Towards EQS assessment in groundwater bodies:

ammonium contamination and response of groundwater copepods

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ENVIRONMENTAL QUALITY STANDARS
Groundwater Daughter Directive
2006/118/EC

POINT 7

“Having regard to the need to achieve consistent levels of protection for groundwater, **environmental quality standards** (**EQS)** and **threshold values (TV)** should be established”.

Article 2(1) (EQS)

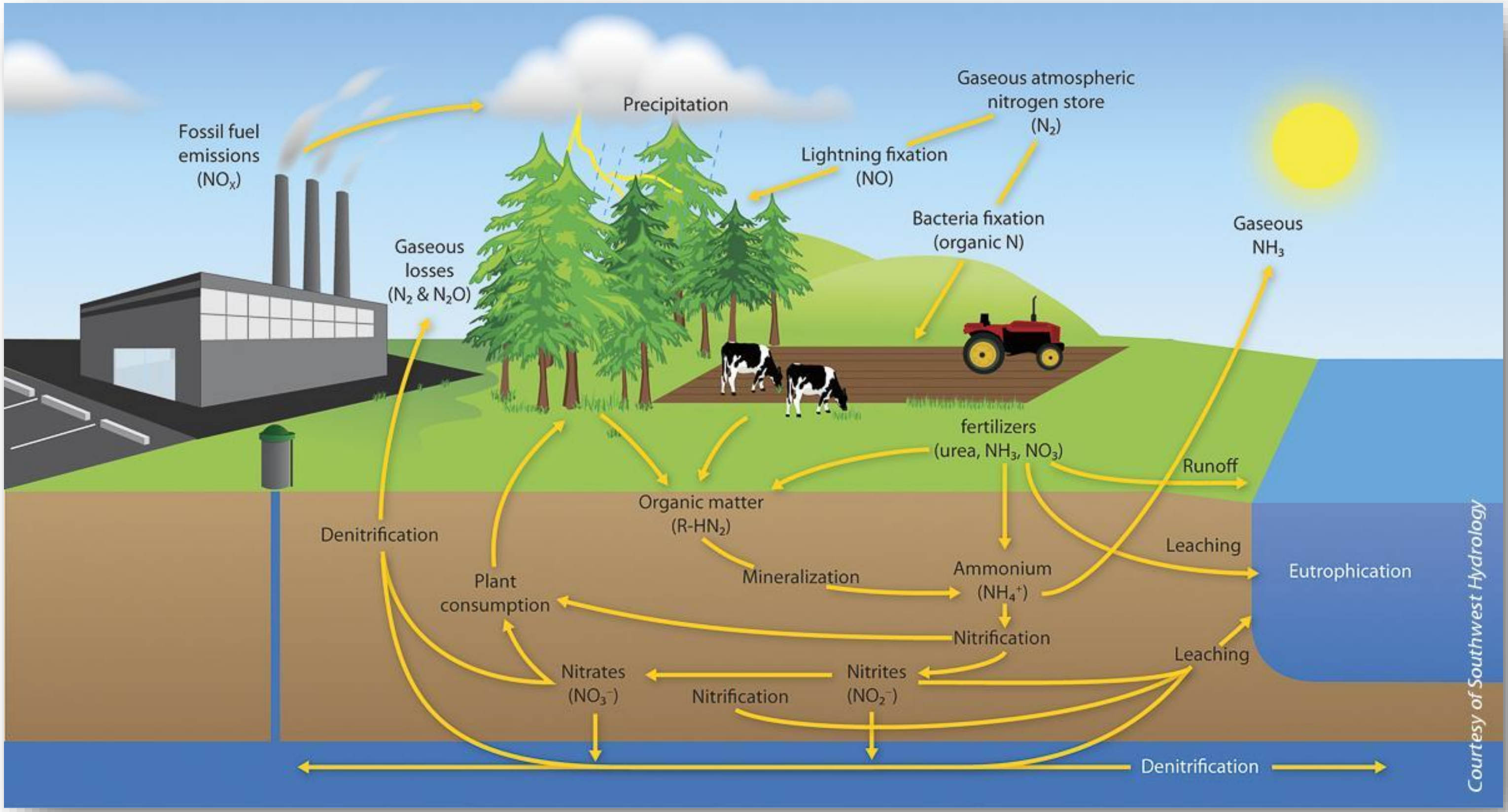
Groundwater quality standard means an environmental quality standard expressed as the concentration of a particular pollutant, group of pollutants or indicator of pollution in groundwater, which should not be exceeded in order to protect human health **and the environment**.

Article 2(2) (TV)

Threshold value means a groundwater quality standard set by Member States in accordance with Article 3.

WHY IONIZED AMMONIA?

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_{4(aq)}^{+} + OH^{-}_{(aq)}$$



AMMONIUM TVs in EUROPE

ID	MS	min TV (mg/L)	max TV (mg/L)	unique TV (mg/L)
1	Austria			0.5
2	Belgium	0.3	3.9	
3	Bulgaria			0.5
4	Cyprus			0.5
5	Czech Republic			0.5
6	Denmark			
7	Estonia	ammonium has been never found in gw		
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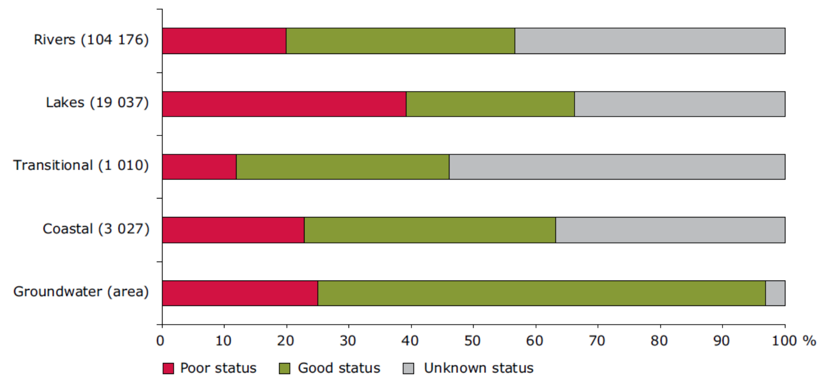
10	Germany	0.5	52	
11	Hungary	0.5	5	
12	Ireland	0.084	0.22	0.2
13	Italy			0.5
14	Latvia			0.8
15	Lithuania			3
16	Luxembourg			0.5
17	Malta			0.25
18	Poland			1.92
19	Portugal	ammonium does not pose gw bodies at risk		
20	Romania	0.5	9.9	
21	Slovak Republic	0.25	0.5	
22	Slovenia	ammonium does not pose gw bodies at risk		
23	Spain			0.5
24	Sweden			1.5
25	The Netherlands	no anthropogenic origin		
26	UK			0.37

