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Author:

Andersen, Martin; Jakobsen, R

Publication details:

Groundwater Quality: Securing Groundwater Quality in Urban and Industrial Environments

pp. 459-466

9781901502794 (ISBN)

Event details:

GQ07: Securing Groundwater Quality in Urban and Industrial Environments
Freemantle, Australia

Publication Date:

2007

DOI:

<https://doi.org/10.26190/unsworks/656>

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From the aquifer to the sea – mapping and quantifying groundwater discharge and nitrate flux and transformations – a review of methods

M. S. ANDERSEN¹ & R. JAKOBSEN²

¹ *Water Research Laboratory, School of Civil and Environmental Engineering, University of New South Wales, 110 King St, Manly Vale, 2093, New South Wales, Australia*
m.andersen@wrl.unsw.edu.au

² *Institute of Environment and Resources, Technical University of Denmark, Bygningstorvet Building 115, DK-2800 Kgs Lyngby, Denmark*

Abstract This paper reviews methods available for addressing fluxes of water and nitrate, as well as the process affecting nitrate concentrations in the transition from groundwater to surface water, in a comprehensive tabular compilation. Small-scale methods, typically involving direct measurements, give the most quantitative information, while methods working on a larger scale, e.g. airborne or waterborne techniques, can give information on a larger and, in many contexts, more useful scale, but rarely with appropriate quantification. Bridging the gap may be possible by simultaneously applying large-scale measurements and small-scale direct measurements covering the range of values, using these for calibration.

Key words groundwater; surface water; submarine; flux; nitrate; geophysics; geochemistry

INTRODUCTION

Groundwater entering the sea directly through coastal aquifers may carry contaminants that enter the sea by various pathways and in unknown quantities. Options for finding these pathways, quantifying the amount, the composition and processes occurring in groundwater in transit can roughly be divided into: (i) direct or indirect physical measurements of the flux using quantitative, semi-quantitative and qualitative methods; (ii) geophysical methods for mapping the distribution of discharging groundwater and controlling geology; (iii) numerical modelling; (iv) sampling the water and measuring its composition; and (v) direct or indirect measurements of the rates of various geochemical transformations and attenuation of compounds. This is a compact tabulated comprehensive overview of the pros and cons of methodologies available for providing answers on water and contaminant fluxes, here exemplified by nitrate, from groundwater into a surface water body. Possibilities for further development by a closer integration of local and large-scale methods are suggested.

METHODOLOGIES AND POSSIBILITIES

Tables 1–4, in combination with the references, are the core part of this contribution and summarize methods available for mapping and quantifying groundwater discharge and nitrate flux and transformations. The text is without references and mainly serves as an entry point and provides some general perspectives (see tables for references).

Physical measurements Table 1 lists methods for determining water flux more or less directly. Seepage meters give the most direct measurements, but up-scaling is

Table 1 Hydrological (physical) methods.

