

Groundwater Quality: An Ecotoxicology Perspective

Jenny Stauber, Grant Hose and Andrew Boulton



www.csiro.au

Bizarre new species stops Pilliga mining

BY HSIN-YI LO AUGUST 09, 2013

THE DISCOVERY OF NEW stygofauna species in the groundwater of Pilliga State Forest in New South Wales has brought a \$1 billion drilling project to a pause...



21 Aug 2018 Adelaide Advertisor, Adelaide

> Author: Clare Peddie • Section: General News • Article Type: News Item Audience : 112,097 • Page: 3 • Printed size: 234,00cm² • Market: SA • Country: Australia ASR: AUD 3,481 • words: 349 • Item ID: 997733879

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Water contamination probe

Long-term exposure

manufacturing

Industrial Complex.

CLARE PEDDIE SCIENCE REPORTER

RESIDENTS of 900 homes at risk of contamination from past use of industrial chemicals are being advised not to use bore water for any purpose while the Environmental Protection Agency investigates.

Yesterday residents in the Woodville North assessment will find." area, north of Torrens Rd to Grand Junction Rd, received advice in a letterbox dron about testing to begin next up through the soil. month.

The EPA will engage consultants to drill groundwater bores in road verges and footpaths, not on private proper ties, to sample and test groundwater for chemicals and vapour coming up through the soil.

EPA regulation director Peter Dolan said they were particularly interested in chlorinated hydrocarbons such as trichloroethene or TCE, but also some petroleum products that may have eached through the soil into groundwater

"I would be very surprised if identified. As well as writing to it was perfectly clean, I'll put it residents, the EPA is conduct that way. I think we will find ing a community information contamination," he said. session in Sentember and has "The question is, is it in a translated information into place or form that's going to Vietnamese, with a Vietnamese interpreter available at the

hurt people or not and that we don't know. session. "We're concerned enough The assessment relates to that we want to find out, but it's groundwater (bore water) only very hard to predict what we and mains water and rainwater

are safe to use There is a potential risk to Home grown vegetables are human health from using bore safe to eat, provided they are water or from vapour coming not being watered with bore water.

> to EXPLAINER: ADVERTISER.COM.AU

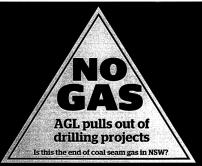
TCE has been linked to cancer Gratel Innction Rd 43 818 111 of the liver or kidneys and non-Hodgkin lymphoma. Mr Dolan said the testing

would target residential areas around the former Finsbury Factory, which made ammu nition during World War II Since then other large companies have worked in the area now known as the Woodville North

The EPA conducts assess ments into so-called "orphan" sites where the original polluter no longer exists or cannot be



Public still in dark on CSG chemicals





Sydney Moming Herald, Sydney

Author: Patrick Begley • Section: General News • Article Type: News Item Audience : 88,634 • Page: 2 • Printed size: 179.00cm* • Market: NSW Country: Australia • ASR: AUD 14,326 • words: 349 • Item ID: 969373185

15 Jun 2018

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Page 1 of 1

Contaminated water found near air base

Patrick Beglev

Chemicals from the RAAF air base at Richmond on Sydney's outskirts have leached into groundwater, potentially risking the health of nearby residents, an investigation has found.

From 1976 to 2004, the base used a form of firefighting foam that contained per- and polyfluoroalkyl substances, cancercausing chemicals known commonly as PFAS.

The NSW Environment Protection Authority refers to PFAS as an "emerging contaminant" - one that has unknown effects on human health.

But a growing body of international evidence has associated exposure with a slew of health effects, including immune suppression, liver dysfunction, high cholesterol and some forms of cancer.

Last year the ADF launched an investigation into the Richmond base and the surrounding area, releasing results to local residents vesterday. The report, completed by savir-

onmental consultancy firm Aecom, found chemicals had entered groundwater in a plume 2km long and 5km wide, extending beyond the base perimeter.

Concentrations of PFAS were found at all major drainage systems on the base but also in nearby

waterways including Rickabys Creek and Bakers Lagoon.

"Ultimately, all surface water discharges into major drainage networks and creeks flowing from the site towards the Hawkesbury River," the report said.

Assistant secretary of PFAS Investigation and Management Luke McLeod said people did not need to avoid swimming in the water. "People don't drink the surface

water," he told the ABC. A survey of 157 respondents in the area found only one used hore water, for cattle, but PFAS can also be spread through the atmo-

chemicals included residents living on the base, employees and children attending the base's child

sphere in soil and dust.

care centre Blue House. "Off-site receptors" included nearby residents, recreational users of creeks and rivers in the area, commercial workers such a farmers, and livestock.

According to the report, poten-

tial "on-site receptors" of the

Defence investigators are preparing to assess any effects on human health, monitoring exposures through soil and water contact but also through food, such as seafood, eggs and home-grown crops from the area.

The Department of Defence will develop a management plan to handle any unacceptable risks to human health.

NEWS 0

Condamine River's mysterious bubbling 'intensifying'

By Mark Willacy

Updaled Sun 14 Fab 2016, 7:57pm



125 20.0



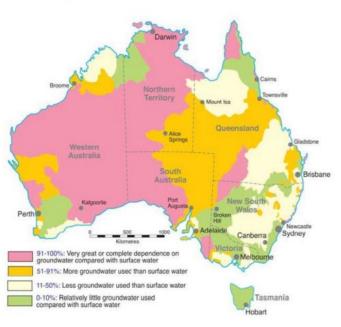
Groundwater resources in Australia

Service Type

Provisioning

Supplies 30% of Australia's total water consumption (~15% of Australia's drinking waters and in some areas 100%)

Figure 1.2: Australia's reliance on groundwater



	Irrigation Industrial uses
Regulating	Bioremediation Nutrient recycling Refugia Baseflow to wetlands and rivers Flood and erosion mitigation
Cultural	Tourism to caves, natural springs Indigenous spiritual values

