Università Ca'Foscari Venezia

Ca' Foscari University of Venice
Department of Environmental Science,
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Environmental impacts research and smart monitoring strategy development focused on the DETOX Programme

Technical Report

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SOMMARIO

ABBREVIATIONS

AC	ACute toxicity
AC AQ	ACute AQuatic toxicity
AGTS	Analyte Global Toxicological Score
AHP	Analytical Hierarchy Process
CARC	CARCinogenicity
CAT	CATegory
CHR AQ	CHRonic AQuatic toxicity
CI	Consistency Index
CR	Consistency Ratio
EC	Effective Concentration
FGTS	Facility Global Toxicological Score
GR	GRoup
IARC	International Agency for Research on Cancer
IW	Incoming Water
LC	Lethal Concentration
LD	Lethal Dose
LOD	Limit Of Detection
MCA	Multi-Criteria Analysis
NOEC	No Observed Effect Concentration
REP	REProductive toxicity
RI	Random consistency Index
TV	Toxicological Value
TWW	Treated WasteWater
UNECE	United Nations Economic Commission for Europe
UWW	Untreated WasteWater
W	Weight

1. INTRODUCTION

Measuring the concentration of toxic compounds provides fundamental information about the chemical composition of an environmental compartment. However, it is also important to critically evaluate the obtained concentration values and to give them the appropriate weight. For example, a high concentration could have a very different significance depending on the compound's toxicological characteristics.

The evaluation of the concentration data based on the toxicity of the compounds can be very difficult, due to the lack of a formal assessment system. In recent years several chemical hazard screening methods have been developed. Generally, they establish a few classes of toxicity and distinguish between chemicals of high concern and chemicals that can be used with precautions or safer chemicals. As a consequence, the same class can include compounds with very different toxicity levels.

Indeed, the comparison between compounds with different kinds of toxicity is not a trivial aspect. As an example, is a compound more toxic if it has immediate lethal effects or if it is carcinogenic? Is an endocrine disruptor more toxic than a compound that it is toxic for aquatic systems? The relative importance of the different types of toxicity must first be defined. The resulting ranking should be specific to the purpose and to the analysed matrix. One should also consider that compounds can have different types of toxicity at the same time and different values, which complicates the evaluation.

In this work we tried to overcome this limitation by creating a ranking of compounds based on different types of toxicity at the same time. We applied and readapted the multi-criteria analysis (MCA), a technique that permits to evaluate a phenomenon by simultaneously using different criteria, in decision-making environments. The application of MCA allowed us to obtain a single value of toxicity for every compound, which includes different types of toxicity, after determining the relative importance of each criterion with respect to the others.

Globally, the work was been organised in three phases:

1. **Data evaluation.** In this phase concentration data of chemicals in water were assessed. Given that most data were under the limit of detection, great attention was paid to the trend of detected compounds among classes and facilities. These considerations were completed by analysing of trends and by further statistical treatment. Correspondence analysis, which permits to individuate compounds with a specific profile, was performed; outliers (extreme values of concentration) were individuated.
2. **Toxicological evaluation.** In this phase the methodology used to evaluate the global toxicology of compounds was described. Applying multi-criteria analysis, a global toxicity score for every compound was calculated.
3. **Site evaluation.** Finally, the global toxicity score of each analyte was used to measure the concentration of chemicals and to evaluate the toxicological impact of facilities.

2. DATA EVALUATION

OVERALL VIEW

The evaluation conducted in this work includes data from three types of samples:

- incoming water (IW);
- untreated wastewater (UWW);
- treated wastewater (TWW).

177 different chemical compounds were analysed and divided into 12 classes. Each compound was assigned a Axxyy code (Table 2.2), where xx represent the class and yy the arbitrary order of the compound into the class. A description of the classes and of the number of analytes per class is reported in Table 2.1.

Table 2.1. Number of analysed compounds per class.

	Class	Number analytes		Class	Number analytes
C01	Alkylphenols	4	**C07**	Chlorobenzenes	6
C02	Phthalates	20	**C08**	Chlorinated Solvents	14
C03	Brominated and Chlorinated Flame Retardants	32	**C09**	Chlorophenols	18
C04	Azo Dyes	33	**C10**	Short-Chain Chlorinated Paraffins	1
C05	Organotin Compounds	10	**C11**	Total Heavy Metals	12
C06	Perfluorinated Chemicals (PFCs)	26	**C12**	Cyanide	1

Table 2.2. Analyzed chemical compounds, CAS and internal code for classification (A).

A	CAS	Name
C01 – Alkylphenols		
A0101	1806-26-4,140-66-9	Octylphenols (OPs)
A0102	Various	Octylphenolethoxylates (OPEOs)
A0103	54852-15-3,104-40-5,1173019-62-9	Nonylphenols (NPs)
A0104	Various	Nonylphenolethoxylates (NPEOs)
C02 – Phthalates		
A0201	85-68-7	Benzyl-butyl-phthalate (BBP)
A0202	84-74-2	Di-butyl-phthalate (DBP)
A0203	117-81-7	Di-(2-ethyl-hexyl)-phthalate (DEHP)
A0204	117-84-0	Di-n-octyl-phthalate (DNOP)
A0205	68515-48-0	Di-iso-nonyl-phthalate (DINP)
A0206	26761-40-0	Di-iso-decyl-phthalate (DIDP)
A0207	131-11-3	Di-methyl-phthalate (DMP)
A0208	84-66-2	Di-ethyl-phthalate (DEP)
A0209	131-16-8	Di-n-propyl-phthalate (DPP)
A0210	84-69-5	Di-iso-butyl-phthalate (DIBP)
A0211	84-61-7	Di-cyclo-hexyl-phthalate (DCHP)
A0212	84-75-3	Di-n-hexyl-phthalate (DNHP)
A0213	84-76-4	Di-nonyl-phthalate (DNP)
A0214	27554-26-3	Di-iso-octyl-phthalate (DIOP)
A0215	117-82-8	Bis-(2-methoxy-ethyl)-phthalate (DMEP)
A0216	605-50-5	Di-iso-pentyl-phthalate (DIPP)
A0217	71888-89-6	Di-iso-heptyl-phthalate (DIHP)
A0218	84777-06-0	1,2-Benzene-di-carboxylic acid di-pentyl-esters, branched and linear (DHNUP)
A0219	776297-69-9	N-iso-pentyl-iso-pentyl-phthalate (PIPP)
A0220	3648-20-2	Di-heptyl-phthalate (DHP)
C03 - Brominated and Chlorinated Flame Retardants		
A0301	Various	Polybromodiphenyls (PBBs)
A0302	126-72-7	Tri-(2,3-di-bromo-propyl)-phosphate (TRIS)
A0303	Various	Polybromodiphenyl ethers (PBDEs)
A0304	79-94-7	Tetra-bromo-bisphenol-A (TBBPA)
A0305	5412-25-9	Bis-(2,3-di-bromo-propyl)-phosphate
A0306	3194-55-6	Hexa-bromo-cyclo-dodecan (HBCDD)
A0307	3296-90-0	2,2-Bis(bromomethyl)-1,3-propanediol (BBMP)
A0308	115-96-8	Tris-(2-chloro-ethyl)-phosphate (TCEP)
A0309	13674-87-8	Tris-(1,3-di-chloro-iso-propyl)-phosphate (TDCPP)
A0310	Various	Bromo-diphenyl
A0311	Various	Di-bromo-diphenyl
A0312	Various	Tri-bromo-diphenyl
A0313	Various	Tetra-bromo-diphenyl
A0314	Various	Penta-bromo-diphenyl
A0315	Various	Hexa-bromo-diphenyl
A0316	Various	Hepta-bromo-diphenyl
A0317	Various	Octa-bromo-diphenyl
A0318	Various	Nona-bromo-diphenyl
A0319	13654-09-6	Deca-bromo-diphenyl
A0320	Various	Bromo-diphenyl-ether
A0321	Various	Di-bromo-diphenyl-ether
A0322	Various	Tri-bromo-diphenyl-ether
A0323	Various	Tetra-bromo-diphenyl-ether
A0324	Various	Penta-bromo-diphenyl-ether
A0325	Various	Hexa-bromo-diphenyl-ether
A0326	Various	Hepta-bromo-diphenyl-ether
A0327	Various	Octa-bromo-diphenyl-ether
A0328	Various	Nona-bromo-diphenyl-ether
A0329	1163-19-5	Deca-bromo-diphenyl-ether
A0330	21850-44-2	Tetra-bromo-bisphenol A bis-(di-bromo-propyl-ether) (TBBPA-BDPE)

Table 2.2. (continued)

A	CAS	Name
A0331	13674-84-5	Tris-(2-chloroisopropyl)-phosphate (TCPP)
A0332	Various	Tris-(aziridinyl)-phosphinoxide (TEPA)
C04 - Azo Dyes		
A0401	92-67-1	4-Aminodiphenyl
A0402	92-87-5	Benzidine
A0403	95-69-2	4-Chloro-o-toluidine
A0404	91-59-8	2-Naphthylamine
A0405	97-56-3	o-Aminoazotoluene
A0406	99-55-8	5-Nitro-o-toluidine
A0407	106-47-8	4-Chloroaniline
A0408	615-05-4	2,4-Diaminoanisole
A0409	101-77-9	4,4'-Diaminodiphenylmethane
A0410	91-94-1	3,3'-Dichlorobenzidine
A0411	119-90-4	3,3'-Dimethoxybenzidine
A0412	119-93-7	3,3'-Dimethylbenzidine
A0413	838-88-0	3,3'-Dimethyl-4,4'-diaminodiphenylmethane
A0414	120-71-8	p-Cresidine
A0415	101-14-4	4,4'-Methylene-bis(2-chloroaniline)
A0416	101-80-4	4,4'-Oxydianiline
A0417	139-65-1	4,4'-Thiodianiline
A0418	95-53-4	o-Toluidine
A0419	95-80-7	2,4-Diaminotoluene
A0420	137-17-7	2,4,5-Trimethylaniline
A0421	90-04-0	o-Anisidine
A0422	60-09-3	4-Aminoazobenzene
A0423	95-68-1	2,4-Xylidine
A0424	87-62-7	2,6-Xylidine
A0425	62-53-3	Aniline
A0426	106-50-3	1,4-Phenylenediamine

A	CAS	Name
A0427	95-51-2	2-Chloroaniline
A0428	99-59-2	5-Nitro-o-anisidine
A0429	108-44-1	m-Toluidine
A0430	91-66-7	n,n-Diethylanaline
A0431	103-69-5	n-Ethylaniline
A0432	100-61-8	n-Methylaniline
A0433	106-49-0	p-Toluidine
C05 - Organotin Compounds		
A0501	Various	Monobutyltin (MBT)
A0502	Various	Dibutyltin (DBT)
A0503	Various	Dioctyltin (DOT)
A0504	Various	Tributyltin (TBT)
A0505	Various	Triphenyltin (TPhT)
A0506	Various	Tricyclohexyltin(TCyHT)
A0507	Various	Trioctyltin(TriOT)
A0508	Various	Tripropyltin (TPT)
A0509	Various	Monooctyltin (MOT)
A0510	Various	Tetrabutyltin (TeBT)
C06 - Perfluorinated Chemicals (PFCs)		
A0601	335-67-1	Perfluoro-n-octanoic acid (PFOA)
A0602	2795-39-3 / Various	Perfluorooctane sulphonates (PFOS)
A0603	307-24-4	Perfluoro-n-hexanoic acid (PFHxA)
A0604	3871-99-6	Perfluorohexane sulphonates (PFHxS)
A0605	375-22-4	Perfluorobutyric Acid (PFBA)
A0606	375-73-5	Perfluoro-butane-sulfonic acid
A0607	754-91-6	Perfluoro-octane-sulfon- amide (PFOSA)
A0608	31506-32-8	N-Methyl-Perfluoro-octane-sulfon-amide (N-Me-FOSA)
A0609	4151-50-2	N-Ethyl-Perfluoro-octane-sulfon-amide (N-Et-FOSA)

Table 2.2. (continued)

A	CAS	Name
A0610	24448-09-7	N-Methyl-Perfluoro-octane-sulfon-amido-ethanol (N-Me-FOSE alcohol)
A0611	1691-99-2	N-Ethyl-Perfluoro-octane-sulfon-amido-ethanol (N-Et-FOSE alcohol)
A0612	2706-90-3	Perfluoro-pentanoic acid
A0613	375-85-9	Perfluoro-heptanoic acid
A0614	375-95-1	Perfluoro-nonanoic acid
A0615	335-76-2	Perfluoro-n-decanoic acid (PFDA)
A0616	2058-94-8	Perfluoro-undecanoic acid
A0617	307-55-1	Perfluorododecanoic Acid (PFDoA)
A0618	72629-94-8	Perfluoro-tridecanoic acid
A0619	376-06-7	Perfluoro-tetradecanoic acid
A0620	355-46-4 / 432-50-7	Perfluoro-hexane-sulfonic acid
A0621	375-92-8	Perfluoro-heptane-sulfonic acid
A0622	355-77-3	Perfluor-decane-sulfonic acid
A0623	27619-97-2	1H,1H,2H,2H-Perfluoro-octane-sulphonic acid
A0624	34598-33-9	2H,2H,3H,3H-Perfluoroundecanoic acid (PFUnA)
A0625	172155-07-6	Perfluoro-3-7-dimethyl octane carboxylate
A0626	1546-95-8	7H-Dodecafluoro heptane carboxylate
C07 - Chlorobenzenes		
A0701	108-90-7	Chlorobenzene
A0702	Various	Dichlorobenzenes
A0703	Various	Trichlorobenzenes
A0704	Various	Tetrachlorobenzenes
A0705	608-93-5	Pentachlorobenzene
A0706	118-74-1	Hexachlorobenzene
C08 - Chlorinated Solvents		
A0801	75-09-2	Dichloromethane
A0802	67-66-3	Chloroform
A0803	56-23-5	Carbon tetrachloride

A	CAS	Name
A0804	107-06-2	1,2-dichloroethane
A0805	71-55-6	1,1,1-trichloroethane
A0806	79-00-5	1,1,2-trichloroethane
A0807	630-20-6	1,1,1,2-tetrachloroethane
A0808	79-34-5	1,1,2,2-tetrachloroethane
A0809	76-01-7	Pentachloroethane
A0810	75-35-4	1,1-dichloroethylene
A0811	156-59-2	cis-1,2-Dichloroethylene
A0812	156-60-5	trans-1,2-Dichloroethylene
A0813	79-01-6	Trichloroethylene
A0814	127-18-4	Tetrachloroethylene
C09 - Chlorophenols		
A0901	Various	Monochlorophenols
A0902	Various	Dichlorophenol (DiCP)
A0903	Various	Trichlorophenols (TriCP)
A0904	25167-83-3	Tetrachlorophenols (TeCP)
A0905	87-86-5	Pentachlorophenol (PCP)
A0906	95-57-8	2-Chlorophenol
A0907	108-43-0	3-Chlorophenol
A0908	106-48-9	4-Chlorophenol
A0909	576-24-9	2,3-Dichlorophenol
A0910	95-77-2	3,4-Dichlorophenol
A0911	120-83-2, 583-78-8, 87-65-0, 591-35-5	2,4-Dichlorophenol, 2,5-Dichlorophenol, 2,6-Dichlorophenol, 3,5-Dichlorophenol
A0912	933-78-8	2,3,5-Trichlorophenol
A0913	95-95-4	2,4,5-Trichlorophenol
A0914	88-06-2	2,4,6-Trichlorophenol
A0915	609-19-8, 15950-66-0	3,4,5-Trichlorophenol, 2,3,4-Trichlorophenol
A0916	4901-51-3	2,3,4,5-Tetrachlorophenol
A0917	58-90-2	2,3,4,6-Tetrachlorophenol

Table 2.2. (continued)

A	CAS	Name
A0918	935-95-5	2,3,5,6-Tetrachlorophenol
C10 - Short-Chain Chlorinated Paraffins		
A1001	85535-84-8	Short-chain chlorinated paraffins (C10-C13)
C11 - Total Heavy Metals		
A1101	7440-47-3	Chromium (Cr)
A1102	18540-29-9	Hexavalent Chromium (Cr VI)
A1103	7439-95-4	Manganese (Mn)
A1104	7440-48-4	Cobalt (Co)
A1105	7440-02-0	Nickel (Ni)

A	CAS	Name
A1106	7440-50-8	Copper (Cu)
A1107	7440-66-6	Zinc (Zn)
A1108	7440-38-2	Arsenic (As)
A1109	7440-43-9	Cadmium (Cd)
A1110	7440-36-0	Antimony (Sb)
A1111	7439-97-6	Mercury(Hg)
A1112	7439-92-1	Lead(Pb)
C12 - Cyanide		
A1201	74-90-8	Cyanide

Each facility was assigned an internal code, composed by F and a three-digit number. In some facilities, chemical analyses were conducted twice; in those cases an additional letter is present: A for the first investigation and B for the second one. Globally, 112 studies were conducted in 102 facilities located in 10 countries. China is the most represented country, with 49 facilities out of 102, followed by Bangladesh. Globally, 72% of all facilities are located in Asia (Figure 2.1).

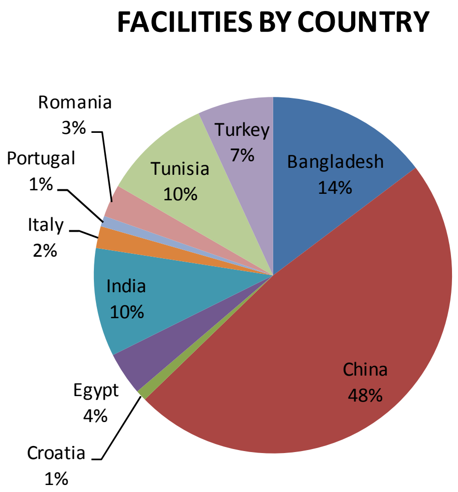


Figure 2.1. Facilities involved in this work, divided by country.

The chemical analysis were conducted from 2013 to 2015. The studies were distributed as follows:

- 42 studies were performed in 2013;
- 43 studies were performed in 2014;
- 27 studies were performed in 2015.

The data are inhomogeneous: not all of the 177 compounds were analysed in each facility; moreover, the three types of samples did not have the same amount of available data. Generally, the monitoring strategy required that, for those classes for which all analytes were under the limit of detection (LOD) in UWW, samples from IW and TWW would not be analysed. As a consequence, most data relates to UWW, with 141 compounds analysed for each facility, on average, followed by IW (60 compounds) and TWW (53 compounds). This difference must be taken into consideration during the comparison of results. In Table 2.3 various information about data are reported: the average number of compounds analysed for every facility with the range, the number of studies conducted and the global amount of data, for IW, UWW and TWW.

Table 2.3. Average number of compounds per facility (range in brackets), number of studies conducted and global amount of data, for incoming water, untreated wastewater and treated wastewater.

INCOMING WATER	UNTREATED WASTEWATER	TREATED WASTEWATER
60 (11-143) compounds	141 (96-156) compounds	53 (1-147) compounds
111 studies	112 studies	65 studies
6611 data	15822 data	3425 data

DETECTED ANALYTES

The first step of the study was the evaluation of detected and undetected analytes. The assessment initially focused on UWW samples, given the great data size. Thereafter the comparison with IW and TWW samples was performed.

Untreated wastewater

The first conclusion that can be inferred from the available data is that 112 compounds out of 177 were under the limit of detection (LOD) in all studies. The LOD is the lowest quantity of a substance that can be distinguished from the absence of such substance. Therefore being under LOD does not mean being absent, rather it indicates that the concentration of a substance is certainly below a specific value. Accordingly, in order to assess the real concentration of chemicals, it is very important to choose pre-analytical and analytical methods characterised by a minimum LOD.

Considering an average facility, about 8% of the compounds were detected (i.e., they were above LOD). The most representative class is C11 (total heavy metals), followed by C04 (Azo dyes), as shown in Figure 2.2. Table 2.4 reports the detected analytes in more detail. On the contrary, class C03 is characterised by a very low percentage of detected analytes (average 0.1%). This should be taken into account, in view of a reduction of the analytes.

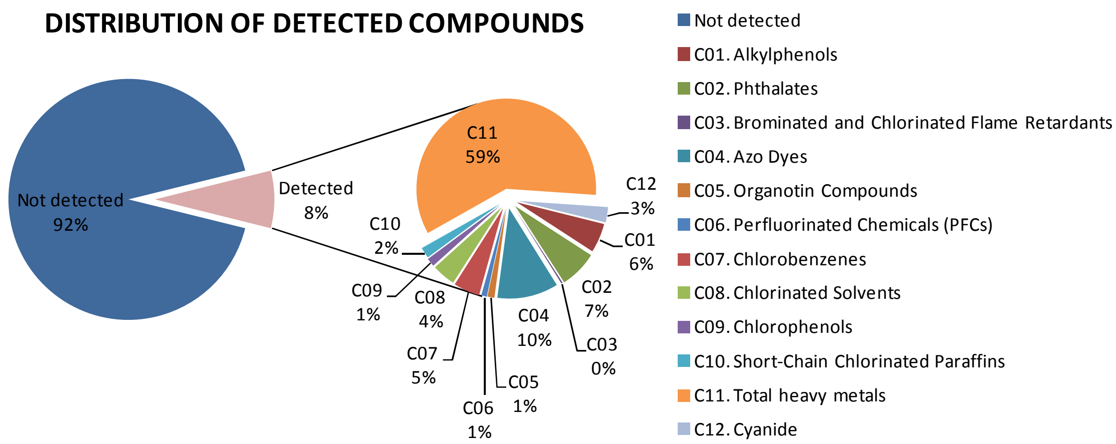


Figure 2.2. Distribution of the detected analytes among classes, in untreated wastewater.

