</tbody>
</table>

*downward flow –ve, upward flow +ve; bcomposite sample taken in 2016; cstart and d end of depth-specific sampling.

Contribution to 27% of the total ambient flow (red line in Figure 4a). Although this flow profile is a slightly poorer fit to the flowmeter data it provides a plausible explanation for the measured CFC-12 concentrations. Beneath this, the measured difference of flow and concentration in the well before (115 m) and after (135 m) the distinct inflowing zone gave an inflow concentration of 18.5 ±39 pg/kg of CFC-12. This was only slightly affected (15.0 ±45 pg/kg) by the alternative flow profile fit in the overlying zone. The concentration of intraborehole flow invading the aquifer between 130–140 m is given by the sample from 135 m (38.1 ±8 pg/kg).
When LHRP4 was pumped, the same flowing zones were observed both using a borehole flowmeter (Figure 4c and 4d) and a tracer dilution test (Poulsen et al., 2019). Thus, all possible opportunities to sample aquifer chemistry were already provided in the ambient flow regime. The lowermost zone, which was not sampled in ambient conditions, only provided the returning intraborehole flow when pumped. This was evidenced by the high concentration of the sample from 135 m (55.6 pg/kg ±11 CFC-12), a depth at which native groundwater should have been near zero CFC-12 concentration (i.e. less than the overlying zone, identified in ambient conditions Figure 4a). The fact that the returning concentration was not identical to that of the invading ambient flow (38.1 ±8 pg/kg CFC-12) is probably due to variable outflow concentration over time, mixing in the aquifer, or/and imprecision in CFC measurements.

The flowmeter’s head-loss threshold (101/min, see Section 4.2 and Figure 4c) was exceeded above 130 m in the pumped regime, so flow was increasingly under-measured as it was raised in the well. This problem with flow measurement creates uncertainty with using the mass balance approach to calculate inflow concentrations from the in-well samples. Figure 4c shows two possible versions of the flow profile: one (black dashed lines) is consistent with the flow profile identified in the earlier tracer test (Poulsen et al., 2019) and allows the mass balance to give the inflow concentration from the 70–66 m zone identified in the ambient regime (i.e. a known concentration); while the other (red line) shows...
the flow required to explain the measured in-well concentrations in the 123–70 m interval by assigning the minimum possible concentration (i.e. 0 pg/kg CFC-12) to inflows. This 22% of total discharge is similar to the proportion of the ambient flow regime (27%) required to explain the same decreasing concentrations, but it is inconsistent with the flowmeter and tracer test, neither of which showed inflow from this interval. We provide further discussion of this situation in Section 6.

In terms of purging the intraborehole flow plume, we can look at the CFC-12 concentration of pumped discharge. Given that the invading plume contained more CFCs than native groundwater in that interval, we expect to see CFCs in discharge decrease with pumping, until the plume is fully purged. We obtained three composite samples from this well, each after different durations of pumping and found that this was indeed the case (April 2018: 37.5 ±8 pg/kg after 4.6 well vol. and 30.2 ±6 pg/kg after 6.5 well vol.; June 2016: 9.0 ±2 pg/kg after 8.3 well vol., Figure 4e). So evidently the pumped flow regime was not chemically steady during our sampling. However, we sidestep that, and the flow measurement problem, entirely because the ambient flow regime actually provided more reliable information on native groundwater inflows. Figure 4e shows these depth-resolved aquifer concentrations compared to results from the adjacent nest of piezometers (described further below and in Figure 7) and the pumped composite samples taken from LHRP4.

**5.2 WB11HD6001**

A weak upward ambient flow regime was present in WB11HD6001 (Figure 5a and 5b), with small inflows over much of the well (a similar flow profile was measured in June 2016). Flow rates were indistinguishable from zero below 140 m, but a distinct inflow (0.3 l/min) was measured between 137–140 m, which was captured by the sample at 136 m (13.3 ±3 pg/kg CFC-12). Above, the samples were widely spaced and changes in concentration were negligible until 40 m depth, where a significant increase was measured (27.2 ±5 pg/kg). If we take the overall change in flow and concentration between the samples from 70–40 m then the average inflow concentration would be 83.8 ±16 pg/kg. The upward ambient flow (totalling 1 l/min) then invaded the aquifer at the very top of the screen (40–34.5 m), with the outflowing concentration identified by the sample at 40 m (27.2 ±5 pg/kg).