Ammonium TV (21 MS): Min value = 0.084 mg/L, max value: 52 mg/L

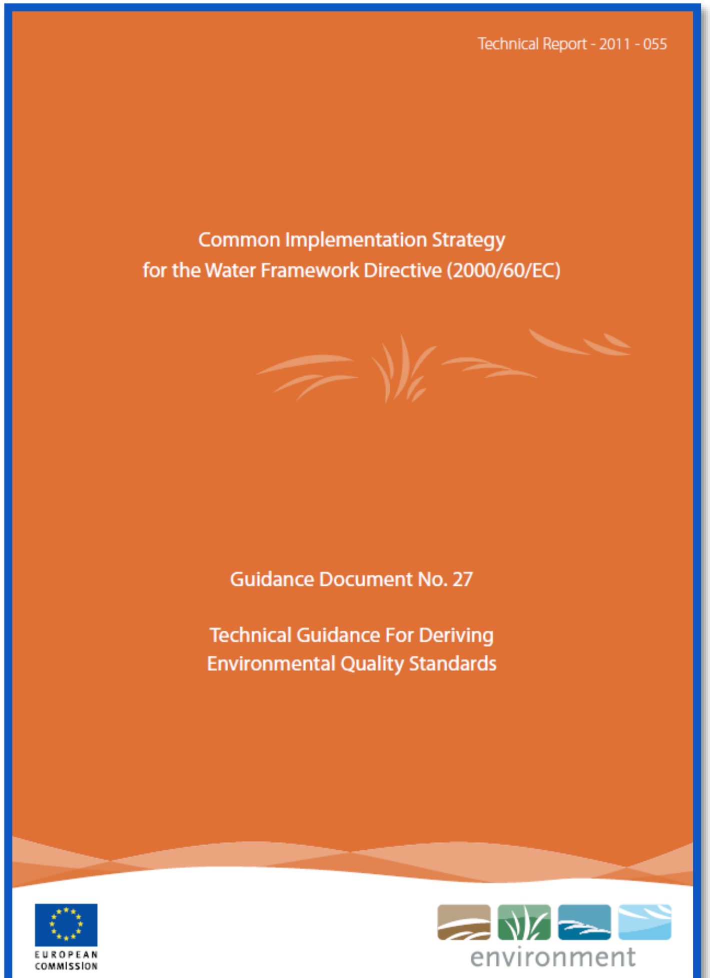
Table 6: Seven pollutants posing risk to more than 100 groundwater bodies in Europe

Pollutants	posing risk		poor status	
	GWBs	Member States	GWBs	Member States
Nitrate*	**478**	17	504	14
Ammonium	**276**	14	147	13
Chloride	**256**	18	117	13
Sulphate	**216**	16	117	15
Arsenic	**128**	13	42	11
Benzo(a)pyrene	**110**	4	51	3
Cadmium	**101**	11	55	5

*partial information



THRESHOLD VALUES
Guidance Document n. 27


Technical Report - 2011 - 055

Common Implementation Strategy
for the Water Framework Directive (2000/60/EC)

Guidance Document No. 27

Technical Guidance For Deriving
Environmental Quality Standards

EUROPEAN COMMISSION

environment

ANNEX II: 2. the assessment of TVs should take into account:

1) the origins of the pollutants;
2) their possible natural occurrence;
3) their **toxicology;**
4) their dispersion tendency;
5) their persistence;
6) their bioaccumulation potential

2.6.1.2 Ecotoxicological data

According to Annex V of the WFD, the <u>base set of taxa</u> that should be used in setting quality standards for water are **algae** and/or **macrophytes**, ***Daphnia*** (or representative invertebrate organisms for saline waters), and **fish** <u>in relation to water column standards</u>. **However, for the purpose of quality standard setting, the data should not be restricted to this base set.** All available data for **any taxonomic group or species should be considered**, provided the data meet quality requirements for relevance and reliability (Section 2.6.2).

WHAT IS STILL MISSING?

Deliberate omission or unfortunate oversight: Should stygofaunal surveys be included in routine groundwater monitoring programs?

**Moya Tomlinson · Andrew J. Boulton ·
Peter J. Hancock · Peter G. Cook**

Introduction

With burgeoning global exploitation of groundwater, there is increasing urgency for sustainable groundwater management (Kalf and Woolley 2005). Escalating groundwater exploitation is outstripping social and scientific understanding of the sustainability of this resource. To date, groundwater management has largely concerned quantity and hydrological sustainability of supply, water quality and protection from pollution, and more recently, economic and social governance (see *Hydrogeology Journal*, Vol 14 (3), 2006). However, increasing public and political recognition of the importance of ecological sustainability heralds a new paradigm in groundwater management integrating hydrogeology and groundwater ecology (Hancock et al. 2005). This paradigm emphasises the close links between hydrogeology, biogeochemistry, and ecology in holistic management of water supply and quality, explicitly acknowledging the connectivity between surface and groundwaters, aquifers as biologically active systems (e.g., capable of bioremediation of pollutants, Gounot 1994) and the ubiquity of groundwater dependence in terrestrial ecosystems (Eamus et al. 2006).

Aquifers support interstitial assemblages of bacteria and associated biofilms as well as specialized obligate groundwater fauna termed "stygofauna". Full assessment of aquifer condition includes not only traditional sampling of physical and chemical variables but also consideration of the biota. This requires the combined expertise of hydrogeologists and ecologists, but as in any multidisciplinary field, successful collaboration is hampered by different knowledge structures, disciplinary paradigms, and field experiences (Boulton et al. 2005). Traditionally, managers of groundwater have hydrogeological and engineering backgrounds and work in resource management agencies responsible for water supply. Conversely, groundwater ecologists mainly work in universities, museums and conservation agencies, seldom have direct responsibility for groundwater management, and currently grapple with the uncertainties of an infant discipline (Gibert et al. 1994). Thus, the potential benefits of groundwater ecology to resource management are seldom readily accessible to groundwater managers despite some efforts to bridge the divide (Sophocleous 2002; Danielopol et al. 2003). Questions of whether the contents of a bore are representative of the aquifer community, how results can be compared among aquifer types, and how to interpret the data given gaps in taxonomic and ecological knowledge currently hamper acceptance of stygofaunal sampling in the toolbox of techniques for assessing and monitoring environmental impacts of groundwater exploitation.