Table 2.4. Analysed and detected compounds (percentage and maximum) per class, in untreated wastewater. C01: Alkylphenols; C02: Phthalates; C03: Brominated and Chlorinated Flame Retardants; C04: Azo Dyes; C05: Organotin Compounds; C06: Perfluorinated Chemicals (PFCs); C07: Chlorobenzenes; C08: Chlorinated Solvents; C09: Chlorophenols; C10: Short-Chain Chlorinated Paraffins; C11: Total Heavy Metals; C12: Cyanide.

Classes	Analysed compounds (average)	Detected compounds	Detected compounds (maximum)
C01	4	14%	2
C02	18	4.1%	5
C03	21	0.1%	1
C04	29	4.2%	5
C05	10	1.4%	2
C06	21	0.5%	3
C07	6	8.9%	4
C08	12	4.0%	3
C09	8	2.0%	2
C10	1	2.1%	1
C11	12	55%	10
C12	1	34%	1

Metals (C11) are not only the most represented class on average, but they were also detected in almost all the investigated facilities, as shown in Figure 2.3. The second most frequent class is azo dyes (C04), present in two thirds of the sites; other classes were detected less frequently than C11 and C04. The less frequent class is C03, which is present (with maximum 1 compound out of 21, as reported in Table 2.4) in only 3% of the facilities.

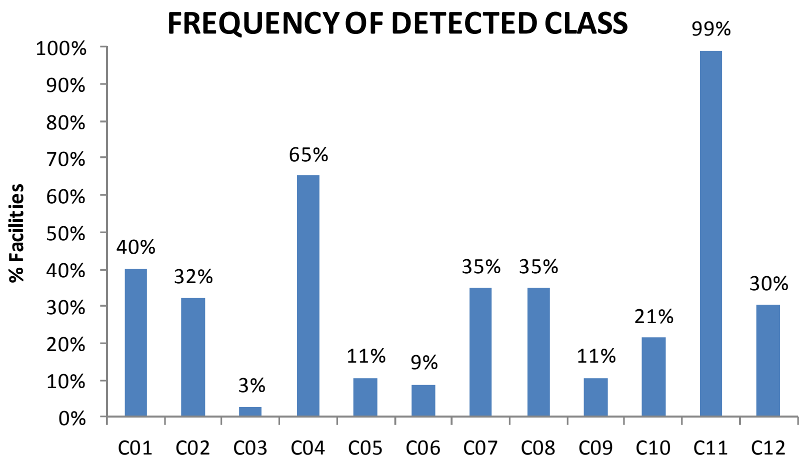
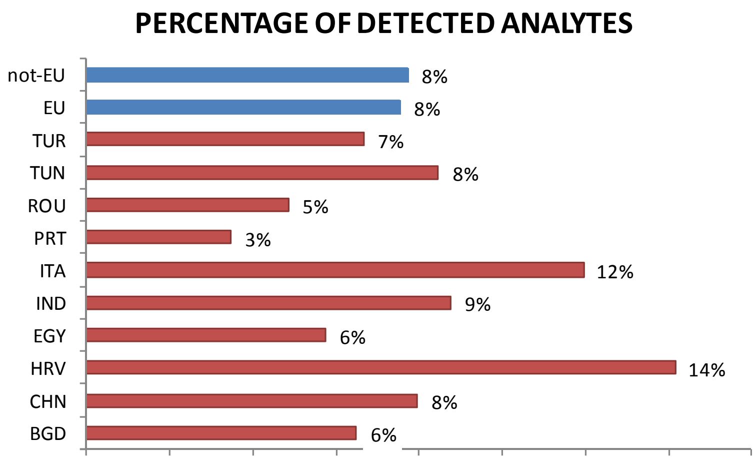


Figure 2.3. Frequency of detected class of compounds in facilities. C01: Alkylphenols; C02: Phthalates; C03: Brominated and Chlorinated Flame Retardants; C04: Azo Dyes; C05: Organotin Compounds; C06: Perfluorinated Chemicals (PFCs); C07: Chlorobenzenes; C08: Chlorinated Solvents; C09: Chlorophenols; C10: Short-Chain Chlorinated Paraffins; C11: Total Heavy Metals; C12: Cyanide.

Figure 2.4. Percentage of detected analytes, per country and community of countries. EU: European Union; TUR: Turkey; TUN: Tunisia; ROU: Romania; PRT: Portugal; ITA: Italy; IND: India; EGY: Egypt; HRV: Croatia; CHN: China; BGD: Bangladesh.



Finally, the number of detected analytes was assessed considering the country were facilities were located. The percentage of detected analytes ranges from 3% in Portugal to 14% in Croatia. No significant difference was noticed between countries within and outside of the European Union.

Obviously, the assessments reported in this section must be considered in combination with the information about the concentration and toxicity of the compounds, described in the following pages.

Comparison of sampling sites

In this section detected analytes in UWW are compared with IW and TWW. As expected, the number of analytes above the LOD is higher in UWW (11) than in the other samples: TWW and IW samples are characterised by 7 and 4 detected analytes on average, respectively (Figure 2.5a). Figure 2.5b shows the number of compounds with all values under the LOD. This increases from 112 for UWW to 134 for UWW, and 140 for TWW, out of the 177 total analysed chemicals.

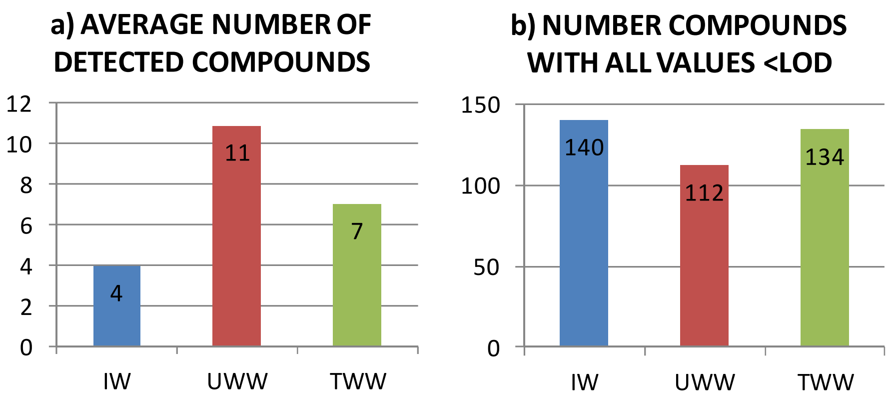


Figure 2.5. a) Average number of detected compounds (above the limit of detection); b) number of compounds with all values under the limit of detection (LOD) in incoming water (IW), untreated wastewater (UWW) and treated wastewater (TWW).

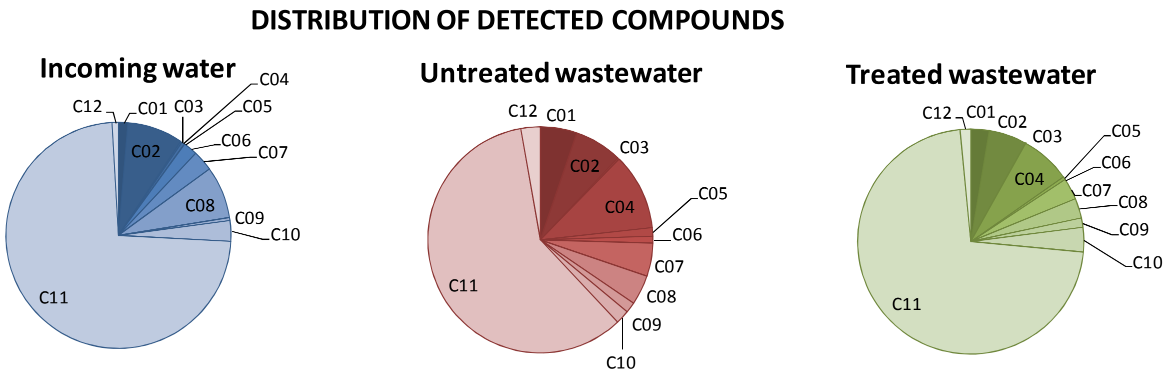


Figure 2.6. Distribution of detected analytes among classes, in incoming water, untreated wastewater and treated wastewater. C01: Alkylphenols; C02: Phthalates; C03: Brominated and Chlorinated Flame Retardants; C04: Azo Dyes; C05: Organotin Compounds; C06: Perfluorinated Chemicals (PFCs); C07: Chlorobenzenes; C08: Chlorinated Solvents; C09: Chlorophenols; C10: Short-Chain Chlorinated Paraffins; C11: Total Heavy Metals; C12: Cyanide.

The distribution per class of the detected analytes shows a few differences in the three samples (Figure 2.6). The most represented class is C11 (total heavy metals) for all the sites, the other classes are present with various percentages. It seems that in UWW the percentage of metals (C11) decreases respect to IW and TWW. This trend was associated with an increase in the percentage of the other minor classes. As an example, C04 is almost absent in IW and increases to about 10% in UWW; C01 increases from 1% in IW to 5% in UWW. In TWW the percentage of C11 is close to that in IW and all the other classes decrease in percentage compared to UWW. It should also be noted that azo dyes (C04) are reduced in percentage in TWW with respect to UWW, but anyway remain much higher than in IW; the same goes for C01. On the contrary, other classes shows an opposite trend (C05, C06, C07, C08).

To further investigate which class is more influenced by the presence of the facilities, a detailed comparison about the detected classes in the three samples is reported in Figure 2.7, expressed as difference between concentration of classes.

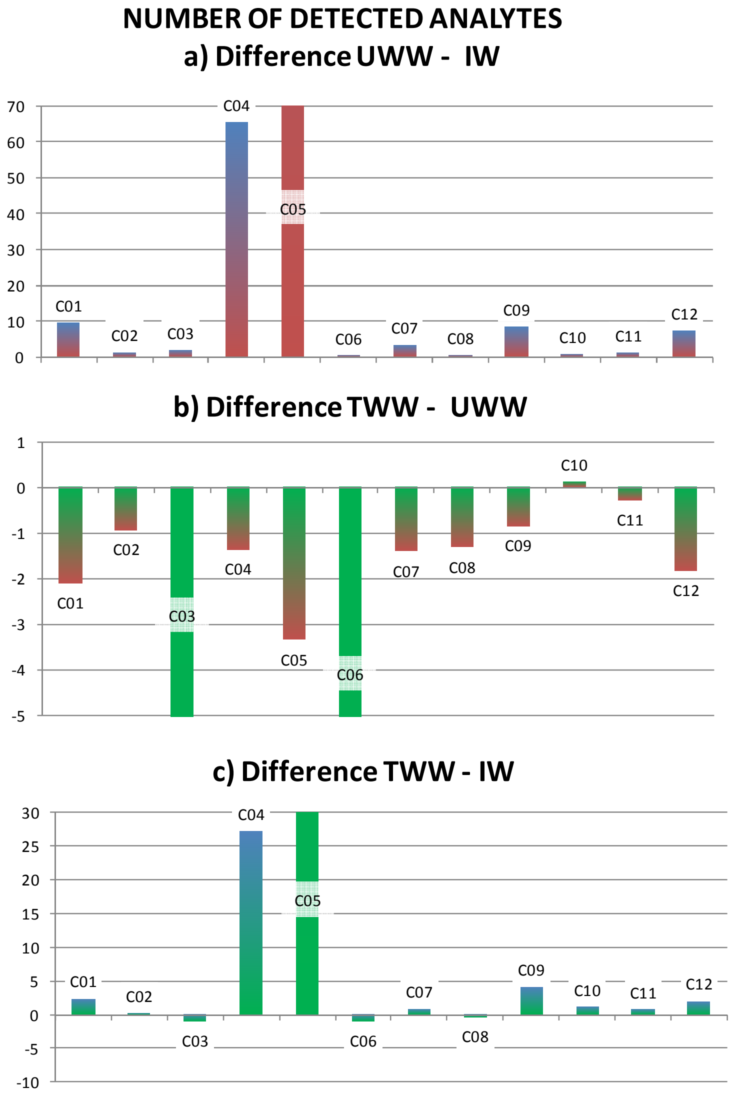


Figure 2.7. Difference of detected values in classes of chemicals, comparing various types of samples. a) Difference between untreated wastewater (UWW) and incoming water (IW); b) Difference between treated wastewater (TWW) and untreated wastewater (UWW); c) Difference between treated wastewater (TWW) and incoming water (IW). C01: Alkylphenols; C02: Phthalates; C03: Brominated and Chlorinated Flame Retardants; C04: Azo Dyes; C05: Organotin Compounds; C06: Perfluorinated Chemicals (PFCs); C07: Chlorobenzenes; C08: Chlorinated Solvents; C09: Chlorophenols; C10: Short-Chain Chlorinated Paraffins; C11: Total Heavy Metals; C12: Cyanide.

Figure 2.7a shows that azodyes (C04) and organotin compounds (C05) are the most influenced by the activities of the facilities, representing a high difference between UWW and IW; C05 shows a very high increase from IW to UWW due to the fact that the entire class was totally absent in IW. Alkylphenols (C01), chlorophenols (C09) and cyanide (C12) are also noteworthy, as they show an almost 10-fold increase in the number of detected analytes, from IW to UWW.

Comparing UWW with TWW, C03 (brominated and chlorinated flame retardants) and C06 (perfluorinated compounds) seem to be completely removed from the wastewater (Figure 2.7b). It should be consider that these results are affected by the difference in data size among the samples. In particular, in classes C03 and C06, 2 compounds were analysed on average for TWW (Table 2.5), while in UWW they were 21. C04 and C05 show also a decrease in the number of detected analytes, but it is not enough to compensate for the extreme increment that was previously observed. This is confirmed by Figure 2.7c, where C04 and C05 are still the most important classes, in term of relative increase of number of detected analytes from IW to TWW.

Table 2.5. Analysed and detected compounds (percentage and maximum) per class, in incoming water and treated wastewater. C01: Alkylphenols; C02: Phthalates; C03: Brominated and Chlorinated Flame Retardants; C04: Azo Dyes; C05: Organotin Compounds; C06: Perfluorinated Chemicals (PFCs); C07: Chlorobenzenes; C08: Chlorinated Solvents; C09: Chlorophenols; C10: Short-Chain Chlorinated Paraffins; C11: Total Heavy Metals; C12: Cyanide.

	INCOMING WATER			TREATED WASTEWATER		
Classes	Analysed compounds (average)	Detected compounds	Detected compounds (maximum)	Analysed compounds (average)	Detected compounds	Detected compounds (maximum)
C01	2	2.9%	1	1	13%	1
C02	7	4.5%	4	6	6.9%	4
C03	3	0.3%	1	2	0%	0
C04	19	0.1%	1	17	3.0%	3
C05	2	0%	0	3	1.2%	1
C06	3	2.3%	4	2	0%	0
C07	2	4.9%	2	2	8.7%	14
C08	5	5.6%	2	4	4.5%	2
C09	2	1.1%	1	2	4.3%	2
C10	0.4	33%	1	0.4	59%	1
C11	12	25%	7	12	43%	10
C12	1	5.3%	1	1	14%	1

EVALUATION OF CONCENTRATION VALUES

After the evaluation of detected compounds in general, a specific assessment of concentration values was conducted. Given the little size of values above the limit of detection, drawing conclusions considering only the median concentration as an importance indicator of compounds and classes could be misleading. Therefore, all the results reported in this paragraph must be evaluated in this perspective and always compared with the corresponding results in term of presence of compounds.

Comparison of concentration values

A comparison of concentration values among samples is difficult, not only because of the different data size in IW, UWW and TWW, as mentioned above, but also because the majority of data is <LOD, hence it is not possible to express their value quantitatively.

As in the previous paragraph, a comparison was conducted among the three type of samples, in order to investigate which class is more affected by the presence of the facilities, in terms of concentration. Given the low number of the detected analytes, the results reported in Figure 2.8 must be compared to those reported in Figure 2.7, in order to better understand the situation in its entirety.

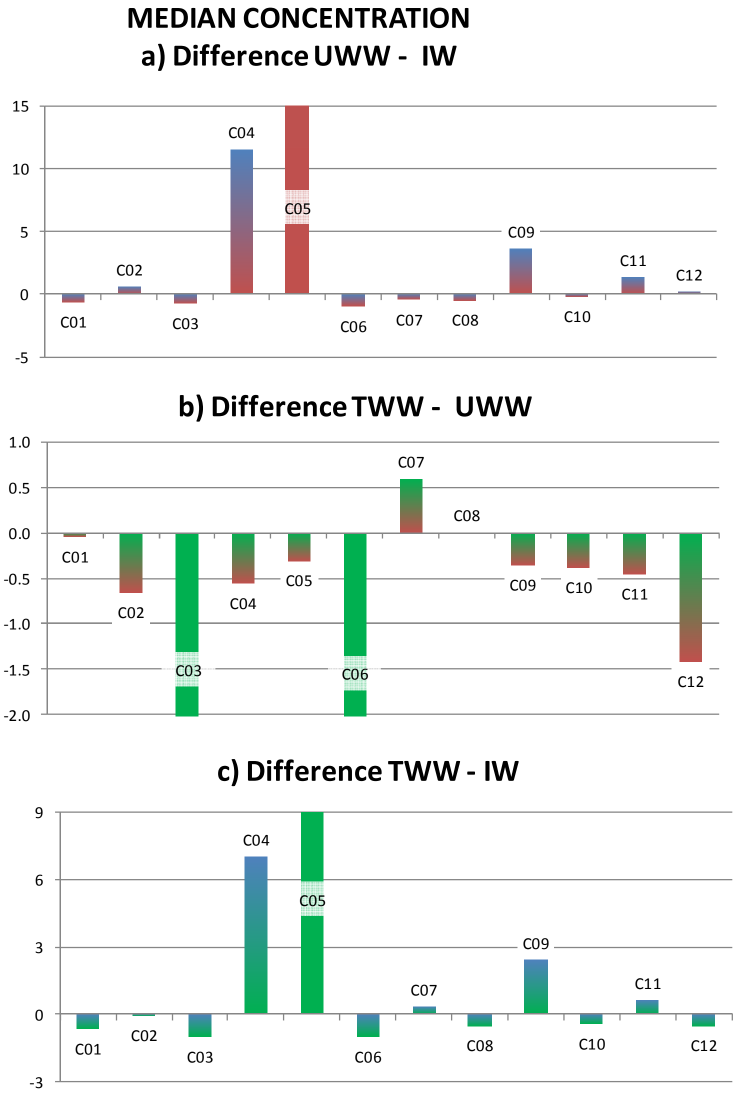


Figure 2.8. Difference of median concentration of classes of chemicals, comparing various types of samples. a) Difference between untreated wastewater (UWW) and incoming water (IW); b) Difference between treated wastewater (TWW) and untreated wastewater (UWW); c) Difference between treated wastewater (TWW) and incoming water (IW). C01: Alkylphenols; C02: Phthalates; C03: Brominated and Chlorinated Flame Retardants; C04: Azo Dyes; C05: Organotin Compounds; C06: Perfluorinated Chemicals (PFCs); C07: Chlorobenzenes; C08: Chlorinated Solvents; C09: Chlorophenols; C10: Short-Chain Chlorinated Paraffins; C11: Total Heavy Metals; C12: Cyanide.

Classes C04 and C05 show the greatest increase from IW to UWW in median concentration, followed by C09 (Figure 2.8a). C1 and C12 seem to be characterised by an almost 10-fold increase in the number of detected analytes (Figure 2.7a), but the median concentration remains at the same levels. C03 and C06 are absent from TWW, leading to a very high decrease passing from UWW to TWW in both assessments (Figure 2.7b and Figure 2.8b). Regarding the other classes, C12 and C05 show a decrease in both evaluations; a number of detected analytes of class C01 decreased, with a stable median concentration; the analytes of class C07 were detected less in TWW with than in UWW, but, when quantified, they show a higher median concentration.

As in the previous evaluation, the decrease in concentration due to water treatment does not compensate for the impact of the facilities. Figure 2.8c shows a higher concentration of classes C04 and C05, when comparing TWW to IW.

Considering only the median concentration allows us to understand the general tendency of data, but sometimes it prevents us from identifying specific cases differing from the average trend. In order to individuate anomalies, a data-to-data comparison was conducted for every possible couple of sample tpes:

UWW-IW; UWW-TWW and IW-TWW (Figure 2.9). It must remind that only analytes detected in both sample types for each couple can enter the comparison.

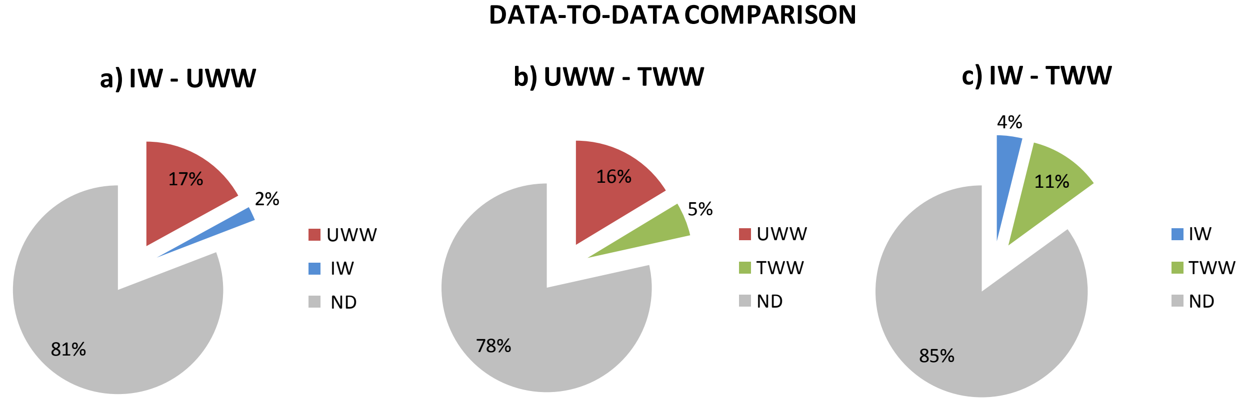


Figure 2.9. Data-to-data comparison of the concentration in UWW (untreated wastewater), IW (incoming water) and TWW (treated wastewater). a) Comparison between UWW and IW; b) comparison between UWW and TWW; c) comparison between IW and TWW. ND represents a comparison with both values under the limit of detection.

