

Contaminanti Prioritari ed Emergenti: Recenti Sviluppi nell'ambito dell'implementazione della Direttiva Quadro Acque

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Convegno Microinquinanti e Contaminanti Emergenti Politecnico Milano, 11-12 Giugno 2018

WFD-2° River Basin Management Plan Consultations on-going



Ι

(Legislative acts)

DIRECTIVES

DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 12 August 2013

amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy

(Text with EEA relevance)

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty on the Functioning of the European Union, and in particular Article 192(1) thereof,

Having regard to the proposal from the European Commission,

preventive action should be taken, that environmental damage should, as a priority, be rectified at source and that the polluter should pay.

(3) Treating waste water can be very costly. In order to facilitate cheaper and more cost effective treatment, the development of innovative water treatment technologies could be stimulated.



Prioritization Methodology





Joint Research Centre



Substances	SQA-MA µg/L (inland waters)	SQA-MA µg/L (other surface waters)	SQA-MAC μg/L (inland waters)	SQA-MAC µg/L (other surface waters)	SQA-biota (µg/kg fresh weight)
Dicofol	1,3 x 10 ⁻³	3,2 x 10 ⁻⁵	Non appl.	Non appl.	33
PFOS	<u>6,5 x 10⁻⁴</u>	<u>1,3 x 10 -4</u>	<u>36</u>	<u>7,2</u>	<u>9,1</u>
Quinoxifen	0,15	0,015	2,7	0,54	
«Dioxins»			Non appl.	Non appl.	0,008 TEQ
Aclonifen	0,12	0,012	0,12	0,012	
Bifenox	0,012	0,0012	0,04	0,004	
Cibutrina (irgarol)	0,0025	0,0025	0,016	0,016	
Cipermetrina	8x10 ⁻⁵	8x10 ⁻⁶	6x10 ⁻⁴	6x10 ⁻⁵	

Biota EQS (directive 2013/39/UE)

BDEs	0.0085 µg/kg
Fluoranthene	30 µg/kg
Hexachlorobenzene	10 µg/kg
Hexachlorobutadiene	55 µg∕kg
Mercury	20 µg/kg
Benzo(a)pyrene	5 µg/kg
Dicofol	33 µg/kg
PFOS	9.1 µg/kg
Dioxins and dioxin-like PCBs	0.0065 µg∕kg TEQ
Hexabromocyclododecane	167 µg/kg
Heptachlor (epoxide)	0.0067 µg∕kg



(Responsible: NN)

(Responsible: NN)



COMMISSION IMPLEMENTING DECISION (EU) 2015/495

of 20 March 2015

establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council

(notified under document C(2015) 1756)

(Text with EEA relevance)

THE EUROPEAN COMMISSION,

Having regard to the Treaty on the Functioning of the European Union,

Having regard to Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 environmental quality standards in the field of water policy, amending and subsequently repealing Council Directive 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the Europ Parliament and of the Council (1), and in particular Article 8b(5) thereof,



1st Watch List substances

- 1. 17-Alpha-ethinylestradiol (EE2) (contraceptive pill ingredient)
- 2. 17-Beta-estradiol (E2) (natural hormone/pharmaceutical), to be monitored with Estrone (E1)
- 3. Diclofenac (painkiller)
- 4. 2,6-ditert-butyl-4-methylphenol (industrial chemical-antioxidant)
- 5. 2-Ethylhexyl 4-methoxycinnamate (uv filter sunscreen)
- 6. *Macrolide antibiotics* (*Erythromycin*, *Clarithromycin*, *Azithromycin*)
- 7. Methiocarb (plant protection product)
- 8. Neonicotinoid pesticides (Imidacloprid, Thiacloprid, Thiamethoxam, Clothianidin, Acetamiprid) (plant protection products/biocides)
- 9. Oxadiazon (plant protection product)
- 10.Tri-allate (plant protection product)

Clarithromycin-reasons for watch-list inclusion

2. Reason for proposal as candidate for the Watch list and suspected environmental risk Clarithromycin, a semisynthetic macrolide antibiotic derived from erythromycin, inhibits bacterial protein synthesis by binding to the bacterial 50S ribosomal subunit. Binding inhibits peptidyl transferase activity and interferes with amino acid translocation during the translation and protein assembly process¹.

Clarithromycin has been classified as Category 2 according to the NORMAN Prioritisation Methodology², with a frequency of exceedance of 15% and an extent of exceedance of 2.33-fold of the lowest PNEC¹, considering monitoring data from 2002-2011in the NORMAN database³.