This essay briefly reviews perceived values of stygofauna and benefits of their inclusion in hydrogeological surveys of groundwater, and summarises the legislative and policy framework for stygofaunal surveys. Although focused on Australia, the issues discussed are of broad, international concern. A staged approach to surveys is advocated where investigations progressively increase in complexity. This aims to overcome the current paradox of omitting stygofauna from groundwater monitoring because there is insufficient information for the interpretation of survey results—yet, if stygofauna are not sampled, then the information will never be collected to address the knowledge gaps.

Received: 14 February 2007 / Accepted: 11 July 2007
Published online: 1 August 2007

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Stygofauna and their perceived values

The term stygofauna refers only to obligate groundwater fauna (stygobionts, Gibert et al. 1994). It excludes organisms which may occur in groundwaters but lack specialisations for the aquifer environment. Most stygofauna are unpigmented, elongate and small, adapted for life in dark and often confined spaces. Stygofauna include crustaceans, molluscs, worms, beetles and other less familiar invertebrates, and occur in many calcrete, alluvial and fractured rock aquifers. Surveys worldwide reveal stygofauna to be more widespread, abundant and diverse than previously expected (Sket 1999). Currently, stygofauna are valued as (1) a reserve of biodiversity, (2) potential providers of

 DOI 10.1007/s10040-007-0211-z

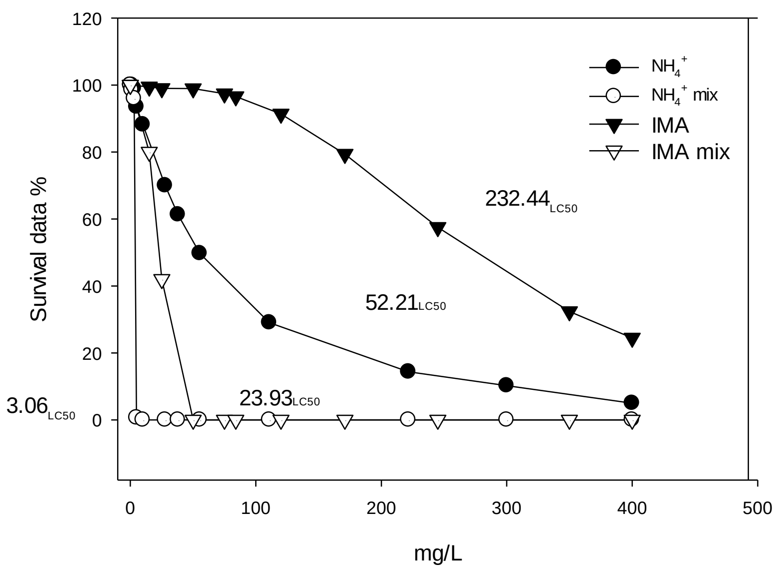
2006/118/EC Recital – point 20

Research should be conducted in order to provide better criteria for ensuring groundwater ecosystem quality and protection.

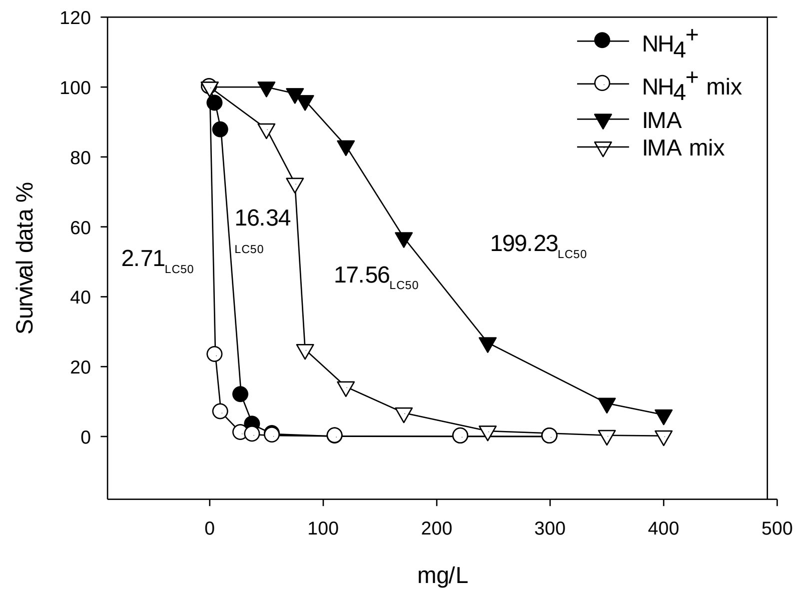
Where necessary, the findings obtained should be taken into account when implementing or revising this Directive. Such research, as well as dissemination of knowledge, experience and research findings, needs to be encouraged and funded.

