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Risk assessment

ENVIRONMENTAL EXPOSURE AND EFFECTS OF SOME MICROPOLLUTANTS FOUND IN THE ROMANIAN SURFACE WATERS

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Abstract. Ecological risk assessment is required by the European norms to predict or evaluate the effects of chemicals, which are discharged into the receiving 'environment'. Usually the aquatic risk involves two major components: occurrence and hazard effects. In order to estimate the predicted exposure concentrations of chemicals in the water (PEC aquatic) and the predicted no-effect concentration on organisms (PNEC aquatic), literature data collecting and laboratory testing data were necessary. A ratio of PEC/PNEC < 1 indicated no aquatic risk and no future assessments is deemed necessary. In the period of 2009–2013, within different national projects, our aquatic risk studies has been initiated for some micropollutants, such as hazardous chemicals (4-chloroaniline, 1-chloro-4-nitrobenzene and 4-chloro-2-nitrotoluene), pesticides (azinphos-methyl and bentazone), pharmaceuticals (diclophenac, acetaminophen, ketoprophen, indomethacin, naproxen, ibuprophen, carbamazepine, caffeine, ciprofloxacine and trimethoprim) and surfactants (benzenthonium chloride and cocamidopropyl betaine). Several toxicity bioassays using the sensitivity of living organisms at different trophic levels (fish, planktonic crustacean, green algae and different bacteria species) were performed. The studied chemicals showed a relatively limited acute toxicity and generally the final results have revealed insignificant or low risks on aquatic organisms. Two chemicals (ciprofloxacin and benzenthonium chloride) showed high environmental risk. The ranking organism sensitivity was crustacean, bacteria and algae. The risk assessment studies were based on environmental concentrations detected in Romanian surface waters (Danube river, Danube delta, Arges river, Mures river, Ciorogarla river and Ghimbasel stream) comparatively with other international rivers.

Keywords: toxicity bioassays, aquatic risk assessment, chemicals, PEC, PNEC.

AIMS AND BACKGROUND

The purpose of this work was to assess the effects and risks of some micropollutants using the sensitivity of aquatic organisms at different trophic levels. The risk assessment was characterised for the Romanian surface waters according to international norms and based on laboratory and literature data. The studied pollutants were hazardous industrial chemicals, pesticides, pharmaceuticals compounds (PHCs) and surfactants.

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At present, large volumes of hazardous chemicals are manufactured and their increasing and diversified use, led to a significant concern of scientific communities for their occurrence in the environment and their adverse effects on ecological systems. The European countries have a large and comprehensive legislation for chemicals manufacture and commercialization, spearheaded by REACH Regulation[1] and Classification, Labelling and Packaging (CLP) Regulation[2]. Chemicals such as pesticide, biocides, pharmaceuticals, cosmetics or recently endocrine disruptors and nanocompounds are covered by their own legislation. Considering the REACH requirements different testing strategies for environmental toxicity of chemicals were implemented to provide risk assessment information in safety conditions, with low costs and low distress[3]. In this context is intended to limit or decrease the number of testing animals or replace the conventional methods with alternative bioassays[4].

In the European continental waters the monitoring of hazardous chemicals is required by Water Framework Directive (WFD) in order to protect the quality of water sources[5]. An important aim of WFD is to achieve a good chemical status of surface waters by 2015 (Ref. 6). Instead many countries report annually high consumptions of hazardous chemicals such as industrial chemicals[7,8], pesticides[9], surfactants[10,11] or human pharmaceuticals[12,13].

The most significant way of chemicals to enter in the aquatic environment is through wastewater discharge or migration between soil and water after usage. The presence of these pollutants in Waste Water Treatment Plants (WWTPs) effluents is especially due to the fact that most of these compounds have low removal efficiencies under sludge microorganisms action.

Environmental risk assessment of these compounds on aquatic system started from the idea that they may have significant toxic effects at very low concentrations (μg/l or ng/l)[14]. All the European norms related to chemicals risk characterisation require the aquatic risk evaluation using different responses of living organisms as a measure of environmental protection[15]. Usually the aquatic risk involve literature data collecting and laboratory testing data to estimate the predicted exposure concentrations of chemicals in the water (PEC aquatic) and the predicted no-effect concentration on organisms (PNEC aquatic). If the ratio of PEC/ PNEC is < 1, the chemicals present no risk for aquatic environment.