The graphs of Figure 2.9 show that most data are characterised by values under the limit of detection in both the samples. Considering the comparison UWW-IW and only data with both values > LOD, the majority of data are characterised by a higher concentration in UWW respect to IW (Figure 2.9a), but there are some exceptions: in 2% of cases (142 out of the 6595 comparable couples of data) compounds have a higher concentration in incoming water respect to untreated wastewater. Exceptions are widely distributed among compounds and sites. The reasons of this particular trend should be investigated.

A similar profile was obtained when comparing UWW to TWW (Figure 2.9b): 16% of the total data-to-data comparisons show a higher concentration in UWW than in TWW, but 5% of comparisons (178 out of 3425 comparable couples of data) shows the opposite trend. In this case anomalies are mainly concentrated in a few facilities: in particular F036 with 14 cases of TWW>UWW and 2 cases of UWW>TWW, F066 (TWW>UWW: 9 cases; UWW>TWW: 3 cases) and F089 (TWW>UWW: 5 cases; UWW>TWW: 2 cases). Such an increase of concentration of toxic compounds after the treatment is quite alarming. Given that this effect is localised to specific sites, the need of further investigation about the efficiency of the purifiers is evident.

Figure 2.9c shows that generally compounds are in higher concentration in wastewater after treatment than in incoming water (11%), with a frew exceptions (4%).

Correspondence analysis

In the previous section similarities and anomalies in the concentration values were assessed separately from values under the LOD. This partial view should now be completed. In order to bridge the gap, advanced statistical techniques can be used.

Correspondence analysis is a descriptive/exploratory technique designed to analyze simple two-way and multiway tables containing some measure of correspondence between the rows and columns. The advantage in using this technique is that values above and below LOD can be included in the same evaluation recurring to an appropriate categorisation.

Correspondence analysis was conducted starting from three datasets, containing the concentration values of toxic compounds from different type of samples: IW, UWW and TWW. All values were categorised as reported in Table 2.6.

Table 2.6. Categorisation of concentration values, for correspondence analysis.

Category		Limits
ND	Not detected	Under LOD
LOW	Low concentration	From LOD to one-third of the maximum value
MED	Medium concentration	From one-third to two-thirds of the maximum value
HIGH	High concentration	From two-thirds of the maximum value to the maximum value

Datasets were rearranged as matrices with categories as columns and compounds as rows; i. e. every analyte was represented by a profile of frequencies of its values. The resulting table of frequencies was standardised, so that the relative frequencies across all cells amounted to 1. Correspondence analysis was performed using STATISTICA 8.0. Since the main objective was to individuate the distance between rows (or the differences in the compound profiles), standardisation of coordinates on row profile was chosen. Results can be plotted in a two-dimension graph, where compounds are grouped on the basis of the similarity of their profile. The 2D plots resulting from the application of correspondence analysis in the three datasets are presented in Figure 2.10, Figure 2.12 and Figure 2.14. In all plots, near the origin of the graph, a group containing many overlapping analytes is evidenced ("ND" group). It represents all the compounds with all (or most of the) values <LOD. Precisely because they have a very similar profile, they are represented in the same region of the graph, resulting in a overlap. The more distant is the compounds are from the ND group, the more their profile differs.

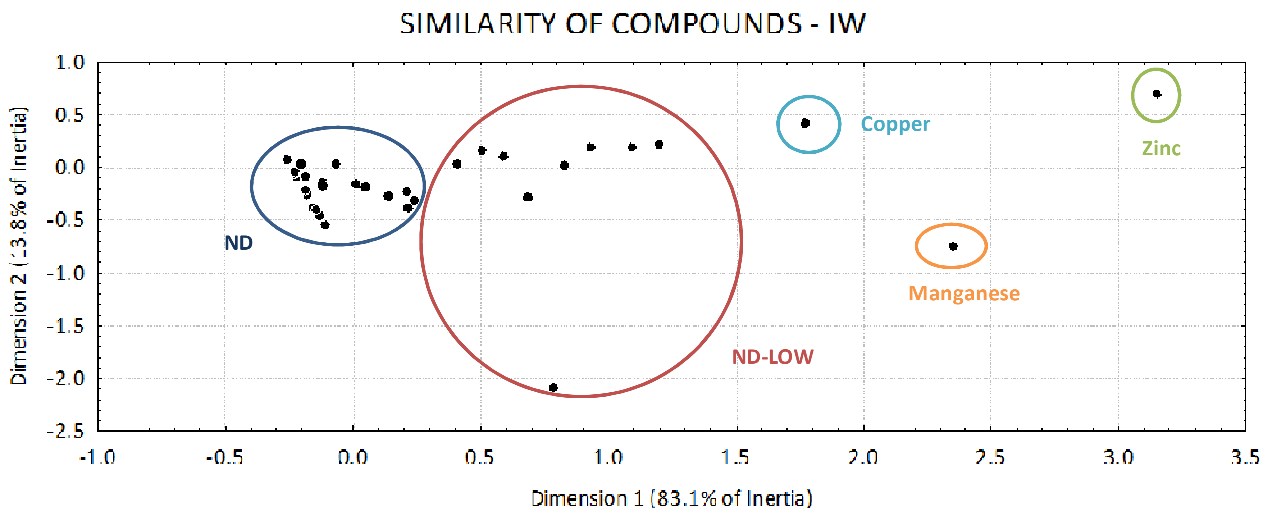


Figure 2.10. Correspondence analysis of incoming water (IW) data. 2D plot of row coordinates; Dimensions: 1x2; Input Table (Rows x Columns): 177x4; Standardisation: row profiles.

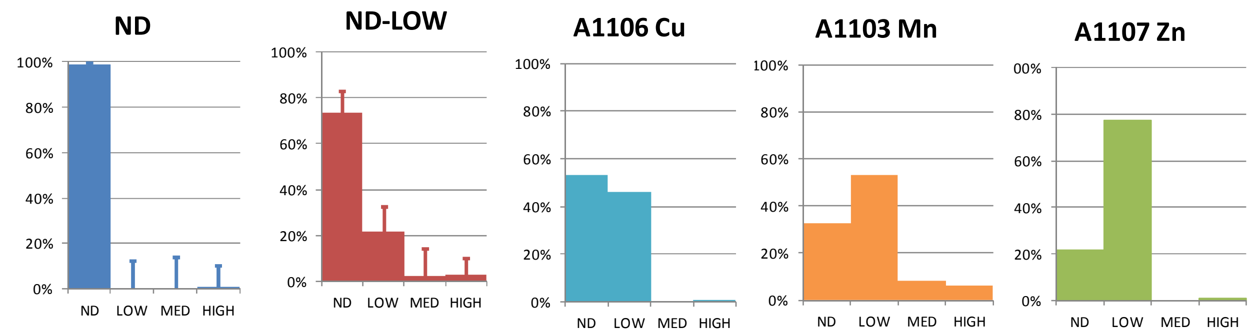


Figure 2.11. Concentration profiles of: group ND, group ND-LOW, zinc (Zn), manganese (Mn) and copper (Cu), in incoming water. For groups the average profile is reported; whiskers represent the range of values.

In IW data, compounds that differ the most from ND group are zinc, manganese and copper. Zinc and manganese are characterised by a greater number of values above LOD, variously distributed among categories; copper profile shows approximately half of the values > LOD. Figure 2.11 reports those profiles, with the average profile of the ND group and the so-called ND-LOW group, the latter characterised by about 75% of values <LOD and 20% of values in low concentration.

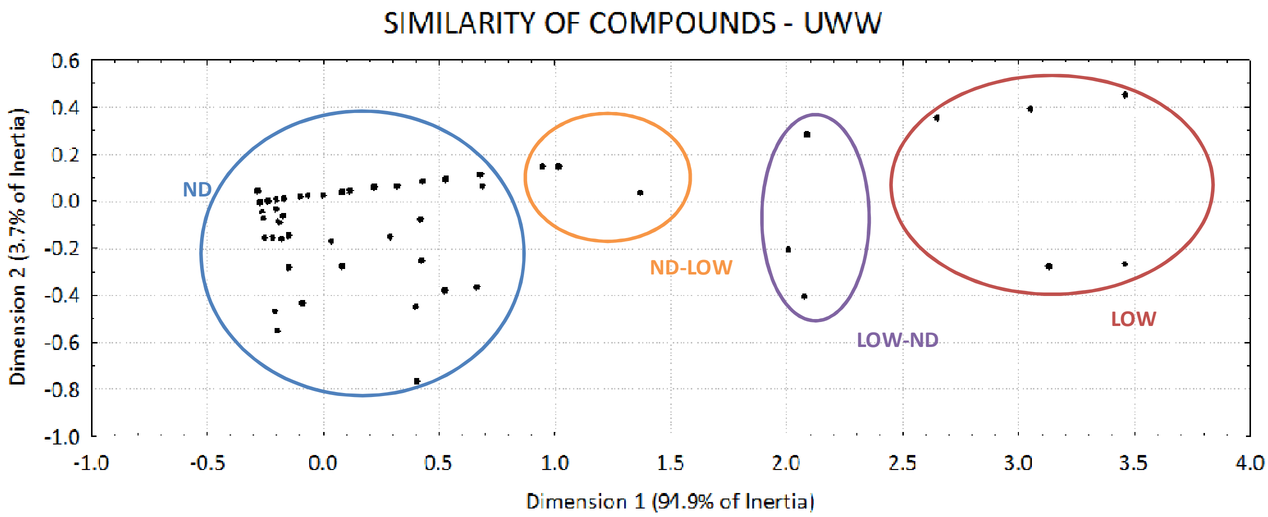


Figure 2.12. Correspondence analysis of untreated wastewater (UWW) data. 2D plot of row coordinates; Dimensions: 1x2; Input Table (Rows x Columns): 177x4; Standardisation: row profiles.

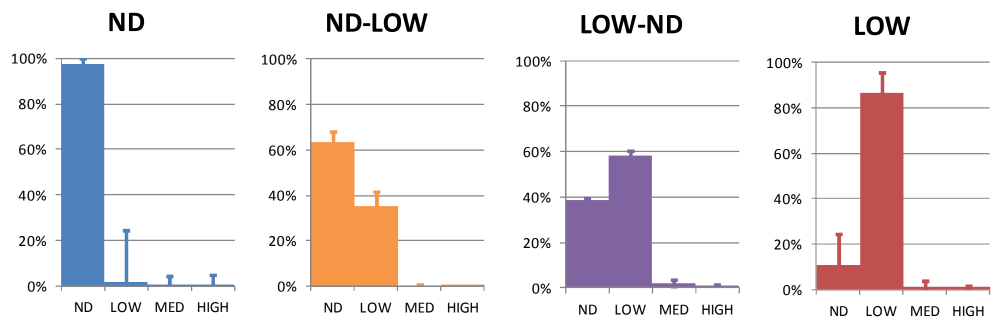


Figure 2.13. Average concentration profiles of groups ND, ND-LOW, LOW-ND and LOW. Whiskers represent the range of values.

2D plot resulting from UWW data highlighted 11 compounds that were different from those included in the ND group. They were classified by their profile in ND-LOW, LOW-ND and LOW groups. The ND-LOW group includes nonylphenolethoxilates (NPEOs), arsenic and cyanide. Despite the fact that most values for arsenic and cyanide are <LOD (Figure 2.13), their presence could be alerting, because of their known high toxicity. Lead, antimony and aniline are present in low concentration in almost 60% of the cases and under the LOD in 40% of the cases; hence they were classified in the LOW-ND group. Contrary to what we observed for IW, most of the compounds in UWW had values above LOD: nickel, chromium, zinc, copper and manganese. This category of compound must be kept under control due to its high prevalence in wastewater.

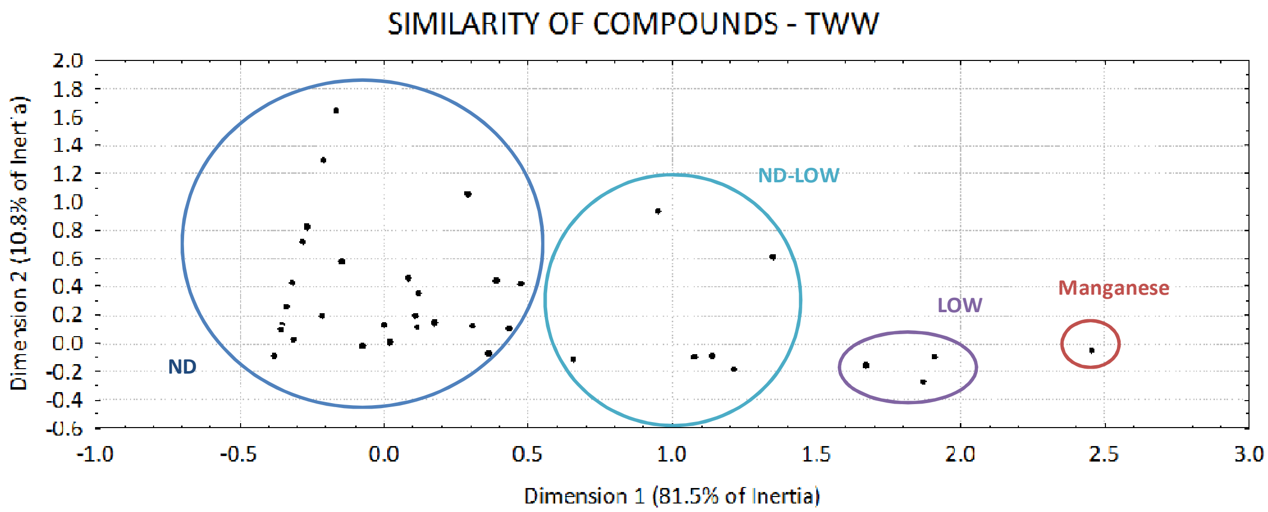


Figure 2.14. Correspondence analysis of treated wastewater (TWW) data. 2D plot of row coordinates; Dimensions: 1x2; Input Table (Rows x Columns): 175x4; Standardisation: row profiles.

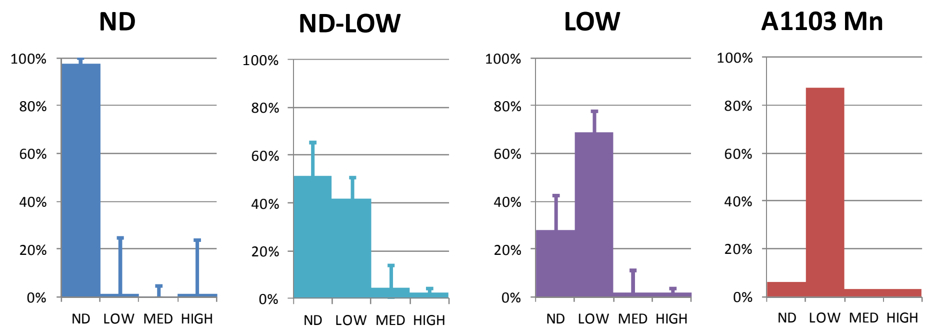


Figure 2.15. Concentration profiles of: group ND, group ND-LOW, group LOW and manganese (Mn), in treated wastewater. For groups the average profile is reported; whiskers represent the range of values.

UWW includes four compounds with most values >LOD, and which must be kept under control: manganese concentration was above LOD in 90% of the cases; regarding the average profiles of nickel, copper and zinc, about 70% of the values indicated low concentrations and 25% were <LOD. Di-(2-ethyl-hexyl)-phthalate (DEHP), lead, aniline, short-chain chlorinated paraffin (C10-C13), antimony and chromium are classified in the ND-LOW group.

To conclude, correspondence analysis permits to individuate compounds with a peculiar concentration profile, which is particularly useful for datasets where most values are under LOD. 2D plots of row coordinates show that a set of compounds with high frequency (>80%) of values >LOD can be individuated for UWW and TWW. The set could be composed of only one compound (in TWW) or more (UWW). A secondary set with 60-80% of values >LOD should be taken into consideration. A summary of all highlighted compounds is reported in Table 2.7.

Table 2.7. List of compounds individuated by correspondence analysis for their concentration profile in incoming water, untreated wastewater and treated wastewater. DET>>ND: more than 80% of values >LOD; DET>ND: from 60% to 80% of values >LOD.

	INCOMING WATER	UNTREATED WASTE WATER	TREATED WASTE WATER
DET >> ND		Zinc (Zn) Manganese (Mn) Copper (Cu) Chromium (Cr) Nickel (Ni)	Manganese (Mn)
DET > ND	Zinc (Zn) Manganese (Mn)	Lead (Pb) Antimony (Sb) Aniline ($PhNH_3$)	Copper (Cu) Zinc (Zn) Nickel (Ni)

Outliers individuation

The study of concentration profiles also led to the conclusion that the distribution generally tended towards low values: the typical profile of chemicals was characterised by high values in the ND or LOW categories and very low or absent values in MEDIUM and HIGH categories. A possible cause for this distribution could be the presence of outliers, which are extreme values that greatly differ from the distribution of the others. The presence of outliers could "press" all the other values in the LOW category, leaving only a few elements in the HIGH category.

In this work extreme outliers were individuated using the quartile method. If Q_1 and Q_3 are the lower and the upper quartiles respectively, an extreme value is defined by being it is higher than the following equation (Equation 1.1).

$$Q_3 + 3(Q_3 - Q_1) \quad (1.1)$$

An example of outlier is reported in Figure 2.16.

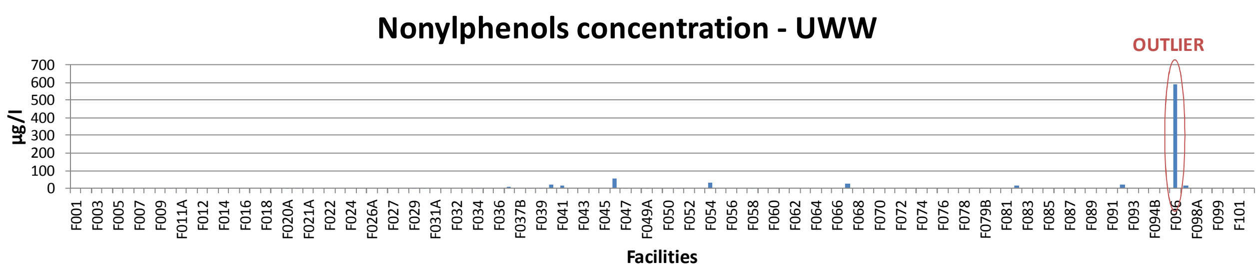


Figure 2.16. Distribution of concentration values of nonylphenols (A0103) in untreated wastewater.

In this work extreme outliers were calculated for all compounds and the frequency of outliers was consider as an indication of the possible criticality of the facility. In Figure 2.17 the number of extreme outliers in facilities is reported, dividing data of IW, UWW and TWW. As expected the greater amount of outliers is in UWW. In IW and TWW the number of outliers per facility ranges from 1 to 3, while in UWW there are facilities with 4 outliers and more. The more critical sites in UWW seems to be:

1. F096: characterised by 8 outliers (nonylphenols, chromium, manganese, cobalt, nickel, copper, zinc and lead);
2. F091: characterised by 7 outliers (chromium, manganese, cobalt, nickel, copper, zinc and lead);
3. F021: characterised by 4 outliers (cobalt, nickel, arsenic and cyanide).