IN THE LAB
Ecotoxicity of Imazamox and ionized ammonia binary mixture

Eucyclops serrulatus

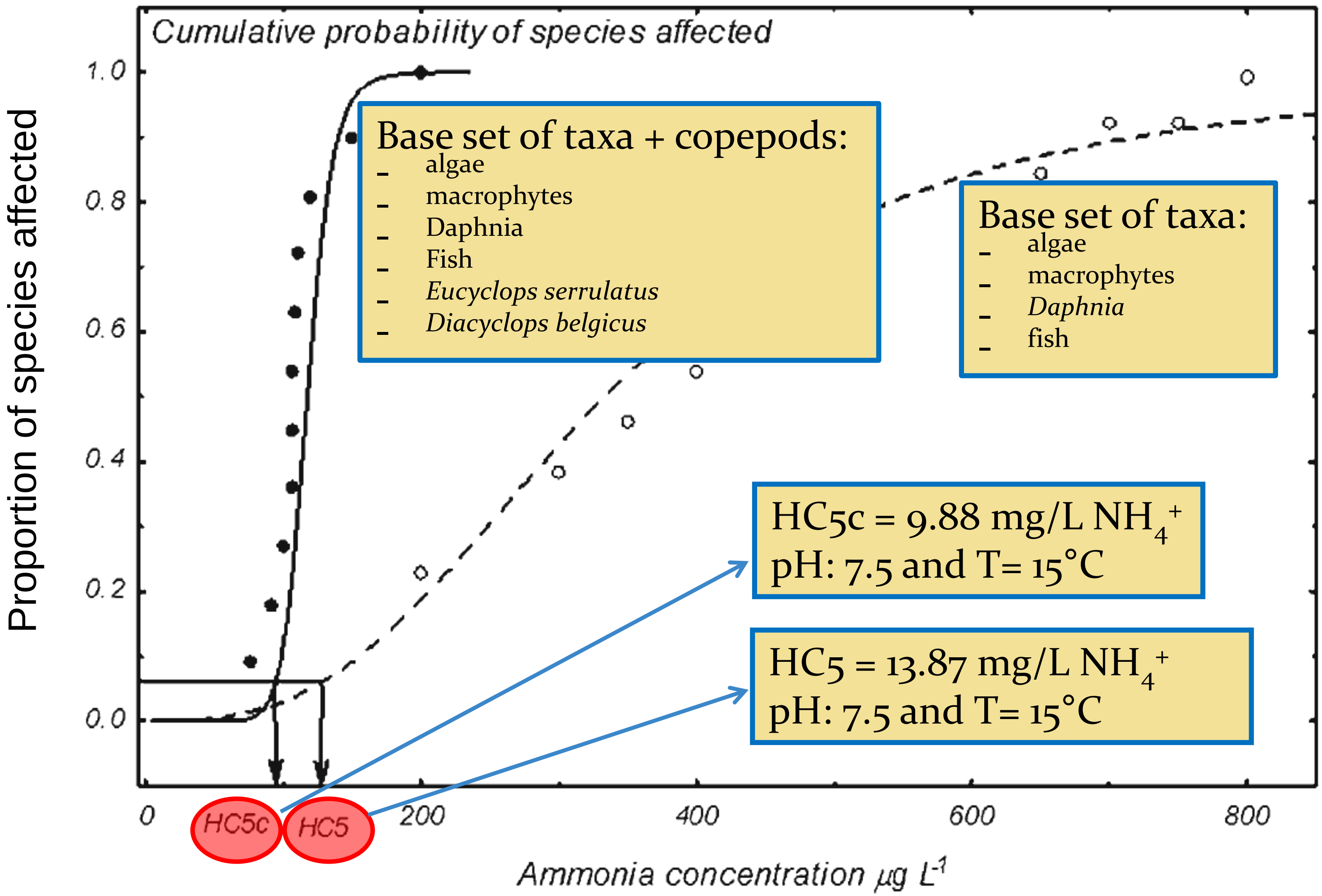


Diacyclops belgicus

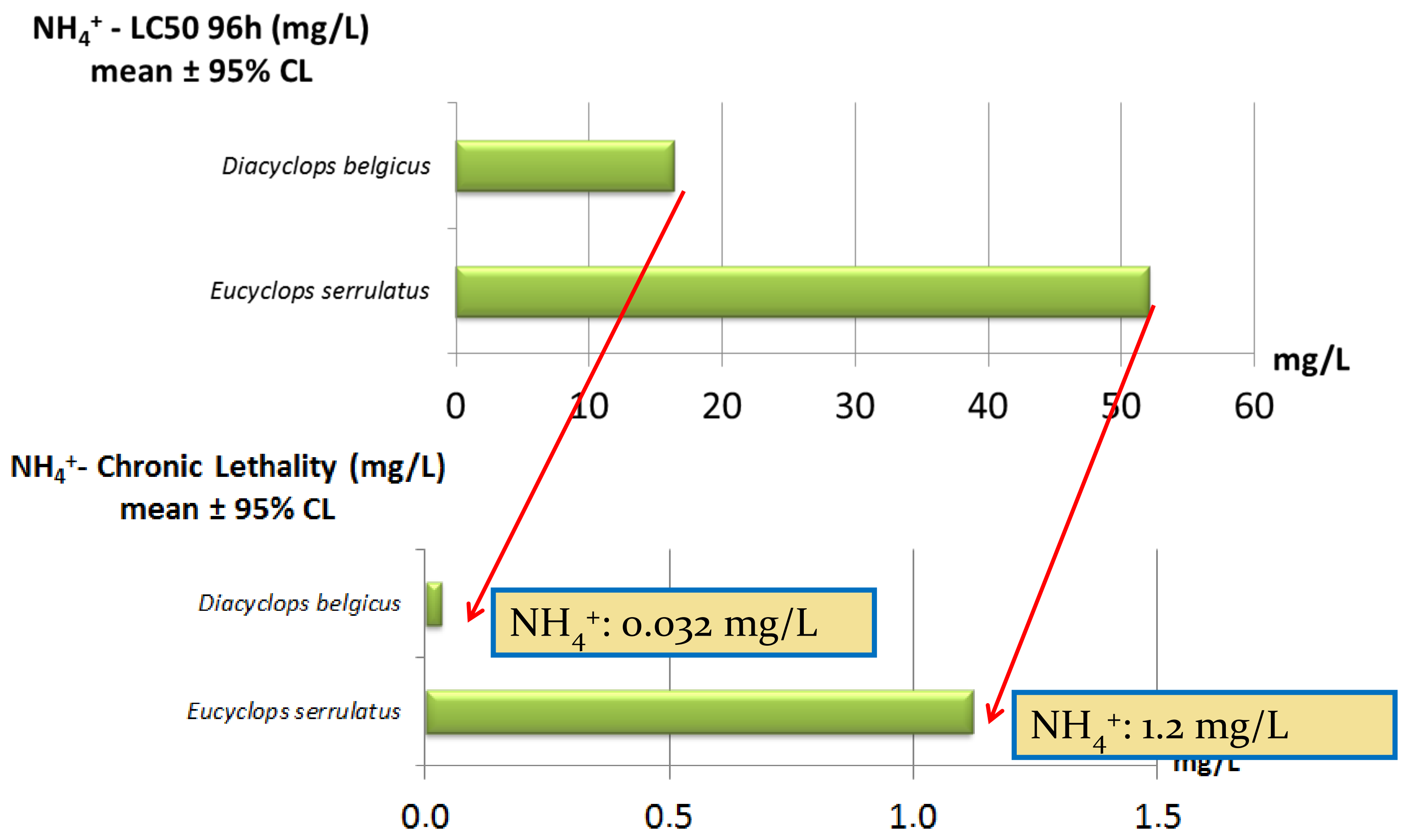


LC50: concentration of the chemical that kills 50% of the exposed individuals.

