Risk assessment of emerging contaminants in aquatic systems

Peter-Diedrich Hansen

For risk assessment and "risk-assessment tools", new recommendations are described in the second edition of the Technical Guidance Document of REACH, the new chemicals legislation of the European Union (EU), and in the status report for toxicological methods of the European Centre for the Validation of Alternative Methods. For the description of a "good physical-chemical status" of aquatic systems, effects-monitoring tools are needed.

Chemical toxicity and related information cannot be obtained by instrumental analysis. The effects-related quality norms for emerging single contaminants are generated by conventional bioassays and new emerging bio-analytical systems. Concepts are available for the classification of waterways using bio-analytical systems with respect to the EU Water Framework Directive.

Exposure assessment and effect assessment and their deliverables comprise the scientifically-generated baseline for a valid risk assessment, risk communication and risk management for the sustainable development for protection of surface water, soil and human health.

Keywords: Decision-support system; Emerging contaminant; Environmental Quality Standard; EQS; QN; Quality Norm; Risk assessment; Risk communication; Risk management; Water Framework Directive

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1. Introduction

There is a need for unified strategies for risk assessment of emerging contaminants in aquatic systems. In the European Union (EU) Water Framework Directive (WFD) [1], a general requirement for ecological protection, and a general minimum chemical standard was introduced to cover all surface waters. For the description of a "good physical-chemical status", effects-monitoring tools are needed to describe the ecological and the chemical status of river-basin systems and aquatic systems in general. On the analytical chemistry side, there are certain needs and further steps for standards for WFD, Annex V; there are needs for research (new methods) and the revision and optimization of existing methods, so there are ongoing standardization activities in the field of exposure and effects-related data.

It is rather difficult to transfer exposure data and effects-related data into an operational effects-related standard. The contaminants that are present in aquatic systems have to be discussed in the context of the so-called Environmental Quality Standards (EQSs) and their Quality Norms (QNs). QNs [1–3] were developed after the WFD corresponding to "good chemical status" and dangerous substances (76/464/EEC List I and List II) as well as priority substances and hazardous substances [1]. Priority hazardous substances should be enlarged to include new emerging contaminants with deleterious effects on aquatic systems in function and structure.

2. Emerging contaminants and risk assessment

The aim of this type of investigation and research is to improve our understanding regarding environmental threats, and the risks they pose to human health. In addition, improved assessment methods are needed to be able to estimate the possible cumulative risk of several contributing factors (biotic and a-biotic parameters). The probability and quantification of disruptions by hazards and the process of the environmental risk assessment (ERA) will be served by two major elements: characterization of effects and characterization of exposure.

Implementation of operational monitoring in support of the ERA concept should be adequate for characterization of exposure and effects, thus enabling sustainable development for aquatic systems. QNs for water will serve as management tools for environmental quality, protecting water resources as a valuable natural resource supporting drinking water, human health, aquatic communities, commercial and sports fishing, outdoor recreation, and in general the integrity of the ecosystem.

For sustainable use of water resources and the exposure to newly emerging substances under extreme situations of temperature and precipitation, site-specific and effects-related QNs for water need to be developed so that that water management guarantees the quality of drinking water and irrigation in agriculture, and protects the ecosystem as well as quality of life. Table 1 summarizes the strategies on risk assessment for the sustainable development for surface water, soil and human health protection.

The main elements of the strategies and their applications for environmental risk assessment are the characterization of exposure and effects, as set out in Tables 1 and 2.

For the exposure assessment (Table 1), there are several exposure parameters of interest: commercial compounds, structural properties of the compound, matrices and routes, formulation (e.g., of pesticides) and the active gradient, biotransformation and metabolites, biological degradation kinetics (persistence) and bioavailability.

In Table 2, the baseline data for effects assessment are generated by bioassays [1] and QNs [1–3]. The endpoints of the bioassays are in terms of acute and chronic toxicities expressed in clear numbers by LC50 (LC50 = Lethal concentration 50%) and or NOEC (NOEC = No Observed Effect Concentration). In addition to the classical bioassays, bioaccumulation assays and reproduction toxicology, there are several validated biomarkers (biochemical responses) available and also standardized under ISO (International Standardization Organization) [4].