EXPERIMENTAL

In the period of 2009–2013, within 3 national projects, our researches on aquatic ecological risk of hazardous chemicals, human pharmaceuticals and detergents started.

Aquatic toxicity bioassays were performed for three hazardous industrial chemicals (4-chloroaniline, 1-chloro-4-nitrobenzene and 4-chloro-2-nitrotoluene),

two pesticides (azinphos methyl and bentazone), ten human pharmaceuticals (diclophenac, acetaminophen, ketoprophen, indomethacin, naproxen, ibuprophen, carbamazepine, caffeine, ciprofloxacine and trimethoprim) and two surfactants (benzenthonium chloride and cocamidopropyl betaine). All studied chemicals had analytical purity >99% and were purchased from Sigma-Aldrich (Seelze, Germany) or Merck KGaA (Darmstadt, Germany). In Table 1 are presented summarily information concerning identification of studied chemicals, the representative samples chosen for chemicals detection in the field in order to assess their aquatic risks, the monitoring period, and the used analytical methods.

Table 1. Sampling and detection methods

Chemical	CAS number	Samples	Monitoring period	Analytical method / equipment
Diclofenac	15307-79-6	wastewater effluents from Brasov, Targu Mures, Pitesti and Magurele WWTPs	January–September 2011	LC-UV/Agilent 1100 (Agilent Technologies, USA)
Acetaminophen	103-90-2			
Ketoprofen	22071-15-4			
Indomethacin	53-86-1			
Naproxen	22204-53-1	surface water from Ghimbasel stream (Brasov area), Mures river (Targu Mures town area) and Arges river (for Pitesti town area) upstream and downstream of WWTPs	March 2011 and January 2013	HPLC-MS/MS (EPA Method 1694) Agilent 1290 Infinity coupled to an Agilent 6410 triple quadrupole MS equipped with an electrospray ionization (ESI) source (Agilent Technologies, Germany)
Ibuprofen	15687-27-1			
Carbamazepine	298-46-4			
Caffeine	58-08-2			
Trimethoprim	738-70-5		March 2011 and January 2013	
Ciprofloxacin	85721-33-1			
		surface water from Danube river (Bazias, Giurgiu and Tulcea) and Danube delta (Mahmudia, Uzlina, Murighiol, Sf. Gheorghe and Black Sea confluence)		
Benzenthonium chloride	121-54-0	wastewater effluents from different WWTPs	January 2010 – March 2011	DIN 38409/20:1989
Cocamidopropil betaine	4292-10-8	surface water from Danube river (Bazias, Giurgiu and Tulcea) and Danube delta (Mahmudia, Uzlina, Murighiol, Sf. Gheorghe and Black Sea confluence)		Boiteux 1984
4-Chloroaniline	106-47-8		January 2013	HPLC-UV/ Agilent 1100 (Agilent Technologies, USA)
1-Chloro-4-nitrobenzene	100-00-5		February – April 2012	
4-Chloro-2-nitrotoluene	89-59-8			
Azinphos methyl	86-50-0	surface water from Ciorogarla River (Ilfov County)	May 2013	HPLC-DAD (diode aray detector) – UV-vis./Agilent 1200 (Agilent Technologies, Germany)
Bentazone	25057-89-0			

Toxicity assessment was carried out according to OECD and ISO methodologies using conventional and alternative methods (microbiotests). In Table 2 are presented the biological tests battery, the monitored endpoints and the ranges of tested concentrations.