A significant ecotoxicological risk due to the presence of clarithromycin in treated waste water in EL was estimated from acute and chronic toxicity data in algae ⁴. In addition, a risk indicator considered adverse to ecosystems was calculated for clarithromycin ⁵ considering the presence of this substance in the Llobregat river in ES⁶. Furthermore, clarithromycin was considered to pose a potential risk to the environment considering the predicted exposure in Turkey ⁷.



PNEC Clarithromycin

7.3 PNEC derivation

PNEC	Endpoint	Endpoint value	AF	PNEC value
PNEC _{fw}	Anabaena flos-aquae, 72 h, EC ₁₀	2.6 μg/L	10*2	0.13 μg/L ª
PNECsed	-	-	-	0.0012 mg/kg dw ^b
PNEC _{biota,sec} pois	-	-	-	Info missing
PNEC _{biota, hh}	ADI	0.0002 mg/kg bw/day	-	0.012 mg/kg food ^c

^a The PNEC value was retrieved from the UBA factsheet²³ on the substance. The additional AF of 2 was used because the toxic metabolite 14-Hydroxy-Claritromycin occur up to about 50% in surface water and is equivalent toxic. ^b Calculated using the equilibrium partitioning method. The following values were used: K_{sed-water} = 4.55 m³m⁻³ (calculated with eq. D of section 3.3.2), RHO_{sed} = 1300 kg m⁻³ (default value), Fsolid_{sed} = 0.2 (default value), RHO_{solid} = 2500 kg m⁻³ (default value), Kp_{sed} = 7.5 L/kg (calculated, K_{oc} x Foc_{sed}), K_{oc} = 150 L/kg (from PubChem⁸), Foc_{sed} = 0.05 kg kg-1 (default value). Conversion from wet weight to dry weight was done with eq. B (see section 3.3.2). ^cADI value retrieved from Leung et al., 2013 (see reference 25) used in equation E as TL. See section 3.3.4 for calculation

^d ADI value used in equation F as TL_{hh}. See section 3.3.5 for calculation



Update of the 1st watch list

- <u>2-step process :</u>
- Reviewing the substances in the 1st WL to assess whether substances can be removed (substances having sufficient high-quality monitoring data)
- Identifying new substances (substances posing a potential risk at EU level but for which the monitoring data doesn't allow to confirm the risk)

Review of the substances from the first watch list-Decision 5/06/2018

Analysis of the 1st year of monitoring data for the 1st WL performed by the JRC, in consultation with the WG Chemicals.

Identification of the following substances to be removed from the list because they have sufficient high-quality data : Diclofenac, antioxidant, triallate, oxadiazon.

Retention of EE2, E2, E1, macrolide antibiotics, methiocarb, neonicotinoids.

New substances-Watch List Decision 5/06/2018

Metaflumizone, former veterinary medicine, currently used as a PPP, identified based on results of last prioritisation

Amoxicillin and Ciprofloxacin, antibiotics, based on research projects on ecotoxicological effects and taking account of the revised European Antimicrobial Resistance (AMR) Action Plan, which supports the use of the WL to "improve knowledge of the occurrence and spread of antimicrobials in the environment". Also some indications of possible risk (respectively some monitored exceedances / modelled exceedances).



Commissione europea > Consultazioni >

CONSULTAZIONE

Consultazione pubblica sui prodotti farmaceutici nell'ambiente

	INDICE	Informazioni sulla consultazione			
	Informazioni sulla consultazione	Durata della	22 Novembre 2017 - 21 Febbraio 2018		
	Destinatari Settori Obiettivo della consultazione		Ambiente, Sostanze chimiche, Salute pubblica, Risorse idriche, Qualità del suolo,		
			Rifiuti e riciclaggio		
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Emerging Contaminants-Science and Policy

Watch list-Water Framework Directive

- 1. 17-Alfa-ethinilestradiol (EE2) (pillola contraccettiva)
- 2. 17-Beta-estradiol (E2) (ormone estrogenico), Estrone (E1)
- 3. Diclofenac (antiinfiammatorio-voltaren)
- 4. 2,6-ditert-butyl-4-metilfenol (antiossidante)
- 5. 2-Etilexil 4-metoxicinnamate (filtri crème solari)
- 6. Eritromicin, Claritromicine, Azitromcin (antibiotics)
- 7. Methiocarb (pesticide)
- 8. Imidacloprid, Thiacloprid, Thiamethoxam, Clothianidin, Acetamiprid) (neonicotinoids)
- 9. Oxadiazon (pesticide)
- 10. Triallate (pesticide)

