Hydrogeological Techniques

# Chemical Sampling to estimate groundwater inflow



This resource describes how longitudinal chemical sampling of rivers can be used to identify both the quantity and source of groundwater that is contributing to river flow.

Estimates of groundwater flux to rivers facilitate conjuntive management of connected aquifers and rivers. Longitudinal chemical sampling adds valuable additional information to stream gauging. The measurement of chemistry enables the identification of both the quantity and source of groundwater that is contributing to river flow.

#### **HOW DOES IT WORK?**

Stream water is sampled at a number of locations along the course of the river and downstream changes in water chemistry are then interpreted in terms of groundwater discharge. The length of river sampled and number of samples collected is likely to depend upon the purpose of the study and the accessibility of sample sites.

A number of tracers have been used in these studies including electrical conductivity, conservative ions such as chloride, and dissolved gases including radon, helium and chlorofluorocarbons.

## BACKGROUND: SOLUTE MASS BALANCES

Often the concentration of dissolved ions is higher in groundwater than in river water. Electrical conductivity and conservative (non-reactive) ions such as chloride therefore tend to increase downstream as groundwater enters the river. The volume of groundwater discharging into a river may be quantified by accounting for this increase, as shown

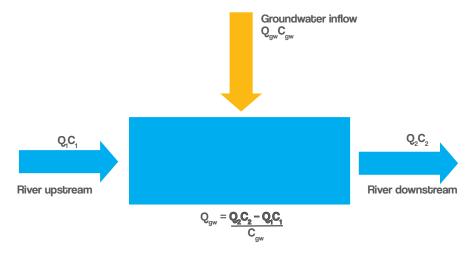


Figure 1. Conceptual model of how inflowing groundwater may be quantified from the change in concentration in river water ( $Q_1$ ,  $Q_2$  = flow upstream, downstream,  $C_1$ ,  $C_2$  = concentration upstream, downstream,  $Q_{aw}$ ,  $C_{aw}$  = groundwater inflow, groundwater concentration)

in Figure 1. If we ignore evaporation, then the water balance is

$$Q_1 + Q_{gw} = Q_2$$

and salt mass balance is

$$Q_1c_1 + Q_{gw}c_{gw} = Q_2c_2$$

These two equations can be combined to calculate the groundwater inflow as a fraction of the riverflow, if  $c_1$  and  $c_2$  are measured and  $c_{\rm qw}$  is known. Thus:

$$Q_{gw}/Q_2 = (c_2 - c_1)/(c_{gw} - c_1)$$

This method allows groundwater inflow to be calculated along a length of river, if measurements of concentration are made at points along the river. If the river flow rate is also measured at one or more points, then we can calculate the absolute groundwater inflow rate (rather than as a fraction of river flow).

In very slow flowing streams, it can be important to include the effect of evaporation. We can re-write the solute balance as

$$Q \frac{dc}{dx} = I (c_i - c) + wEc$$

where I = groundwater inflow per metre of river (m²/day); c = concentration in river (mg/l); c<sub>i</sub> = concentration in groundwater (mg/l); w = stream width (m); E = evaporation (m/day); Q = river discharge (m³/day); x = distance downstream (m).





Here the change in chloride concentration downstream

<u>dc</u>

is related to groundwater input, which can be estimated from measuring all other parameters.

Another tracer that has been widely used for these mass balance calculations is radon (222Rn). Even quite low rates of groundwater inflow can be measured with radon, because the concentration difference between groundwater and river water is usually very high. (Radon is produced by uranium bearing minerals in the parent rock.)

The mass balance radon can be written:

$$Q \frac{dc}{dx} = I(c_i - c) + wEc - kwc - dwc$$

where is the radioactive decay constant (/day), k is the gas loss rate (m/day) and d is the river depth (m). Once in the river radon will decay ( ), and as the atmosphere however contains very low amounts of radon there is also a net diffisuve gas transfer (loss) to the atmosphere (k).

These terms are all included in the mass balance. Values for the gas transfer coefficient can be estimated from a number of gas transfer models (see Mullinger et al., 2007). Leaney and Herczeg (2006) provide an overview of the method used to collect radon samples in surface water using 1.25L soft drink bottles.

#### LIMITATIONS AND UNCERTAINTIES

There are a number of assumptions involved in applying these methods, and these must be assessed on a case-by-case basis. Firstly, the mass balance equations assume that the system is at steady state when measurements are taken. Hence, the method should only be applied during stable flow conditions, and may not be applied during river flow events.

In practical terms, steady state flow can be assessed by inspection of the

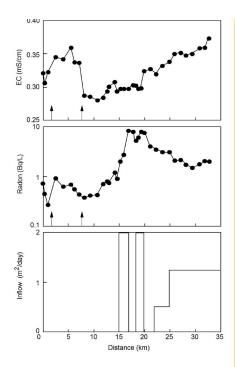


Figure 2. Groundwater inflow rates determined by the measurement of electrical conductivity and radon activity in the Cockburn River, New South Wales (Cook et al., 2006).

river hydrograph over the course of the sampling program, and repeat measurement at a number of locations at different times.

If the river receives inflow from tributaries, then the contribution of tributaries must be identified and sampled and incorporated into the mass balance. Finally, it is assumed that groundwater input concentrations are well-known and temporally constant. Uncertainty of the groundwater input concentration can cause large uncertainty in the calculated inflow rate. Sampling of groundwater in proximity to the river is one way in which this value may be constrained.

The selection of appropriate analytes is essential to minimise uncertainty in estimates of groundwater inflows to rivers using this method. The method will be most accurate where concentrations

#### CASE STUDY

Cook et al. (2006) measured dissolved ions and gases and performed stream gauging at multiple points along a stretch of the Cockburn River, NSW. Figure 2 shows their measurements of electrical conductivity and radon activity as well as their modelled groundwater inflow rates.

Electrical conductivity of the river increases between 15 and 33 km, and modelling of this data suggests that groundwater inflow occurs over most of this river reach. The highest radon activities occur between 15 and 20 km, and the model also has highest rates of groundwater inflow in this area.

in surface water and groundwater are very distinct.

When radon is used, care must be taken to separate the radon contribution from groundwater inflow from that due to hyporheic exchange (movement of water into and out of the streambed). The choice of tracers also drives the selection of an appropriate sampling interval, as described by Cook (2012).

It is also possible to use this approach to calculate the chemical composition of groundwater discharging to the river. Comparison of this data with measurements of the chemical composition of different aquifers can then be used to identify which aquifers are discharging groundwater to the river, and potentially to calculate the proportion of water from different aquifers.

### Want to know more?

Cook, PG, Favreau, G, Dighton, JC & Tickell, S 2003, 'Determining natural groundwater influx to a tropical river using radon, chlorofluorocarbons and ionic environmental tracers', Journal of Hydrology, vol. 277.1–2, pp. 74–88

Cook, PG 2012, 'Estimating groundwater discharge to rivers from river chemistry surveys', Hydrological Processes, online, DOI: 10.1002/ hyp.9493

Mullinger, NJ, Binley, AM, Pates, JM, Crook, NP 2007, 'Radon in chalk streams: spatial and temporal variation of groundwater sources in the Pang and Lambourn catchments, UK', Journal of Hydrology, vol. 339,1, pp172–182.