**Figure 5.** WB11HD6001 (see Figure 4 caption for description).
When the well was pumped (Figure 5c and 5d), similar inflows continued below 45 m and nearly all discharge (98%) came from between 34.5–45 m. While pumping, CFC-12 concentrations at depth remained near the lower limit of resolution, but an increase was measured in the well at 50 m (18.7 ±4 pg/kg). A mass balance with the underlying 100 m sample indicates an average inflow concentration of 28.5 ±9 pg/kg over that rather large interval. Above this, the major aquifer zone was calculated to contribute inflow with an average concentration of 17.5 pg/kg, which is lower than expected. But on closer inspection, the measured flows indicate that while some of the discharge (11%) would be native groundwater from the 40–45 m interval, most (87%) was from the 34.5–40 m interval and likely to have anomalously low CFCs due to the presence of the intraborehole flow plume. If we assume the concentration of the plume (27.2 pg/kg) and inflowing native groundwater (83.8 pg/kg) identified from the ambient regime and use the in-well concentration from below (18.7 pg/kg), a mass balance indicates that the sample above the screen should contain 34 pg/kg CFC-12. However, it actually had a lower concentration (17.5 ±4 pg/kg). This mass balance is most sensitive to the concentration of the intraborehole flow plume because that was the majority of discharge. If we consider that perhaps the 40–45 m zone does not always contribute to ambient flows (apparent in the flow profile measured in June 2016, within the generally similar flow pattern), then the concentration of intraborehole flow would actually be more similar to that measured from below (e.g. 13.3 pg/kg, ambient regime). In that case it is possible to account for the low concentration in the pumped sample above the screen while maintaining the higher concentration of native groundwater in the main aquifer zone.

There was little change in the CFC-12 concentration of the composite samples taken at the start and end of the depth-specific sampling (17.5 ±4 and 16.3 ±3 pg/kg after purging 2.8 and 4.1 well vol. respectively). But a sample taken on a previous occasion, after significantly more pumping (June 2016, 9.9 well vol.), showed a higher CFC-12 concentration (28.7 ±6 pg/kg), as would be expected with a reduced fraction of intraborehole flow in the sample (i.e. intraborehole flow plume had lower CFC-12 concentration). Figure 5e compares these composite samples for the entire well screen with the depth-specific interpretations of aquifer concentrations from the ambient and pumped flow regimes.

5.3 WB11AH001

The ambient flow regime in WB11AH001 (Figure 6a and 6b) reflects a hydrogeological situation complicated by a fault zone in the Hamersley Group geology. The transition from Hamersley Group (fault gouge) to overlying Tertiary Detritals at 102 m (Figure 3) coincides with a split in the flow regime. Downward flow in the Hamersley of up to 5 l/min occurred in a relatively discrete interval (110–122 m), with CFC-12 concentration of inflowing native groundwater measured at 15.7 ±3 pg/kg. While in the Detritals, 2 l/min of upward flow was sourced between 104–90 m, with a measured concentration of 14.5 ±3 pg/kg. The flow profile then showed further inflow between 60–55 m, nearly all of which left the well between 55–47 m, before inflowing again between 47–41 m, with an overall addition of 5.2 l/min. These aquifer-well interactions between 60–41 m increased the CFC-12 concentration in the well, so the aquifer concentration must be higher than that of water already in the well from below. The mass balance gives an average of the inflow concentrations (28.0 ±7 pg/kg) using the overall change of flow and concentration in the well across this interval. The intraborehole flow (7.21/min, 25.4 ±5 pg/kg) then invaded the aquifer surrounding the uppermost part of the well (35–40 m).

In the pumped regime (Figure 6c and 6d) inflow was mainly from the upper aquifer zone (60–35 m, 91%). Below this, the ambient regime continued, but with slightly enhanced upward flow above 75 m and half the rate of downward flow at depth (110–122 m). CFC-12 concentrations in these inflows (7.9 ±2 pg/kg) were even closer to zero than in the fully ambient condition. A lower concentration was also estimated for the 60–40 m interval (16.9 ±3 pg/kg), while the topmost zone produced water that was estimated to
have higher than expected concentration (67.0 ± 38 pg/kg) given that it had received the intraborehole flow (25.4 ± 5 pg/kg). However, it is possible that the sample was a mixture with even higher concentration native groundwater. Although the two composite samples taken at the start and end of the depth-specific sampling procedure contrarily showed a decrease in concentration with pumping (25.4 ± 5 and 8.5 ± 2 pg/kg after purging 3 and 5 well vol. respectively), a previous composite sample taken after more pumping at a higher rate (May 2016: 180 l/min, 9.6 well vol.) did show a small increase in CFC-12 (28.5 ± 6 pg/kg, Figure 6e). When considered as a whole, the interpreted concentrations from both the ambient and pumped regimes (Figure 6e) indicate appreciable CFC-12 concentrations in the upper aquifer zone, and near zero below.

