

1 **Assessment of the Water Chemical Quality Improvement based on Human Health**  
2 **Risk Indexes: application to in Drinking Water Treatment Plants incorporating**  
3 **membrane technologies**

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17 **ABSTRACT**

18  
19 A methodology has been developed in order to evaluate the potential risk of drinking  
20 water for the health of the consumers. The methodology used for the assessment  
21 considers systemic and carcinogenic effects caused by oral ingestion of water based on  
22 the reference data developed by the World Health Organization (WHO) and the Risk  
23 Assessment Information System (RAIS) for chemical contaminants. The exposure  
24 includes a hypothetical dose received by drinking this water according to the analysed  
25 contaminants. The assessment of the chemical quality improvement of produced water  
26 in the Drinking Water Treatment Plant (DWTP) after integration of membrane  
27 technologies using human health risk indexes has been performed.

28  
29 Series of concentration values covering up to 261 chemical parameters during 5 years  
30 (2008-2012) of raw and treated water in the Sant Joan Despi DWTP, at the low part of  
31 the Llobregat River basin (NE Spain), have been used. After the application of the  
32 methodology, resulting global indexes are located below the thresholds except for  
33 carcinogenic risk in the output of DWTP, where the index is slightly above the  
34 threshold during 2008 and 2009 before the upgrade of the treatment works with  
35 membrane technologies was executed. Annual evolution of global indexes shows a  
36 decrease on the global values for all situations: H<sub>Q</sub> systemic index based on RAIS  
37 descends from 0.64 to 0.42 for surface water and from 0.61 to 0.31 for drinking water;  
38 R carcinogenic index based on RAIS is negligible for input water and varies from  
39  $4.2 \times 10^{-05}$  to  $7.4 \times 10^{-06}$  for drinking water; W systemic index based on WHO moves from  
40 0.41 to 0.16 for surface water and from 0.61 to 0.31 for drinking water. A specific  
41 analysis for the indexes associated to trihalomethanes (THMs) shows the same pattern.  
42 Those indexes have been presented as a tool to show the improvement of the produced  
43 water, especially after the year 2009 where the ultrafiltration (UF) and reverse osmosis  
44 (RO) membrane technologies were installed.

45  
46 **KEYWORDS**

47  
48 Human health risk assessment; Global risk indexes; Membrane technologies; Llobregat  
49 River; Trihalomethanes

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## HIGHLIGHTS

- Indexes based on health risk assessment for the treatment of surface water (Llobregat river) to drinking water have been designed
- Annual evolution of indexes shows a decrease on the global index for all situations
- An upgrade in the water treatment is specially remarkable to improve the carcinogenic risk index for drinking water

## 1. INTRODUCTION

In developed countries, a wide implementation of water treating technologies and a proper management has led to a remarkable reduction of the risks associated to water ingestion. Good practices have led to a decrease of the pollution in origin and to a better removal of the contaminants. In the European Union (EU) the Drinking Water Directive (98/83/EC) concerns the quality of water intended for human consumption. According to this legislation, a total of 48 microbiological, chemical and indicator parameters must be monitored and tested regularly. Nevertheless, the list of contaminants that should be taken into account is continuously growing as the studies to define the effects on health are progressing.

Water safety plans are considered by the World Health Organization (WHO) as the most effective means of maintaining a safe supply of drinking water to the public. Hazards and risks should be identified, and appropriate steps towards minimizing these risks are then investigated (WHO, 2005). Additionally, the incidence of global driving forces, including climate change, increasing water scarcity, population growth, demographic changes and urbanization are expected to affect the resilience of water supply and sanitation systems and services, forcing also managers to adapt their infrastructures to these driving forces (Guha-Sapir et al., 2011).

Membrane technologies have been identified as the most robust and flexible technologies used to improve water quality and taste by removing undesirable compounds and pathogens (Rahardianto et al., 2007; Reverberi and Gorenflo, 2007). Reverse osmosis (RO), nanofiltration (NF) and reverse electrodialysis (RED) are being applied worldwide to meet these needs (Birnhack and Lahav, 2007; Greenlee et al., 2009; Wang et al., 2006). The selection of a suitable membrane technology is based on technical criteria (removal of contaminants) and economic aspects (capital operation and maintenance). Implementation of new technologies in drinking water treatment plants (DWTP), as membrane technologies, improves quality of potable water as remove toxic contaminants and reduces human health risk associated to its consumption.