Threshold value setting through the hazardous concentration (HC5)

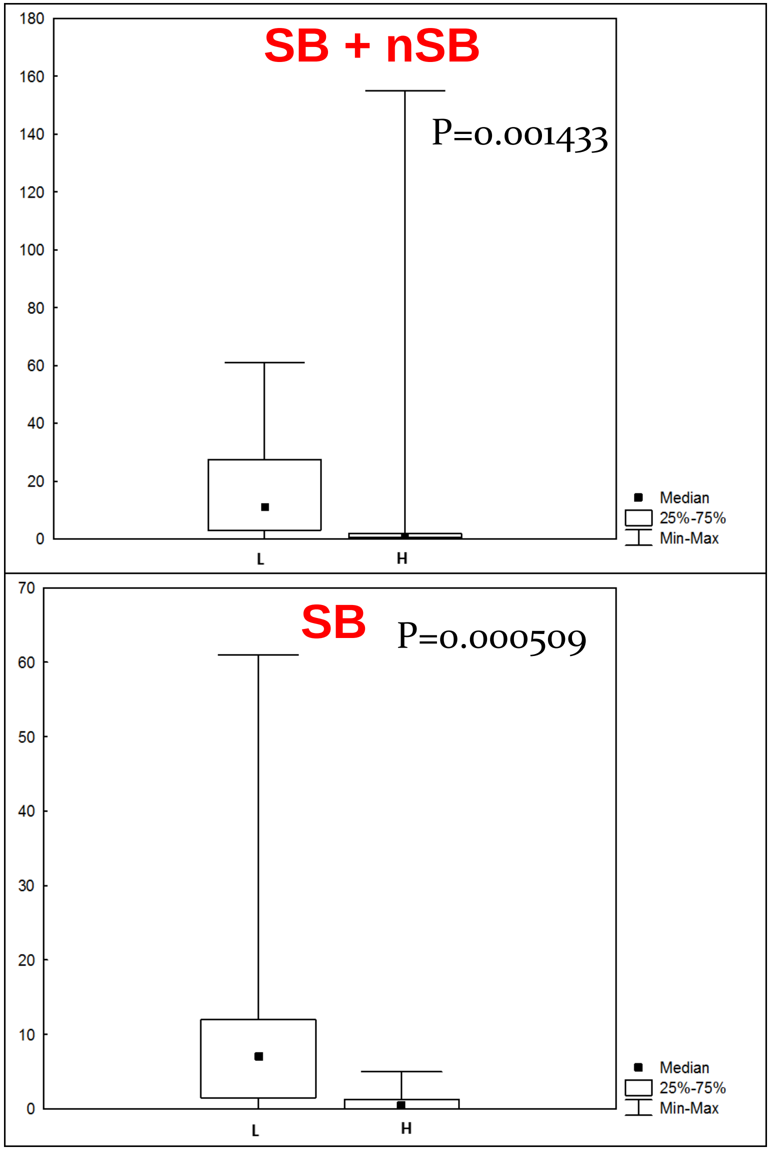


Acute to Chronic Estimation (ACE) method (Mayer et al., 1999)



On the field

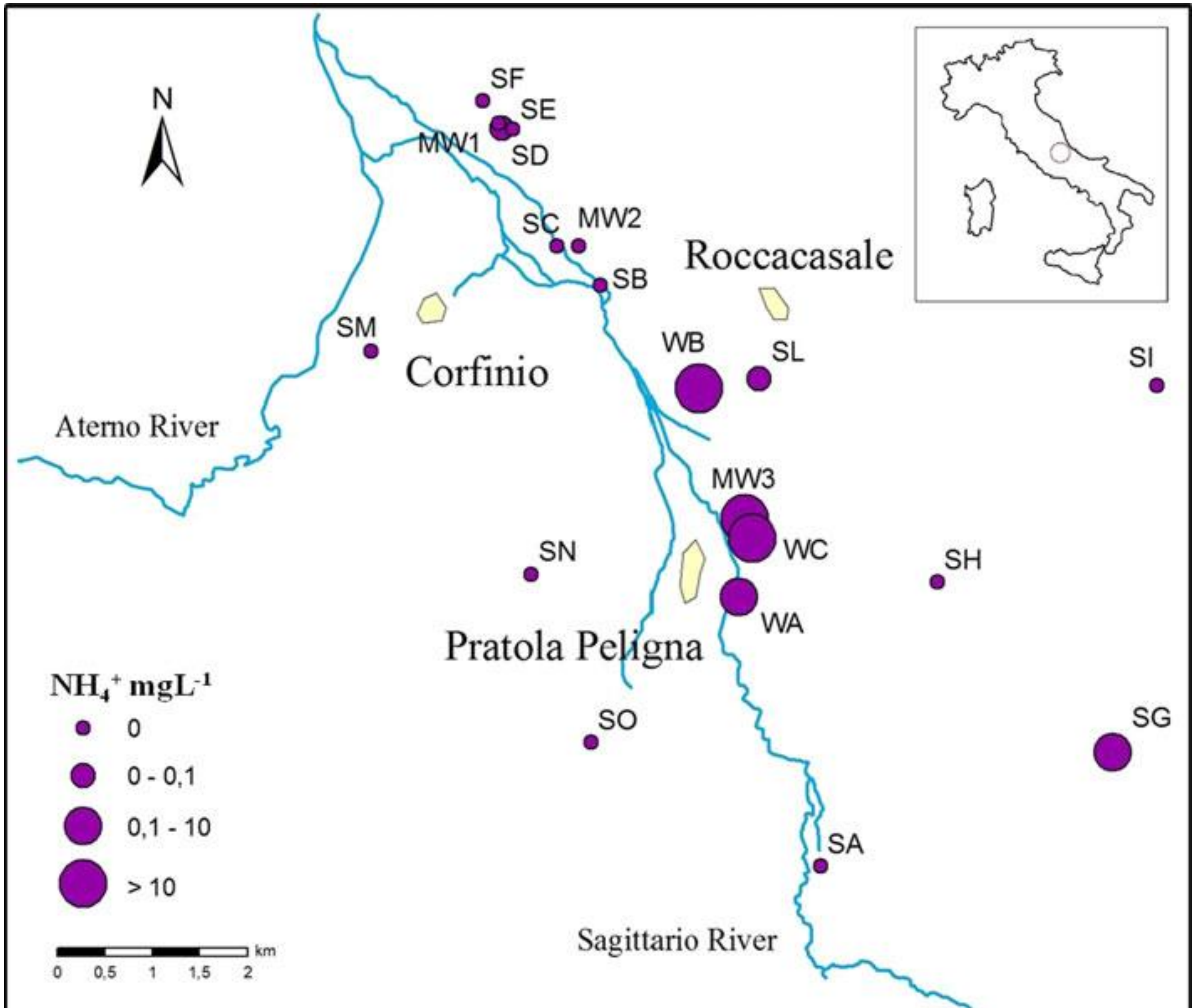
DBE Chronic Lethality: 32 µg/L



TV= 0.032 mg/L
H bores: NH_4^+ > 32 µg/L
L bores: NH_4^+ < 32 µg/L

Di Lorenzo T., Cifoni M. Lombardo P., Fiasca B., Galassi D.M.P. (2015) Ammonium threshold values for groundwater quality in the EU may not protect groundwater fauna: evidence from an alluvial aquifer in Italy. Hydrobiologia, 743:139–150.