### 5.4 Aquifer Concentration Profiles

Figure 7 shows aquifer concentration profiles for each of the four tracers. There was evidence of appreciable CFC concentrations at shallower depths in the groundwater systems intersected by all three long-screened wells (65-84 pg/kg, Figure 7a), indicating a fraction was recharged less than 60 years ago. The piezometers (Table 3 and Figure 7) showed generally good agreement with LHRP4, and although CFC-12 concentrations were slightly more elevated at depth, this was within the error of the estimate from LHRP4.

#### Table 3. Tracers sampled from nested piezometers adjacent to LHRP4.

<table>
<thead>
<tr>
<th>Source depth interval (m)</th>
<th>$^{14}$C (pmC)</th>
<th>CFC-12 (pg/kg)</th>
<th>He (ccSTP/g)</th>
<th>TDS (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>38-40</td>
<td>27.3</td>
<td>139.1</td>
<td>1.45e-6</td>
<td>578</td>
</tr>
<tr>
<td>58-60</td>
<td>24.4</td>
<td>81.0</td>
<td>4.26e-6</td>
<td>588</td>
</tr>
<tr>
<td>78-80</td>
<td>25.4</td>
<td>37.5</td>
<td>4.40e-6</td>
<td>590</td>
</tr>
<tr>
<td>108-110</td>
<td>26.0</td>
<td>54.4</td>
<td>4.42e-6</td>
<td>591</td>
</tr>
<tr>
<td>138-140</td>
<td>19.3</td>
<td>31.4</td>
<td>5.14e-6</td>
<td>597</td>
</tr>
</tbody>
</table>

Interpreted aquifer $^{14}$C activities equated to values in the range 17-30 pmC for all samples (Figure 7b), without correction for exchange with carbonate minerals. The youngest
Figure 7. All depth-resolved aquifer concentrations interpreted from the three long-screened wells and those measured from a nest of piezometers (for direct comparison with LHRP4 only): (a) CFC-12 (grey line: max. atmospheric concentration), (b) $^{14}$C, (c) He (grey line: water in equilibrium with the atmosphere at 25°C), and (d) TDS. Vertical bars represent the inflow interval (less than symbol size for piezometers). Horizontal bars represent combined uncertainty of in-well flow and concentration measurement (less than symbol size for He, not shown for TDS). There are a different number of values for each well because the flow regimes in each offered different opportunities to sample aquifer concentrations. There are fewer data points for He because fewer samples were analysed.

(30 pmC) is similar to the minimum pmC (i.e. oldest) measured in nearby mine dewatering (composite samples from long-screened wells), which Cook et al. (2017) estimated to be 9900 years without corrections and $\sim$5000–7000 years with corrections. Corrections aside, this indicates a fraction of old (>5000 years) groundwater at all depths. LHRP4 and the adjacent piezometers showed decreasing values with depth (27-19 pmC), consistent with the CFCs and the downward head gradient, all pointing to the occurrence of groundwater recharge. WB11HD6001 showed a slight decrease with depth (22-17 pmC) but this was within the uncertainty of the estimates. While WB11AH001 potentially indicated a slight increase with depth (19-21 pmC), in keeping with groundwater discharge driven by the observed upward head gradient, but again this variation was within the uncertainty.

There was measureable enrichment of helium in all samples, with distinctly different characteristics between the two sites (Figure 7c). At WB11HD6001 and WB11AH001 He was enriched by about half an order of magnitude above the atmospheric equilibrium concentration expected in recharge, and concentrations were essentially constant with depth ($\sim$1.1×10$^{-7}$ ccSTP/g). While at the LHRP4 site the long-screened well and piezometers showed He enrichment by two orders of magnitude, with evidence of concentrations increasing with depth (1.5 – 5.1 × 10$^{-6}$ ccSTP/g). At both sites these data suggest a fraction of the water is at least in the order of 10$^3$ years old, and the lower concentrations at shallower depths at LHRP4 could be due to enhanced recharge from Pebble Mouse Creek.