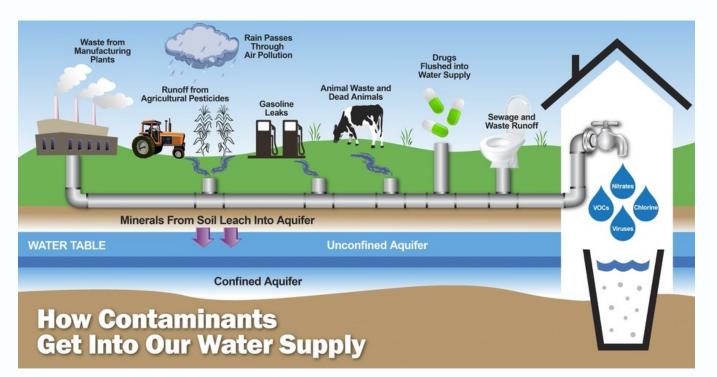
Examples

Drinking water

Source: National Centre for Groundwater Research and Training, 2013

Groundwater management

Management previously based on environmental values (beneficial uses) – irrigation, drinking water supply, with concerns mainly for human health







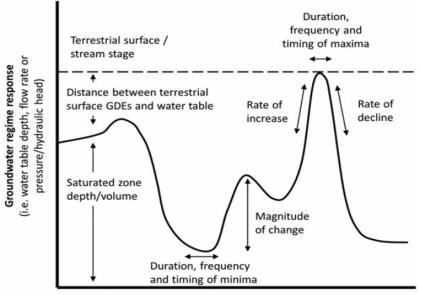
Environmental impacts historically only considered when GW infiltrated surface waters



Groundwater ecosystems

GW supports a range of groundwater-dependent ecosystems (GDEs) GDEs depend on GW regime:

- Residence time
- Flux
- Pressure
- Depth
- Dynamics (frequency, duration, timing)



Time



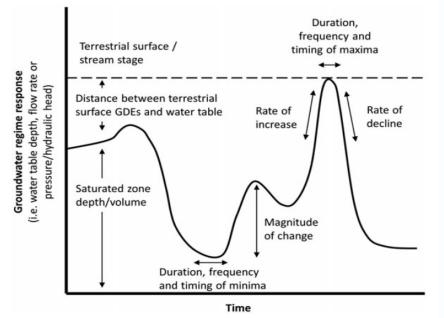
Groundwater ecosystems

GW supports a range of groundwater-dependent ecosystems (GDEs) GDEs depend on GW regime:

- Residence time
- Flux
- Pressure
- Depth
- Dynamics (frequency, duration, timing)
- Quality
 - Physical (e.g. temp, turbidity)
 - Chemical (e.g. TDS, minerals)
 - **Biological** (e.g. pathogens, microbes, fauna)

Water quality (EC, nitrate and carbonate) shown to have greatest influence on GW microbial assemblages (together with seasonality) in an alluvial aquifer (Korbel and Hose, 2015)

Kath et al. (2018)



Outline

Why is groundwater quality important?

How do we measure groundwater health?

Are ecotoxicological tools that we use for surface waters also applicable to assessing groundwater quality?

Case studies

- eDNA to assist bioremediation
- VOCs
- PFAS

How can this help improve groundwater management?



Why is groundwater quality important?



Sub-surface groundwater ecosystems

Aquifers are not just conduits for water

Wide variety of sub-surface GW ecosystems

Habitats for biota (microbes and invertebrates) which form a unique ecosystem

Aquifers contain diverse and unique fauna found only in GW systems

GW must be fit for purpose to support these unique GDEs – this means GW quality as well as GW quantity/regime



Limbodessus bennetti





Stygofauna

Animals occupying groundwater ecosystems (from Styx River, portal to Hades)

Like Hades – lightless, confined, low DO, low energy i.e. hell for most animals unless adapted for subterranean life:

- reduced/lost eyes but other sensory structures
- elongated appendages on flexible bodies
- low metabolic rates and low reproductive rates

Occur in caves and interstitial spaces in alluvial, karstic or fractured rock aquifers, usually in low densities

Most are short-range endemic species (>4,500) dominated by crustaceans, but also includes beetles, snails, mites, worms

Burrow/bioturbate which may enhance water flow in some aquifers and graze on microbes, improving water quality

Increased vulnerability to habitat loss through altered groundwater regime/water quality therefore vulnerable to extinction









Hydrobiidae sp. B02 – a stygofaunal snail from the eastern Pilbara



Neoniphargidae

Pilbarophreotoicus

Photos from Bennelongia and P. Hancock



Billibathynella sp. B01 – another stygofaunal syncarid crustacean





Gomphodella yandi – Ostracod species currently only known from Australia

Hydrobiidae



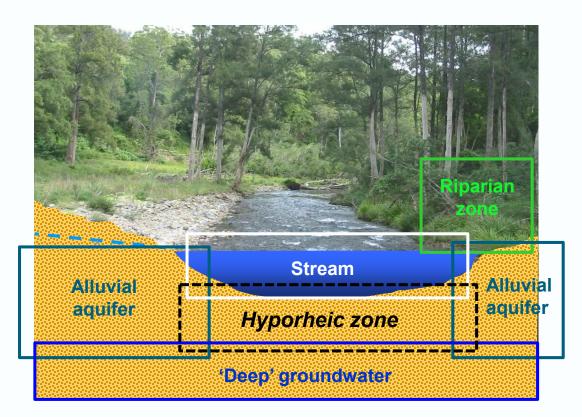




Peter Hancock

Groundwater-surface water connectivity

GW quality influenced by residence time underground and by subsurface and surface conditions



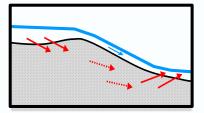
Hydrologically connected vertically and laterally via hyporheic zone