Method	Description	Advantages	Disadvantages	References	
Manual seepage meters	Measurements of volumetric flow through a benthic chamber. Tend to work best with high flux rates. Can separate fresh and saline water fluxes by concurrent Cl/EC measurements	Direct quantitative fluid flux measurements	Labour and time consuming. Measures only small areas. Subject to artefacts depending on deployment conditions, e.g. flow generated by waves and currents.	Andersen <i>et al.</i> , 2007 Bokuniewicz, 1980 Burnett <i>et al.</i> , 2002 Cable <i>et al.</i> , 1997a/b Chanton <i>et al.</i> , 2003 Gallagher <i>et al.</i> , 1996 Giblin & Gaines, 1990	Lee, 1977 Martin <i>et al.</i> , 2004 Mulligan & Charette, 2006 Nowicki <i>et al.</i> , 1999 Rutkowski <i>et al.</i> , 1999 Taniguchi <i>et al.</i> , 2003
Automated seepage meters	As above with a sensor detecting a heat pulse or ultrasonic pulse	As above, but less laborious and automation makes it easier to obtain time series	As above	Chanton <i>et al.</i> , 2003 Paulsen <i>et al.</i> , 2001 Taniguchi & Fukuo, 1993	Taniguchi & Iwakawa, 2004 Taniguchi <i>et al.</i> , 2003
Head gradient/permeability relationships	Based on head gradients and permeability in piezometers along the direction of groundwater flow and calculating flux from Darcy's law	A direct measure of groundwater flux given a adequately homogeneous permeability distribution	Needs a good delineation of groundwater flow paths and the installation of many piezometers and therefore often only cover local scale investigations	Andersen <i>et al.</i> , 2007 Cambareri & Eichner, 1997 Harvey & Odum, 1990 Mulligan & Charette, 2006 Oberdorfer <i>et al.</i> , 1990	Portnoy <i>et al.</i> , 1998 Robinson <i>et al.</i> , 1998 Staver & Brinsfield, 1996 Tobias <i>et al.</i> , 2001a
Direct temperature measurements	Measuring of temperature contrasts between groundwater and receiving seawater. Works best when contrast is large (i.e. summer or winter). Optical fibres have potential but have not yet been used in marine settings.	Qualitative method to identify outflow zones. Optical fibres may cover large areas in great detail rapidly and precisely and as a function of time.	Cannot quantify the groundwater flux. Only works at times of the year when there is a temperature contrast. Potential problems keeping optical fibres in place in a marine environment.	Taniguchi <i>et al.</i> , 2003 Selker <i>et al.</i> , 2006 Lowry <i>et al.</i> , 2007	
Infrared imaging	As above, but by remote sensing. Either by airborne thermal/IR photography or from satellite IR images, depending on scale	Covers large areas fast. Resolution can be adjusted for airborne data collection.	Only successful during quiet weather and when temperature contrasts between discharging and receiving waters are high	Banks <i>et al.</i> , 1996 Mulligan & Charette, 2006 Portnoy <i>et al.</i> , 1998	
Modelling	Varying in complexity from simple water balance calculations to 3-D time-varying density dependent distributed models	Data integration conceptualisation Complex scenarios	"Never better than the data"	Andersen <i>et al.</i> , 2007 Cambareri & Eichner, 1997 Destouni & Prieto, 2003 Kaleris <i>et al.</i> , 2002	Langevin 2003 Mulligan <i>et al.</i> , 2007 Smith & Nield, 2003 Smith & Zawadzski, 2003

Table 2 Geophysical methods.

Method	Description	Advantages	Disadvantages	References
Multi-electrode profiling (MEP)/ Resistivity Imaging	Land-based line surveys along coastlines	Fast data acquisition	May not adequately reflect discharge patterns offshore. Non-uniqueness in clayey environments	Andersen <i>et al.</i> , 2007 Tronick <i>et al.</i> , 1999 Turner & Acworth, 2004
Resistivity streamers (UMEP)	Offshore towed resistivity arrays	As above	Ambiguity of resistivity–porosity relationships at low freshwater contents. Pore water EC is needed to verify UMEP data	Andersen <i>et al.</i> , 2007 Krantz <i>et al.</i> , 2004 Manheim <i>et al.</i> , 2004 Vanek & Lee 1991
Electromagnetic (EM) streamers	Offshore towed array (1–2 knots)	Fast data acquisition using towed streamers	As above	Mulligan <i>et al.</i> , 2007 Hoefel & Evans, 2001
Electromagnetic (EM) Helicopter surveys	Equipment is flown across area during measurements	Well suited given a scarcity of wires, etc.	As above, and furthermore substantial post-processing is often needed for correcting method errors	Fitterman, 1996 Fitterman & Deszcz-P, 1998 Paine, 2003*
Seismic reflection	Marine seismic surveys reflecting geo-structures	Comparatively large survey depth	Only indirect evidence – no flow or salinity information. Needs independent data verification	Krantz <i>et al.</i> , 2004 Mulligan <i>et al.</i> , 2007
Side-scan sonar	Measuring anomalies in the bathymetry, i.e. pockmarks	Fast data acquisition	As above	Schlüter <i>et al.</i> , 2004

Table 3 Geochemical methods.

Method	Description	Advantages	Disadvantages	References
Large-scale mass balance on salinity (CI or EC)	Measuring salinity distribution within area of groundwater discharge and calculating exchange with surrounding surface water bodies	Large-scale deriving total integrated fluxes	Subject to large mass balance errors of determining exchange between water bodies.	Giblin & Gaines, 1990
Pore fluid salinity (CI or EC)	Extraction of discrete fluid samples from within the sea-bottom.	Direct measurements of salinity. Depth profiles can be used to derive fluxes of pore water with assumptions of advection and diffusion	Very small-scale, time consuming. Many assumptions inherent in deriving fluxes from salinity profiles	Andersen <i>et al.</i> , 2007 Bratton <i>et al.</i> , 2004 Capone & Bautista, 1985 Harvey & Odum, 1990 Martin <i>et al.</i> , 2004 Rutkowski <i>et al.</i> , 1999 Schlüter <i>et al.</i> , 2004 Vanek & Lee, 1991
Natural tracers				Swarzenski <i>et al.</i> 2001
Radon-222	Measurement of water column (and sediment pore water) activities of ²²² Rn	Low levels in seawater, high in groundwater, conservative. Can provide estimates on both point and system scale	Cannot distinguish between fresh and saline water discharging. Short-lived isotope, samples needs fast processing	Burnett <i>et al.</i> , 2002 Hussain <i>et al.</i> , 1999 Lambert & Burnett, 2003 Mulligan & Charrette, 2006 Schlüter <i>et al.</i> , 2004 Chanton <i>et al.</i> , 2003