Table 2. Biological tests battery

Bioassay/microbiotest	Species	Type of test	End points	Test period
OECD 203	fish *Cyprinus carpio*	acute	mortality	96 h, 21–22°C
OECD 202, Daphtoxkit F	Planktonic crustacean *Daphnia magna*	acute	mortality	24–48 h, 20°C
OECD 201, Algaltoxkit F	green microalgae *Selenastrum capricornutum*	acute/ chronic	growth inhibition	72 h, 21–25°C
DIN EN ISO 11348-3 BioFix Lumi, Multi-shot kit	marine luminescent bacteria *Vibrio fischeri*	acute	luminescence inhibition	15 min, 20°C
MARA test (Microbial array for toxicity risk assessment)	*Bacteria species of Microbacterium*, *Brevundimonas*, *Citrobacter*, *Comamonas*, *Enterococcus*, *Delftia*, *Kurthia*, *Sthaphilococcus*, *Pseudomonas*, *Serratia*, *Pichia.*	acute	microbial growth inhibition	18 h, 30°C
ASTM Standard Guide E1440-9, Rotoxkıt F	rotifers *Brachiounus calyciflorus*	acute	mortality	24 h, 25°C
OECD test proposal of further validation , Protoxkit F	Ciliates *Tetrahymena thermophila*	chronic	growth inhibition	24 h, 30°C

Aquatic risk assessment methodology. The aquatic risk assessment of the studied chemicals was conducted according to Technical Guidance for Risk Assessment (2003) and Guideline of Environmental Risk Assessment of Medicinal Products for Human Use (2006), adapted at our laboratory conditions and indigenous organisms. For hazard characterisation of the studied chemicals PEC and PNEC values were estimated. The PNECs were calculated using the lowest acute toxicity values (LC_{50}/EC_{50}) obtained in laboratory or from literature. The PECs were estimated based on monitoring data (chemicals concentrations occurred in different Romanian surface waters and also in the effluents of some WWTPs). The PEC/PNEC ratio is widely accepted as endpoint in aquatic risk assessment models taking into account the unfavourable scenarios.

RESULTS AND DISCUSSION

Environmental concentrations. The concentrations of the studied micropolutants are variable and influenced by several factors such as: population sizes which define the consumptions, industrial activities, historical events, WWTPs performances and laboratory analytical methods and detection equipments.

All PHCs were found in the influents and effluents from the three monitored WWTPs with a mean concentrations varying from 0.13 μg/l for naproxen to 21.48 μg/l for ibuprofen. Values of PHCs in wastewater in the same range are specified by Roberts and Thomas[17] and Lin et al.[18] Their removal rates in the monitored WWTPs were >80% for acetaminophen, indomethacin, naproxen and caffeine and >50% for diclofenac and ketoprofen. Lower removal rates were observed for carbamazepine, trimethoprim (<20%) and ibuprofen (25%).

The concentrations averages of PHCs in surface water were between 0.22 and 11.05 μg/l, and the most abundant compounds were ibuprofen and caffeine. Generally, in the Mures river, Arges river, Danube river and Danube delta (Sf. Gheorghe Branch), PHCs concentrations were detected less than 1 μg/l, excepting ibuprofen (2.16 μg/l) and caffeine (1.78 μg/l). The concentrations of studied PHCs obtained in Romanian surface water were almost similar with those found in the surface waters in Germany, Slovenia, USA and France (0.001to 18 μg/l) even they have a larger population and therefore a higher consumption of PHCs (Refs 19–23). Nowadays Romania is facing an increased incidence of infectious disease and uncontrolled consumption of pharmaceuticals products.

In case of the studied cationic and amphoteric surfactants they were frequently detected in the wastewater effluents in mean concentrations about 0.05 mg/l for cocamidopropyl betaine and 0.2 mg/l for benzenthonium chloride, with removal rates >70%. Lower concentrations of 0.003 to 0.01 mg/l for cationic and 0.002 mg/l for amphoteric compounds were detected in the Danube river in 2010–2011. The cationic surfactants were found in surface waters from Austria, Germany, Norway, Japan and Malaysia in concentrations from <0.1 to 34 μg/l (Refs 24–26). Concerning the amphoteric surfactants they were detected recently in the range of <0.01 to 1.9 μg/l (Ref. 25).

The monitoring of nitroderivates (1-chloro-4-nitrobenzene and 4-chloro-2-nitrotoluene) and 4-chloroaniline in the Danube river revealed concentrations under detection limits. 1-Chloro-4-nitrobenzene was detected in the Rhine river in concentration<0.1 μg/l, in the Elbe river – 0.04 μg/l and in the Main river – 0.01 μg/l (Refs 27 and 28). The 4-chloro-2-nitrotoluene was detected in the Rhine river in concentration <0.02–10 μg/l (1989–1990), in the Elbe river – 0.06–0.4 μg/l and in the Danube river – <0.02 μg/l (1999) (Refs 29 and 30). Some studies from Germany revealed that 4-chloroaniline was detected in the Rhine river and its tributaries in the range of 0.1 to 1 μg/l (1980–1990) and under detection limit

(0.05 μg/l) in 1995. In Japanese rivers this was detected in the range of 0.024 to 0.39 μg/l and in the Elbe river and its tributaries about 0.002 μg/l (Ref. 31).