Commission Decision 2015/495/UE

Emerging Contaminants in River Ecosystems

- Biocides
- Disinfectants
- Drugs
- Flame Retardants
- Industrial Chemicals
- Nanomaterials (organic ed inorganic)
- PFAS
- Personal care products
- Pharmaceuticals (human and veretrinary use)
- Pesticides and Metabolites/Transformation Products
- Plastificizers
- Surfactants
- Microplastics

Emerging contaminants in River Ecosystems-Springer International Volume-2015

CHEMICAL CONTAMINATION OF AQUATIC ECOSYSTEMS-EMERGING ISSUES

- Only a minimal part of substances included in the legislation
- Majority of substances currently in use not included
 - Adverse effects of emerging contaminants often ignored for human and environment
- Evidence of Mixtures risks









RESEARCH

Open Access

The European technical report on aquatic effect-based monitoring tools under the water framework directive

Ann-Sofie Wernersson¹, Mario Carere^{2*}, Chiara Maggi³, Petr Tusil⁴, Premysl Soldan⁴, Alice James⁵, Wilfried Sanchez⁵, Valeria Dulio⁵, Katja Broeg⁶, Georg Reifferscheid⁷, Sebastian Buchinger⁷, Hannie Maas⁸, Esther Van Der Grinten⁹, Simon O'Toole¹⁰, Antonella Ausili³, Loredana Manfra³, Laura Marziali¹¹, Stefano Polesello¹¹, Ines Lacchetti², Laura Mancini², Karl Lilja¹², Maria Linderoth¹², Tove Lundeberg¹², Bengt Fjällborg¹, Tobias Porsbring¹, DG Joakim Larsson¹³, Johan Bengtsson-Palme¹³, Lars Förlin¹³, Cornelia Kienle¹⁴, Petra Kunz¹⁴, Etienne Vermeirssen¹⁴, Inge Werner¹⁴, Craig D Robinson¹⁵, Brett Lyons¹⁶, Ioanna Katsiadaki¹⁶, Caroline Whalley¹⁷, Klaas den Haan¹⁸, Marlies Messiaen¹⁹, Helen Clayton²⁰, Teresa Lettieri²¹, Raquel Negrão Carvalho²¹, Bernd Manfred Gawlik²¹, Henner Hollert²², Carolina Di Paolo²², Werner Brack²³, Ulrike Kammann²⁴ and Robert Kase¹⁴

Abstract

The Water Framework Directive (WFD), 2000/60/EC, require Pr assessment of the quality of surface water bodies. The che ht legally binding Environmental Quality Standards (EQSs) for m

Wernersson Ann-Sofie; Carere Mario, et al. (2015): The European technical report on aquatic effect-based monitoring tools under the water framework directive. Environmental Sciences Europe, 2015; 27 (1) DOI: 10.1186/s12302-015-0039-4. <u>http://www.enveurope.com/content/pdf/s12302-015-0039-4.pdf</u> Press release at: <u>http://www.sciencedaily.com/releases/2015/03/150313083449.ht</u>

Technical Report on Aquatic Effect-Based Monitoring Tools



Technical Report on Aquatic Effect Based Monitoring Tools.

Technical Report 2014-077. EU Commission. doi: 102779/7260. Effect-based tools described in three main groups:

- ✓ Bioassays in vitro and in vivo bioassays that measure the toxicity of environmental samples
- Biomarkers biological responses at individual level (or below) observed in field exposed organisms
- Ecological indicators biological responses at higher organisation levels, e.g. population and community

In vitro assays in Europe

Table 1 <i>In vitro</i> assay	s and their modes of action	and the second se
Name/s of assay	Mode of action/endpoint	
AR CALUX (anti-)	Androgen receptor (activation or blocking)	European Commission
DR CALUX	AH receptor binding	
ER CALUX (anti-)	Alpha and beta/estrogen receptors	Technical Report - 2014 - 07
GR CALUX (anti-)	Glucocorticoid receptor	
PAH CALUX	AH receptor binding	
PR CALUX	Progesterone receptor	
Acetylcholinesterase inhibition assay	Inhibition of acetylcholinesterase activity	
Carboxylesterase inhibition assay	Inhibition of carboxylesterase activity	
Ames	Mutagenicity	TECHNICAL REPORT ON AQUATIC
umuC	Primary DNA damage	EFFECT-BASED MONITORING TOOLS
TTR-binding	Competition with thyroid hormone for binding to TTR (transport protein)	
TRb CALUX	Thyroid receptor beta	
EROD	EROD induction	
YES	ER receptor	
YAS	AR receptor	
P-53 accumulation	Genotoxicity	
Green screen	Genotoxicity	
RYA	ER receptor	
ABC assay	Antibiotic activity	Environment