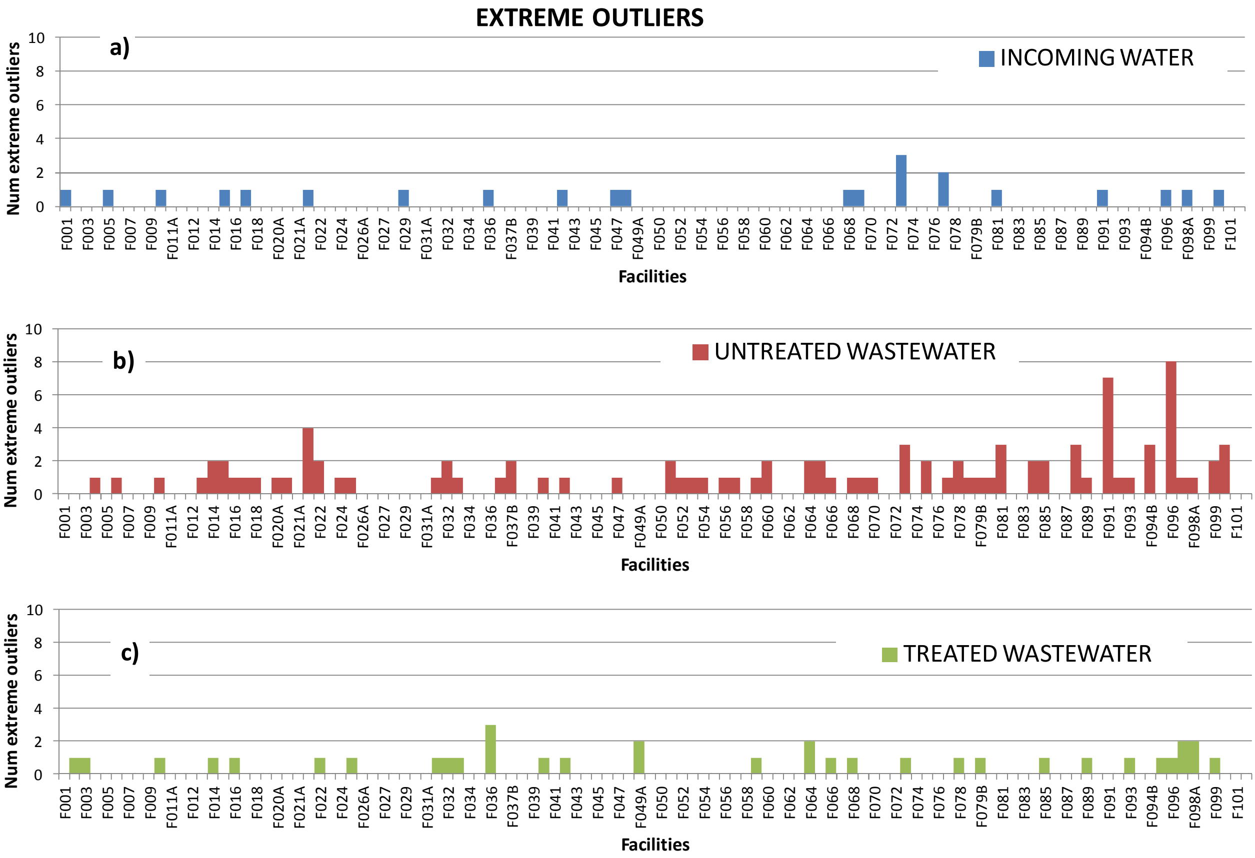


Figure 2.17. Number of extreme outliers in facilities: a) incoming water; b) untreated wastewater; c) treated wastewater.

The evaluation of critical sites using outliers is only an indication, because the importance of an extreme concentration of a chemical mainly depends on its toxicity. As an example, in F021 only 4 outliers were individuated, but among them there are arsenic and cyanide, which are known to be poisons. A specific evaluation of the toxicity of compounds is needed, in order to better understand the meaning of concentration values assessed in this chapter.

3. TOXICOLOGICAL EVALUATION

Conducting a global toxicological evaluation of analysed compounds is a considerable challenge, since every chemical is characterised by a specific kind of toxicology (lethal effects, carcinogenicity, etc.), that makes the comparison complex. Given the increasing concern regarding the use of chemicals in everyday life and workplaces, in recent years several chemical hazard screening methods have been developed, but they generally only discriminate chemicals of high concern from those that can be used with precautions and from safer chemicals.

To better evaluate the concentration values detected in this study, a toxicological ranking of chemicals has been developed, using a multi-criteria method, specifically developed for this purpose. Multi-criteria analysis is a family of decision-making tools that can be used in strategic environmental assessment procedures to ensure that environmental, societal and economic aspects can be integrated and taken into consideration. The multi-criteria tool used in this work is the analytical hierarchy process (AHP), a mathematical technique that enables people to make decisions involving many kinds of concerns, selecting the best among a number of scenarios. Since the aim of this work was to make a ranking of analytes, instead of selecting the best analyte, the method was adapted, to fit this goal. In particular, an AHP approach consists of three phases:

1. Criteria identification and selection.
2. Calculation of the relative weight of each criterion.
3. Comparison of the alternatives.

In the next sections each phase will be described in detail.

CRITERIA IDENTIFICATION AND SELECTION

In order to conduct a global toxicological evaluation, the following kinds of toxicity were identified as criteria:

1. Acute toxicity (AC);
2. Carcinogenicity (CARC);
3. Reproductive Toxicity (REP);
4. Acute aquatic toxicity (AC AQ);
5. Chronic aquatic toxicity (CHR AQ).

At this stage, the decision-maker usually selects a score from a range of values that expresses the performance of each criterion on each alternative. In this specific study toxicological scores were assigned to each compound on the basis of the previous above mentioned five kinds of toxicity. The toxicity data used were provided by internationally recognised organisations and can be considered standard values. Specifically, the sources of toxicity data are listed in Table 3.1. To the UNECE (United Nations Economic Commission for Europe) categories of reproductive toxicity we added a further category (CAT *), for specific cases where there is an evidence of an adverse effect on reproduction, but the analyte is not classified in any other UNECE category. Additional information about groups and categories used in this work are reported in Annex I.

Table 3.1. Data source for each kind of toxicity. LD_{50}: Median lethal dose. UNECE: United Nations Economic Commission for Europe; IARC: International Agency for Research on Cancer.

Toxicity	Data Source
Acute toxicity	LD_{50} (oral toxicity on rat, mg/kg of body weight) or UNECE categories or LD_{50} (oral toxicity on mouse, mg/kg of body weight)
Carcinogenicity	IARC groups
Reproductive toxicity	UNECE categories
Acute aquatic toxicity	UNECE categories
Chronic aquatic toxicity	UNECE categories

The list of analytes examined in this work includes not only single compounds, but also classes of chemicals composed by members of different toxicity. As an example, A0310 (bromo-diphenyl) includes 2-bromo-diphenyl (2-BB), 3-bromo-diphenyl (3-BB) and 4-bromo-diphenyl (4-BB), which have kind of different toxicity: 2-BB is classified in group 2B for carcinogenicity; 4-BB is not only carcinogenic 2B, but also shows acute toxicity (category 4) and acute aquatic toxicity (category 1); 3-BB does not show any of the five kinds of toxicity studied in this work. For classes of compounds and for chemicals that can be present in different formes in the environment (i.e. metals), the principle of precaution was followed: for every kind of toxicity, the toxicity of the analyte corresponds to the toxicity of the most dangerous compound of the class. Toxicity data used in the evaluation are reported in Annex I (Table A.5).

In order to obtain a numerical value that describes the toxicity of compounds, each group and category was converted into a numerical value ranging from 0 (no toxicity) to 1 (maximum toxicity), as shown in Table 3.2. The acute toxicity was expresses by the normalised reciprocal of LD_{50}; the UNECE categories were used only when LD_{50} was not available.

Table 3.2. Converted values for categories and groups representative of acute toxicity, carcinogenicity, reproductive toxicity, acute and chronic aquatic toxicity.

ACUTE TOXICITY		CARCINOGENICITY		REPRODUCTIVE TOXICITY		ACUTE AQUATIC TOXICITY		CHRONIC AQUATIC TOXICITY	
CAT 1	1	**CAT 1**	1	**CAT 1A**	1	**CAT 1**	1	**CAT 1**	1
CAT 2	0.1	**CAT 2A**	0.1	**CAT 1B**	0.1	**CAT 2**	0.1	**CAT 2**	0.1
CAT 3	0.005	**CAT 2B**	0.01	**CAT 2**	0.01	**CAT 3**	0.01	**CAT 3**	0.01
CAT 4	0.001	**CAT 3**	0.001	**CAT ***	0.001				
CAT 5	0.0002	**CAT 4**	0						

WEIGHTS OF CRITERIA

Multi-criteria analysis enables the operator to weight criteria according to their importance. This feature makes the method universal and applicable to a wide range of situations, after proper assessment of the criteria weights.

In AHP, relative weights are determined by pair-wise comparison: the latter is a mathematical technique that determines the relative weights of criteria by dividing the complex decision problem into a series of one-to-one judgements about the significance of each criterion relative to the others. For each pair-wise comparison between two criteria, a value from 1/9 (extremely less important) to 9 (extremely more important) is given, 1 being representative of equally important criteria. The comparison values are inserted in a square matrix where the criteria names are used as row and column heads. The final weights of the factors are the components of the main eigenvector calculated from that square matrix. Finally, a statistical index (Consistency Ratio, CR) is calculated, to check whether the criteria weights are consistent. CR is the ratio between the Consistency Index (CI), defined in Equation 2.1, and the Random consistency Index (RI).

$$CI = \frac{\lambda_{max} - n}{n - 1} \quad (2.1)$$

where λ_{max} is the largest eigenvalue of the matrix and n is the number of criteria. RI is obtained averaging the CIs of many randomly-generated pair-wise comparison matrices and it is a tabulated value, depending on n. As a consequence, much smaller the ratio between CI and RI, much lower the probability for matrix values to be generated randomly. When this probability becomes greater than 10% (CR > 0.1) the choices of the comparison values must be reassessed.

Table 3.3 reports the pair-wise comparison values of the five above mentioned kinds of toxicity. The weights were calculated using MATLAB R2015b. The consistency ratio was 0.008, meaning a very high consistency of the matrix.

Table 3.3. Pair-wise comparison between criteria and calculated weight. AC: Acute toxicity; CARC: Carcinogenicity; REP: Reproductive toxicity; AC AQ: Acute aquatic toxicity; CHR AQ: Chronic aquatic toxicity.

	AC	CARC	REP	AC AQ	CHR AQ		WEIGHT
AC	1	2	3	7	9	→	0.481
CARC	1/2	1	2	3	4	→	0.242
REP	1/3	1/2	1	2	3	→	0.147
AC AQ	1/7	1/3	1/2	1	2	→	0.080
CHR ACQ	1/9	1/4	1/3	1/2	1	→	0.050

COMPARISON OF THE ALTERNATIVES

For every analyte, the sum of the toxicological values, each weighted for the importance of its toxicity, corresponds to the analyte global toxicity score (AGTS), that can be considered as an expression of the hazard proper of that analyte.

$$AGTS = \sum_{i=1}^{n} (TV_i \cdot W_i) \cdot 100 \quad (2.2)$$

where TV is the toxicological value of the analyte with respect to the type of toxicity i; W is the weight of the criterion (or type of toxicity) i and n is the number of criteria. The Equation 2.2 was applied for all the analytes investigated in this work. The resulting toxicological score is reported in Table 3.4.

Table 3.4. Ranking of analytes, with internal code for classification (A) and CAS number, based on the analyte global toxicity score (AGTS), % of toxicity with respect to the sum of toxicity of all analytes, and cumulative % toxicity.

	A	CAS	Name	AGTS	%	% cum
1	A1108	7440-38-2	Arsenic (As)	65	5.0%	
2	A1201	74-90-8	Cyanide	61	4.7%	
3	A1102	18540-29-9	Hexavalent Chromium (Cr VI)	42	3.2%	
4	A1109	7440-43-9	Cadmium (Cd)	41	3.1%	
5	A1105	7440-02-0	Nickel (Ni)	40	3.1%	
6	A0402	92-87-5	Benzidine	38	2.9%	
7	A0415	101-14-4	4,4'-Methylene-bis(2-chloroaniline)	37	2.9%	
8	A0410	91-94-1	3,3'-Dichlorobenzidine	37	2.9%	
9	A0418	95-53-4	o-Toluidine	33	2.5%	
10	A1112	7439-92-1	Lead (Pb)	31	2.3%	
11	A1111	7439-97-6	Mercury (Hg)	27	2.1%	
12	A0404	91-59-8	2-Naphthylamine	25	1.9%	
13	A0401	92-67-1	4-Aminodiphenyl	25	1.9%	
14	A0813	79-01-6	Trichloroethylene	24	1.9%	
15	A0905	87-86-5	Pentachlorophenol (PCP)	22	1.7%	
16	A0502	Various	Dibutyltin (DBT)	19	1.5%	
17	A0301	Various	Polybromodiphenyls (PBBs)	16	1.2%	
17	A0311	Various	Di-bromo-diphenyl	16	1.2%	
18	A0426	106-50-3	1,4-Phenylenediamine	16	1.2%	
19	A1104	7440-48-4	Cobalt (Co)	16	1.2%	
20	A0403	95-69-2	4-Chloro-o-toluidine	16	1.2%	
21	A0416	101-80-4	4,4'-Oxydianiline	16	1.2%	
21	A0904	25167-83-3	Tetrachlorophenols (TeCP)	16	1.2%	
21	A0917	58-90-2	2,3,4,6-Tetrachlorophenol	16	1.2%	
22	A0505	Various	Triphenyltin (TPhT)	15	1.2%	
23	A0427	95-51-2	2-Chloroaniline	15	1.2%	
23	A0432	100-61-8	n-Methylaniline	15	1.2%	
24	A0504	Various	Tributyltin (TBT)	15	1.1%	
25	A0201	85-68-7	Benzyl-butyl-phthalate (BBP)	15	1.1%	
26	A0210	84-69-5	Di-iso-butyl-phthalate (DIBP)	15	1.1%	
27	A0425	62-53-3	Aniline	14	1.1%	
28	A0702	Various	Dichlorobenzenes	14	1.1%	
29	A1106	7440-50-8	Copper (Cu)	14	1.1%	
30	A1107	7440-66-6	Zinc (Zn)	14	1.1%	
31	A0903	Various	Trichlorophenols (TriCP)	14	1.0%	
31	A0913	95-95-4	2,4,5-Trichlorophenol	14	1.0%	
31	A0914	88-06-2	2,4,6-Trichlorophenol	14	1.0%	
32	A0312	Various	Tri-bromo-diphenyl	14	1.0%	
32	A0506	Various	Tricyclohexyltin(TCyHT)	14	1.0%	
32	A0912	933-78-8	2,3,5-Trichlorophenol	14	1.0%	
32	A0915	609-19-8, 15950-66-0	3,4,5-Trichlorophenol, 2,3,4-Trichlorophenol	14	1.0%	
33	A0703	Various	Trichlorobenzenes	13	1.0%	
34	A0706	118-74-1	Hexachlorobenzene	13	1.0%	
35	A0422	60-09-3	4-Aminoazobenzene	13	1.0%	
35	A1001	85535-84-8	Short-chain chlorinated paraffins (C10-C13)	13	1.0%	
36	A0705	608-93-5	Pentachlorobenzene	13	1.0%	
37	A0704	Various	Tetrachlorobenzenes	13	1.0%	
38	A0510	1461-25-2	Tetrabutyltin (TeBT)	13	1.0%	
39	A0103	54852-15-3,104-40-5,1173019-62-9	Nonylphenols (NPs)	13	1.0%	80%
40	A0303	Various	Polybromodiphenyl ethers (PBDEs)	13	1.0%	
40	A0320	Various	Bromo-diphenyl-ether	13	1.0%	
41	A0206	26761-40-0	Di-iso-decyl-phthalate (DIDP)	13	1.0%	

Table 3.4. (continued)

	A	CAS	Name	AGTS	%	% cum
42	A0304	79-94-7	Tetra-bromo-bisphenol-A (TBBPA)	13	1.0%	
43	A0101	1806-26-4,140-66-9	Octylphenols (OPs)	13	1.0%	
43	A0306	3194-55-6	Hexa-bromo-cyclo-dodecan (HBCDD)	13	1.0%	
43	A0508	Various	Tripropyltin (TPT)	13	1.0%	
44	A0310	Various	Bromo-diphenyl	11	0.83%	
45	A0302	126-72-7	Tri-(2,3-di-bromo-propyl)-phosphate (TRIS)	11	0.82%	
46	A0916	4901-51-3	2,3,4,5-Tetrachlorophenol	10	0.79%	
47	A0202	84-74-2	Di-butyl-phthalate (DBP)	10	0.73%	90%
48	A0216	605-50-5	Di-iso-pentyl-phthalate (DIPP)	9.5	0.73%	
48	A0217	71888-89-6	Di-iso-heptyl-phthalate (DIHP)	9.5	0.73%	
48	A0219	776297-69-9	N-iso-pentyl-iso-pentyl-phthalate (PIPP)	9.5	0.73%	
49	A1101	7440-47-3	Chromium (Cr)	9.1	0.69%	
50	A0433	106-49-0	p-Toluidine	8.7	0.67%	
51	A0429	108-44-1	m-Toluidine	8.5	0.65%	
52	A0419	95-80-7	2,4-Diaminotoluene	7.5	0.58%	
53	A0902	Various	Dichlorophenol (DiCP)	5.6	0.43%	
53	A0911	120-83-2, 583-78-8, 87-65-0, 591-35-5	2,4-Dichlorophenol, 2,5-Dichlorophenol, 2,6-Dichlorophenol, 3,5-Dichlorophenol	5.6	0.43%	95%
54	A0615	335-76-2	Perfluoro-n-decanoic acid (PFDA)	4.0	0.30%	
55	A0814	127-18-4	Tetrachloroethylene	3.0	0.23%	
56	A0423	95-68-1	2,4-Xylidine	2.8	0.21%	
57	A0602	2795-39-3 / Various	Perfluorooctane sulphonates (PFOS)	2.4	0.19%	
58	A0431	103-69-5	n-Ethylaniline	2.3	0.17%	
58	A0918	935-95-5	2,3,5,6-Tetrachlorophenol	2.3	0.17%	
59	A0308	115-96-8	Tris-(2-chloro-ethyl)-phosphate (TCEP)	2.2	0.17%	
60	A1103	7439-95-4	Manganese (Mn)	2.1	0.16%	
61	A0601	335-67-1	Perfluoro-n-octanoic acid (PFOA)	1.9	0.15%	
62	A0203	117-81-7	Di-(2-ethyl-hexyl)-phthalate (DEHP)	1.7	0.13%	
62	A0204	117-84-0	Di-n-octyl-phthalate (DNOP)	1.7	0.13%	
63	A0808	79-34-5	1,1,2,2-tetrachloroethane	1.7	0.13%	
64	A0215	117-82-8	Bis-(2-methoxy-ethyl)-phthalate (DMEP)	1.5	0.12%	
65	A0212	84-75-3	Di-n-hexyl-phthalate (DNHP)	1.5	0.11%	
66	A0412	119-93-7	3,3'-Dimethylbenzidine	1.3	0.10%	
67	A0408	615-05-4	2,4-Diaminoanisole	1.2	0.09%	
68	A1110	7440-36-0	Antimony (Sb)	1.2	0.09%	
69	A0810	75-35-4	1,1-dichloroethylene	1.2	0.09%	
70	A0424	87-62-7	2,6-Xylidine	1.0	0.08%	
71	A0417	139-65-1	4,4'-Thiodianiline	1.0	0.08%	
72	A0407	106-47-8	4-Chloroaniline	1.0	0.08%	
73	A0104	Various	Nonylphenolethoxylates (NPEOs)	1.0	0.07%	
74	A0901	Various	Monochlorophenols	0.92	0.07%	
75	A0609	4151-50-2	N-Ethyl-Perfluoro-octane-sulfon-amide (N-Et-FOSA)	0.92	0.07%	
76	A0907	108-43-0	3-Chlorophenol	0.90	0.07%	
77	A0908	106-48-9	4-Chlorophenol	0.86	0.07%	
78	A0906	95-57-8	2-Chlorophenol	0.84	0.06%	
79	A0309	13674-87-8	Tris-(1,3-di-chloro-iso-propyl)-phosphate (TDCPP)	0.82	0.06%	
80	A0809	76-01-7	Pentachloroethane	0.77	0.06%	99%
81	A0409	101-77-9	4,4'-Diaminodiphenylmethane	0.75	0.06%	
82	A0701	108-90-7	Chlorobenzene	0.71	0.05%	

Table 3.4. (continued)