Other readily degradable hazardous chemicals such as azinphos-methyl and bentazon were detected in Ciorogarla river (in Magurele WWTP area) in mean concentrations about 0.22 μg/l, respectively 0.6 μg/l. In other rivers such as the Rhine River the bentazon was detected frequently about <0.1 μg/l and sporadically >1 μg/l (Ref. 32). Some studies highlighted concentrations of azinphos-methyl in the range of <0.001–0.826 μg/l in the Californian rivers[9].

Aquatic toxicity. According to Globally Harmonised System for Classification and Labelling of Chemicals[33], the results indicated moderate and low acute toxicity values, in case of PHCs. $LC_{50(96h)}$ ranged from 43.65 to >100 mg/l (for fish *Cyprinus carpio*), $EC_{50(48h)}$ ranged from 12.02 to >100 mg/l (for planktonic crustacean *Daphnia magna*) and $IC_{50(15\ min)}$/MTC ranged from 6.02 to 77.62 mg/l (bacteria, *Vibrio fischeri* and other). Antibiotics showed an acute toxicity to bacteria < 5 mg/l. As it is known that antibiotic are harmless for microbial flora[34,35], the studied antibiotics (ciprofloxacin and trimethoprim) revealed a high toxicity on bacteria using MARA test, the most sensitive bacteria being the *Microbacterium* sp.

In case of azinphos methyl and benzenthonium chloride[36] the LC_{50}/EC_{50} were ≤ 1 mg/l, 'acute toxic, first class' for the tested organisms, especially for crustaceans. The other chemicals such as bentazone, cocamidopropyl betaine[36], 1-chloro-4-nitrobenzene, 4-chloro-2-nitrotoluene and 4-chloroaniline were 'acute toxic, second class' especially for algae and crustaceans, where $1 < LC_{50}/EC_{50} \leq 10$ mg/l.

Aquatic risk assessment characterisation. For each studied chemical the risk coefficients were calculated taking into consideration multiple risk scenarios. All chemicals were found in the investigated surface waters in concentrations ≥0.01 μg/l and the risk evaluation started with toxicity assessment using aquatic organisms. In order to estimate the PNEC values, the lowest LC_{50}/EC_{50} values were selected and an extrapolation factor of 1000 was applied. Table 3 presents the data used for aquatic risk assessment estimation such as: predicted environmental concentrations, the most sensitive species and the toxicity data (mostly obtained in our studies), risk ratios, level of risk and the recommended maximum admissible concentrations of studied compound for the surface wasters according to the worst scenario.