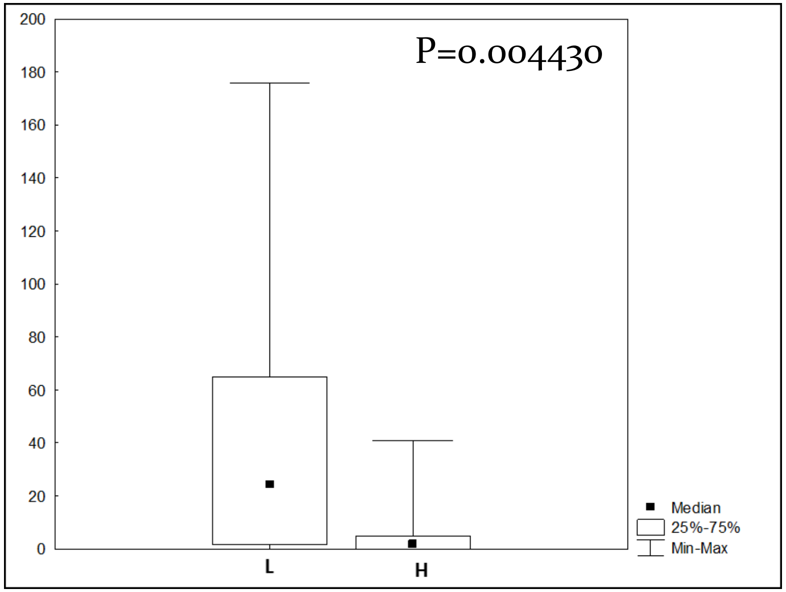
NH_4^+ IN THE HYPORHEIC ZONE OF THE SAGITTARIO RIVER (ABRUZZO)



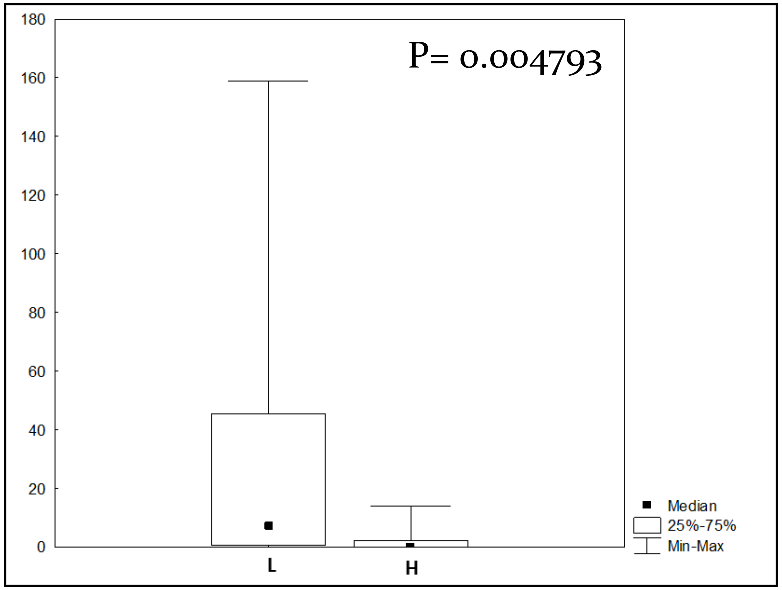
Map of distribution of NH_4^+ concentrations across sampling sites (after Caschetto et al., 2014)

THE COPEPOD RESPONSE TO NH_4^+ CONCENTRATION IN THE HYPORHEIC ZONE OF THE RIVER SAGITTARIO

SB + nSB



SB

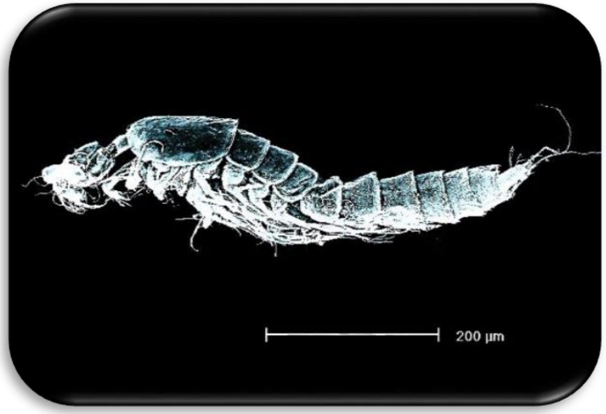


L = sites with NH_4^+ concentrations < **32 µg/L** NH_4^+

H = sites with ammonium concentration > **32 µg/L** NH_4^+

Caschetto M., Galassi D.M.P., Petitta M. & Aravena R. (2016, in press) Evaluation of the sources of nitrogen compounds and their influence on the biological communities in the hyporheic zone of the Sagittario River, Italy: an isotopic and biological approach, *Italian Journal of Geosciences* DOI: 10.3301/IJG.2016.07

Beyond regulation: the use of GDE species for assessing EQS in groundwater and dependent ecosystems