The effects-related parameters or biochemical responses (biomarkers) are very complex, but they will give a clear, additional picture of the molecular level in the context of the health status of the investigated aquatic system. The health status of the aquatic system is sometimes called ecosystem health (EH), which is synonymous with "environmental integrity", from

Table 2. Effects assessment - strategy on environmental risk assessment (ERA) for water, soil and human health protection - from effect assessment to risk management

Effect assessment (effects biomonitoring)	
Short-term, long-term effects, primary molecular damage, biochemical functional effects using bioassays	Population effects (environment and human) fitness, bio-diversity, reproduction, stress factors, mortality
↓	↓
[EQS-QN] Criteria for aquatic life and human health protection to characterize reference conditions and to prove ecological status class boundaries in surface water and soil	
Risk analysis	Risk estimate
↓	↓
Risk management	

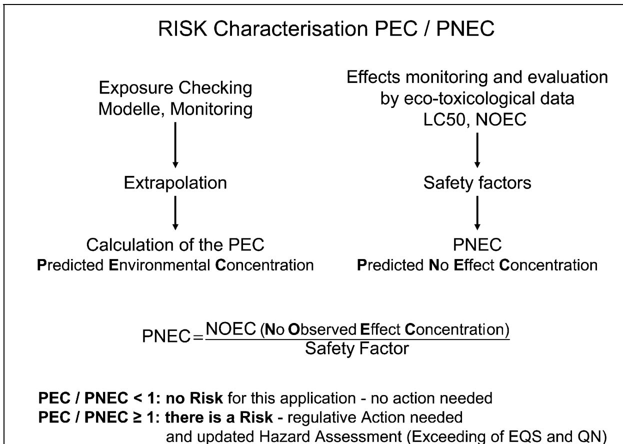

Figure 1. Risk characterization involving exposure and effects using effects-related quality norm (EQS–QN), which is a single-substance concept for dangerous substances and priority hazardous substances. Risk is characterized by predicted environmental concentrations (PECs) and predicted no effect concentrations (PNECs), which may trigger regulatory action and/or updated hazard assessment.

Table 1. Exposure Assessment – Strategy on environmental risk assessment (ERA) for water, soil and human health protection – from exposure assessment to risk management

Exposure assessment (dose biomonitoring)		
Data of exposure using chemical analysis	Fate of the compounds (binding and transport) by characterization of the matrix	Bioavailability (intake and distribution)
↓	↓	↓
[EQS] Criteria for aquatic life and human health protection to characterize reference conditions and to prove ecological status class boundaries in surface water and soil		
↓	↓	↓
Exposure data acquisition	Exposure pathways	Exposure scenarios
Risk management		

Table 3. Safety factors and available eco-toxicological data generated by bioassays [3] used in the calculations of the single-substance concept (see Fig. 2)

Available data	Safety factor
At minimum, one acute assay at one trophic level (Algae, Daphnia or Fish)	1000
One long-term, chronic toxicity assay (NOEC): with Fish or Daphnia	100
Two long-term, chronic toxicity assays (NOEC) at two trophic levels: Algae and/or Daphnia and/or Fish	50
Three long-term, chronic toxicity assay at three species (NOEC): Algae, Daphnia and Fish (three trophical levels)	10

which it follows that the scope of EH research encompasses all the tools and approaches that are efficacious in increasing cognitive, curative and preventive knowledge for preservation of environmental integrity. EH research therefore directs its attention to the prediction of reversible and irreversible insults that human or other activities could potentially inflict on the environment. For the assessment of EH, very promising biomarker approaches centre on quantifying biochemical effects in organisms and populations. An important tool to achieve the acceptance of biomarkers in science and industry and by governmental authorities comprises the so-called inter-laboratory comparison studies of measurements of bioassays and biomarkers [2].