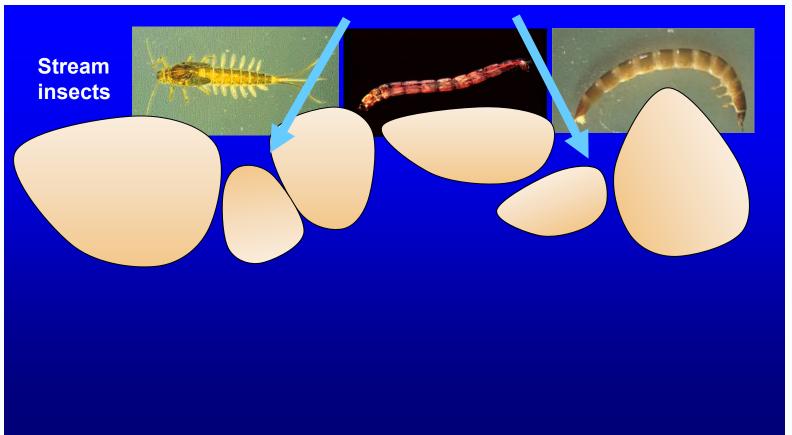
Physical and biochemical filter between river water and groundwater (e.g. microbial activity transforms nutrients along flow path)

Need holistic approach to manage these connected systems

Groundwater-surface water connectivity

Combination of stream and groundwater biota often associated with the direction of SW-GW exchange

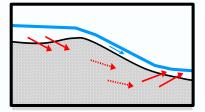


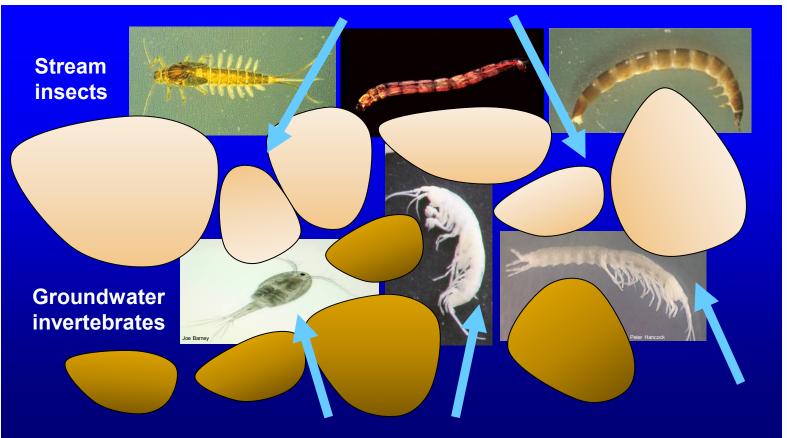




Groundwater-surface water connectivity

Combination of stream and groundwater biota often associated with the direction of SW-GW exchange







	Surface waters	Groundwaters
Physical	Light, variable temp, colour, suspended sediments	Stable, dark, constant temp, pressure, large surface area

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Hydrological	Variable flows -often ephemeral or temporary, floods, erosion, pulse events	Different depths, slow flow, variable age, long distances from source of recharge
Biological	Primary producers basis of most food chains, vertebrates common, high species diversity and abundance, diverse feeding strategies	No photoautrophs, few vertebrates, invertebrates (crustaceans) dominate, sparse fauna, short-range endemics, limited resilience, low fecundity and metabolism, omnivores, low diversity of microbes (mostly attached), difficult to culture

How do we measure groundwater health?



Groundwater health

"A healthy groundwater system is one that sustains its ecological structure and function (including vigour and resilience) while sustainably providing ecosystem services" Korbel and Hose (2011)

Threats to groundwater systems

- Climate change
- Over-extraction
 - Irrigation
 - Mining/gas
- Contaminants
 - Salinity, acidity
 - Pesticides, organics, metals, nutrients, radionuclides, emerging contaminants
 - Pathogens









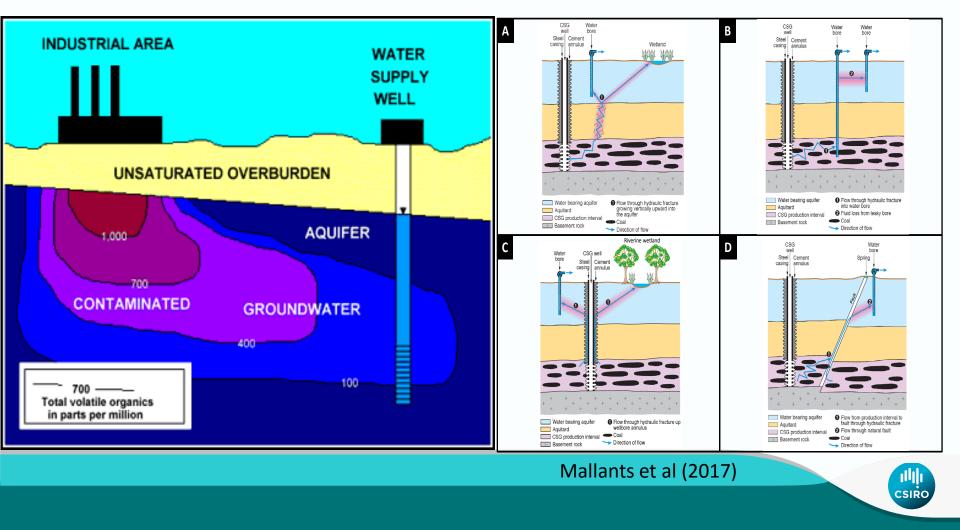


Contaminants in groundwater

Contaminants are substances present in the environment at concentrations above natural background (biological, physical, chemical)

Surface to GW pathway

GW to surface water pathway



So managed differently?

	Surface waters	Groundwaters
Physical	Light, variable temp, colour, suspended sediments	Stable, dark, constant temp, pressure, large surface area
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Management	Water Quality Guidelines (WQGs) based on ecotoxicological effects or reference condition	Often regulated based on salinity Insufficient taxonomic diversity to derive GW-specific WQGs WQGs for surface waters usually used to protect GW biota