Expert Group of WG chemicals «Effect-based Methods»

- Identification and Selection of relevant modes of Actions of Chemical Substances
- Identification and Selection of «Effect based methods» for the detection of the relevant Modes of Actions
- Selection of «effect based methods» to detect the effect of complex mixtures in the environment
- Identification of «trigger values/assessment criteria» for the Effect Based Methods
- Evaluation of methods connected with the Ecological Status
- Link with Marine strategy
- Use in the WFD and Identification of sources
- Feasibility of the approach based on EBM in complement with chemical analysis.

ACTIVITY: EFFECT-BASED METHODS

for WG Chemicals as part of the Water Framework Directive CIS Work Programme (2016-2018) endorsed by the Water Directors

"Effect-based assays; links between chemical and ecological status; mixtures. Possible follow-up of estrogen-screening project. Exchange of information on innovative techniques, approaches and potential application in WFD context"

TERMS of REFERENCE

Introduction

In the aquatic environment¹ thousands of chemical substances are discharged daily, from point and



Kick Off meeting Effect Based Methods Task: Istituto Superiore di Sanità, Roma, 2-3 October 2017

71201

Which bioassays are relevant for water quality assessment?

1. Bioassay that have known anchors in known AOPs



2. Bioassays that cover relevant effects for water quality



Grouping of the chemicals according to the common MoA and / or effect (JRC Draft report: D.Napierska, T. Lettieri et al)

Esempio erbicidi

Substanc e	Target species	Specific MoA (target species)	Potential EBM (target species)	Non-target organism	Non-specific MoA (reported for non-target species)	Effect on the organism level (reported for non-target species)	Potential EBM (non-target species)
Atrazine	Plant	Photosystem II inhibition	PSII inhibition Chlorophyll concentration ROS production / lipid peroxidation	Snail Fish Amphibians	Changes in biochemical/ detoxification parameters (SOD, CAT, GR, LDH) Induction of aromatase (Cyp19A1) - Adrenotoxicant Changes in sex hormones concentration (decrease of testosterone and induction of estrogen)	Reduced egg production Demasculinizati on and feminization	Oxidative stress markers / Xenobiotic- metabolizing enzymes activity Zebrafish repr. CYP19A1/aromatase induction (gene expression) T/E2 assay Hist. examin. of
Diuron	Plant	Photosystem II inhibition	PSII inhibition Chlorophyll concentration ROS production / lipid peroxidation	Oyster Fish Amphibians	ROS production / Genotoxicity (CAT activity, formation of 8-oxodGuo) Decrease of testosterone level Cytochrome P450 stimulation Steroid biosynthesis, cholesterol metabolism and pregnane X receptor activation	Embryotoxicity Changes in GSI and germ cells/oocytes quantity	Oxidative stress markers T/E2 assay Cytochrome P4501A activity /EROD CYP19A1/aromatase induction (gene expression)

EUROPEAN PROJECT ON E1, E2, EE2 UNDER THE WATER FRAMEWORK DIRECTIVE

High end HPLC MS/MS:

1-3) JRC, Lab in Germany, Swiss Centre for Applied Ecotoxicology

In vitro effect-based methods:

- 4) ER-Calux
- 5) pYES
- 6) MELN
- 7) Hela 9903
- 8) ER-GeneBlazer

17 Waste water 16 Surface water



9) In vivo fish toxicity data with EASZY (INERIS)





Accepted Manuscript

Effect-based and chemical analytical methods to monitor estrogens under the European Water Framework Directive

Sarah Könemann, Robert Kase, Eszter Simon, Kees Swart, Sebastian Buchinger, Michael Schlüsener, Henner Hollert, Beate I. Escher, Inge Werner, Selim Aït-Aïssa, Etienne Vermeirssen, Valeria Dulio, Sara Valsecchi, Stefano Polesello, Peter Behnisch, Barbora Javurkova, Olivier Perceval, Carolina Di Paolo, Daniel Olbrich, Eliska Sychrova, Rita Schlichting, Lomig Leborgne, Manfred Clara, Christoph Scheffknecht, Yves Marneffe, Carole Chalon, Petr Tušil, Přemysl Soldàn, Brigitte von Danwitz, Julia Schwaiger, Maria Isabel San Martín Becares, Francesca Bersani, Klara Hilscherová, Georg Reifferscheid, Thomas Ternes, Mario Carere