	A	CAS	Name	AGTS	%	% cum
83	A0102	Various	Octylphenolethoxylates (OPEOs)	0.63	0.05%	
84	A0804	107-06-2	1,2-dichloroethane	0.59	0.05%	
85	A0606	375-73-5	Perfluoro-butane-sulfonic acid	0.53	0.04%	
86	A0209	131-16-8	Di-n-propyl-phthalate (DPP)	0.50	0.04%	
86	A0430	91-66-7	n,n-Diethylanaline	0.50	0.04%	
87	A0802	67-66-3	Chloroform	0.49	0.04%	
88	A0313	Various	Tetra-bromo-diphenyl	0.45	0.03%	
88	A0314	Various	Penta-bromo-diphenyl	0.45	0.03%	
88	A0319	13654-09-6	Deca-bromo-diphenyl	0.45	0.03%	
88	A0501	Various	Monobutyltin (MBT)	0.45	0.03%	
88	A0611	1691-99-2	N-Ethyl-Perfluoro-octane-sulfon-amido-ethanol (N-Et-FOSE alcohol)	0.45	0.03%	
88	A0613	375-85-9	Perfluoro-heptanoic acid	0.45	0.03%	
88	A0616	2058-94-8	Perfluoro-undecanoic acid	0.45	0.03%	
88	A0620	355-46-4	Perfluoro-hexane-sulfonic acid	0.45	0.03%	
88	A0910	95-77-2	3,4-Dichlorophenol	0.45	0.03%	
89	A0421	90-04-0	o-Anisidine	0.44	0.03%	
90	A0414	120-71-8	p-Cresidine	0.40	0.03%	
91	A0803	56-23-5	Carbon tetrachloride	0.39	0.03%	
92	A0307	3296-90-0	2,2-Bis(bromomethyl)-1,3-propanediol (BBMP)	0.36	0.03%	
93	A0807	630-20-6	1,1,1,2-tetrachloroethane	0.36	0.03%	
94	A0411	119-90-4	3,3'-Dimethoxybenzidine	0.36	0.03%	
95	A0305	5412-25-9	Bis-(2,3-di-bromo-propyl)-phosphate	0.36	0.03%	
96	A0806	79-00-5	1,1,2-trichloroethane	0.34	0.03%	
97	A0205	68515-48-0	Di-iso-nonyl-phthalate (DINP)	0.24	0.02%	
97	A0405	97-56-3	o-Aminoazotoluene	0.24	0.02%	
97	A0801	75-09-2	Dichloromethane	0.24	0.02%	
98	A0812	156-60-5	trans-1,2-Dichloroethylene	0.23	0.02%	
99	A0626	1546-95-8	7H-Dodecafluoro heptane carboxylate	0.21	0.02%	
100	A0331	13674-84-5	Tris-(2-chloroisopropyl)-phosphate (TCPP)	0.21	0.02%	
101	A0428	99-59-2	5-Nitro-o-anisidine	0.10	0.01%	
102	A0909	576-24-9	2,3-Dichlorophenol	0.10	0.01%	
103	A0330	21850-44-2	Tetra-bromo-bisphenol A bis-(di-bromo-propyl-ether) (TBBPA-BDPE)	0.09	0.01%	
104	A0406	99-55-8	5-Nitro-o-toluidine	0.07	0.01%	
105	A0811	156-59-2	cis-1,2-Dichloroethylene	0.05	0.004%	
106	A0805	71-55-6	1,1,1-trichloroethane	0.05	0.004%	
107	A0208	84-66-2	Di-ethyl-phthalate (DEP)	0.04	0.003%	
108	A0207	131-11-3	Di-methyl-phthalate (DMP)	0.03	0.002%	
109	A0329	1163-19-5	Deca-bromo-diphenyl-ether	0.02	0.002%	
109	A0420	137-17-7	2,4,5-Trimethylaniline	0.02	0.002%	
110	A0507	Various	Trioctyltin(TriOT)	0.01	0.001%	100%
111	A0211	84-61-7	Di-cyclo-hexyl-phthalate (DCHP)	0	0%	
111	A0213	84-76-4	Di-nonyl-phthalate (DNP)	0	0%	
111	A0214	27554-26-3	Di-iso-octyl-phthalate (DIOP)	0	0%	
111	A0218	84777-06-0	1,2-Benzene-di-carboxylic acid di-pentyl-esters, branched and linear (DHNUP)	0	0%	
111	A0220	3648-20-2	Di-heptyl-phthalate (DHP)	0	0%	
111	A0315	Various	Hexa-bromo-diphenyl	0	0%	
111	A0316	Various	Hepta-bromo-diphenyl	0	0%	
111	A0317	Various	Octa-bromo-diphenyl	0	0%	
111	A0318	Various	Nona-bromo-diphenyl	0	0%	
111	A0321	Various	Di-bromo-diphenyl-ether	0	0%	

Table 3.4. (continued)

	A	CAS	Name	AGTS	%	% cum
111	A0322	Various	Tri-bromo-diphenyl-ether	0	0%	
111	A0323	Various	Tetra-bromo-diphenyl-ether	0	0%	
111	A0324	Various	Penta-bromo-diphenyl-ether	0	0%	
111	A0325	Various	Hexa-bromo-diphenyl-ether	0	0%	
111	A0326	Various	Hepta-bromo-diphenyl-ether	0	0%	
111	A0327	Various	Octa-bromo-diphenyl-ether	0	0%	
111	A0328	Various	Nona-bromo-diphenyl-ether	0	0%	
111	A0332	Various	Tris-(aziridinyl)-phosphinoxide (TEPA)	0	0%	
111	A0413	838-88-0	3,3'-Dimethyl-4,4'-diaminodiphenylmethane	0	0%	
111	A0503	Various	Dioctyltin (DOT)	0	0%	
111	A0509	Various	Monooctyltin (MOT)	0	0%	
111	A0603	307-24-4	Perfluoro-n-hexanoic acid (PFHxA)	0	0%	
111	A0604	3871-99-6	Perfluorohexane sulphonates (PFHxS)	0	0%	
111	A0605	375-22-4	Perfluorobutyric Acid (PFBA)	0	0%	
111	A0607	754-91-6	Perfluoro-octane-sulfon-amide (PFOSA)	0	0%	
111	A0608	31506-32-8	N-Methyl-Perfluoro-octane-sulfon-amide (N-Me-FOSA)	0	0%	
111	A0610	24448-09-7	N-Methyl-Perfluoro-octane-sulfon-amido-ethanol (N-Me-FOSE alcohol)	0	0%	
111	A0612	2706-90-3	Perfluoro-pentanoic acid	0	0%	
111	A0614	375-95-1	Perfluoro-nonanoic acid	0	0%	
111	A0617	307-55-1	Perfluorododecanoic Acid (PFDoA)	0	0%	
111	A0618	72629-94-8	Perfluoro-tridecanoic acid	0	0%	
111	A0619	376-06-7	Perfluoro-tetradecanoic acid	0	0%	
111	A0621	375-92-8	Perfluoro-heptane-sulfonic acid	0	0%	
111	A0622	355-77-3	Perfluor-decane-sulfonic acid	0	0%	
111	A0623	27619-97-2	1H,1H,2H,2H-Perfluoro-octane-sulphonic acid	0	0%	
111	A0624	34598-33-9	2H,2H,3H,3H-Perfluoroundecanoic acid (PFUnA)	0	0%	
111	A0625	172155-07-6	Perfluoro-3-7-dimethyl octane carboxylate	0	0%	

Since acute toxicity was indicated as the most important type of toxicity, the most toxic analytes extracted from MCA are arsenic (As) and cyanide, which have the strongest lethal acute effect, with LD_{50} of 4.7 and 8 mg/kg of body weight, respectively. The third most toxic analyte is hexavalent chromium (Cr VI), which has a lower acute toxicity compared to other compounds, such as mercury (Hg) and some of the chlorophenols, but which was considered the most dangerous among them, due to the classification in the highest group for carcinogenicity (Group 1). In the same way, cadmium (Cd) and nickel (Ni) show a smaller acute toxicity than the previous mentioned compounds (LD_{50} of 107 and 186 mg/kg of body weight), but are dangerous for the reproductive system (Category 1B). The first five most toxic compounds are also classified in the highest category for acute and chronic aquatic toxicity (Category 1).

This method overcomes the simple toxicological evaluation, based on one specific type of toxicology: MCA takes potentially into consideration an unlimited number of factors at the same time, leading to a ranking of compounds based on a global hazard concept. Moreover, it leads to the construction of a dynamic ranking of analytes (or scenarios, in general), that may change with the relative importance of the criteria. This feature makes multi-criteria analysis a very versatile technique, applicable to various fields.

Two further comments are in order, regarding the ranking listed in Table 3.4:

- 21% of the analytes (37 of the 177 analysed compounds) shows a zero value of AGTS, coming from a zero value for all the types of toxicity examined. This result does not necessary mean that those compounds have no toxicity at all: they could have a different type of toxicity from those examined or their toxicity could be not yet included in the official hazard categories. However, the fact the approximately one fifth of the analytes shows no toxicity should be taken into account in view of a possible modification of the monitoring strategy.
- The Pareto principle (also known as the 80–20 rule) states that, for many events, roughly 80% of the effects comes from 20% of the causes. In this specific case, the rule is approximately verified, since the most dangerous 49 analytes (28%) represent 80% of the toxicity of all the analytes. From this event we can infer that, if the aim is to reduce toxicity with abatement strategies, it could be more effective to focus on a few carefully selected analytes, rather than act on the entire list of chemical compounds.

In Table 3.5 the average AGTS for every class of compounds is reported. The most dangerous class is C12 (Cyanide). The second most toxic class is C11 (Total heavy metals), especially due to the high toxicity of arsenic (As, A1108), hexavalent chromium (Cr VI, A1102), cadmium (Cd, A1109) and nickel (Ni, A1105), also included in the first five more toxic analytes of the list.

Table 3.5. Ranking of class of analytes, based on the average analyte global toxicity score (AGTS, range in brackets), % of toxicity and cumulative % toxicity.

	Class	Average AGTS (range)	%	% cum
C12	Cyanide	61	5%	5%
C11	Total Heavy Metals	25 (1.2-65)	23%	28%
C10	Short-Chain Chlorinated Paraffins	13	1%	29%
C07	Chlorobenzenes	11 (0.7-14)	5%	34%
C04	Azo Dyes	10 (0-38)	26%	60%
C05	Organotin Compounds	8.9 (0-19)	7%	67%
C09	Chlorophenols	8.2 (0.1-22)	11%	78%
C01	Alkylphenols	7.0 (0.6-13)	2%	80%
C02	Phthalates	4.4 (0-15)	7%	87%
C03	Brominated and Chlorinated Flame Retardants	3.9 (0-16)	10%	97%
C08	Chlorinated Solvents	2.4 (0.05-24)	3%	99%
C06	Perfluorinated Chemicals (PFCs)	0.45 (0-4.0)	1%	100%

The less toxic class is C06 (PFCs): perfluorinated compounds show very low scores in all the five types of toxicity considered in this work. This does not mean that they are guarantee to be safe. Animal studies have shown that some PFCs have adverse effects on endocrine activities and on specific organs; data on humans are contradictory, because some human studies suggests that PFCs may also have effects on human health, while other studies have failed to find conclusive links. The toxicological information collected in this work could surely be used for future evaluation, but periodically checks of changes in the classification of compounds are needed.

The combination of toxicological and concentration data evidenced that C03 and C06 are rarely detected in water and are not very toxic at the same time. For these kinds of classes, if there is the intent to modify the monitoring strategy, the frequency of analysis could be reduced.

4. FACILITY EVALUATION

The information analysed in Chapter 2 and the toxicological scores calculated in Chapter 3 are joined, in order to conduct a toxicological evaluation of all facilities. For every facility and for every sampling site (IW, UWW and TWW) a facility global toxicological score (FGTS) was calculated, applying Equation 3.1. FGTS is the sum of the concentration of all the compounds analysed, weighted for their toxicity.

$$FGTS = \sum_{j=1}^{m}(C_j \cdot AGTS_j) \cdot 10^{-3} \quad (3.1)$$

where C_j is the concentration (µg/l) of the analyte j; AGTS is the global toxicity score of the analyte m; j and m is the number of analytes. In the calculation of FGTS the following principles were adopted:

- for all the analytes that have a concentration <LOD, the value of half LOD was considered;
- the concentration of total chromium (A1101) included the concentration of chromium hexavalent (A1102). In order to not overestimate the toxicity of sites, the concentration of A1102 was subtracted to the concentration of A1101, obtaining a value referred to total chromium with the exception of Cr VI, indicated with A1101*. The same overestimation could occur due to other overlaps (i. e. a class of compounds, with its components). In all the other cases, if a class of compounds was analysed, none of the components of that class were analysed and vice versa.

UNTREATED WASTEWATER FACILITY RANKING

Based on the calculated FGTS, sites were classified into five impact categories. For IW and UWW measurements, the limits of the impact categories are listed in Table 4.1.

Table 4.1. Impact categories for incoming water (IW) and untreated wastewater (UWW), based on the site global toxicological score (FGTS).

IMPACT	FGTS
MINIMUM IMPACT	From 0 to 12
WEAK IMPACT	From 12 to 23
MEDIUM IMPACT	From 23 to 47
STRONG IMPACT	From 47 to 93
EXTREME IMPACT	From 93 to 360

The site ranking listed in Table 4.2 is refers to UWW measurements. Globally facilities are distributed among the impact categories as follows:

- Extreme impact: 1 facility;
- Strong impact: 4 facilities;
- Medium impact: 7 facilities;
- Weak impact: 19 facilities;
- Minimum impact: 81 facilities.

UWW in F096 shows an extreme impact, with a score that differs significantly from the others. It is due to the strong concentration of highly toxic compounds, such as nickel (4050 µg/l; n. 5 of the ranking); zinc (6880 µg/l; n. 30 of the ranking), lead (1800 µg/l ; n. 10 of the ranking); chromium (2050 µg/l ; n. 49 of the ranking) and copper (320 µg/l ; n. 29 of the ranking). The second most toxic facility (F21B) is characterised by a very high concentration of cyanide (1010 µg/l; n. 2 of the ranking) and arsenic (346 µg/l; n. 1 of the ranking).

In Figure 4.1 we reported the average FGTS for every country involved in this study. The graph shows that the most toxic facilities are located in Asia, with India and China as the most important contributors to the global toxicity. The FGTS decreased from a value of 21 in 2013 to 7 in 2015 (Figure 4.2).

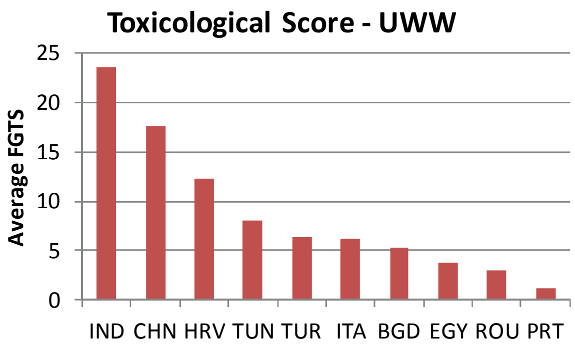


Figure 4.1. Average facility global toxicity score (FGTS) for every country, for untreated wastewater.

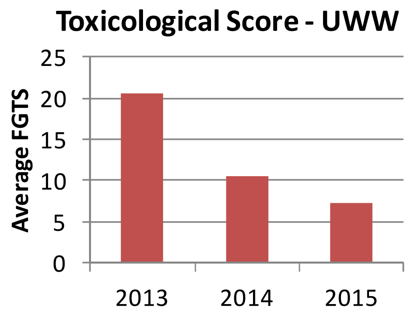


Figure 4.2. Average facility global toxicity score (FGTS) per year, for untreated wastewater.

Table 4.2. Ranking of the facilities, based on the site global toxicological score (FGTS), referred to untreated wastewater (UWW) measurements.

Facility			Year	FGTS	Impact
F096	CHN	ASIA	2013	360	EXTREME
F021B	CHN	ASIA	2014	92	STRONG
F018	IND	ASIA	2013	60	STRONG
F091	CHN	ASIA	2015	54	STRONG
F073	IND	ASIA	2013	51	STRONG
F060	TUN	AFR	2013	36	MEDIUM
F080	CHN	ASIA	2015	33	MEDIUM
F088	IND	ASIA	2013	28	MEDIUM
F085	IND	ASIA	2013	26	MEDIUM
F098A	CHN	ASIA	2013	26	MEDIUM
F064	IND	ASIA	2013	25	MEDIUM
F022	CHN	ASIA	2014	24	MEDIUM
F094B	CHN	ASIA	2014	21	WEAK
F084	CHN	ASIA	2014	21	WEAK
F100	CHN	ASIA	2014	18	WEAK
F079B	CHN	ASIA	2014	17	WEAK
F032	CHN	ASIA	2014	16	WEAK
F020A	CHN	ASIA	2013	16	WEAK
F016	TUN	AFR	2014	16	WEAK
F079A	CHN	ASIA	2013	16	WEAK
F081	CHN	ASIA	2014	16	WEAK
F093	BGD	ASIA	2014	16	WEAK
F012	CHN	ASIA	2013	15	WEAK
F078	IND	ASIA	2013	15	WEAK
F051	CHN	ASIA	2014	14	WEAK
F070	TUR	ASIA	2015	14	WEAK
F057	CHN	ASIA	2014	13	WEAK
F039	CHN	ASIA	2013	13	WEAK
F024	TUR	ASIA	2015	13	WEAK
F066	CHN	ASIA	2014	13	WEAK
F010	HRV	EUR	2013	12	WEAK
F033	CHN	ASIA	2013	11	MINIM
F029	IND	ASIA	2013	11	MINIM
F075	TUR	ASIA	2015	11	MINIM
F099	CHN	ASIA	2013	11	MINIM
F052	CHN	ASIA	2013	11	MINIM
F049B	CHN	ASIA	2014	10	MINIM
F082	CHN	ASIA	2013	10	MINIM
F098B	CHN	ASIA	2014	10	MINIM
F037A	CHN	ASIA	2013	10	MINIM
F101	CHN	ASIA	2014	10	MINIM
F077	BGD	ASIA	2014	9.2	MINIM
F020B	CHN	ASIA	2014	9.0	MINIM
F095	IND	ASIA	2013	9.0	MINIM
F049A	CHN	ASIA	2013	8.8	MINIM
F056	CHN	ASIA	2014	8.6	MINIM
F059	BGD	ASIA	2014	8.5	MINIM
F068	ITA	EUR	2013	8.3	MINIM
F065	CHN	ASIA	2015	8.0	MINIM
F040	CHN	ASIA	2015	7.8	MINIM
F042	TUN	AFR	2013	7.6	MINIM
F026A	TUN	AFR	2013	7.3	MINIM
F037B	CHN	ASIA	2015	7.1	MINIM
F074	ROU	EUR	2015	6.3	MINIM
F015	CHN	ASIA	2013	6.2	MINIM
F014	BGD	ASIA	2014	5.8	MINIM
F076	IND	ASIA	2013	5.7	MINIM
F055	CHN	ASIA	2014	5.6	MINIM
F031A	TUN	AFR	2013	5.3	MINIM
F053	CHN	ASIA	2014	5.3	MINIM
F019	BGD	ASIA	2014	5.2	MINIM
F094A	CHN	ASIA	2013	5.0	MINIM
F092	CHN	ASIA	2013	4.9	MINIM
F006	CHN	ASIA	2015	4.8	MINIM
F026B	TUN	AFR	2014	4.7	MINIM
F041	IND	ASIA	2013	4.7	MINIM
F025	BGD	ASIA	2014	4.6	MINIM
F030	TUN	AFR	2013	4.6	MINIM
F058	TUN	AFR	2015	4.5	MINIM
F083	CHN	ASIA	2013	4.4	MINIM
F013	EGY	AFR	2014	4.3	MINIM
F017	TUN	AFR	2014	4.2	MINIM
F035	BGD	ASIA	2015	4.2	MINIM
F027	EGY	AFR	2014	4.1	MINIM
F054	CHN	ASIA	2015	4.1	MINIM
F069	ITA	EUR	2013	4.1	MINIM
F046	CHN	ASIA	2013	4.0	MINIM
F031B	TUN	AFR	2014	4.0	MINIM
F008	BGD	ASIA	2014	4.0	MINIM
F004	EGY	AFR	2014	3.8	MINIM
F061	BGD	ASIA	2014	3.5	MINIM
F087	BGD	ASIA	2014	3.5	MINIM
F044	BGD	ASIA	2014	3.5	MINIM
F009	BGD	ASIA	2014	3.3	MINIM

Table 4.2. (continued)

Facility			Year	FGTS	Impact
F089	BGD	ASIA	2014	3.0	MINIM
F097	CHN	ASIA	2013	3.0	MINIM
F001	TUR	ASIA	2015	2.9	MINIM
F090	BGD	ASIA	2014	2.9	MINIM
F050	CHN	ASIA	2014	2.9	MINIM
F045	CHN	ASIA	2015	2.8	MINIM
F062	EGY	AFR	2014	2.7	MINIM
F086	CHN	ASIA	2013	2.5	MINIM
F047	CHN	ASIA	2015	2.4	MINIM
F071	BGD	ASIA	2014	2.4	MINIM

Facility			Year	FGTS	Impact
F102	CHN	ASIA	2015	1.9	MINIM
F021A	CHN	ASIA	2013	1.8	MINIM
F003	TUR	ASIA	2015	1.8	MINIM
F028	ROU	EUR	2015	1.7	MINIM
F038	TUN	AFR	2013	1.6	MINIM
F063	TUR	ASIA	2015	1.6	MINIM
F005	CHN	ASIA	2013	1.5	MINIM
F007	CHN	ASIA	2015	1.4	MINIM
F011B	CHN	ASIA	2014	1.4	MINIM
F067	CHN	ASIA	2015	1.3	MINIM

Facility			Year	FGTS	Impact
F002	PRT	EUR	2015	1.2	MINIM
F072	ROU	EUR	2015	1.2	MINIM
F034	CHN	ASIA	2015	1.1	MINIM
F043	TUN	AFR	2014	0.89	MINIM
F011A	CHN	ASIA	2013	0.87	MINIM
F036	CHN	ASIA	2013	0.73	MINIM
F048	CHN	ASIA	2015	0.41	MINIM
F023	TUR	ASIA	2015	0.13	MINIM

INCOMING WATER SITE RANKING

Obviously, for a global evaluation of the responsibility of the suppliers in the calculated toxicity from UWW data, the situation of the UWW must be compared to the toxicity of IW. Equation 3.1 was applied also to incoming water data and facilities were classified into five impact categories (Table 4.1). Results are reported in Table 4.3. F023 is missing because of the lack of data in IW.

Unexpectedly, one facility (F081) was classified having an extreme impact. It was characterised by an exceptional concentration of zinc (7709 µg/l ; n. 30 of the ranking) and N-Et-FOSA (7709 µg/l ; n. 75 of the ranking). The other facilities are categorised having weak (5 facilities) or minimum impact (105 facilities).

As shown in Figure 4.3 the average FGTS is much lower in IW, than UWW. The country with the highest FGTS is Croatia, with a value around 9. The chronological evolution reported in Table 4.4 does not indicate a specific trend; probably the relative high FGTS in 2014 is due to the extreme score of the facility F081.