Groundwater quality management

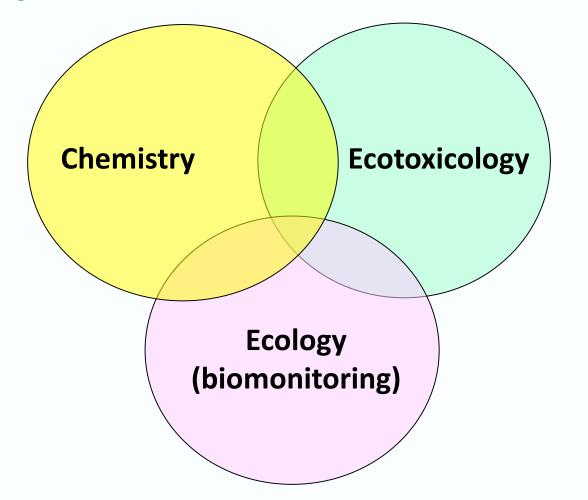
- National Water Quality Management Strategy – guidelines for different environmental values
- Guidelines for Groundwater Quality Protection in Australia 2013
 - General framework
 - No specific WQOs or WQGs
- State/territory responsibility
- Some states have catchmentspecific WQOs

e.g. Qld has a range of WQ parameters for alluvial aquifers of different depths



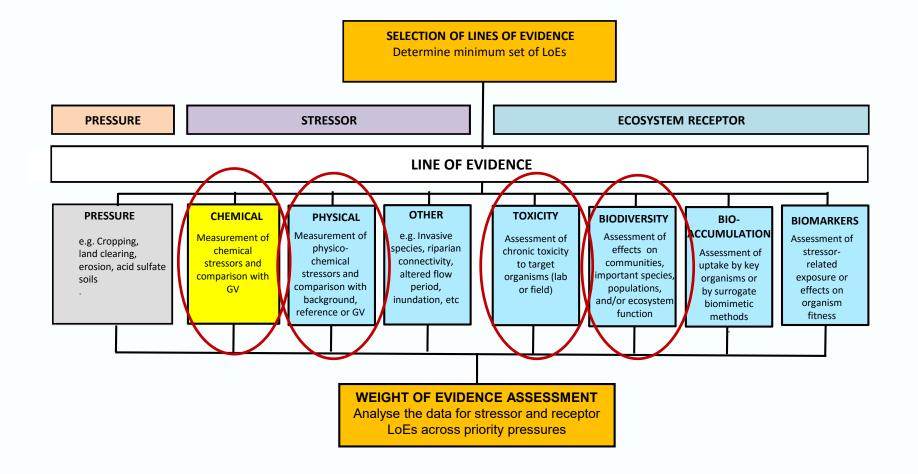


Integrated approaches to assessing groundwater quality and health



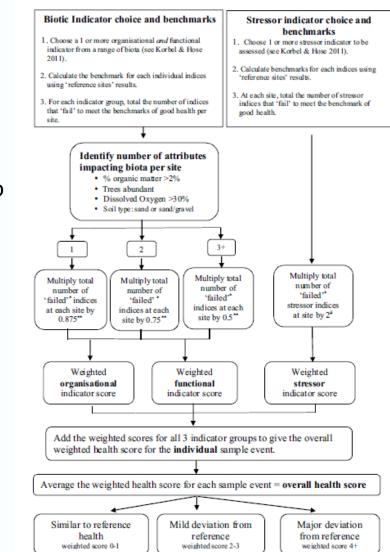


Weight of evidence approach



GW health index

- A two tiered framework using biotic and abiotic components to assess GW ecosystem health
- Tier 1 uses 6 functional (e.g. DOC), organisational (e.g. taxa abundance) and stressor (e.g. pesticides) indicators to compare with universal benchmarks and rank as 'pass' or 'fail'
- Tier 2 refines assessment (12 indicators compared to benchmarks from 'best available' reference sites)
- GW ecosystem health weighted to account for natural factors (e.g. aquifer type, DO) and classified as:
 - 1. Similar to reference
 - 2. Mild deviation from reference
 - 3. Major deviation from reference





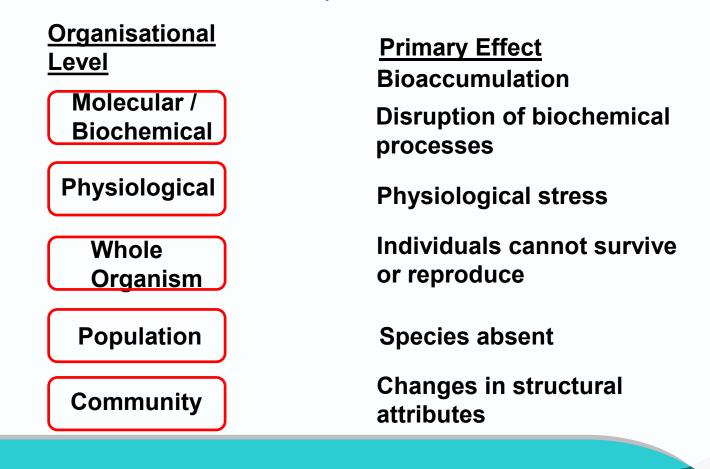
Are ecotoxicological tools that we use for surface waters also applicable to assessing groundwater quality?



Ecotoxicology

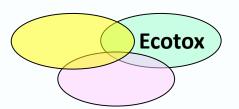
Ecotox

Ecotoxicology is the study of the fate and effects of contaminants on individual organisms, species, populations, communities and ecosystems



Ecotoxicity tests

- Measure an organism's response to contaminants
- Can be short-term (acute toxicity e.g. survival, behaviour) or long-term (chronic toxicity e.g. growth, reproduction)
- Response depends on:
 - organism (species, health, prior exposure, measured endpoint)
 - contaminant bioavailability
 - route and duration of exposure







Ecotoxicity tests

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- Response depends on:
 - organism (species, health, prior exposure, measured endpoint)
 - contaminant bioavailability
 - route and duration of exposure
- Useful to assess complex mixtures of unknown chemicals
- Early warning
- Predict impacts
- Identify contaminants of concern (TIE)
- Derive water quality guidelines (WQGs)



Cirrhosis of the river.