PII:	S0165-9936(17)30433-8
DOI:	10.1016/j.trac.2018.02.008
Reference:	TRAC 15103

Highlights

In vitro effect-based methods integrate effects of mixtures of chemical compounds with the same mode of action

- E2 equivalents are highly correlated with LC-MS/MS
- E2 equivalents are highly correlated among effect-based methods

Implementation of effect-based methods in the water framework directive is highly recommended



Screening and risk management solutions for steroidal estrogens in surface and wastewater

Robert Kase, Barbora Javurkova, Eszter Simon, Kees Swart, Sebastian Buchinger, Sarah Könemann, Beate I. Escher, Mario Carere, Valeria Dulio, Selim Ait-Aissa, Henner Hollert, Sara Valsecchi, Stefano Polesello, Peter Behnisch, Carolina di Paolo, Daniel Olbrich, Eliska Sychrova, Michael Gundlach, Rita Schlichting, Lomig Leborgne, Manfred Clara, Christoph Scheffknecht, Yves Marneffe, Carole Chalon, Petr Tusil, Premysl Soldan, Brigitte von Danwitz, Julia Schwaiger, Antonio Moran Palao, Francesca Bersani, Olivier Perceval, Cornelia Kienle, Etienne Vermeirssen, Klara Hilscherova, Georg Reifferscheid, Inge Werner

PII:	S0165-9936(17)30437-5
DOI:	10.1016/j.trac.2018.02.013
Reference:	TRAC 15108



WG Chemicals (WFD) other activities

- Drafting of a new guidance document on how to implement metal EQSs (e.g. Use of biotic ligand model)
- Member States sharing experiences in particular on biota monitoring and assessment.
- Derivation of EQSs ongoing for selected substances in dedicated subgroups (silver, omethoate, nicosulfuron) and call for interest to join the subgroup for uranium.
- Update and Sharing Knowledge on Chemical Analytical Methods

The Handbook of Environmental Chemistry 46 Series Editors: Damià Barceló · Andrey G. Kostianoy

Mira Petrovic Sergi Sabater Arturo Elosegi Damià Barceló *Editors*

Emerging Contaminants in River Ecosystems

Occurrence and Effects Under Multiple Stress Conditions



The Emerging Contaminants in the Context of the EU Water Framework Directive

Mario Carere, Stefano Polesello, Robert Kase, and Bernd Manfred Gawlik

Abstract The WFD (Water Framework Directive) requires that good chemical status of surface waterbodies is achieved by all member states of the European Union by 2015. The assessment of the chemical status is based on monitoring of the list of priority substances included in the Annex X of the WFD. In August 2013, the Directive 2013/39/EU has been published and contains a revised list of priority substances for the European aquatic environments and the derivation of environmental quality standards in the water column and biota; 12 new substances were selected through a procedure of prioritisation based on a simplified risk assessment methodology with the use of monitoring and modelling data collected over a period of 4 years. In the list of the 12 new substances, also emerging contaminants and some biocides are included. The Commission is establishing a so-called watch list of substances for which Union-wide monitoring data are to be gathered for the purpose of supporting future prioritisation exercises. For the substances diclofenac, betaestradiol (E2) and 17-alpha-ethinylestradiol (EE2), the Directive has foreseen a monitoring obligation in order to gather data to facilitate the determination of appropriate measures to address the risk to surface waters posed by those substances. Furthermore, on the basis of the outcome of a study on the risks posed by medicinal products in the environment and of other relevant studies and reports, the Commission shall develop a strategic approach to pollution of water by pharmaceutical substances.

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 M. Petrovic et al. (eds.), Emerging Contaminants in River Ecosystems, Hdb Env Chem, DOI 10.1007/698_2015_5011,
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Conclusions

- The Activity of the WFD on Emerging Pollutants is relevant and the Mechanism of the Watch-List it is an important starting point but is not enough.
- The Risk caused by emerging pollutants for human health and aquatic ecosystems is often unknown. Long procedures to derive EQS, TDI and Analitycal Methods.
- The Strategy on Pharmaceuticals (mentioned in 2013) should be reinforced and implemented.
- Need for a more «olistic» approach including the possibility to include tools/methods for the detection of the real effects caused by chemical contaminants

Thanks to Stephanie Schaan and Helen Clayton (DG Environment, EU Commission)