Table 3. Risk assessment

Chemicals	$PEC_{surface\ water}$ (µg/l)	PNEC water (the lowest EC_{50}/1000) (µg/l)	Risk coefficients ($PEC_{surface\ water}$ / $PNEC_{water}$)	Level of risk[14,15]	Recommended limits for national surface water according to the worst scenario
1	2	3	4	5	6
		Pharmaceuticals			
Diclofenac	mean: 2.10 max: 4.82	22.04 (crustacean)[37] 17.37 (bacteria)	0.17 (mean of four scenarios)	low risk	20 µg/l
Acetaminophen	mean: 1.38 max: 4.15	6.02 (bacteria) 9.2 (crustacean)[38]	0.37 (mean of four scenarios)	low risk	8 µg/l
Ketoprofen	mean: 0.91 max: 2.45	16.21 (bacteria) 15.6 (bacteria)[38]	0.1 (mean of four scenarios)	low risk	16 µg/l
Indomethacin	mean: 0.38 max: 0.43	7.94 (bacteria) 16.14 (crustacean)[38]	0.08 (mean of four scenarios)	negligible risk	8 µg/l
Naproxen	mean: 0.40 max: 0.69	19.95 (bacteria)[37] (crustacean)[38]	0.04 (mean of four scenarios)	negligible risk	20 µg/l
Ibuprofen	mean: 11.05 max: 30.61	39.89 (bacteria) 13.4 (crustacean)[38]	0.62 (mean of three scenarios)	low risk	13 µg/l
Carbamazepine	mean: 0.09 max: 0.22	21.87 (crustacean) 13.8 (crustacean)[38]	0.008 (mean of four scenarios)	negligible risk	14 µg/l
Caffeine	mean: 4.82 max: 16.4	77.20 (bacteria) 87 (fish)[38]	0.12 (mean of four scenarios)	low risk	80 µg/l
Trimethoprim	mean: 0.058	100 (fish) 16 (algae)[34]	0.001 (mean of two scenarios)	negligible risk	16 µg/l
Ciprofloxacin	mean: 0.32	0.005 (algae)[34] 0.08 (bacteria)[34]	34 (mean of two scenarios)	high risk	0.005 µg/l
		Surfactants			
Benzenthonium chloride	max: 10 max: 200 (Ref. 39) min: 2 (Ref. 39)	0.39 (algae)	180 (mean of three scenarios)	high risk	0.4 µg/l
Cocamidopropyl betaine	max: 2 max: 1.9 (Ref. 25)	5.55 (algae)	0.37 (mean of two scenarios)	low risk	5.5 µg/l
		Anilines			
4-Chloroaniline	max: 0.01 surface water; 0.007 effluents (dilution factor of 10)	0.11 (crustacean)	0.05 (mean of two scenarios)	negligible risk	0.11 µg/l G.D.351/2005 – 0.05 µg/l (Ref. 40)

to be continued

Continuation of Table 3

1	2	3	4	5	6
Nitroderivates					
1-Chloro-4-nitrobenzene	max: 0.04 min: 0.01	2.15 (algae)	0.09 (mean of two scenarios)	negligible risk	2 µg/l G.D. 1038/2010 – 10 µg/l (Ref. 41)
4-Chloro-2-nitrotoluene	mean: 0.02	1.14 (algae)	0.017 (one scenarios)	negligible risk	1.2 µg/l G.D. 1038/2010 – 10 µg/l (Ref. 41)
Pesticides					
Azinphos methyl	max: 0.26 min: 0.18	0.002 (crustacean)	110 (mean of two scenarios)	high risk	G.D.1038/ 2010 – 0.1 µg/l (Ref. 41)
Bentazone	max: 0.85 min: 0.1	1.4 (ciliate)	0.33 (mean of two scenarios)	low risk	1.4 µg/l

Using literature and laboratory data, the PEC/PNEC ratios of studied PHCs revealed that the presence of these compounds in the aquatic environment leads to a low aquatic risk (most of PEC/PNEC ratios were <0.1 and in the range 0.01–1) excepting the ciprofloxacin that showed a high environmental risk (PEC/PNEC ratios was 34) as a result of high effects on bacteria.

Low risk to negligible risk was obtained also for cocamidopropyl betaine, nitroderivates, 4-cloroaniline and bentazon, taken into account our toxicity laboratory data. Benzenthonium chloride and azinphos-methyl highlighted high environment risk with inhibitory effects on small aquatic organisms like algae and crustacean, at very low concentrations.

CONCLUSIONS

The studied chemicals showed a relatively limited acute toxicity and generally the final results reveled insignificant or low risks on aquatic organisms, excepting ciprofloxacin, benzenthonium chloride and azinphos-methyl with risk quotients higher than one. In the most cases the bacteria, algae and crustacean showed highest sensitivity. For each pollutant the risk coefficients were calculated by different risk scenarios based on environmental concentrations detected in the national waters and toxicity data obtained in-house and also from literature databases. These data allowed the estimation of the chemicals admissible limits in natural water in order to complete the national norms concerning the surface water quality.

Our research will continue with the development of new analytical methods to assess the Romanian surface waters contamination with a wide range of micro pollutants as well as, ecotoxicological assessment, especially in chronic and sub-lethal effects area. There are still many gaps in national chemicals risk assessment concerning the indirect risks, bioaccumulation, recalcitrant metabolites, synergisms and absence of public chemicals consumption databases.

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