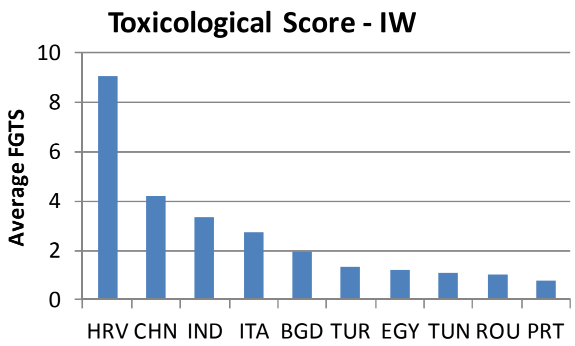


Figure 4.3. Average facility global toxicity score (FGTS) for every country, for incoming water.

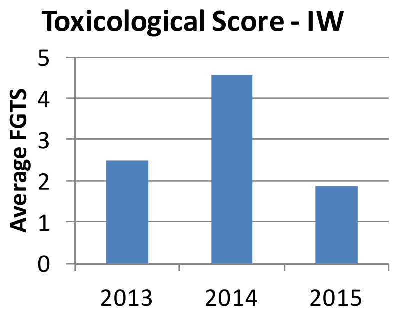


Figure 4.4. Average facility global toxicity score (FGTS) per year, for incoming water.

Table 4.3. Ranking of the facilities, based on the facility global toxicological score (FGTS), referred to incoming water (IW) measurements.

Facility			Year	FGTS	Impact
F081	CHN	ASIA	2014	118	EXTREME
F047	CHN	ASIA	2015	20	WEAK
F100	CHN	ASIA	2014	16	WEAK
F073	IND	ASIA	2013	16	WEAK
F005	CHN	ASIA	2013	13	WEAK
F036	CHN	ASIA	2013	12	WEAK
F010	HRV	EUR	2013	9.1	MINIM
F077	BGD	ASIA	2014	6.5	MINIM
F021B	CHN	ASIA	2014	5.9	MINIM
F017	TUN	AFR	2014	5.6	MINIM
F096	CHN	ASIA	2013	5.1	MINIM
F029	IND	ASIA	2013	4.7	MINIM
F071	BGD	ASIA	2014	4.1	MINIM
F091	CHN	ASIA	2015	3.9	MINIM
F087	BGD	ASIA	2014	3.7	MINIM
F041	IND	ASIA	2013	3.4	MINIM
F068	ITA	EUR	2013	3.3	MINIM
F021A	CHN	ASIA	2013	2.9	MINIM
F053	CHN	ASIA	2014	2.9	MINIM
F084	CHN	ASIA	2014	2.8	MINIM
F037A	CHN	ASIA	2013	2.6	MINIM
F045	CHN	ASIA	2015	2.3	MINIM
F015	CHN	ASIA	2013	2.2	MINIM
F069	ITA	EUR	2013	2.2	MINIM
F097	CHN	ASIA	2013	2.1	MINIM
F042	TUN	AFR	2013	2.1	MINIM
F064	IND	ASIA	2013	2.1	MINIM

Facility			Year	FGTS	Impact
F001	TUR	ASIA	2015	2.0	MINIM
F007	CHN	ASIA	2015	1.8	MINIM
F088	IND	ASIA	2013	1.8	MINIM
F061	BGD	ASIA	2014	1.7	MINIM
F095	IND	ASIA	2013	1.7	MINIM
F059	BGD	ASIA	2014	1.6	MINIM
F024	TUR	ASIA	2015	1.5	MINIM
F027	EGY	AFR	2014	1.5	MINIM
F006	CHN	ASIA	2015	1.5	MINIM
F082	CHN	ASIA	2013	1.5	MINIM
F018	IND	ASIA	2013	1.4	MINIM
F009	BGD	ASIA	2014	1.4	MINIM
F003	TUR	ASIA	2015	1.4	MINIM
F090	BGD	ASIA	2014	1.4	MINIM
F014	BGD	ASIA	2014	1.4	MINIM
F025	BGD	ASIA	2014	1.3	MINIM
F050	CHN	ASIA	2014	1.3	MINIM
F044	BGD	ASIA	2014	1.3	MINIM
F070	TUR	ASIA	2015	1.3	MINIM
F072	ROU	EUR	2015	1.2	MINIM
F011A	CHN	ASIA	2013	1.2	MINIM
F074	ROU	EUR	2015	1.2	MINIM
F062	EGY	AFR	2014	1.1	MINIM
F054	CHN	ASIA	2015	1.1	MINIM
F093	BGD	ASIA	2014	1.1	MINIM
F013	EGY	AFR	2014	1.1	MINIM
F004	EGY	AFR	2014	1.1	MINIM

Facility			Year	FGTS	Impact
F039	CHN	ASIA	2013	1.1	MINIM
F079B	CHN	ASIA	2014	1.1	MINIM
F089	BGD	ASIA	2014	1.1	MINIM
F058	TUN	AFR	2015	1.1	MINIM
F076	IND	ASIA	2013	1.0	MINIM
F080	CHN	ASIA	2015	1.0	MINIM
F035	BGD	ASIA	2015	1.0	MINIM
F043	TUN	AFR	2014	1.0	MINIM
F066	CHN	ASIA	2014	1.0	MINIM
F049B	CHN	ASIA	2014	0.92	MINIM
F019	BGD	ASIA	2014	0.91	MINIM
F075	TUR	ASIA	2015	0.89	MINIM
F038	TUN	AFR	2013	0.88	MINIM
F063	TUR	ASIA	2015	0.87	MINIM
F051	CHN	ASIA	2014	0.86	MINIM
F085	IND	ASIA	2013	0.86	MINIM
F078	IND	ASIA	2013	0.85	MINIM
F094A	CHN	ASIA	2013	0.84	MINIM
F008	BGD	ASIA	2014	0.84	MINIM
F079A	CHN	ASIA	2013	0.83	MINIM
F086	CHN	ASIA	2013	0.80	MINIM
F040	CHN	ASIA	2015	0.78	MINIM
F002	PRT	EUR	2015	0.77	MINIM
F098A	CHN	ASIA	2013	0.76	MINIM
F033	CHN	ASIA	2013	0.76	MINIM
F028	ROU	EUR	2015	0.74	MINIM
F052	CHN	ASIA	2013	0.65	MINIM

Table 4.3. (continued)

Facility			Year	FGTS	Impact
F012	CHN	ASIA	2013	0.64	MINIM
F060	TUN	AFR	2013	0.64	MINIM
F101	CHN	ASIA	2014	0.59	MINIM
F020B	CHN	ASIA	2014	0.59	MINIM
F055	CHN	ASIA	2014	0.55	MINIM
F102	CHN	ASIA	2015	0.52	MINIM
F067	CHN	ASIA	2015	0.52	MINIM
F057	CHN	ASIA	2014	0.51	MINIM
F083	CHN	ASIA	2013	0.50	MINIM
F098B	CHN	ASIA	2014	0.48	MINIM

Facility			Year	FGTS	Impact
F031A	TUN	AFR	2013	0.48	MINIM
F016	TUN	AFR	2014	0.46	MINIM
F049A	CHN	ASIA	2013	0.46	MINIM
F011B	CHN	ASIA	2014	0.43	MINIM
F026A	TUN	AFR	2013	0.43	MINIM
F020A	CHN	ASIA	2013	0.43	MINIM
F030	TUN	AFR	2013	0.39	MINIM
F099	CHN	ASIA	2013	0.39	MINIM
F092	CHN	ASIA	2013	0.39	MINIM
F037B	CHN	ASIA	2015	0.38	MINIM

Facility			Year	FGTS	Impact
F046	CHN	ASIA	2013	0.36	MINIM
F056	CHN	ASIA	2014	0.33	MINIM
F065	CHN	ASIA	2015	0.27	MINIM
F032	CHN	ASIA	2014	0.26	MINIM
F026B	TUN	AFR	2014	0.24	MINIM
F094B	CHN	ASIA	2014	0.24	MINIM
F022	CHN	ASIA	2014	0.19	MINIM
F034	CHN	ASIA	2015	0.16	MINIM
F031B	TUN	AFR	2014	0.15	MINIM
F048	CHN	ASIA	2015	0.15	MINIM

SUPPLIER RESPONSIBILITY FACILITY RANKING

The supplier responsibility (SR) was calculated by subtracting the measured concentration in IW from the concentration in UWW, data by data, site by site. For those cases in which a value in UWW does not have a correspondence in IW, the missing data in IW was substituted with a value <LOD, therefore it was numerically considered as half LOD. When applying this approximation, the operators consider that, for every compound, the concentration in UWW is usually higher than the concentration in IW, as confirmed by Figure 2.9a. However, the same figure also shows that there are a few exceptions that cannot be properly assessed with available data. Most exceptions are data with value <LOD in UWW, but there are 9 cases characterised by a value >LOD for UWW and no data in IW: 7 cases for A0425 (F002, F004, F013, F028, F058, F072, F074), 1 case for A0304 (F037B) and 1 case for A1201 (F055). These exceptions, due to a lack of additional information, were also assigned a value <LOD for IW. The SR evaluation was conducted in all the facilities involved in this work, with the exception of F023, for which no data was present in IW.

To this new dataset the Equation 3.1 was applied. Since the most toxic facilities for UWW show a minimum impact for IW, it is expected that the evaluation of the SR (reported in Table 4.4) leads to a similar ranking to that one obtained for UWW data (Table 4.2), at least in the initial part. As anticipated, the facility with the highest SR was F096, indicated as "extreme responsibility", followed by F21B, F018 and F091, as in the UWW ranking. As reported in Figure 2.9a, sometimes the concentration of chemicals in IW could be higher than in UWW. As a consequence, in SR ranking an additional category, called "Negative Responsibility" is present: it includes all facilities with a FGTS under zero, representing facilities where IW is "more polluted" than UWW. The facility with a higher negative FGTS is F081, characterised by an extreme impact in IW and weak impact in UWW.

Globally, the distribution of results among the responsibility categories is as follows:

- Extreme Responsibility: 1 facility;
- Strong Responsibility: 3 facilities;
- Medium Responsibility: 5 facilities;
- Weak Responsibility: 18 facilities;
- Minimum Responsibility: 70 facilities;
- Negative Responsibility: 14 facilities.

Table 4.4. Ranking of the facilities, based on the facility global toxicological score (FGTS), referred to the supplier responsibility.

Facility			Year	FGTS	Respons
F096	CHN	ASIA	2013	355	EXTREME
F021B	CHN	ASIA	2014	86	STRONG
F018	IND	ASIA	2013	57	STRONG
F091	CHN	ASIA	2015	50	STRONG
F060	TUN	AFR	2013	35	MEDIUM
F073	IND	ASIA	2013	34	MEDIUM
F080	CHN	ASIA	2015	32	MEDIUM
F088	IND	ASIA	2013	25	MEDIUM
F098A	CHN	ASIA	2013	25	MEDIUM
F022	CHN	ASIA	2014	23	WEAK
F085	IND	ASIA	2013	23	WEAK
F064	IND	ASIA	2013	21	WEAK
F094B	CHN	ASIA	2014	21	WEAK
F084	CHN	ASIA	2014	19	WEAK
F079B	CHN	ASIA	2014	16	WEAK
F032	CHN	ASIA	2014	16	WEAK
F020A	CHN	ASIA	2013	16	WEAK
F016	TUN	AFR	2014	16	WEAK
F079A	CHN	ASIA	2013	15	WEAK
F012	CHN	ASIA	2013	15	WEAK
F093	BGD	ASIA	2014	14	WEAK
F051	CHN	ASIA	2014	13	WEAK
F070	TUR	ASIA	2015	13	WEAK
F057	CHN	ASIA	2014	13	WEAK
F078	IND	ASIA	2013	12	WEAK
F066	CHN	ASIA	2014	12	WEAK
F039	CHN	ASIA	2013	12	WEAK
F024	TUR	ASIA	2015	11	MINIM
F033	CHN	ASIA	2013	10	MINIM
F099	CHN	ASIA	2013	10	MINIM
F075	TUR	ASIA	2015	10	MINIM
F052	CHN	ASIA	2013	10	MINIM
F098B	CHN	ASIA	2014	9.2	MINIM
F049B	CHN	ASIA	2014	9.2	MINIM
F101	CHN	ASIA	2014	8.9	MINIM
F020B	CHN	ASIA	2014	8.4	MINIM
F049A	CHN	ASIA	2013	8.3	MINIM
F082	CHN	ASIA	2013	8.2	MINIM
F056	CHN	ASIA	2014	8.2	MINIM
F065	CHN	ASIA	2015	7.6	MINIM
F037A	CHN	ASIA	2013	6.9	MINIM
F040	CHN	ASIA	2015	6.9	MINIM
F026A	TUN	AFR	2013	6.8	MINIM
F059	BGD	ASIA	2014	6.8	MINIM
F037B	CHN	ASIA	2015	6.6	MINIM
F095	IND	ASIA	2013	5.7	MINIM
F042	TUN	AFR	2013	5.5	MINIM
F068	ITA	EUR	2013	5.1	MINIM
F055	CHN	ASIA	2014	5.0	MINIM
F031A	TUN	AFR	2013	4.8	MINIM
F029	IND	ASIA	2013	4.7	MINIM
F074	ROU	EUR	2015	4.4	MINIM
F092	CHN	ASIA	2013	4.3	MINIM
F014	BGD	ASIA	2014	4.3	MINIM
F026B	TUN	AFR	2014	4.2	MINIM
F030	TUN	AFR	2013	4.2	MINIM
F019	BGD	ASIA	2014	4.1	MINIM
F094A	CHN	ASIA	2013	4.0	MINIM
F015	CHN	ASIA	2013	3.9	MINIM
F083	CHN	ASIA	2013	3.7	MINIM
F046	CHN	ASIA	2013	3.6	MINIM
F031B	TUN	AFR	2014	3.6	MINIM
F006	CHN	ASIA	2015	3.2	MINIM
F010	HRV	EUR	2013	3.2	MINIM
F025	BGD	ASIA	2014	3.2	MINIM
F035	BGD	ASIA	2015	3.0	MINIM
F076	IND	ASIA	2013	3.0	MINIM
F008	BGD	ASIA	2014	3.0	MINIM
F054	CHN	ASIA	2015	2.9	MINIM
F058	TUN	AFR	2015	2.7	MINIM
F077	BGD	ASIA	2014	2.6	MINIM
F053	CHN	ASIA	2014	2.3	MINIM
F044	BGD	ASIA	2014	2.1	MINIM
F100	CHN	ASIA	2014	1.9	MINIM
F069	ITA	EUR	2013	1.9	MINIM
F089	BGD	ASIA	2014	1.8	MINIM
F009	BGD	ASIA	2014	1.8	MINIM
F061	BGD	ASIA	2014	1.6	MINIM
F086	CHN	ASIA	2013	1.5	MINIM
F013	EGY	AFR	2014	1.5	MINIM
F050	CHN	ASIA	2014	1.5	MINIM
F090	BGD	ASIA	2014	1.4	MINIM
F041	IND	ASIA	2013	1.3	MINIM
F102	CHN	ASIA	2015	1.2	MINIM

Table 4.4. (continued)

Facility			Year	FGTS	Respons
F004	EGY	AFR	2014	1.1	MINIM
F027	EGY	AFR	2014	0.94	MINIM
F001	TUR	ASIA	2015	0.81	MINIM
F038	TUN	AFR	2013	0.77	MINIM
F011B	CHN	ASIA	2014	0.74	MINIM
F034	CHN	ASIA	2015	0.73	MINIM
F097	CHN	ASIA	2013	0.65	MINIM
F063	TUR	ASIA	2015	0.64	MINIM
F067	CHN	ASIA	2015	0.54	MINIM

Facility			Year	FGTS	Respons
F045	CHN	ASIA	2015	0.50	MINIM
F003	TUR	ASIA	2015	0.33	MINIM
F028	ROU	EUR	2015	0.23	MINIM
F048	CHN	ASIA	2015	0.02	MINIM
F062	EGY	AFR	2014	-0.13	NEGAT
F011A	CHN	ASIA	2013	-0.31	NEGAT
F002	PRT	EUR	2015	-0.35	NEGAT
F087	BGD	ASIA	2014	-0.36	NEGAT
F043	TUN	AFR	2014	-0.41	NEGAT

Facility			Year	FGTS	Respons
F007	CHN	ASIA	2015	-0.59	NEGAT
F072	ROU	EUR	2015	-0.76	NEGAT
F021A	CHN	ASIA	2013	-1.3	NEGAT
F071	BGD	ASIA	2014	-1.8	NEGAT
F017	TUN	AFR	2014	-1.8	NEGAT
F005	CHN	ASIA	2013	-11	NEGAT
F036	CHN	ASIA	2013	-11	NEGAT
F047	CHN	ASIA	2015	-18	NEGAT
F081	CHN	ASIA	2014	-102	NEGAT

Evaluations of the SR per country and per year were also conducted. As expected, the trend reflects the findings for UWW, with India and China as the countries with higher FGTS and a decreasing trend over the years.

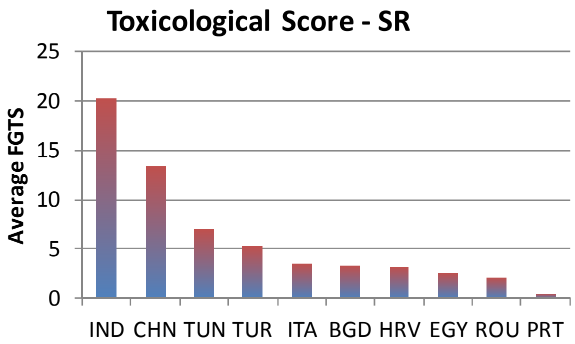


Figure 4.5. Average facility global toxicity score (FGTS) for every country, for supplier responsibility.

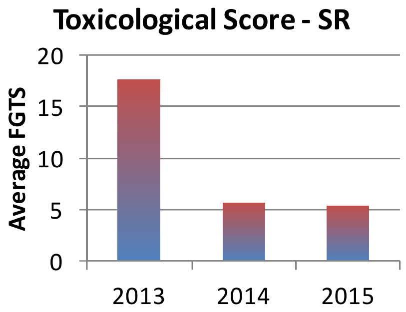


Figure 4.6. Average facility global toxicity score (FGTS) per year, for supplier responsibility.

TREATED WASTEWATER FACILITY RANKING

Facility global toxicological scores (FGTSs) were calculated also from TWW data.

Given that TWW enter directly into the environment, sites were classified into five impact categories, more restricted than those used for the IW and UWW data evaluation. The limits of the impact categories for TWW are listed in Table 4.5. The ranking for TWW is reported in Table 4.6.

Table 4.5. Impact categories for incoming water (IW) and untreated wastewater (UWW), based on the site global toxicological score (FGTS).

IMPACT	FGTS
MINIMUM IMPACT	From 0 to 6.5
WEAK IMPACT	From 6.5 to 13
MEDIUM IMPACT	From 13 to 20
STRONG IMPACT	From 20 to 50
EXTREME IMPACT	From 50 to 100

Table 4.6. Ranking of the facilities, based on the facility global toxicological score (FGTS), referred to treated waste water measured concentration.

Facility			Year	FGTS	Impact
F066	CHN	ASIA	2014	32	STRONG
F022	CHN	ASIA	2014	22	STRONG
F059	BGD	ASIA	2014	17	MEDIUM
F040	CHN	ASIA	2015	12	WEAK
F036	CHN	ASIA	2013	8.9	WEAK
F002	PRT	EUR	2015	8.8	WEAK
F010	HRV	EUR	2013	8.6	WEAK
F016	TUN	AFR	2014	7.6	WEAK
F032	CHN	ASIA	2014	7.3	WEAK
F097	CHN	ASIA	2013	7.2	WEAK
F098A	CHN	ASIA	2013	7.1	WEAK
F049A	CHN	ASIA	2013	6.7	WEAK
F064	IND	ASIA	2013	6.6	WEAK
F003	TUR	ASIA	2015	6.3	MINIM
F079B	CHN	ASIA	2014	6.1	MINIM
F096	CHN	ASIA	2013	5.9	MINIM
F093	BGD	ASIA	2014	5.4	MINIM
F068	ITA	EUR	2013	5.2	MINIM
F031B	TUN	AFR	2014	4.9	MINIM
F069	ITA	EUR	2013	4.6	MINIM
F041	IND	ASIA	2013	3.9	MINIM
F073	IND	ASIA	2013	3.6	MINIM

Facility			Year	FGTS	Impact
F089	BGD	ASIA	2014	3.5	MINIM
F095	IND	ASIA	2013	3.5	MINIM
F049B	CHN	ASIA	2014	3.1	MINIM
F098B	CHN	ASIA	2014	2.9	MINIM
F101	CHN	ASIA	2014	2.9	MINIM
F029	IND	ASIA	2013	2.9	MINIM
F085	IND	ASIA	2013	2.8	MINIM
F078	IND	ASIA	2013	2.7	MINIM
F077	BGD	ASIA	2014	2.6	MINIM
F042	TUN	AFR	2013	2.6	MINIM
F009	BGD	ASIA	2014	2.6	MINIM
F033	CHN	ASIA	2013	2.5	MINIM
F025	BGD	ASIA	2014	2.4	MINIM
F006	CHN	ASIA	2015	2.3	MINIM
F100	CHN	ASIA	2014	2.3	MINIM
F071	BGD	ASIA	2014	2.2	MINIM
F061	BGD	ASIA	2014	2.1	MINIM
F014	BGD	ASIA	2014	2.1	MINIM
F047	CHN	ASIA	2015	2.1	MINIM
F090	BGD	ASIA	2014	2.0	MINIM
F035	BGD	ASIA	2015	2.0	MINIM
F020B	CHN	ASIA	2014	1.8	MINIM

Facility			Year	FGTS	Impact
F044	BGD	ASIA	2014	1.8	MINIM
F091	CHN	ASIA	2015	1.7	MINIM
F028	ROU	EUR	2015	1.7	MINIM
F008	BGD	ASIA	2014	1.7	MINIM
F099	CHN	ASIA	2013	1.6	MINIM
F001	TUR	ASIA	2015	1.6	MINIM
F094B	CHN	ASIA	2014	1.5	MINIM
F076	IND	ASIA	2013	1.2	MINIM
F063	TUR	ASIA	2015	1.2	MINIM
F018	IND	ASIA	2013	1.1	MINIM
F017	TUN	AFR	2014	1.0	MINIM
F088	IND	ASIA	2013	0.90	MINIM
F074	ROU	EUR	2015	0.89	MINIM
F050	CHN	ASIA	2014	0.75	MINIM
F094A	CHN	ASIA	2013	0.73	MINIM
F058	TUN	AFR	2015	0.56	MINIM
F065	CHN	ASIA	2015	0.41	MINIM
F079A	CHN	ASIA	2013	0.38	MINIM
F026B	TUN	AFR	2014	0.38	MINIM
F043	TUN	AFR	2014	0.31	MINIM
F026A	TUN	AFR	2013	0.07	MINIM

Treated wastewater shows a lower FGTS than untreated wastewater, on average. No facility was classified as "extreme impact"; F066 and F022 are categorised as "strong impact", due to the high contribution of zinc and nickel, respectively. F059 is a "medium impact" site and the other facilities show a weak (10 sites) or minimum impact (52 sites).