The TDS concentrations (Figure 7d) give an overall representation of the major water chemistry. There were variations of all ions with depth within a limited range of
concentrations, but without distinct stratification. Bicarbonate was the major component of TDS (46-86%) and sulphate the second most abundant (7-17%).

Previous work on groundwater ages in this type of environment (Darling et al., 2012; Underwood et al., 2018) suggests that the simultaneous occurrence of young and old groundwater is probably explained by dual porosity in the aquifer. Specifically that relatively rapid flow within fractures and other preferential pathways mixes with water that infiltrates the primary porosity of the aquifer material over much longer timescales.

6 Discussion

A normal sampling approach is adequate if a well intersects just one discrete aquifer interval. In contrast, the approach described in this paper provides depth-resolved data from specific inflow zones within a well that intersects two or more permeable intervals or has a long screen in an otherwise homogeneous aquifer. Even in the latter case, it has been shown that small differences in head can drive vertical flow through the well, redistributing solutes between depths and causing significant bias in a pumped sample (e.g. Poulsen et al., 2018). The method presented here avoids or minimises in-well mixing of inflows and better indicates concentrations of a solute of interest for at least some of the aquifer intervals intersected by a well. In this study, the aquifer concentrations of environmental tracers interpreted from the ambient flow regime in LHRP4 are in good agreement with the depth-discrete samples from the adjacent piezometers (Figure 7), supporting the utility of the method. It appears unlikely that the intraborehole flow plume from LHRP4 has affected the chemistry sampled from any of the piezometers. That is, groundwater flows eastwards with Pebble Mouse Creek (Figure 2c) and, assuming that this prevails at all depths intersected by LHRP4, the intraborehole flow plume most likely extends to the east as indicated in Figure 2d, at a depth of approximately 130–140 m (i.e. the outflowing zone in Figure 4a). So the piezometers nearest to LHRP4 are much shallower than the plume and the deeper ones are positioned away from the plume.

Although this approach does not replace the need for piezometers at multiple depths in a groundwater investigation, it does provide a way to obtain more reliable data from certain depths in existing wells, allowing any new (properly designed) sampling installations to target depth intervals that remain un-sampled. Intervals that are typically not sampled with this method are those in which the head is lower than the blended head in the well (because they receive ambient flow), and those that contribute very little inflow. This paper focusses on the sampling method, and as such the principle concern is measuring the prevailing vertical flow regime in the well. However, we do recognise that additional borehole geophysical information helps to resolve the main hydraulically active zones (e.g. Paillet & Pedler, 1996; Paillet & Crowder, 1996; Paillet & Reese, 2000). The broader hydrogeological situation of a well is also important for interpreting the sample results in the context of an investigation, but it is not germane to the sampling or deconvolution method itself. Conversely, one key benefit of measuring the ambient flow regime in a well is that the direction and relative magnitude of the vertical hydraulic gradient is identified, which helps to assess the position of a well in a flow system (e.g. recharge or discharge area), the influence of location specific heterogeneity, and/or hydraulic stresses (e.g. groundwater abstraction, irrigation drainage).

When a pumped sample is said to be an inflow-weighted mixture, it is implicitly assumed that the well has been pumped long enough for the inflow located furthest from the pump to reach the pump intake and contribute to the discharge. To illustrate the time involved in this, we calculated the travel times for the wells used in this study by integrating the velocities indicated by the measured flow profiles. Prior to pumping, the ambient flow regime in LHRP4 was downwards and the in-well chemistry was mainly that of the highest head zone at 66–70 m (Figure 4b). Pumping reversed the flow direction (Figure 4d) and, with a large fraction of inflow from the bottom, it took 2-3 hours for
the most distant inflow to reach the pump. In contrast, both WB11HD6001 and WB11AH001 had upward ambient flow regimes (Figure 5b and Figure 6b) and when pumped, nearly all discharge was sourced from a main aquifer zone near the top of the screen (Figure 5d and Figure 6d). Below, flow velocities remained very slow so inflows would take a long time to reach the pump (e.g. 80 hr from 137 m in WB11HD6001). However, given that pumping hardly altered the ambient flows, except in the main producing zones near the top of these wells, an approximately chemically steady regime occurred once inflow from the base of the main aquifer zone reached the pump (<1 hr). Clearly it is necessary to know the flow profile at the pumping rate used for sampling in order to identify the inflow zones and to determine when the sample can indeed be considered inflow-weighted. Alternatively, this problem can be avoided by depth-specific longitudinal sampling in the ambient flow regime, which is already chemically steady.