However, it should be stressed that in order to ensure the minimization of pathogens the required treatment generates disinfection by-products (DBPs), one of the main drawbacks of the drinking water production. Those compounds are produced by the reaction between chemical disinfectants and naturally occurring organic material in the source water (Boorman et al., 1999; Krasner, 2009). The trihalomethanes (THMs), the most abundant DBPs, are human carcinogens according to the WHO (2005). From January 1<sup>st</sup> 2009, a limit of total THMs of 100 µgL<sup>-1</sup> is established in the EU

100 (98/83/EC). Although values have been established for a number of DBPs, risks  
101 associated with an inadequate disinfection are far greater than potential risks from long-  
102 term exposure to DBPs (WHO, 2014).

103  
104 It is widely accepted that all stakeholders responsible for water safety should place  
105 efforts in improving risk management and risk communication to the consumers, that is,  
106 the provision of information and health-based assessments on the various microbial,  
107 chemical, radiological and physical human health hazards that may be present in the  
108 water cycle. Evaluation of existing and emerging hazards in water should include a  
109 proper monitoring at source, after treated and along the distribution network for  
110 reducing the risks and a proper approach to manage those associated risks.

111  
112 Assessing exposure and the health consequences of chemicals in drinking water is  
113 challenging: exposures are typically at low concentrations, measurements in water are  
114 frequently insufficient, chemicals are present in mixtures, exposure periods are usually  
115 long, multiple exposure routes may be involved, and valid biomarkers reflecting the  
116 relevant exposure period are scarce. In addition, the magnitude of the relative risks  
117 tends to be small (Villanueva et al., 2013). Studies to assess the exposure of  
118 contaminants due to drinking water ingestion detected values of arsenic and THMs  
119 above the threshold in Turkey (Caylak, 2012) and perfluorooctane sulfonate (PFOS) in  
120 Taiwan (Chimeddulam and Wu, 2013). Industrial contamination led to high risk indexes  
121 due to metals in India (Krishna and Mohan, 2014) and Pakistan (Muhammad et al.,  
122 2011). Studies in developed countries are more oriented to emerging compounds but  
123 they are limited to the availability of reference data. Risk of adverse health effects of  
124 pharmaceuticals appeared to be negligibly low in the Netherlands (Houtman et al.,  
125 2014). Schriks (2010) concluded that the majority of the compounds evaluated pose  
126 individually no appreciable concern to human health in the Rhine and Meuse Rivers.  
127 Ribera (2014) used a combination of Life Cycle Assessment (LCA) and human health  
128 risk assessment in order to select the percentage of water in DWTPs that should be  
129 nanofiltered. Results show a reduction of one order of magnitude for the carcinogenic  
130 risk index when NF produces 100% of drinking water when is compared to the direct  
131 consumption without treatment.

132  
133 In this work, a methodology to determine the evolution of the chemical hazard of water  
134 has been developed. Additionally, an assessment is included on how this risk has been  
135 impacted after the implementation of the new treatment processes. The methodology is  
136 supported on toxic effects assessment, exposure assessment and risk indexes  
137 characterization (Durham and Swenberg, 2013). The exposure assessment in the present  
138 work only considers ingestion of drinking water containing pollutants through oral route  
139 as unique pathway and two typologies of effects on the human health have been  
140 considered: a) systemic toxicity that refers to adverse effects on any organ system  
141 following absorption and distribution of a chemical throughout the body; and b)  
142 carcinogenic effects.

143  
144 A set of water quality data registered during five years from the DWTP monitoring  
145 program has been used to implement the risk assessment methodology. The results  
146 obtained will be used to quantify numerically the improvement of the water quality by  
147 the use of risk indexes. This study should contribute to develop new managing  
148 practices based, not only on the occurrence, but also on the potential hazard of the  
149 chemical contaminants.