To follow the scheme in Fig. 1 for effects monitoring and evaluation of single substances by single substances, we have to confirm the relevance of the data for the aquatic system using safety factors that relate to the trophic levels available for the acute and long-term, chronic bioassays being investigated.

The safety factors in Table 3 are used to calculate the predicted no effect concentration (PNEC) from Fig. 1 to generate the EQS-QN [1,2] for single substances in Table 4. The contaminants are substances actually measured in German surface waters [3]. According to Table 3, the classical trophical level-related test battery of bioassays [2] was used. The relevance for the aquatic system was roughly estimated by exposure assessment and EQS-QN. In addition to the endpoints for the organisms and sub-organisms (i.e. genotoxicity), the endocrine effects are mentioned for those substances with valid effects [6,7] in the aquatic system.

Table 4. Proposed environmental quality standard (EQS) with respective quality norms (QNs) of substances actually measured in German surface waters (modified after Moltmann et al. [3] and Huschek et al. [5]) and relevance for the aquatic system (protection of the aquatic communities): +++ = high aquatic relevance; + = aquatic relevance; ? = relevance unclear

Compounds	Safety factor	Proposed EQS – QN water [ng/L]	Relevance for the aquatic system
p,p′-DDT	10	7.1	+++
p,p′-DDE	10	0.1	+e
Tributyltin-cation (TBT)	10	0.1	+++e
Tributyltin oxide (TBTO)	10	0.3	?e
Tributyltin (TTBT)	100	2	+++e
Nonylphenol	10	3.3	?e
4-Nonylphenol (4-NP;P-NP)	10	3.3	+++e
4-tert-Octylphenol	10	200	+e
4-tert-Pentylphenol	1000	30	?e
4-Nonylphenol-diethoxylate	1000	30	+++e
Bisphenol A	10	0.8	+++e
β-HCH	100	320	+e
γ-HCH (Lindane)	10	66	+
Atrazin	10	10	+++
Aldrin	10	5	+e
Dieldrin	10	20	+
Endosulfan	10	4	+
Malathion	10	1	+
Methylparathion	10	0.025	+
Benzo(a)pyren	10	14	+++
17ß-Oestradiol (E2)	10	0.5	+e
17α-Ethinyloestradiol (EE2)	10	0.03	+e
Testosteron	50	20	+e
Genistein	100	13	+e
Bromocycline	1000	700	?
Metamitron	10	4000	?
Ibuprofen	1000	7100	?
Metroprolol	1000	7300	?
Sulfamethoxazol	100	150	?
1.2.3.4 Tetrachlorbenzol	50	200	?

Effect-related endpoint (e) = endocrine effect.

3. Risk management

QNs for water will serve as management tools for environmental quality protecting the waterways as a valuable natural source supporting drinking water, human health, outdoor recreation, and in general EH and quality of life.

QNs for water in relation to the possible use of different sources should be determined by bioassays, real-time bioassays and bio-sensing (bio-analytical) systems. QNs for water [1,2] are for testing whether or not sufficient measures have been taken to protect the individual body of water and especially its valuable and exploitable resources from ''dangerous substances and emerging contaminants''. In order to secure the functioning and stability of a body of water (ecosystem) or to re-establish these qualities, concrete ecological knowledge is necessary concerning the interaction of functions and structures of the living systems under these extreme conditions, as well as nutrient cycles and energy fluxes in temporal succession. Salinity is especially important as an a-biotic parameter of endocrine-active substances in transitional waters [7]. Kase et al. provide the first example of endocrine effects [7]. It is also always a question of the endocrine endpoints and the assays investigated [8].