In this work, the ambient flow regime in all three wells provided equal or better sampling opportunities as the pumped regime. Zones that receive intraborehole flow do not provide useful data in either flow regime unless they are fully purged, which is usually unrealistic. An everted liner (e.g. Cherry et al., 2007) could be used to prevent ambient intraborehole flow if the need for sampling is known in advance and such resources are available. In general, a key advantage of the ambient flow regime is that the chemically steady flow in the well is not disrupted (as it is with pumping), so it is not necessary to wait for a new one to establish. Sampling in the ambient regime is also simpler and more efficient because it does not require a discharge pump in addition to the sampling pump or device (e.g. grab sampler). Even for an active pumping well, stopping the pump and allowing the ambient flow regime to establish enables a discrete unmixed sample to be obtained from the highest head zone. Although one caveat is that a well must have a clearly defined ambient flow regime so that samples are attributable to specific inflow zones. But given that vertical head gradients, and hence ambient vertical flows, are ubiquitous in groundwater systems (Elçi et al., 2003), this is likely to be common. The main reasons to sample in a pumped flow regime are if the ambient flow regime is inadequate, or to induce inflow from zones of intermediate head, which were inactive in the ambient regime (although we did not see these cases in this study). Another caveat, which applies to sampling in all wells, is that only the major flowing zones are elucidated, in both ambient and pumped conditions. Without using packers (or depth-discrete piezometers) to specifically sample low permeability zones, it is generally only possible to resolve inflows from zones that are within two orders of magnitude of the most permeable zone (e.g. Paillet, 1998, 2001).

The most certain estimate of aquifer chemistry is that from a single inflowing zone of a clearly defined ambient flow regime, which is only subject to analytical error. As a worst case, this was ±20% of the measured value for CFC-12 (66–70 m in LHRP4, CFC-12: 70.7 ±14 pg/kg, Figure 4e). If a well is always pumped then the same applies to the inflow zone most distant from the pump (e.g. A3 sample, Figure 1b). It is important to note here that most solutes can be measured much more accurately than dissolved gases like CFCs, so the resulting error would be considerably less. Greater uncertainty arises where in-well flow and concentration measurements are combined in a mass balance (e.g. Eq. (1)) to estimate inflowing aquifer concentration. A statistical analysis, like the Monte Carlo approach used here, helps to quantify the error on calculated tracer concentrations, as shown by the larger error bars in Figure 7. As a worst case this was ±200% of the measured value for CFC-12 (123–130 m in LHRP4, 18.5 ±39 pg/kg, Figure 4e). But again, most of this was analytical error in CFC-12 measurement. If the analytical error is removed, the mass balance error due to ±5% in flow measurement is ±30% for the CFC-12 concentration.

Clearly, accurate flow measurements are critical for accurate calculation of inflow concentrations using a mass balance. An inherent limitation with long-screened wells is the potential for vertical flow in the gravel pack (or void) in the borehole annulus to en-
ter the well at a point downstream of where it was released from the aquifer. This can reduce resolution of flow zone boundaries and increase the apparent inflow from downstream low conductivity zones (Ruud & Kabala, 1997), and it can potentially enhance apparent inflow from the top part of the screen, where the deficit of a pumped discharge rate must be met (e.g., Boman et al., 1997). The use of a flow diverter on a borehole flowmeter increases resistance to flow within the well, potentially exacerbating the above issues and causing flows to be under-measured until near the top of the screen. However, it is important to remember that these uncertainties exist within the limits of zero flow at one end of the screen and the pumping rate at the other end (usually the top), or zero at both ends in ambient conditions. A further limit on uncertainty is that flow rate changes occur incrementally in the direction of flow, so there is only so much error that can be tolerated whilst honouring the overall shape of the flow profile. We believe our use of ±5% error on flows reasonably captures uncertainty in our imperfect field data for flow rates below the 10 l/min head-loss threshold. Defining the pumped flow regime in LHRP4 was problematic because the flowmeters head-loss threshold was exceeded over much of the well (Figure 4c). Thus it is likely that the lack of apparent inflows from the intermediate zone (70–123 m) is because discharge was preferentially sourced from the much more productive zone at the top of the well, or it bypassed the flowmeter in the gravel pack. If the proportion of inflow from that intermediate zone is less than that required to explain the in-well concentrations (red line in Figure 4c) then it would be necessary to invoke well-aquifer exchanges that change concentration without changing the flow rate. As such, the mass balance may be insufficient to resolve specific aquifer concentrations where the spacing between samples incorporates multiple aquifer-well fluxes. This was apparent for the 60–40 m interval in WB11AH001, although the out fluxes could simply be flow bypassing the flowmeter. We have highlighted challenges with using a borehole flowmeter to measure a wide range of flow rates, and strongly encourage careful consideration to the flow measuring methodology for future work. As suggested by Ruud et al. (1999), with a borehole flowmeter this could include an undersized flow diverter to manage the flow rate through the sensor, and/or measuring low and high flow intervals in separate profiles in the same well. Despite the obvious difficulties with in-well flow measurement, with careful interpretation the practitioner can still obtain a clear picture of the distribution of inflows. Depth-resolved estimates of solute concentrations derived from these inflows can provide valuable evidence for many groundwater studies.

