Assessing groundwater toxicity of emerging contaminant mixtures

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Introduction

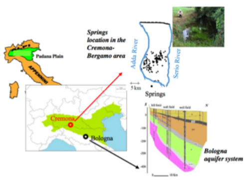
Groundwater is one of the most important natural resources, as globally it comprises the primary available source of freshwater. Groundwater aquifers consist an important drinking source in many parts of the world, a point of supply for irrigation in agriculture, as well as, are considered valuable in sustaining ecosystems´ health and functioning.

The Groundwater Directive (2006/118/EC) was created to protect groundwater bodies from contamination but to date it does not consider a diverse array of emerging contaminants used in great quantities by society. These emerging contaminants often occur in mixtures rather than alone, therefore understanding and predicting the toxicity of such mixtures, will eventually lead the way to developing new strategies for setting adaptations in regulations. Additionally, adapting surface water protocols to groundwater contamination scenarios might lead to erroneous results due to water different composition.

In the context of the European Research Project WE-NEED (Water JPI- WATERWORKS2014 ERA-NET), the present work focused on assessing the toxicity of contaminants alone and in mixtures in order to assist in developing new management strategies to sustainably exploit groundwater resources. A thorough identification of emerging contaminants took place in two well-characterized case-studies, the Bologna and Cremona aquifers, three contaminants were chosen as model chemicals and synthetic water was built to mimic groundwater composition of the two aquifers.

Materials & Methods

Bologna and Cremona aquifer systems (Italy)



1 Groundwater caracterization

Table 1: Synthetic groundwater composition

	Bologna	Cremona
	mg/L	mg/L
$CaCO_3$	475	158.3
$MgSO_4$	138	46.1
$Ca(HCO_3)_2$	673	224.2
NaCl	67	22.4
$NaNO_3$	34	11.3
Humic acid (sodium salt)	5	5
	µg/L	µg/L
tetrachloroethylene (PCE)	30	10.0
NaF	75	25
$(NH_4)OH$	100	33.3
H_3BO_3	800	266.7

2 Identification of emergent contaminants (EC)

Acetaminophen (AC), Triclosan (TCS), Perfluorooctanic acid (PFOA)

Single exposures

Acute Toxicity Test OECD 202 [1]

Cremona

Acetaminophen (µmol/L):
4.54; 8.17; 14.70; 26.46; 47.63; 85.74

Triclosan (µmol/L):
0.69; 1.04; 1.55; 2.33; 3.50; 5.25

Perfluorooctanic acid (mmol/L):
0.05; 0.10; 0.19; 0.39; 0.77; 1.55; 3.09

Bologna

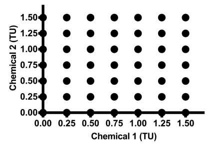
Acetaminophen (µmol/L):
2.07; 4.13; 8.27; 16.54; 33.08; 66.15

Triclosan (µmol/L):
1.64; 2.46; 3.68; 5.53; 8.29; 12.43

Perfluorooctanic acid (mmol/L):
0.05; 0.10; 0.19; 0.39; 0.77; 1.55; 3.09

Binary combinations

Acute Toxicity Test OECD 202 [1]



Full factorial design

MIXTOX framework

Jonker et al (2005) [2]

Ternary combinations

Acute Toxicity Test OECD 202 [1]

Table 2: Experimental design

Cremona Mixture	AC TU	TCS TU	PFOA TU	∑ TU
M1	0.0078	0.0078	0.0078	0.02
M2	0.0156	0.0156	0.0156	0.05
M3	0.03125	0.03125	0.03125	0.09
M4	0.0625	0.0625	0.0625	0.19
M5	0.125	0.125	0.125	0.38
M6	0.25	0.25	0.25	0.75
M7	0.375	0.375	0.375	1.13
M8	0.5	0.5	0.5	1.50
M9	1	1	1	3.00
M10	2	2	2	6.00

Fixed-ratio design / LC_{50} ratio

Toxic Unit-based approach

Concentration Addition (CA)

Results and Discussion

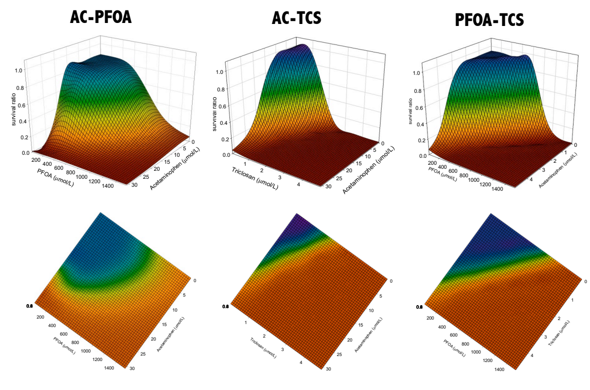
Single exposures

Table 3: Acute toxicity of three emergent contaminants in groundwater. LC50 values after a 48 h exposure presented in µmol/L. CI in brackets.

Single exposures	Cremona water	Bologna water
Acetaminophen	21 (19-24)	32 (28-38)
Triclosan	3.3 (3-3.6)	7.6 (5.9-12.1)
Perfluorooctanic acid	1035.3 (878.4-1224.2)	1048.4 (915.5-1218.9)

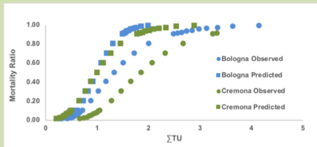
- Higher toxicity observed in the Cremona water for acetaminophen and triclosan → Differences in chemical composition of the 2 waters
- No statistical difference for PFOA between the 2 waters

Binary combinations



Ternary combinations

AC-TCS-PFOA



- Higher toxicity (increased mortality) observed in the Bologna water when compared to Cremona water caused by the ternary mixtures → Differences in the chemical composition of the two synthetic groundwaters
- CA model → conservative towards Cremona and Bologna ternary mixture
- Ternary mixture in Cremona water caused lower toxicity than in Bologna water

Conclusions

In both binary and ternary mixtures, the CA model generally appears to explain the observed mixture toxicity patterns. Deviations to additivity showed to be non significant in the binary mixture.

Testing sublethal endpoints in longer-term experiments will be critical to understand the effects of complex mixtures at realistic concentrations.

Toxicity showed a high dependency of the chemical composition of the synthetic groundwaters.

Development of new groundwater adapted protocols for toxicity studies are paramount for realistic evaluations of emergent pollutants in groundwater ecosystems since current standardized protocols may give misleading results when adopted to groundwater scenarios.

Acknowledgments

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References

1.OECD (2004). OECD guidelines for the testing of chemicals. Guideline 202: *Daphnia* sp., Acute immobilisation test, adopted April 2004.
2.Jonker, M. J. et al. (2005). *Environ Toxicol Chem*, 24, 2701–2713.