Radium isotopes (223, 224, 226 & 228)	Measurement of water column (and sediment pore water) activities of the various radium isotopes	As above. The short-lived isotopes (²²³ Ra and ²²⁴ Ra) have been used to derive mixing ratios between the open ocean and regions impacted by groundwater discharge	As above Budget, mixing and gas-exchange calculations can have considerable uncertainties in their assumptions	Burnett <i>et al.</i> , 1990 Burnett <i>et al.</i> , 2002 Corbett <i>et al.</i> , 2000 Hussain <i>et al.</i> , 1999 Moore, 1996 Moore, 2003 Mulligan & Charette, 2006 Schlüter <i>et al.</i> , 2004
Methane	Measurement of water column and sediment pore water concentrations	Easily sampled and measured using gas chromatography	Reactive, may be produced <i>in situ</i> by degradation of organic matter and in turn easily re-oxidised.	Corbett <i>et al.</i> , 2000

Table 4 Methods to assess chemical attenuation of nitrate.

Method	Description	Advantages	Disadvantages	References	
Assessments of NO ₃ ⁻ pore fluid concentrations	Discrete samples from sea-bottom. Depth profiles together with Cl ⁻ or EC data can be used to derive fluxes of pore water nitrate and/or degree of attenuation by denitrification	Gives direct flux and attenuation estimates given known water flux on local to intermediate scale	Subject to errors caused by spatial or temporal variations in nitrate source levels. Possible variations in the conservative tracers (EC or Cl) in a coastal environment.	Andersen <i>et al.</i> , 2006 Bratton <i>et al.</i> , 2004 Capone & Bautista, 1985 Capone & Slater, 1990 DeSimone & Howes, 1996* Gallagher <i>et al.</i> , 1996	Giblin & Gaines, 1990 Nowicki <i>et al.</i> , 1999 Portnoy <i>et al.</i> , 1998 Rutkowski <i>et al.</i> , 1999 Staver & Brinsfield, 1996 Tobias <i>et al.</i> , 2001b
Pore fluid concentrations of potential attenuation products (e.g. Fe ²⁺ , SO ₄ ²⁻ , HCO ₃ ⁻)	Qualitative or stoichiometric comparisons of catchment groundwater nitrate levels with potential attenuation products in the coastal discharge zone	Parameters are often measured anyway	May not be direct evidence of nitrate attenuation. The levels could be caused by other processes	Andersen <i>et al.</i> , 2006 Böhlke <i>et al.</i> , 2002* Puckett <i>et al.</i> , 2002* Tesoriero <i>et al.</i> , 2000*	
Redox balance calculations	As above, but a more rigorous budgeting of transfers of electrons in relevant redox reduction reactions	Can elucidate the relative importance of different electron donors (org-C or FeS ₂) within the sediment	May be hampered by variations in infiltration chemistry	Andersen <i>et al.</i> , 2006 Postma <i>et al.</i> , 1991* Tesoriero <i>et al.</i> , 2000*	
N ₂ -flux	Measured in water samples from pore water profiles, at the sea bottom in benthic chambers, or in the lab from sediment cores or slurry incubations	Measures a direct unique product of denitrification.	Small increases in N ₂ from denitrification against high atmospheric N ₂ . Variations in dissolved background N ₂ due to variable recharge conditions. High risk of contamination from atmosphere in lab experiments.	Nowicki <i>et al.</i> , 1999	
Gas phase composition, i.e. the N ₂ /Ar-ratio	Excess N ₂ levels compared to Ar, above the atmospheric component, provides a measure for bulk denitrification along the total flow path	The assessment is independent of current variations in the source level of nitrate.	The method does not reveal information on the location of the denitrification. (i.e. it could have occurred far upstream)	Andersen <i>et al.</i> , 2006 Blicher-Mathiesen <i>et al.</i> , 1998* Böhlke <i>et al.</i> , 2002* Bratton <i>et al.</i> , 2004	Puckett <i>et al.</i> , 2002* Tesoriero <i>et al.</i> , 2000* Tobias <i>et al.</i> , 2001b