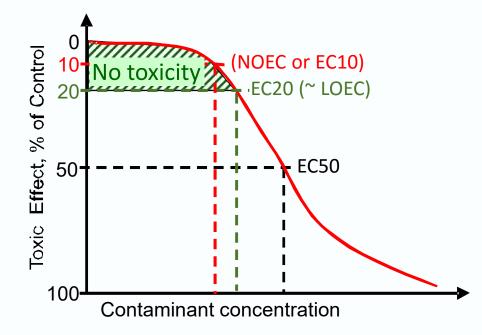






Deriving water quality guideline values

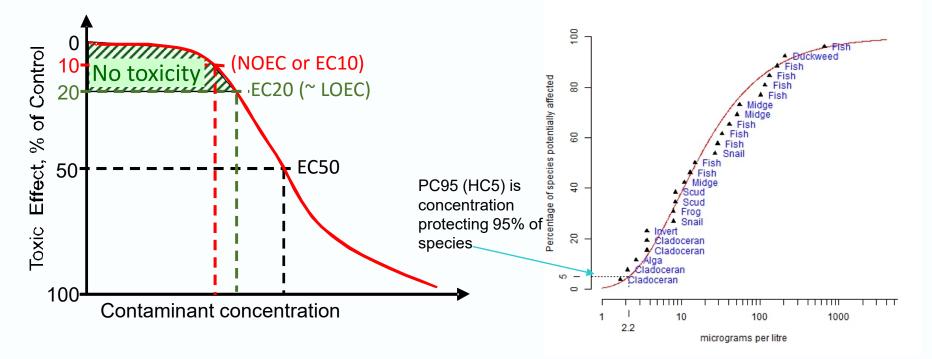
Derived from chronic toxicity tests with aquatic biota





Deriving water quality guideline values

Derived from chronic toxicity tests with aquatic biota



Ecotox

If sufficient data, chronic toxicity endpoints (EC10 or NOEC) are plotted in a species sensitivity distribution (SSD) and the 5th percentile is the WQG for slightly to moderately disturbed receiving waters

Can we use SW ecotox tests as a LOE to protect GW quality?

- Toxicity depends on contaminant bioavailability. Different aquifers have different geology and ionic compositions which will alter contaminant bioavailability
- Significant differences in sensitivities of GW and SW biota found
 - GW biota have lower metabolic rates so uptake of contaminants may be reduced but detoxification/elimination rates also slower
 - GW invertebrates tend to be less sensitive to metals
 - GW biota may be more sensitive to some pesticides e.g. chlorpyrifos

Yes, but prefer GW test species rather than SW surrogates



Groundwater toxicity tests - invertebrates

Groundwater invertebrates (2 cyclopoid and 1 harpacticoid copepods) collected from a GWfed upland peat swamp (1.8 m) and a fractured sandstone aquifer (22 m), NSW

GW spiked with As(III), Cr(VI) and Zn separately

Mortality measured over 96 h, 14 and 28 days

Parameter	Peat swamp (Budderoo)	Fractured sandstone aquifer (Somersby)
рН	4.6 - 5.0	4.2 - 5.6
Conductivity (µS/cm)	95	131 - 195
DO (%sat)	18 - 52	59 - 83
Hardness (mg CaCO ₃ /L)	8 - 37	25 - 44
TOC (mg/L)	21 - 35	3 - 13
As (mg/L)	<0.01	<0.01
Cr (mg/L)	<0.01	0.03
Zn (mg/L)	0.07	0.02



Groundwater toxicity tests – invertebrates 14-day LC50s (mg/L)

Metal/metalloid	Budderoo cyclopoid	Somersby cyclopoid	Somersby harpacticoid
As (III)	5.6	0.79	1.5
Cr(VI)	0.54	1.1	0.03
Zn	2.4	3.1	0.74

All GW species less sensitive than SW copepods to Zn and Cr(VI)

Issues:

Collection of sufficient nos. of copepods (large volumes of GW filtered) Taxonomic identification difficult Matching test conditions to GW e.g. DO Insufficient taxa for SSD and GWQG

Hose et al. (2016) Environ Sci Pollut Res 23, 18704-18713







GW microbial tests- fungi

GW microbial communities dominated by bacteria and fungi

Test developed with *Penicillium* fungi isolated from alluvial aquifer in Bylong Valley, NSW

This fungi dominant and widespread in different aquifer types due to tolerance to physicochemical conditions

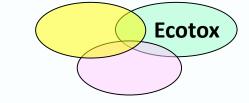
Not present in HC contaminated aquifers

2 tests developed:

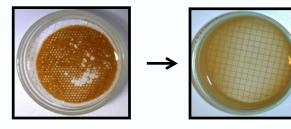
- 1. Hyphae growth on agar plates over 4 and 21 days
- 2. Hyphae growth and viability (absorbance) in microtitre plates over 48 h

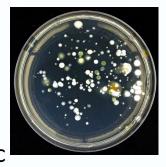
Low sensitivity Cr(VI) > Cu (1mg/L) >> Zn (100mg/L) >> As (III)(1000mg/L)

Yeast (from sand aquifer) test (24-h cell viability) also developed - more sensitive to metals at GW relevant conc











Lategan and Hose (2014) ET&C 33, 2826-2834; Lategan et al. (2016) EES 132, 18-25



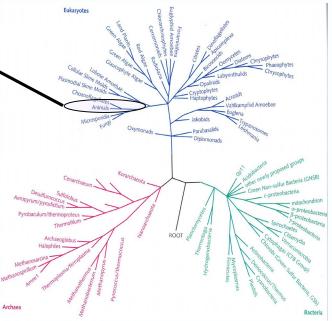
New metagenomics (eDNA) approaches

Limitations of traditional biological monitoring

- Time-consuming
- Costly
- Requires good taxonomic expertise
- Most studies examine 50-60 relatively large metazoan taxa
- Sparse and heterogeneous GW biota no detections
- Focus is on structure and not ecological function



Ecology





New metagenomics (eDNA) approaches

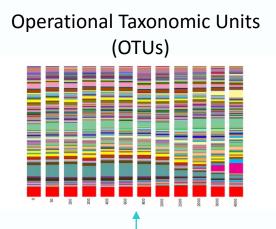
Genetic material recovered directly from environmental samples

Rapid and cost-effective genetic approaches for assessing ecological status (structure and function)