In contrast to what happens in IW and UWW, the countries with higher average toxicity score in treated wastewater are Portugal and Croatia, indicating Europe as the most polluting continent (Figure 4.7). It should be noted that the evaluation of TWW was conducted using much less data than IW and UWW, therefore any comparison should be made carefully. No chronological trend was observed for TWW toxicological scores (Figure 4.8).

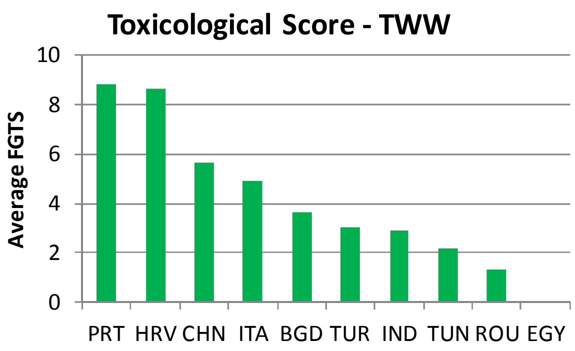


Figure 4.7. Average facility global toxicity score (FGTS) for every country, for untreated wastewater.

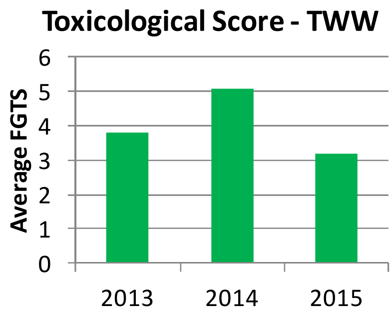


Figure 4.8. Average facility global toxicity score (FGTS) per year, for untreated wastewater.

Given the great difference in the amount between UWW and TWW data (Table 2.3), no evaluation about the purifier efficiency was made. In particular, we individuated 543 values >LOD in UWW with no correspondence in TWW. Some of these represented a very high concentration of chemicals: for instance, zinc in F080 is 2183 μg/l, chromium in F084 is 1360 μg/l, cyanide in F021B is 1010 μg/l. From available data, we cannot assume that these toxic compound were abated by the treatment. Therefore, the approximation used for the evaluation of the supplier responsibility cannot be applied.

5. CONCLUSIONS

DATA EVALUATION

- In all datasets, the majority of analysed values were under the limit of detection. This could be an encouraging result in terms of environmental impact. However, the evaluation strongly depends on the absolute value of LOD. A specific study focusing on the evaluation of the analytical methods used is suggested.

- The order of samples, both in terms of number of detected analytes and median concentration of toxic compounds is: untreated wastewater > treated wastewater > incoming water.

- The most represented class, in all types of samples (incoming water, untreated wastewater and treated wastewater), is total heavy metals (C11). It is also the class more frequently present in facilities. The percentages of the other classes vary with the different type of samples: specifically, azodyes (C04) and organotin compounds (C05) show an increase in the number of detected analytes and median concentration, passing from incoming water to untreated wastewater. These classes of compounds are not efficiently removed during the treatment process.

- The least present class in untreated wastewater is brominated and chlorinated flame retardants (C03): it is present in 3% of facilities; moreover, the class is located in the last part of the toxicological ranking. If there is the intent to modify the monitoring strategy, the frequency of analysis of this class could be reduced. Periodical checks should be maintained, in order to verify the concentration of C03 and return to the current analysis frequency, if necessary. The monitoring strategy could be modified in a smiliar way for perfluorinated coumpounds (C06).

- The data size is very different in the three datasets (incoming water, untreated wastewater and treated wastewater). This is a problem in terms of comparability, because a large percentage of data does not have a corresponding value in the other sampling sites. The current monitoring strategy requires that, if a class is not detected in untreated wastewater, the class is not analysed in incoming water and wastewater after treatment, assuming that untreated wastewater is always the most polluted among the three samples. Data analysis demonstrated that, although this trend is generally verified, there is a significant amount of exceptions. We suggest updating the monitoring strategy, in order to analyse all the collected samples, because the exceptions may be more numerous than those already encounted. It will also permit to have a global view of the chemical composition of the three sites, to make more meaningful comparisons

TOXICOLOGICAL EVALUATION

- The application of the multi-criteria analysis in this work allows us to obtain a single score for every analyte representing five different types of toxicity, which would otherwise be hardly comparable. The relative importance of the criteria must be specified; we thereby obtained a dynamic ranking that changed if the relative importance of criteria was modified. This feature makes the method universal and applicable to different kind of samples (formulations, textiles, ...), after proper assessment of the criteria weights.

- In this evaluation, the resulting most toxic compounds were arsenic and cyanide, which show the strongest lethal acute effect; these were followed by hexavalent chromium (Cr VI), that has a weaker acute toxicity than other compounds, but that is highly carcinogenic. The most toxic classes are cyanide and total heavy metals, the latter especially due to the high toxicity of arsenic, hexavalent chromium, cadmium and nickel.

FACILITY EVALUATION

- In incoming water one facility was classified as "extreme impact", because of the exceptional concentration of zinc and N-Ethyl-Perfluoro-octane-sulfon-amide. The other facilities, as expected, have weak or minimum impact.

- For the untreated wastewater, one facility was individuate as a very critical facility (extreme impact), due to the strong concentration of highly toxic compounds, such as nickel, zinc, lead, chromium and copper. Other four facilities were considered to have a strong impact. The responsibility for the high measured impact in wastewater has to be assigned to the supplier, since in the same facilities incoming water has a low concentration of toxic compounds (minimum impact). In a few cases a negative supplier responsibility was observed, with incoming water more polluted than untreated wastewater.

- The treated wastewater ranking shows two facilities with strong impact; the others are mainly of weak and minimum impact. The evaluation of the treatment efficiency could not be conducted, because of lacking data.

- Countries with the highest toxicological scores are: China and India for untreated wastewater and supplier responsibility; Croatia, China and India for incoming water. While for incoming water and untreated wastewater Asia remains the continent with the highest toxicological impact, a turnaround was observed for treated wastewater: Portugal and Croatia, with their high toxicological scores, makes Europe more polluting than Asia and Africa.

- A decreasing chronological trend was observed in the toxicological scores for untreated wastewater and supplier responsibility. Surprisingly, it seems that this favourable tendency does not be maintained after water purification.

ANNEX I - TOXICITY EVALUATION

In the following paragraphs the classification of compounds, based on the five type of toxicity used in this work (acute toxicity, carcinogenicity, reproductive toxicity, acute and chronic aquatic toxicity) are described. The last table of the annex reports the classification of all the analysed compounds, based on the same type of toxicity.

ACUTE TOXICITY EVALUATION

The acute toxicity is evaluated using oral LD_{50} on rats, when present. LD_{50} or median lethal dose is the dose required to kill half the members of a tested population after a specified test duration. LD_{50} is frequently used as a general indicator of a substance's acute toxicity. If LD_{50} values were not available, UNECE categories were used (Table A.1)

Table A.1. UNECE (United Nations Economic Commission for Europe) oral classification. LD_{50}: median lethal dose.

CATEGORY	THRESHOLDS
CATEGORY 1	LD_{50} ≤ 5 mg/kg bodyweight
CATEGORY 2	LD_{50} > 5 mg/kg bodyweight but ≤ 50 mg/kg bodyweight
CATEGORY 3	LD_{50} > 50 mg/kg bodyweight but ≤ 300 mg/kg bodyweight
CATEGORY 4	LD_{50} > 300 mg/kg bodyweight but ≤ 2000 mg/kg bodyweight
CATEGORY 5	LD_{50} > 2000 mg/kg bodyweight but ≤ 5000 mg/kg bodyweight

CARCINOGENIC TOXICITY EVALUATION

The IARC (International Agency for Research on Cancer) categories are the followings:

- Group 1: The agent is carcinogenic to humans
  This category is used when there is *sufficient evidence of carcinogenicity* in humans. Exceptionally, an agent may be placed in this category when evidence of carcinogenicity in humans is less than *sufficient* but there is *sufficient evidence of carcinogenicity* in experimental animals and strong evidence in exposed humans that the agent acts through a relevant mechanism of carcinogenicity.
- Group 2
  This category includes agents for which, at one extreme, the degree of evidence of carcinogenicity in humans is almost *sufficient*, as well as those for which, at the other extreme, there are no human data but for which there is evidence of carcinogenicity in experimental animals. Agents are assigned to either Group 2A (*probably carcinogenic to humans*) or Group 2B (*possibly carcinogenic to humans*) on the basis of epidemiological and experimental evidence of carcinogenicity and mechanistic and other relevant data. The terms *probably carcinogenic* and *possibly carcinogenic* have no quantitative significance and are used simply as descriptors of different levels of evidence of human carcinogenicity, with *probably carcinogenic* signifying a higher level of evidence than *possibly carcinogenic*.
- Group 2A: The agent is probably carcinogenic to humans
  This category is used when there is *limited evidence of carcinogenicity* in humans and *sufficient evidence of carcinogenicity* in experimental animals. In some cases, an agent may be classified in this category when there is *inadequate evidence of carcinogenicity* in humans and *sufficient*

evidence of carcinogenicity in experimental animals and strong evidence that the carcinogenesis is mediated by a mechanism that also operates in humans. Exceptionally, an agent may be classified in this category solely on the basis of *limited evidence of carcinogenicity* in humans. An agent may be assigned to this category if it clearly belongs, based on mechanistic considerations, to a class of agents for which one or more members have been classified in Group 1 or Group 2A.

- Group 2B: The agent is possibly carcinogenic to humans
  This category is used for agents for which there is *limited evidence of carcinogenicity* in humans and less than *sufficient evidence of carcinogenicity* in experimental animals. It may also be used when there is *inadequate evidence of carcinogenicity* in humans but there is *sufficient evidence of carcinogenicity* in experimental animals. In some instances, an agent for which there is *inadequate evidence of carcinogenicity* in humans and less than *sufficient evidence of carcinogenicity* in experimental animals together with supporting evidence from mechanistic and other relevant data may be placed in this group. An agent may be classified in this category solely on the basis of strong evidence from mechanistic and other relevant data.
- Group 3: The agent is not classifiable as to its carcinogenicity to humans
  This category is used most commonly for agents for which the evidence of carcinogenicity is *inadequate* in humans and *inadequate* or *limited* in experimental animals. Exceptionally, agents for which the evidence of carcinogenicity is *inadequate* in humans but *sufficient* in experimental animals may be placed in this category when there is strong evidence that the mechanism of carcinogenicity in experimental animals does not operate in humans. Agents that do not fall into any other group are also placed in this category. An evaluation in Group 3 is not a determination of non-carcinogenicity or overall safety. It often means that further research is needed, especially when exposures are widespread or the cancer data are consistent with differing interpretations.
- Group 4: The agent is probably not carcinogenic to humans
  This category is used for agents for which there is *evidence suggesting lack of carcinogenicity* in humans and in experimental animals. In some instances, agents for which there is *inadequate evidence of carcinogenicity* in humans but *evidence suggesting lack of carcinogenicity* in experimental animals, consistently and strongly supported by a broad range of mechanistic and other relevant data, may be classified in this group.

REPRODUCTIVE TOXICITY EVALUATION

For the reproductive toxicity evaluation, the UNECE categories were used. The categories are:

- CATEGORY 1: Known or presumed human reproductive toxicant
  This category includes substances which are known to have produced an adverse effect on sexual function and fertility or on development in humans or for which there is evidence from animal studies, possibly supplemented with other information, to provide a strong presumption that the substance has the capacity to interfere with reproduction in humans. For regulatory purposes, a substance can be further distinguished on the basis or whether the evidence for classification is primarily from human data (Category 1A) or from animal data (Category 1B).
- CATEGORY 1A: Known human reproductive toxicant
  The placing of the substance in this category is largely based on evidence from humans.
- CATEGORY 1B: Presumed human reproductive toxicant

The placing of the substance in this category is largely based on experimental animals. Data from animal studies should provide clear evidence of an adverse effect on sexual function and fertility or on development in the absence of other toxic effects, or if occurring together with other toxic effects the adverse effect on reproduction is considered not to be a secondary non-specific consequence of other toxic effects. However, when there is mechanistic information that raises doubt about the relevance of the effect for humans, classification in Category 2 may be more appropriate.

- CATEGORY 2: Suspected human reproductive toxicant
  This category includes substances for which there is some evidence from humans or experimental animals, possibly supplemented with other information, of an adverse effect on sexual function and fertility, or on development, in the absence of other toxic effects, or if occurring together with other toxic effects the adverse effect on reproduction is considered not to be a secondary non-specific consequence of the other toxic effects, and where the evidence is not sufficiently convincing to place the substance in Category 1. For instance, deficiencies in the study may take the quality of evidence less convincing, and in view of this Category 2 could be the more appropriate classification.

To the official UNECE categories, an additional category was added, for specific cases:

- CATEGORY *:
  The user classified a substance in this category if it is not classified in any UNECE category, but there is an evidence of an adverse effect on reproduction: effects on fertility (post-implantation mortality, litter size), effects on embryo, foetus or newborn, paternal effects, development abnormalities.

ACUTE AQUATIC TOXICITY EVALUATION

Acute aquatic toxicity was evaluated using the three UNECE categories. The categories are calculated from the values of LC_{50} (median lethal concentration), that is the concentration required to kill half the members of a tested population after a specified test duration and EC_{50} (half maximal effective concentration), which is the concentration of a drug, antibody or toxicant which induces a response halfway between the baseline and maximum after a specified exposure time.

Table A.2. UNECE (United Nations Economic Commission for Europe) classification for acute aquatic toxicity. LC_{50}: median lethal concentration; EC_{50}: half maximal effective concentration.

CATEGORY	THRESHOLDS
CATEGORY 1	96h LC_{50} (fish): ≤ 1 mg/l and/or
	48h EC_{50} (crustacea): ≤ 1 mg/l and/or
	72h or 96h EC_{50} (algae or other acquatic plants): ≤ 1 mg/l
CATEGORY 2	96h LC_{50} (fish): > 1 mg/l but ≤ 10 mg/l and/or
	48h EC_{50} (crustacea): > 1 mg/l but ≤ 10 mg/l and/or
	72h or 96h EC_{50} (algae or other acquatic plants):> 1 mg/l but ≤ 10 mg/l
CATEGORY 3	96h LC_{50} (fish): > 10 mg/l but ≤ 100 mg/l and/or
	48h EC_{50} (crustacea): > 10 mg/l but ≤ 100 mg/l and/or
	72h or 96h EC_{50} (algae or other acquatic plants):> 10 mg/l but ≤ 100 mg/l

CHRONIC AQUATIC TOXICITY EVALUATION

UNECE classifies chronic aquatic toxicity in different ways, based on the degradability of the substances in environment.

- For non rapidly degradable substances for which there are adequate chronic toxicity data available, the categories are defined as shown in Table A.3. The categories are calculated from the values of Chronic NOEC (No observed effect concentration), that is the Highest tested concentration of a toxicant that causes no statistically discernable effect and EC_x (effect concentration x), which is the concentration at which x% of inhibition is observed.

Table A.3. UNECE (United Nations Economic Commission for Europe) classification for chronic aquatic toxicity, for non rapidly degradable substances for which there are adequate chronic toxicity data available. NOEC: No Observed Effect Concentration; EC_x: effect concentration x.

CATEGORY	THRESHOLDS
CATEGORY 1	Chronic NOEC or EC_x (fish): ≤ 0.1 mg/l and/or
	Chronic NOEC or EC_x (crustacea): ≤ 0.1 mg/l and/or
	Chronic NOEC or EC_x (algae or other acquatic plants): ≤ 0.1 mg/l
CATEGORY 2	Chronic NOEC or EC_x (fish): > 0.1 mg/l but ≤ 1 mg/l and/or
	Chronic NOEC or EC_x (crustacea): > 0.1 mg/l but ≤ 1 mg/l and/or
	Chronic NOEC or EC_x (algae or other acquatic plants): > 0.1 mg/l but ≤ 1 mg/l

- For rapidly degradable substances for which there are adequate chronic toxicity data available, the categories are defined as shown in Table A.4. The categories are calculated from the values of Chronic NOEC and EC_x.

Table A.4. UNECE (United Nations Economic Commission for Europe) classification for chronic aquatic toxicity, for rapidly degradable substances for which there are adequate chronic toxicity data available. NOEC: No Observed Effect Concentration; EC_x: effect concentration x.

CATEGORY	THRESHOLDS
CATEGORY 1	Chronic NOEC or EC_x (fish): ≤ 0.01 mg/l and/or
	Chronic NOEC or EC_x (crustacea): ≤ 0.01 mg/l and/or
	Chronic NOEC or EC_x (algae or other acquatic plants): ≤ 0.01 mg/l
CATEGORY 2	Chronic NOEC or EC_x (fish): > 0.01 mg/l but ≤ 0.1 mg/l and/or
	Chronic NOEC or EC_x (crustacea): > 0.01 mg/l but ≤ 0.1 mg/l and/or
	Chronic NOEC or EC_x (algae or other acquatic plants): > 0.01 mg/l but ≤ 0.1 mg/l
CATEGORY 3	Chronic NOEC or EC_x (fish): > 0.1 mg/l but ≤ 1 mg/l and/or
	Chronic NOEC or EC_x (crustacea): > 0.1 mg/l but ≤ 1 mg/l and/or
	Chronic NOEC or EC_x (algae or other acquatic plants): > 0.1 mg/l but ≤ 1 mg/l

- If adequate chronic toxicity data are not available, substances are classified using the categories for the acute aquatic toxicity (Table A.2).

Table A.5. Toxicity information. AC: Acute Toxicity, as LD_{50} oral in rat (mg/kg body weight) or UNECE Classification; CARC: Carcinogenicity, as IARC Classification; REP: Reproductive Toxicity, as UNECE Classification; AC AQ: Acute Aquatic Toxicity, as UNECE Classification; CHR AQ: Chronic Aquatic Toxicity, as UNECE Classification. The specific compounds that were evaluated in order to acquire the analyte toxicity information are reported, with CAS number (in brackets) UNECE: United Nations Economic Commission for Europe; IARC: International Agency for research on cancer. CAT: Category. GR: Group.