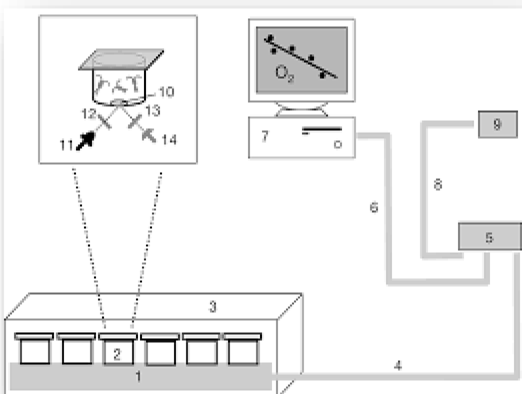

Thank you for your attention

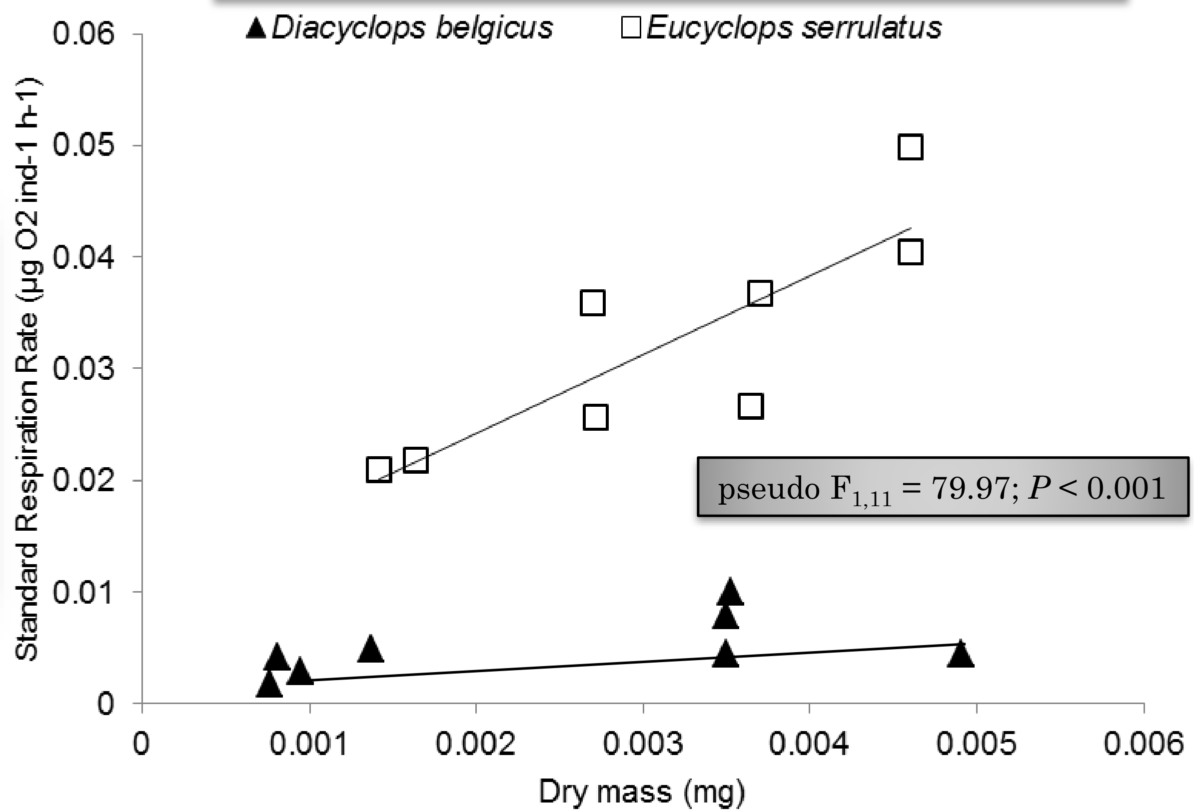
WHAT DO WE HAVE?

*Groundwater associated aquatic ecosystems (GWAAEs) are ecosystems <u>that</u> **<u>belong to surface water bodies</u>** (rivers, lakes, transitional WB or coastal WB), which status (ecological or chemical) or environmental objectives **could be affected by alterations of groundwater level or pollutant concentrations that are transported through groundwater**.*

STANDARD RESPIRATION RATES

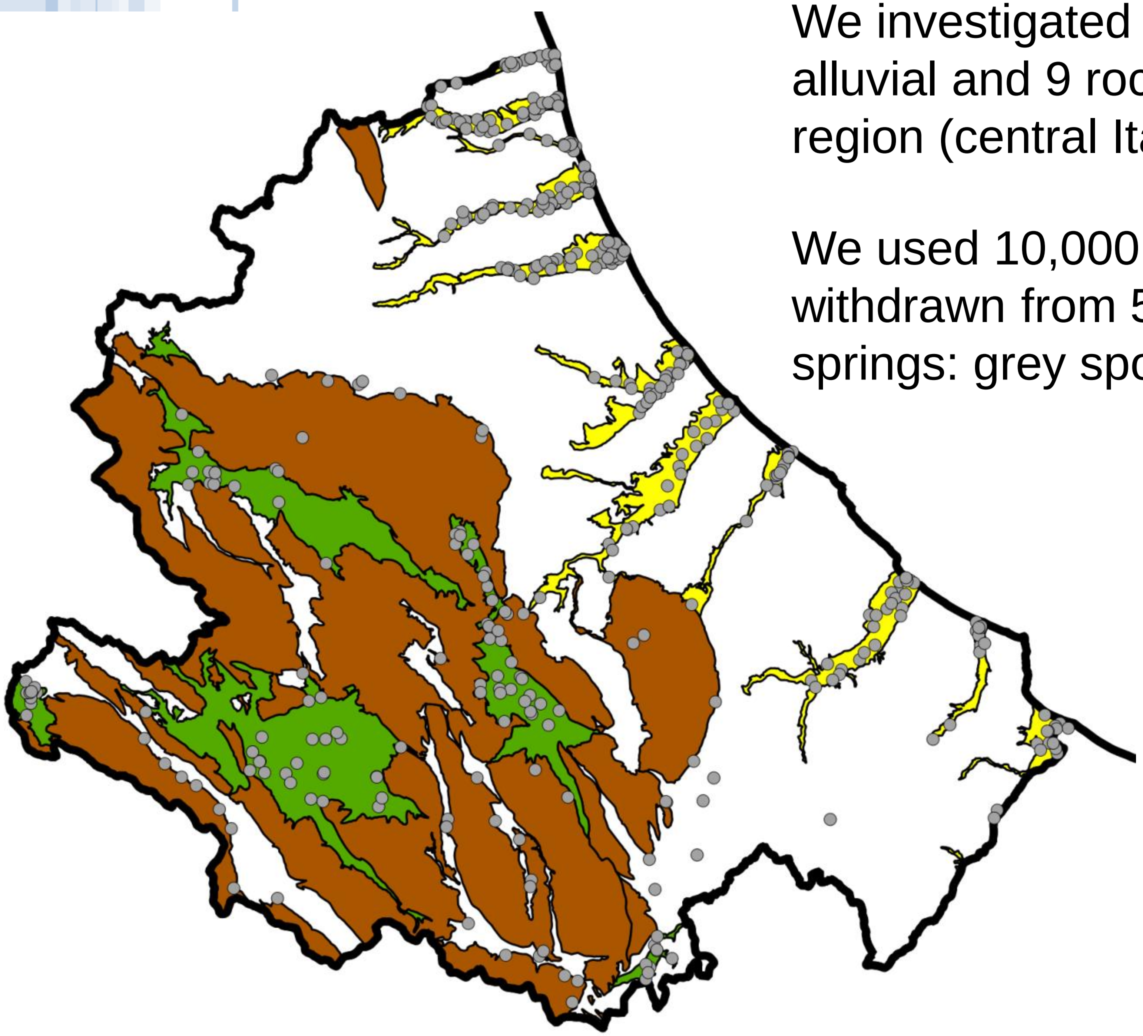
The metabolism of the SB species is about 10 times lower than the metabolism of the nSB one