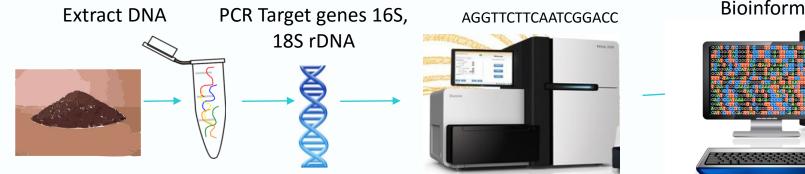
Microbial diversity and abundance

Higher organism diversity

Metabarcoding



Ecology



Sequence DNA

Bioinformatics



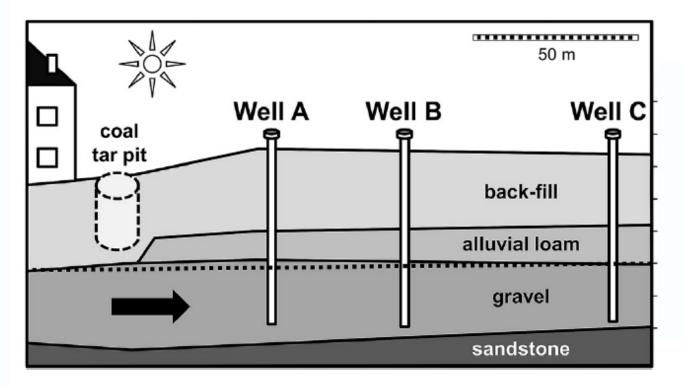
Case studies



Case study 1: Using eDNA to assess bacterial diversity and abundance in a coal tar polluted aquifer

Former gasworks site in Germany – coal tar derived pollutants (BTEX) leaking into GW

LOE included physical and chemical analyses, bacteria sequencing, targeted functional genes for aromatics degradation, culture of GW microbes

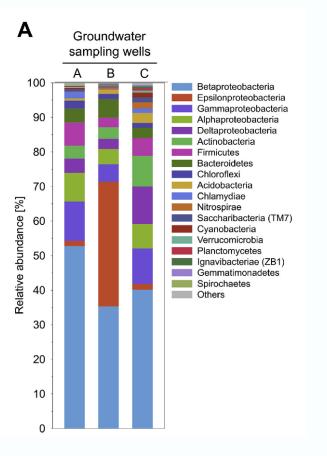




Sperfeld et al. (2018) Wat Res 132, 146-157

Case study 1 con....

Relative abundance of bacteria in GW



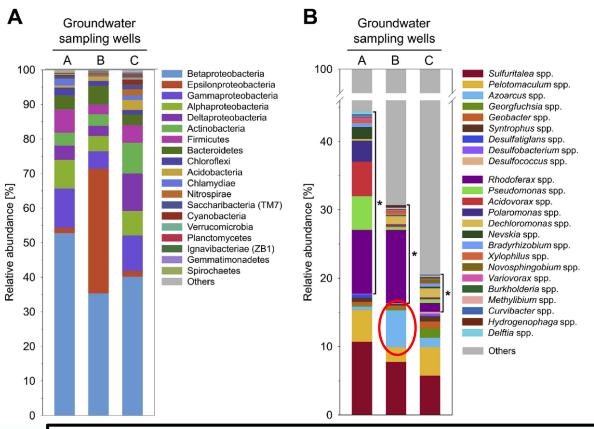
- Betaproteobacteria dominated (facultative anaerobes that degrade HCs)
- Epsilonproteobacteria dominant in Well B (S and N cyclers)



Case study 1 con....

Relative abundance of bacteria in GW

Aromatic compound degrading bacteria (ACDB)



- Betaproteobacteria dominated (facultative anaerobes that degrade HCs)
- Epsilonproteobacteria dominant in Well B (S and N cyclers)

Design of bioremediation approaches can benefit from identifying microbes and their function at a contaminated site



Case study 2: NAPLs in GW

Former diamond-processing operation resulted in contamination of groundwater and surface waters with several volatile organic compounds (VOCs) including 1,1,2,2-tetrabromoethane

Tetrabromoethane breaks down to:

1,2-dibromoethene (DBE)

1,1,2-tribromoethene (TriBE)

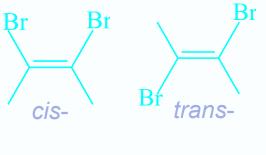
Contamination zone from 2-18 m deep in stratified sands

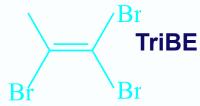
Groundwaters had up to 250 mg/L TriBE and 2 mg/L DBE

Surface waters - 1 μ g/L TriBE and 3 μ g/L DBE

No WQGs for these VOCs to protect either SW or GW fauna



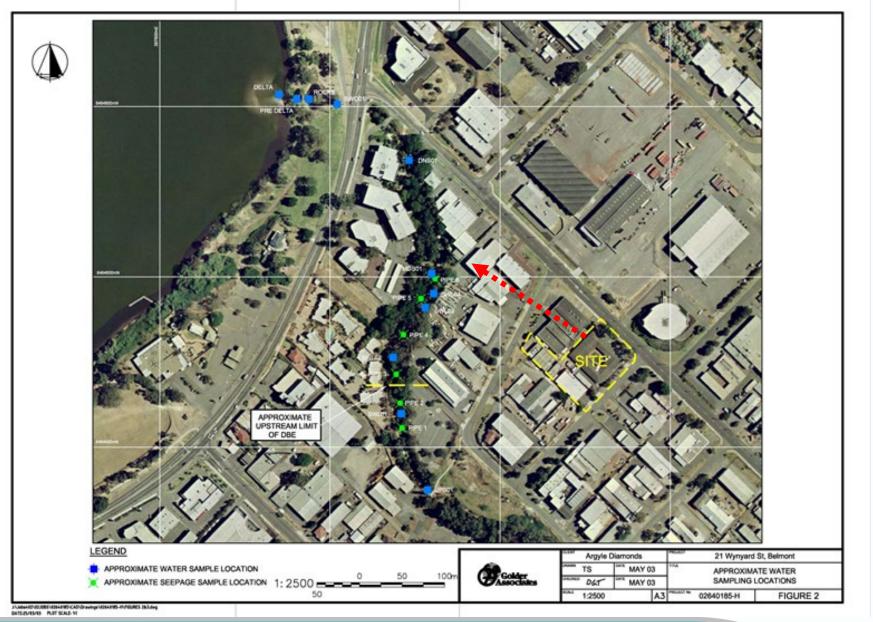




Binet et al. (2010) ET&C 29, 1984-1993

Johnston et al., (2013, 2014) J. Contam Hydrology 144 (122-137) & 164 (100-113)