We measured flow logs on multiple occasions over several years, so the consistency of the ambient flow regimes is fairly well defined. But in the absence of repeat logs, it could be relevant to assess the likelihood that the inflowing zones (h_z > h_avg) are in fact producing native groundwater, rather than potentially being contaminated with intraborehole flow. Heads in the individual aquifer zones can be estimated by combined analysis of ambient and pumped flow logs with an analytical solution (Day-Lewis et al., 2011; Sawdey & Reeve, 2012). The amount of change required to reverse the prevailing head gradient and hence direction of intraborehole flow could then be assessed.

7 Conclusion

The chemistry of specific groundwater inflows to long-screened and open borehole wells can be estimated by measuring and sampling the in-well vertical flow regime. By conceptualising the well-aquifer exchanges in ambient or pumped conditions, inflowing zones can be targeted with depth-specific sampling (low flow rate or grab sampler). Ambient vertical flows within the well, driven by a natural head gradient, provide particularly compelling sampling conditions. In a clearly defined ambient flow regime, sampling of the inflowing zones (h_z > h_avg) does not require pumping or purging in the normal sense. The highest head zone is subject only to analytical error on a single sample, while mixtures can be deconvolved with a simple mass balance, incorporating errors of flow and concentration measurements before and after the inflow. It is difficult to sam-
pene native groundwater from ambient outflowing zones \( h_z < h_{av} \) in wells that are not routinely pumped (even with pumping) because it is displaced by large volumes of intraborehole flow. For wells that are routinely pumped, also sampling in the ambient flow regime (i.e. when the pump is off) can add value by enabling a discrete sample from the highest head zone, rather than having it mixed with other inflows. At our field site, clear ambient flow regimes in all three wells (1–7 l/min) provided multiple opportunities for sampling inflowing native groundwater. Interpreted aquifer concentrations were consistent with discrete samples from a nest of piezometers adjacent to one well. Appreciable CFCs at shallower depths indicate the occurrence of modern recharge (<60 years) particularly at a site along a watercourse. The simultaneous occurrence of consistent levels of \(^{14}C\) in all samples suggests that old groundwater (>5000 years) is present at all depths. Compared to a normal pumped sample, this targeted sampling approach minimises the effect of in-well mixing of water from different depths, enables sample bias caused by intraborehole flow to be avoided, and is particularly relevant where the integrity of packers is compromised. We do not recommend long-screened or long open borehole wells as sampling devices by design, but rather that the method described in this paper enables more reliable depth-resolved estimates of groundwater chemistry to be obtained from such wells where they already exist.

Acknowledgments
This work was undertaken as part of a collaborative project between the National Centre for Groundwater Research and Training (NCGRT) and Rio Tinto Iron Ore (RTIO). Funding was provided by the Australian Government Research Training Program, the Australian Research Council, through Linkage Grant LP150100395 and by RTIO. The authors gratefully acknowledge help from RTIO and NCGRT field staff in collecting data reported in this paper. We also greatly appreciate constructive feedback from James Martin-Hayden, two anonymous reviewers and the Associate Editor, all of which helped to improve the clarity of the manuscript. All data supporting the analysis and conclusions of this study are included in this paper.

References


-20-


Quinn, P., Parker, B. L., & Cherry, J. A. (2015). Blended head analyses to reduce...