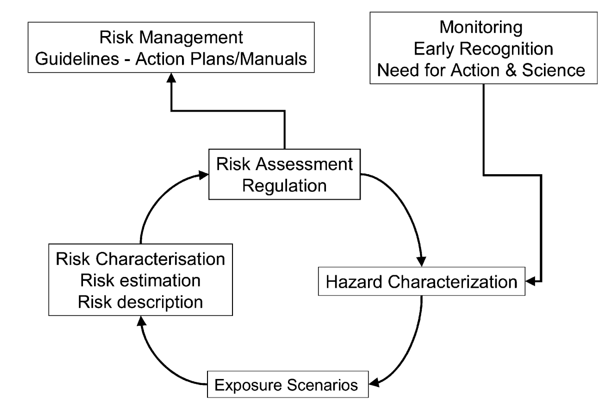

Figure 2. Early recognition, risk assessment and risk management. The illustration shows the strategies for risk assessment of emerging contaminants in aquatic systems as well as risk communication and risk management. Decision concept cycle: monitoring - risk characterization, risk estimation, risk description guiding risk assessment and regulation, action plans, manuals and risk management (Modified from [9]).

The exposure scenarios in Fig. 2 emphasized the need to develop bio-analytical systems that do not only measure ''conventional'' contaminants but also new emerging contaminant parameters (e.g., endocrine effects), which need to be measured for compliance with the EU Drinking Water Directive [10] as well as the WFD, and which are currently used in monitoring programs. The classification of the contamination of river sediments by xenoestrogens using pT values [11,12] and expressed as 17ß-estradiol equivalents contributes to the evaluation by receptor assays for the ERA, risk communication and risk management. To exploit the principal advantage of bio-analytical systems, standardization and harmonization are needed for governmental decision-making in collaboration with industry and governmental authorities.

The aim is the quantification of risk. Fig. 1 sets out the strategies for risk assessment of emerging contaminants in aquatic systems. The indicators in these scenarios (Fig. 2) are shown in Fig. 3 (i.e. groundwater, irrigation water, run-off water and waste-water management). Finally, the decision-support system (DSS) will establish guidelines for environmental risk management (SOPs = Standard Operation Procedures, manuals for monitoring and risk assessment and communication). Research in this area is disseminating solutions for municipality and authorities, especially in urban areas and mega-city regions.

4. Conclusions

In summary, bioassays and bio-analytical systems are early-warning systems that indicate the presence of unknown compounds that are responsible for the signals they detect. It is well known and accepted that, in addition to chemical analysis, effects-related parameters are necessary. Sometimes, chemical toxicity and related information cannot be obtained by measurements using instrumentation for chemical analysis. For diagnosis concerning human health, new technologies (e.g., proteomics) are currently under development. These tools will eventually help to validate effects in humans and in the environment and this could be a relevant direction for the future.

A comprehensive strategy is necessary to protect the ecology and to characterize reference conditions using ''on-site effects monitoring'' and early-warning tools (Fig. 2) to promote an environmentally sensitive and sustainable use of resources in urban areas. The most successful strategy is to include bio-analytical and biosensing systems as well as ''real-time bioassays'' standardized by ISO and CEN (see Fig. 1) in the approaches to defining the quality components (see Table 4). The data generated by following this scheme will be adequate for the characterizing exposure and effects so as to achieve sustainable development for aquatic systems and human health protection in contaminated areas.

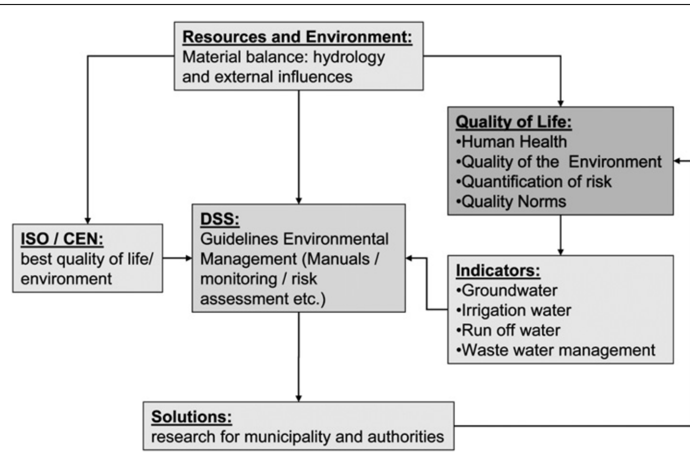

Figure 3. Decision-support system and risk assessment.

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