Lines of evidence

1. GW chemical analyses

17 brominated compounds

60 VOCs

Gas chromatography – mass spectrometry

2. Bioaccumulation in fish



3. Ecotoxicity tests (SW species)

Acute

Bacteria (Microtox[®])

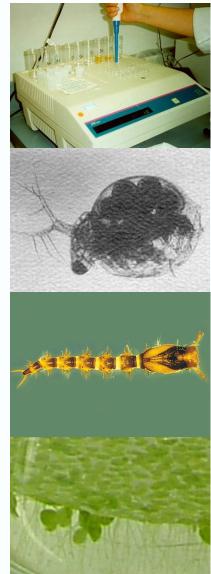
Cladoceran (48-h immobilisation)

Midge (48-h survival)

Chronic

Microalgae (72-h growth rate)

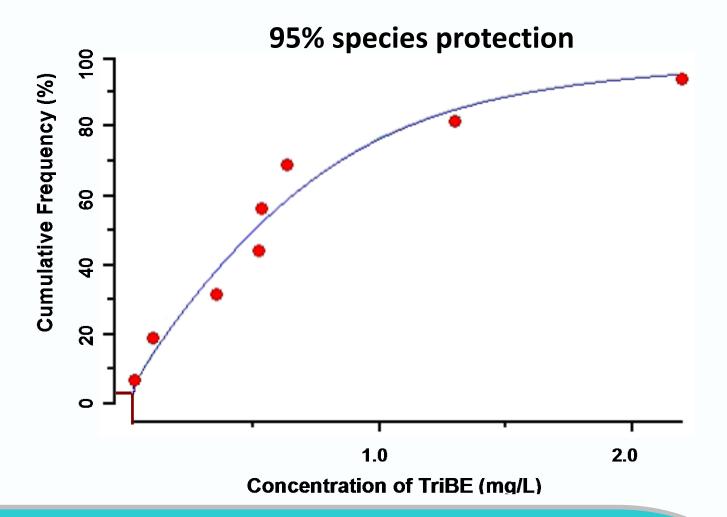
Duckweed (7-day growth rate and biomass)





Species sensitivity distribution - TriBE







Groundwater toxicity

Guidelines:	TriBE 0.03 mg/L,	
	DBE 2.0 mg/L	

SOURCE STREAM

MB01B	MB13B	MB35B
[TriBE] = 250 mg/L	[TriBE] = 9 mg/L	[TriBE] = 3 mg/L
[DBE] = 3 mg/L	[DBE] = 2 mg/L	[DBE] = 3 mg/L
Most toxic	Less toxic (Microtox, cladocerans)	Least toxic
Highest [VOCs] Only site with TBA	Lower [VOCs]	Lowest [VOCs]
5 × more toxic than predicted just from TriBE	Microtox = TriBE toxicity More toxic to cladocerans than predicted	Only toxic to Microtox as predicted
Dilution of 1:1670 needed	Dilution of 1:50 needed	Dilution of 1:18 needed



Surface water toxicity

In the stream, TriBE (3 μ g/L) and DBE (1 μ g/L) ~1000 times lower than in least toxic sample

Therefore groundwater attenuation occurring

Stream concentrations well below guidelines (2 mg/L DBE and 0.03 mg/L TriBE), therefore risk to stream biota is very low

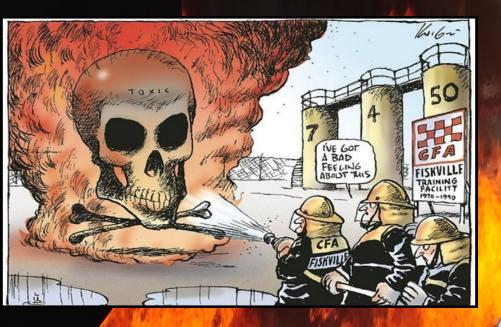
Bioaccumulation in fish negligible

Further attenuation likely, therefore risk to Swan River is even less





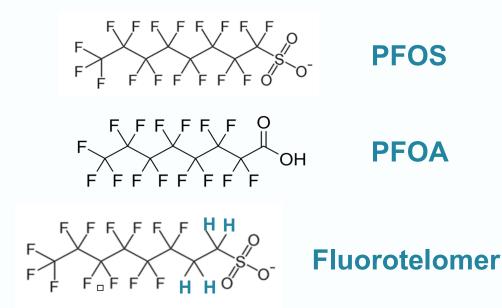
Case study 3: Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)



What is PFAS?

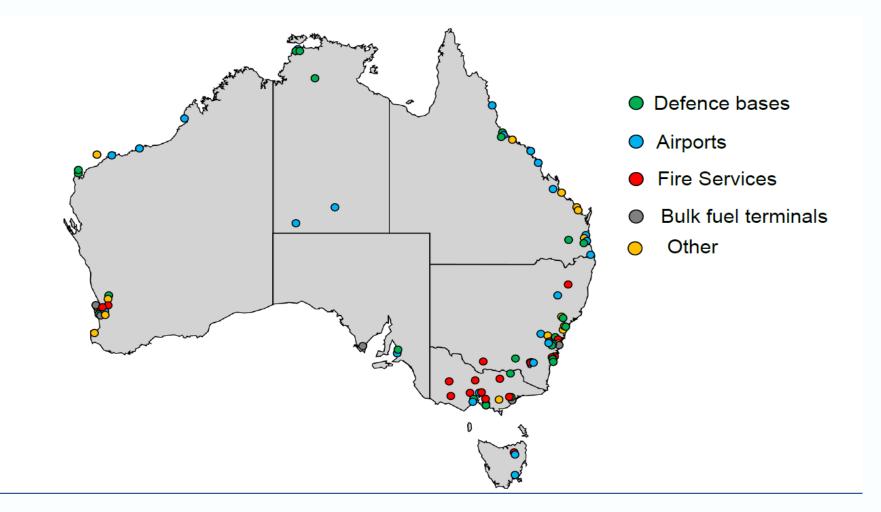
PFAS: per- and polyfluoro alkyl substances (about 2000 compounds)