Nitrogen stable isotopes	Based on the contrasting levels of ^{15}N in different nitrogen species of different sources as well as fractionation due to different processes	Can sometimes pinpoint the most significant or problematic source of N	Variations in ^{15}N isotope levels may be a function of both chemical processes and variable sources	Böhlke <i>et al.</i> , 2002* Bratton <i>et al.</i> , 2004 DeSimone & Howes, 1996* Tobias <i>et al.</i> , 2001b
Incubation tests	Sediment samples incubated in the laboratory, in cores samples, or by <i>in situ</i> experiments	Gives direct rates of nitrate attenuation	Incubation tests only reveal information at a point as opposed to dissolved species (such as N_2) that integrate processes along a flow path.	Smith <i>et al.</i> , 1996*
Acetylene block	Sediment samples can be amended with acetylene to terminate the denitrification of N_2O which can then be collected and used as a measure of denitrification	Gives direct rates of nitrate attenuation. Atmospheric N_2O -levels are low minimizing the risk of contaminating incubations	Acetylene inhibition may be of limited extent especially at low NO_3^- concentrations (Groffman <i>et al.</i> 2006). Acetylene also blocks nitrification giving low denitrification rates when nitrification is a significant source of NO_3^-	Capone & Slater, 1990 DeSimone & Howes, 1996*
Isotope pairing	Sediment samples are amended with labelled $^{15}\text{N}\text{-NO}_3^-$ and incubated. The produced $^{15}\text{N}\text{-N}_2$ can then be assessed as a measure of denitrification	Avoids the inhibition problems of the acetylene block technique		Nielsen, 1992†

* References that only describe methods and results from groundwater environments.

† References that only describe methods and results from marine environments.

virtually impossible in heterogeneous environments due to the point nature of the method. Combining quantitative point measurements and larger-scale qualitative data could potentially provide quantitative data on a larger scale. It may be possible to perform a number of seepage meter measurements in an area simultaneously covered by an IR (infra-red) survey. Assuming the seepage meter measurements cover the range of fluxes, a calibration may be used to obtain quantitative data from the IR survey. The derived data would be ideal for comparison with detailed model results. New methods, exploiting the physics of optical fibres, enable precise metre-scale temperature measurements along 30 km of fibre, providing for detailed 2-D temperature mapping on the bottom of the receiving water body with a system-relevant areal coverage. Fluxes could be derived by combining with seepage meter results.

Geophysical methods Applicable geophysical methods are listed in Table 2. The electrical and the electromagnetic methods have the advantage (at fresh/marine interfaces) that the signal is related to the salinity, but, as clay content is also significant, ambiguous results are possible. Still, the areal distribution of fresh groundwater discharge may be determined precisely. It may be possible to transform electrical/electromagnetic measurements to fluxes using seepage meter results. The use of seismic methods is only relevant in cases where a heterogeneous geology controls the outflow and for cases where good seismic reflections can be obtained.

Geochemical methods With well-defined concentration differences, substantial information can be obtained from geochemical measurements, as shown in Table 3. In principle, any constituent behaving conservatively may be used. Natural tracers may, in the case of well-mixed surface water systems where the influx from streams is negligible or known, be used for calculating the integrated groundwater influx in a very direct manner. The values may be compared to fluxes derived from modelling.

Attenuation Estimating the turnover in the groundwater–surface water transition zone of reacting components is challenging and a vast subject in itself. Table 4 exemplifies the task using nitrate reduction. Some methods measure transformations directly, resulting in good quantitative, but localized potentially-biased, data as the disturbance of sediments by the sampling process may lead to denitrification rates elevated by order of magnitudes (DeSimone & Howes 1996; Smith *et al.*, 1996). Especially for transformation rates depending on, e.g. sedimentary organic matter content, flow rates, etc., the values obtained may be very hard to up-scale.

With regards to the attenuation of groundwater nitrate, there appear to be very few geochemical investigations done in the subsurface coastal interface. This is in stark contrast to the many investigations done in the field of attenuation of groundwater nitrate to fresh surface water bodies and the abundance of studies in the purely marine benthic transformations of nitrogen. This is the reason for the lack of coastal interface references in Table 4 on geochemical studies of nitrate attenuation, and for the inclusion of references on studies entirely from groundwater environments.

SUMMARY

The direct measurements are time consuming and difficult to upscale in heterogeneous environments. The best option, apart from trying to bridge the gap between the direct

measurements and the remote or indirect methods, appears to be a combination of several indirect and/or remote methods (geophysics, geochemistry, modelling, etc.) to constrain groundwater and chemical flux estimates for a given stretch of coast.

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