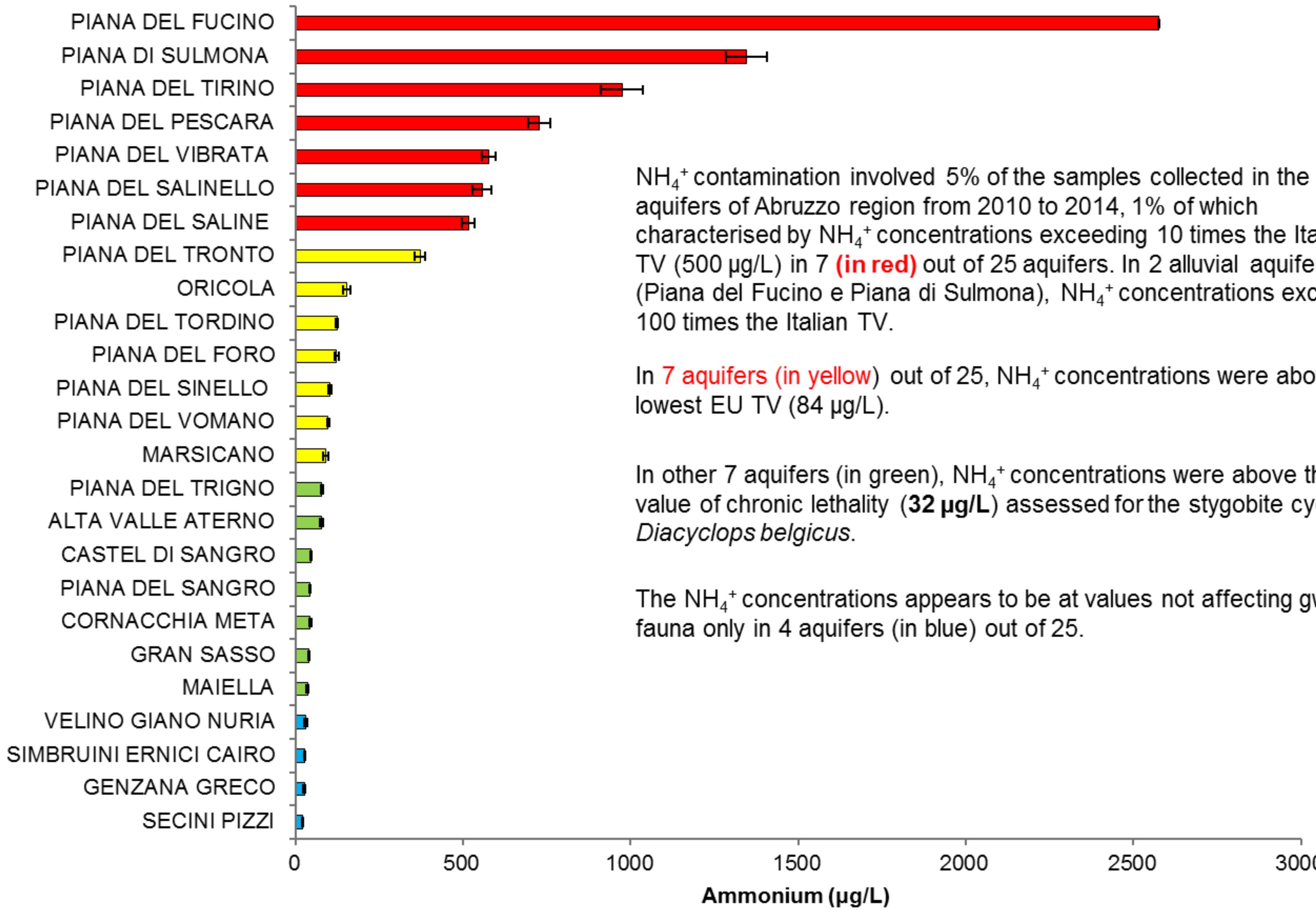
pseudo $F_{1,11} = 79.97$; $P < 0.001$

Di Lorenzo T., *Di Marzio W.D., Spigoli D., Baratti M., Messana G., Cannicci S., Galassi D.M.P., 2015. Metabolic rates of a hypogean and an epigean species of copepod in an alluvial aquifer. Freshwater Biology, 60: 426-435.*



We investigated NH_4^+ contamination in 17 alluvial and 9 rocky aquifers of the Abruzzo region (central Italy).

We used 10,000 groundwater samples withdrawn from 520 sites (bores and springs: grey spots) from 2010 to 2014.



NH_4^+ contamination involved 5% of the samples collected in the alluvial aquifers of Abruzzo region from 2010 to 2014, 1% of which characterised by NH_4^+ concentrations exceeding 10 times the Italian TV (500 µg/L) in 7 **(in red)** out of 25 aquifers. In 2 alluvial aquifers (Piana del Fucino e Piana di Sulmona), NH_4^+ concentrations exceeded 100 times the Italian TV.

In 7 aquifers (in yellow) out of 25, NH_4^+ concentrations were above the lowest EU TV (84 µg/L).

In other 7 aquifers (in green), NH_4^+ concentrations were above the value of chronic lethality (**32 µg/L**) assessed for the stygobite cyclopid *Diacyclops belgicus*.

The NH_4^+ concentrations appears to be at values not affecting gw fauna only in 4 aquifers (in blue) out of 25.

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3	Bulgaria			**0.5**
4	Cyprus			**0.5**
5	Czech Republic			**0.5**
6	Denmark			
7	Estonia	ammonium has been never found in gw		
8	Finalnd			**0.25**
9	France			**0.5**
10	Germany	**0.5**	**52**	
11	Hungary	**0.5**	**5**	
12	Ireland	**0.084**	**0.22**	**0.2**
13	Italy			**0.5**
14	Latvia			**0.8**
15	Lithuania			**3**
16	Luxembourg			**0.5**
17	Malta			**0.25**
18	Poland			**1.92**
19	Portugal	ammonium does not pose gw bodies at risk		
20	Romania	**0.5**	**9.9**	
21	Slovak Republic	**0.25**	**0.5**	
22	Slovenia	ammonium does not pose gw bodies at risk		
23	Spain			**0.5**
24	Sweden			**1.5**
25	The Netherlands	no anthropogenic origin		
26	UK			**0.37**

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Analisi della performance, responsabilità e competenza dell'infermiere di famiglia: ogo