- The famous C8s:
 - Perfluorooctane sulfonate (PFOS)
 - Perfluorooctanoic acid (PFOA)
- Other chain lengths and chemistries
 - Poly-fluorinated e.g. fluorotelomers
 - Precursors
- Used in wide variety of products
- Surfactant properties
- Non-volatile
- Highly mobile
- Persistent (precursors can degrade to stable PFAAs)
- Bioaccumulate differently in plants/animals
- Toxic
- Partitions to protein (not fats) in blood, liver, kidney, muscle (not metabolised)

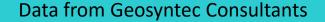




Over 110 PFAS investigation sites



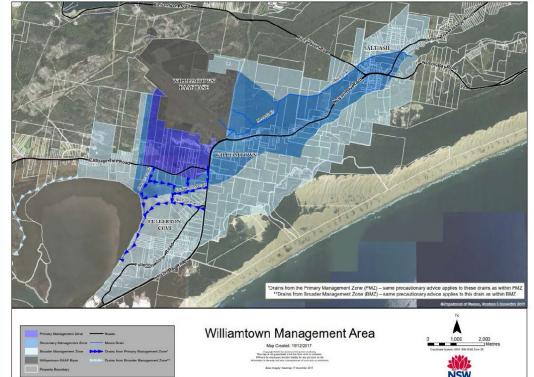
Landfills – sleeping giant – PFAS detected in every landfill leachate tested so far



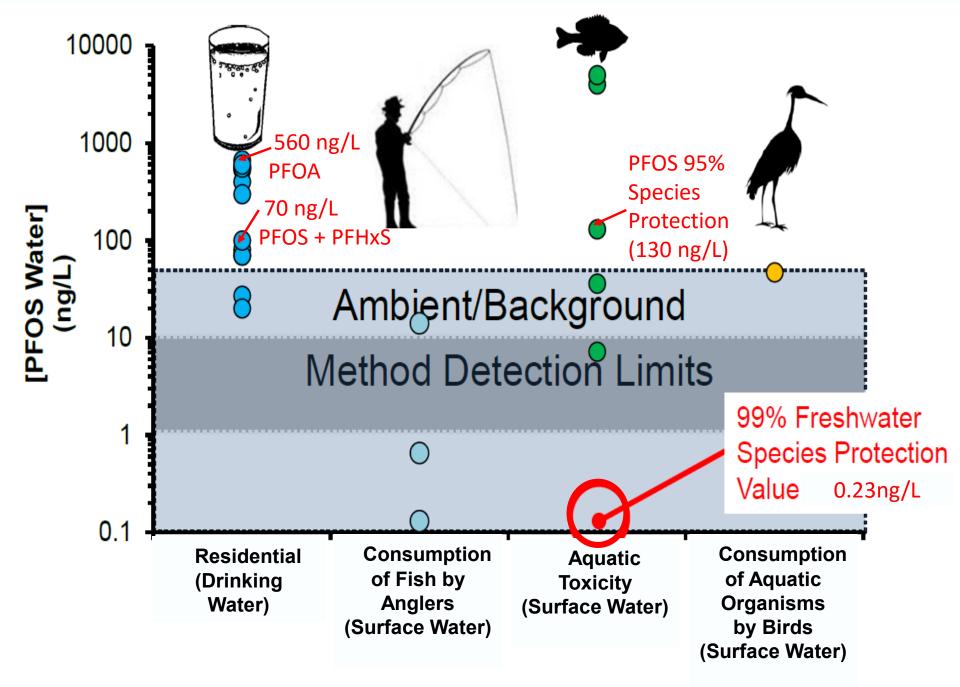


PFAS Williamtown NSW RAAF base

- PFOS and PFOA main concerns, with PFAAs further from source
- 823 ha (on site) and 50 km² (off site) impacted
- 25-km long plume
- PFOS 2,900,000 ng/L in GW (BG < 50 ng/L)
- Human health and ecological risk assessments 2016







No PFOS WQGV for GW but soil criterion (0.009 mg/kg) to protect GW

How can this help improve groundwater management?



So what?

We have multiple LOE/data/tools to assess GW quality:

- 1. Natural uncontaminated GW regime
 - GW quality should be maintained within the natural range of variability
 - Monitor and protect to avoid contamination
 - Prevention better than remediation





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- 2. Moderately disturbed GW system
 - Diffuse, gradual legacy contamination
 - Monitor at source, monitor attenuation zone and boundary, assess impacts

MID

IOW



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 - Monitor and protect to avoid contamination
 - Prevention better than remediation
- 2. Moderately disturbed GW system
 - Diffuse, gradual legacy contamination
 - Monitor at source, monitor attenuation zone and boundary, assess impacts
- 3. Highly degraded GW system
 - Contaminant plume moving slowly (or faster via preferential pathway)
 - WQ monitoring + flow path modelling
 - Engineering solutions remove source, barrier, pump and treat
 - Bioremediate with microbes *in situ*









Key messages

- Inherent value in GW ecosystems that deserve protection in their own right (not just for their env. values/beneficial uses)
- Connectivity between GW and SW demands a holistic approach to their management and protection
- Contaminant sources similar but GW protection may not be achieved by just using SW guidelines. GWs have unique physico-chemical and hydrological properties, and endemic biota, that necessitate development of specific GW quality objectives
- GW quality assessment requires multiple LOE in a WOE approach
- Ecotox tools used for surface water monitoring (toxicity tests, eDNA) can be applied to GW quality assessment with some refinement (e.g. different biota)



The future?

- GW ecosystems are not currently sufficiently valued. We have the science and tools but not the policy, will or resources to protect them
- Australia is leading the way on GW ecotoxicology. Hose group has published 3 of the 10 papers in the global literature!
- Very limited baseline data on GW quality and ecotoxicology is hampering our ability to protect these systems
- Usually only site-specific or industry-specific GW WQ monitoring, except Qld GW pesticides monitoring
- Need a national baseline monitoring program of GW WQ
- Need national repositories for this WQ data (only quantity e.g. BOM's Aust GW Explorer water level database)
- Need national database on GW biota e.g. Qld stygofauna database (https://data.qld.gov.au/dataset/queensland-subterranean-aquatic-fauna-database)

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