A	Name	AC	CARC	REP	AC AQ	CHR AQ	Evaluated Compounds (CAS)
A0101	Octylphenols (OPs)	-	-	-	CAT 1	CAT 1	4-Ter-OP (140-66-9) 4-OP (1806-26-4)
A0102	Octylphenolethoxylates (OPEOs)	1800	-	-	-	CAT 2	Triton X100 (9002-93-1)
A0103	Nonylphenols (NPs)	1412	-	CAT 2	CAT 1	CAT 1	NP (84852-15-3) 4-NP (104-40-5)
A0104	Nonylphenolethoxylates (NPEOs)	CAT 4	-	-	-	CAT 2	Tergitol (127087-87-0)
A0201	Benzyl-butyl-phthalate (BBP)	2330	GR 3	CAT 1B	CAT 1	CAT 1	
A0202	Di-butyl-phthalate (DBP)	8000	-	CAT 1B	CAT 1	-	
A0203	Di-(2-ethyl-hexyl)-phthalate (DEHP)	30000	GR 2B	CAT 1B	-	-	
A0204	Di-n-octyl-phthalate (DNOP)	30000	GR 2B	CAT 1B	-	-	
A0205	Di-iso-nonyl-phthalate (DINP)	-	GR 2B	-	-	-	
A0206	Di-iso-decyl-phthalate (DIDP)	64000	-	*	CAT 1	CAT 1	
A0207	Di-methyl-phthalate (DMP)	8200	-	-	-	-	
A0208	Di-ethyl-phthalate (DEP)	8600	-	*	-	-	
A0209	Di-n-propyl-phthalate (DPP)	-	-	CAT 2	-	CAT 2	
A0210	Di-iso-butyl-phthalate (DIBP)	10382	-	CAT 1B	CAT 1	CAT 1	
A0211	Di-cyclo-hexyl-phthalate (DCHP)	-	-	-	-	-	
A0212	Di-n-hexyl-phthalate (DNHP)	29600	-	CAT 1B	-	-	
A0213	Di-nonyl-phthalate (DNP)	-	-	-	-	-	
A0214	Di-iso-octyl-phthalate (DIOP)	-	-	-	-	-	Diisooctyl Phthalate-d4 (93952-13-7)
A0215	Bis-(2-methoxy-ethyl)-phthalate (DMEP)	3200	-	CAT 1B	-	-	
A0216	Di-iso-pentyl-phthalate (DIPP)	-	-	CAT 1B	CAT 1	-	
A0217	Di-iso-heptyl-phthalate (DIHP)	-	-	CAT 1B	CAT 1	-	
A0218	1,2-Benzene-di-carboxylic acid di-pentyl-esters, branched and linear (DHNUP)	-	-	CAT 2		-	
A0219	N-iso-pentyl-iso-pentyl-phthalate (PIPP)	-	-	CAT 1B	CAT 1	-	
A0220	Di-heptyl-phthalate (DHP)	-	-	CAT 2		-	

Table A.5. (continued)

A	Name	AC	CARC	REP	AC AQ	CHR AQ	Evaluated Compounds (CAS)
A0301	Polybromodiphenyls (PBBs)	CAT 4	GR 2A	-	CAT 1	CAT 1	2,2'-DiBB (13029-09-9) 2-BB (2052-07-5) 3-BB (2113-57-7) 4-BB (92-66-0) 2,4-DiBB (53592-10-2) 2,5-DiBB (57422-77-2) 4,4'-DiBB (92-86-4) 2,6-DiBB (59080-32-9) 3,4',5-TriBB (72416-87-6) 2,2',5-TriBB (59080-34-1) 2,3',5-TriBB (59080-35-2) 2,4,6-TriBB (59080-33-0) 2,4',5-TriBB (59080-36-3) 2,2',5,5'-TeBB (59080-37-4) 2,2',4,5'-TeBB (60044-24-8) 3,3',5,5'-TeBB (16400-50-3) 2,2',4,5',6-PeBB (59080-39-6) 2,2',4,5',5'-PeBB (67888-96-4) 2,2',4,4',6,6'-HexaBB (59261-08-4)
A0302	Tri-(2,3-di-bromo-propyl)-phosphate (TRIS)	810	GR 2A	*	CAT 1	-	
A0303	Polybromodiphenyl ethers (PBDEs)	3200	-	CAT 3	CAT 1	CAT 1	3-BDE (6876-00-2) 4-BDE (101-55-3), DeBDE (1163-19-5)
A0304	Tetra-bromo-bisphenol-A (TBBPA)	-	-	*	CAT 1	CAT 1	
A0305	Bis-(2,3-di-bromo-propyl)-phosphate	636	-	-	-	-	
A0306	Hexa-bromo-cyclo-dodecan (HBCDD)	-	-	CAT 2	CAT 1	CAT 1	
A0307	2,2-Bis(bromomethyl)-1,3-propanediol (BBMP)	1880	GR 2B	-	-	-	
A0308	Tris-(2-chloro-ethyl)-phosphate (TCEP)	1150	GR 3	CAT 1B	-	CAT 2	
A0309	Tris-(1,3-di-chloro-iso-propyl)-phosphate (TDCPP)	-	-	*	CAT 2	-	
A0310	Bromo-diphenyl	CAT 4	GR 2A	-	CAT 1	-	4-BB (92-66-0) 2-BB (2052-07-5) 3-BB (2113-57-7)
A0311	Di-bromo-diphenyl	CAT 4	GR 2A	-	CAT 1	CAT 1	2,2'-DiBB (13029-09-9) 2,4-DiBB (53592-10-2) 2,5-DiBB (57422-77-2) 4,4'-DiBB (92-86-4) 2,6-DiBB (59080-32-9)
A0312	Tri-bromo-diphenyl	CAT 4	-	-	CAT 1	CAT 1	3,4',5-TriBB (72416-87-6) 2,2',5-TriBB (59080-34-1) 2,3',5-TriBB (59080-35-2) 2,4,6-TriBB (59080-33-0) 2,4',5-TriBB (59080-36-3)
A0313	Tetra-bromo-diphenyl	CAT 4	-	-	-	-	2,2',5,5'-TeBB (59080-37-4) 2,2',4,5'-TeBB (60044-24-8) 3,3',5,5'-TeBB (16400-50-3)
A0314	Penta-bromo-diphenyl	CAT 4	-	-	-	-	2,2',4,5',6-PeBB (59080-39-6) 2,2',4,5',5'-PeBB (67888-96-4)
A0315	Hexa-bromo-diphenyl	-	-	-	-	-	2,2',4,4',6,6'-HexaBB (59261-08-4)
A0316	Hepta-bromo-diphenyl						
A0317	Octa-bromo-diphenyl						
A0318	Nona-bromo-diphenyl						
A0319	Deca-bromo-diphenyl	CAT 4	-	-	-	-	
A0320	Bromo-diphenyl-ether	3200	-	-	CAT 1	CAT 1	3-BDE (6876-00-2) 4-BDE (101-55-3)
A0321	Di-bromo-diphenyl-ether	-	-	-	-	-	4,4'-DiBDE (2050-47-7)
A0322	Tri-bromo-diphenyl-ether						

Table A.5. (continued)

A	Name	AC	CARC	REP	AC AQ	CHR AQ	Evaluated Compounds (CAS)
A0323	Tetra-bromo-diphenyl-ether						
A0324	Penta-bromo-diphenyl-ether						
A0325	Hexa-bromo-diphenyl-ether						
A0326	Hepta-bromo-diphenyl-ether						
A0327	Octa-bromo-diphenyl-ether	-	-	-	-	-	
A0328	Nona-bromo-diphenyl-ether						
A0329	Deca-bromo-diphenyl-ether	-	GR 3	-	-	-	
A0330	Tetra-bromo-bisphenol A bis-(di-bromo-propyl-ether) (TBBPA-BDPE)	CAT 5					
A0331	Tris-(2-chloroisopropyl)-phosphate (TCPP)	1101					
A0332	Tris-(aziridinyl)-phosphinoxide (TEPA)						
A0401	4-Aminodiphenyl	500	GR 1	-	-	-	
A0402	Benzidine	309	GR 1	-	CAT 1	CAT 1	
A0403	4-Chloro-o-toluidine	1058	GR 2A	-	CAT 1	CAT 1	
A0404	2-Naphthylamine	727	GR 1	-	-	CAT 2	
A0405	o-Aminoazotoluene	-	GR 2B	-	-	-	
A0406	5-Nitro-o-toluidine	-	GR 3	-	-	CAT 3	
A0407	4-Chloroaniline	300	GR 2B	-	-	-	
A0408	2,4-Diaminoanisole	460	GR 2B	-	-	CAT 2	
A0409	4,4'-Diaminodiphenylmethane	-	GR 2B	-	-	CAT 2	
A0410	3,3'-Dichlorobenzidine	-	GR 1	-	CAT 1	CAT 1	
A0411	3,3'-Dimethoxybenzidine	1920	GR 2B	-	-	-	
A0412	3,3'-Dimethylbenzidine	404	GR 2B	-	-	CAT 2	
A0413	3,3'-Dimethyl-4,4'-diaminodiphenylmethane						
A0414	p-Cresidine	1450	GR 2B	-	-	-	
A0415	4,4'-Methylene-bis(2-chloroaniline)	2000	GR 1	-	CAT 1	CAT 1	
A0416	4,4'-Oxydianiline	CAT 3	GR 2B	2	CAT 1	CAT 1	
A0417	4,4'-Thiodianiline	900	GR 2B	-	-	CAT 2	
A0418	o-Toluidine	670	GR 1	-	CAT 1	-	
A0419	2,4-Diaminotoluene	CAT 3	GR 2B	2	-	CAT 1	
A0420	2,4,5-Trimethylaniline	-	GR 3	-	-	-	
A0421	o-Anisidine	1150	GR 2B	-	-	-	
A0422	4-Aminoazobenzene	-	GR 2B	-	CAT 1	CAT 1	

Table A.5. (continued)

A	Name	AC	CARC	REP	AC AQ	CHR AQ	Evaluated Compounds (CAS)
A0423	2,4-Xylidine	CAT 3	GR 3	-	-	CAT 2	
A0424	2,6-Xylidine	840	GR 2B	-	-	CAT 2	
A0425	Aniline	250	GR 3	-	CAT 1	CAT 1	
A0426	1,4-Phenylenediamine	80	GR 3	-	CAT 1	CAT 1	
A0427	2-Chloroaniline	CAT 3	-	-	CAT 1	CAT 1	
A0428	5-Nitro-o-anisidine	2250	-	-	-	-	
A0429	m-Toluidine	450	-	-	CAT 1	-	
A0430	n,n-Diethylanaline	-	-	-	-	CAT 2	
A0431	n-Ethylaniline	CAT 3	-	-	-	-	
A0432	n-Methylaniline	CAT 3	-	-	CAT 1	CAT 1	
A0433	p-Toluidine	336	-	-	CAT 1	-	
A0501	Monobutyltin (MBT)	CAT 4	-	-	-	-	Butyltin trichloride (1118-46-3)
A0502	Dibutyltin (DBT)	50	-	CAT 1B	CAT 1	CAT 1	Dibutyltin dichloride (683-18-1)
A0503	Dioctyltin (DOT)	-	-	-	-	-	Dioctyltin oxide (870-08-6)
A0504	Tributyltin (TBT)	129	-	-	CAT 1	CAT 1	Tributyltin chloride (1461-22-9)
A0505	Triphenyltin (TPhT)	CAT 3	-	*	CAT 1	CAT 1	Triphenyltin chloride (639-58-7)
A0506	Tricyclohexyltin(TCyHT)	CAT 4	-	-	CAT 1	CAT 1	Tricyclohexyltin chloride (3091-32-5)
A0507	Trioctyltin(TriOT)	29200	-	-		CAT 4	Trioctyltin chloride (2587-76-0)
A0508	Tripropyltin (TPT)	-	-	-	CAT 1	CAT 1	Tripropyltin chloride (2279-76-7)
A0509	Monooctyltin (MOT)						
A0510	Tetrabutyltin (TeBT)	1268	-	-	CAT 1	CAT 1	
A0601	Perfluoro-n-octanoic acid (PFOA)	CAT 4	-	CAT 1B	-	-	
A0602	Perfluorooctane sulphonates (PFOS)	CAT 4	-	CAT 1B	-	CAT 2	Potassium PFOS (2795-39-3) Tetrabutylammonium PFOS (111873-33-7)
A0603	Perfluoro-n-hexanoic acid (PFHxA)	-	-	-	-	-	
A0604	Perfluorohexane sulphonates (PFHxS)	-	-	-	-	-	Potassium PFHxS (3871-99-6)
A0605	Perfluorobutyric Acid (PFBA)	-	-	-	-	-	
A0606	Perfluoro-butane-sulfonic acid	430	-	-	-	-	
A0607	Perfluoro-octane-sulfon- amide (PFOSA)	-	-	-	-	CAT 4	
A0608	N-Methyl-Perfluoro-octane-sulfon-amide (N-Me-FOSA)	-	-	-	-	-	
A0609	N-Ethyl-Perfluoro-octane-sulfon-amide (N-Et-FOSA)	543	-	-	-	CAT 2	
A0610	N-Methyl-Perfluoro-octane-sulfon-amido-ethanol (N-Me-FOSE alcohol)	-	-	-	-	-	
A0611	N-Ethyl-Perfluoro-octane-sulfon-amido-ethanol (N-Et-FOSE alcohol)	CAT 4	-	-	-	-	

Table A.5. (continued)

A	Name	AC	CARC	REP	AC AQ	CHR AQ	Evaluated Compounds (CAS)
A0612	Perfluoro-pentanoic acid	-	-	-	-	-	
A0613	Perfluoro-heptanoic acid	CAT 4	-	-	-	-	
A0614	Perfluoro-nonanoic acid	-	-	-	-	-	
A0615	Perfluoro-n-decanoic acid (PFDA)	57	-	*	-	-	
A0616	Perfluoro-undecanoic acid	CAT 4	-	-	-	-	
A0617	Perfluorododecanoic Acid (PFDoA)	-	-	-	-	-	
A0618	Perfluoro-tridecanoic acid	-	-	-	-	-	
A0619	Perfluoro-tetradecanoic acid	-	-	-	-	-	
A0620	Perfluoro-hexane-sulfonic acid	CAT 4	-	-	-	-	
A0621	Perfluoro-heptane-sulfonic acid						
A0622	Perfluor-decane-sulfonic acid						
A0623	1H,1H,2H,2H-Perfluoro-octane-sulphonic acid	-	-	-	-	-	
A0624	2H,2H,3H,3H-Perfluoroundecanoic acid (PFUnA)	-	-	-	-	-	
A0625	Perfluoro-3-7-dimethyl octane carboxylate	-	-	-	-	-	
A0626	7H-Dodecafluoro heptane carboxylate	1071	-	-	-	-	
A0701	Chlorobenzene	1110	-	-	-	CAT 2	
A0702	Dichlorobenzenes	500	GR 2B	-	CAT 1	CAT 1	1,4-DiCB (106-46-7) 1,2-DiCB (95-50-1) 1,3-DiCB (541-73-1)
A0703	Trichlorobenzenes	756	-	-	CAT 1	CAT 1	1,2,4-TriCB (120-82-1) 1,2,3-TriCB (87-61-6) 1,3,5-TriCB (108-70-3)
A0704	Tetrachlorobenzenes	1167	-	-	CAT 1	CAT 1	1,2,3,4-TetraCB (634-66-2) 1,2,3,5-TetraCB (634-90-2) 1,2,4,5-TetraCB (95-94-3)
A0705	Pentachlorobenzene	1080	-	*	CAT 1	CAT 1	
A0706	Hexachlorobenzene	10000	GR 2B	-	CAT 1	CAT 1	
A0801	Dichloromethane	-	GR 2B	-	-	-	
A0802	Chloroform	908	GR 2B	CAT 2	-	-	
A0803	Carbon tetrachloride	2350	GR 2B	-	-	CAT 3	
A0804	1,2-dichloroethane	670	GR 2B	*	-	-	
A0805	1,1,1-trichloroethane	9600	GR 3	-	-	-	
A0806	1,1,2-trichloroethane	836	GR 3	-	-	CAT 3	
A0807	1,1,1,2-tetrachloroethane	670	GR 3	-	-	-	
A0808	1,1,2,2-tetrachloroethane	200	GR 3	-	-	CAT 2	
A0809	Pentachloroethane	920	GR 3	-	-	CAT 2	
A0810	1,1-dichloroethylene	200	GR 3	-	-	-	
A0811	cis-1,2-Dichloroethylene	-	-	-	-	CAT 3	

Table A.5. (continued)

A	Name	AC	CARC	REP	AC AQ	CHR AQ	Evaluated Compounds (CAS)
A0812	trans-1,2-Dichloroethylene	1235	-	-	-	CAT 3	
A0813	Trichloroethylene	4920	GR 1	-	-	CAT 3	
A0814	Tetrachloroethylene	3005	GR 2A	-	-	CAT 2	
A0901	Monochlorophenols	570	GR 3	-	-	CAT 2	3-CP (108-43-0) 4-CP (106-48-9) 2-CP (95-57-8)
A0902	Dichlorophenol (DiCP)	47	GR 2B	-	-	CAT 2	2,4-DiCP (120-83-2) 2,3-DiCP (576-24-9) 2,5-DiCP (583-78-8) 2,6-DiCP (87-65-0), 3,4-DiCP (95-77-2) 3,5-DiCP (591-35-5)
A0903	Trichlorophenols (TriCP)	820	GR 2B	-	CAT 1	CAT 1	2,4,5-TriCP (95-95-4) 2,4,6-TriCP (88-06-2) 2,3,5-TriCP (933-78-8) 2,3,6-TriCP (933-75-5) 3,4,5-TriCP (609-19-8) 2,3,4-TriCP (15950-66-0)
A0904	Tetrachlorophenols (TeCP)	CAT 3	GR 2B	-	CAT 1	CAT 1	2,3,4,6-TeCP (58-90-2) 2,3,4,5-TeCP (4901-51-3) 2,3,5,6-TeCP (935-95-5)
A0905	Pentachlorophenol (PCP)	27	GR 2B	*	CAT 1	CAT 1	
A0906	2-Chlorophenol	670	-	-	-	CAT 2	
A0907	3-Chlorophenol	570	-	-	-	CAT 2	
A0908	4-Chlorophenol	670	GR 3	-	-	CAT 2	
A0909	2,3-Dichlorophenol	2376	-	-	-	-	
A0910	3,4-Dichlorophenol	CAT 4	-	-	-	-	
A0911	2,4-Dichlorophenol, 2,5-Dichlorophenol, 2,6-Dichlorophenol, 3,5-Dichlorophenol	47	GR 2B	-	-	CAT 2	2,4-DiCP (120-83-2) 2,5-DiCP (583-78-8) 2,6-DiCP (87-65-0), 3,5-DiCP (591-35-5)
A0912	2,3,5-Trichlorophenol	CAT 4	-	-	CAT 1	CAT 1	
A0913	2,4,5-Trichlorophenol	820	GR 2B	-	CAT 1	CAT 1	
A0914	2,4,6-Trichlorophenol	820	GR 2B	-	CAT 1	CAT 1	
A0915	3,4,5-Trichlorophenol, 2,3,4-Trichlorophenol	CAT 4	-	-	CAT 1	CAT 1	3,4,5-TriCP (609-19-8) 2,3,4-TriCP (15950-66-0)
A0916	2,3,4,5-Tetrachlorophenol	CAT 3	-	-	CAT 1	-	
A0917	2,3,4,6-Tetrachlorophenol	CAT 3	GR 2B	-	CAT 1	CAT 1	
A0918	2,3,5,6-Tetrachlorophenol	CAT 3	-	-	-	-	
A1001	Short-chain chlorinated paraffins (C10-C13)	-	GR 2B	-	CAT 1	CAT 1	
A1101	Chromium (Cr)	440	GR 3	-	CAT 1	CAT 2	Cr (7440-47-3) $CrCl_3$ (10025-73-7) Cr_2O_3 (1308-38-9) CrF_3 (7788-97-8) $CrCl_2$ (10049-05-5)
A1102	Hexavalent Chromium (Cr VI)	52	GR 1	CAT 2	CAT 1	CAT 1	CrO_3 (18540-29-9)
A1103	Manganese (Mn)	1330	-	CAT 1B	-	CAT 2	MnI_2 (7790-33-2) $MnCl_2$ (7773-01-5) Mn (7439-96-5) MnO (1344-43-0) Mn_2O_3 (1317-34-6) MnO_2 (1313-13-9)
A1104	Cobalt (Co)	202	GR 2B	CAT 1B	CAT 1	CAT 1	CoO (1307-96-6) $CoCl_2$ (7646-79-9) Co (7440-48-4) CoI_2 (15238-00-3) Co_3O_4 (1308-06-1) $CoBr_2$ (7789-43-7)
A1105	Nickel (Ni)	186	GR 1	CAT 1B	CAT 1	CAT 1	$NiCl_2$ (7718-54-9) Ni (7440-02-0) NiO (1313-99-1) NiI_2 (13462-90-3)

Table A.5. (continued)

A	Name	AC	CARC	REP	AC AQ	CHR AQ	Evaluated Compounds (CAS)
A1106	Copper (Cu)	336	-	-	CAT 1	CAT 1	CuCl (7758-89-6) Cu (7440-50-8) CuBr (7787-70-4) CuO (1317-38-0) CuI (7681-65-4) $CuBr_2$ (7789-45-9) $CuCl_2$ (7447-39-4) Cu_2O (1317-39-1)
A1107	Zinc (Zn)	350	GR 3	-	CAT 1	CAT 1	$ZnCl_2$ (7646-85-7) ZnF_2 (7783-49-5) Zn (7440-66-6) ZnO (1314-13-2) $ZnBr_2$ (7699-45-8) ZnI_2 (10139-47-6)
A1108	Arsenic (As)	8	GR 1	-	CAT 1	CAT 1	As_2O_5 (1303-28-2) As (7440-38-2) As_2O_3 (1327-53-3) $AsCl_3$ (7784-34-1) AsI_3 (7784-45-4)
A1109	Cadmium (Cd)	107	GR 1	CAT 1B	CAT 1	CAT 1	$CdCl_2$ (10108-64-2) Cd (7440-43-9) CdO (1306-19-0) CdI_2 (7790-80-9)
A1110	Antimony (Sb)	525	GR 2B	-	-	CAT 2	Sb_2O_3 (1309-64-4) $SbCl_3$ (10025-91-9) Sb (7440-36-0) $SbCl_5$ (7647-18-9) Sb_2O_5 (1314-60-9) SbF_3 (7783-56-4) SbF_5 (7783-70-2) SbI_3 (7790-44-5)
A1111	Mercury(Hg)	18	GR 3	CAT 1B	CAT 1	CAT 1	Hg (7439-97-6) HgI_2 (7774-29-0) HgO (21908-53-2) $HgCl_2$ (7487-94-7) $HgBr_2$ (7789-47-1) Hg_2Cl_2 (10112-91-1)
A1112	Lead (Pb)	CAT 4	GR 2A	CAT 1A	CAT 1	CAT 1	$PbCl_2$ (7758-95-4) PbI_2 (10101-63-0) $PbBr_2$ (10031-22-8) Pb_3O_4 (1314-41-6) PbO (1317-36-8) PbO_2 (1309-60-0) Pb (7439-92-1) PbF_2 (7783-46-2)
A1201	Cyanide	4.7	-	-	CAT 1	CAT 1	NaCN (143-33-9)