## 2. MATERIALS AND METHODS

### 2.1. Case study description: Llobregat River and Sant Joan Despí DWTP

In recent decades, the drinking water supply network of the Barcelona Metropolitan Area (BMA), 635 km<sup>2</sup> and a population of 4.5 million inhabitants, has been primarily based on surface water resources from the Llobregat and Ter Rivers. Those resources are suffering the effects of mining and industrial discharges, as well as a reduction in quantity, decreasing the quality of the raw water. Additionally, due to the Mediterranean climate, the natural water resource availability is periodically lower than the water demand in the area (López-Roldán et al., 2013).

To improve the water quality of the Llobregat River and its tributaries, more than 30 waste water treatment plants (WWTPs) treating a mixture of urban and industrial wastewaters have been set up along the river. The main industries sited along the Llobregat River are tannery, food products, textile, pulp and paper industries, discharging a broad spectrum of organic chemicals into the river. Therefore the river receives effluents from these WWTPs and surface runoff from agricultural areas. The removal of contaminants by WWTPs is not complete; consequently they can enter into environment via sewage effluents and thus become a potential risk to the receiving bodies and in addition, to the production of drinking water (González et al., 2012; Köck-Schulmeyer et al., 2011; Valero and Arbós, 2010).

Sant Joan Despí DWTP treats water from the Llobregat River following the process flow-sheet described in Figure 1. The plant has a maximum treatment capacity of 5.5 m<sup>3</sup>s<sup>-1</sup>, and provides almost 50% of the annual drinking water in the BMA. In 2009, an improved treatment line began its operation. The new process uses membrane technology and treats 50% of the water flow with a pre-treatment via micro-coagulation and ultrafiltration (UF) as protection for the RO step. Water is remineralised before being blended with water from the conventional treatment and sent to the post-chlorination stages. This process, the membrane treatment line according to Figure 1, is placed after the sand bed filtration where the flow is split and 50% is treated with the new process; the remaining 50% will undergo ozonisation and granular activated carbon (GAC) filtration as before.

### 2.2. Chemical data quality collection and management

The Llobregat River has been object of several studies dealing with the presence of contaminants in surface water and related compartments (e.g. sediments, fishes). In this article only compounds detected in the water matrix are taken into account. Most of these studies focus on the lower and medium part of the river basin, where most of WWTPs, DWTPs and population are located, and therefore, it is the area with higher pressures. Pesticides, surfactants, estrogens, pharmaceuticals and personal care products (PPCPs) and even abuse drugs are the main groups detected in different studies, reporting alterations in species composition, abundance or biomass and endocrine disruption measured by alterations in enzymatic activity or specific protein production (González et al., 2012). Nevertheless, a long list of these compounds is not monitored routinely. The lack of data on their presence and their toxicity makes difficult to include them in risk assessment studies on a large time basis. Table 1 provides a list of the chemical compounds routinely monitored by the Sant Joan Despí DWTP in the year

200 2012. The selection of the parameters to be analysed is done because of the legislation  
201 requirements, local characteristics, occurrence according to historical data and  
202 assessment of the efficiency of treatment technologies, among other causes.

203  
204 Series of data covering monthly averages of 261 chemical parameters during 5 years  
205 (2008-2012) of raw and treated water in Sant Joan Despí DWTP have been used. Not all  
206 parameters were measured along the five years, as monitoring programmes have been  
207 periodically adapted. Moreover, some compounds are only measured in surface water  
208 while other compounds are only measured in drinking water.

### 209 **2.3. Fundamentals of the risk assessment methodology**

210  
211 Chemicals that display environmental and biological persistence, bioaccumulation,  
212 toxicity and long range transport have been previously assessed quantitatively by  
213 national and international health agencies (Szabo and Loccisano, 2012). Among the  
214 databases that offer information on the toxicity of the compounds that can be found in  
215 water, two of the most widely used are the Risk Assessment Information System  
216 (RAIS) and the WHO guidelines (WHO, 2011).

217  
218 RAIS uses the Reference Dose (RfD), expressed as an oral dose per kilogram of body  
219 weight (given in units of  $\text{mgKg}^{-1}\text{day}^{-1}$ ), as an estimate of the lowest daily human  
220 exposure that is likely to occur without appreciable risk of deleterious, non-cancerous  
221 effects during a lifetime. WHO proposes a very similar reference value called the  
222 Tolerable Daily Intake (TDI) as an estimate of the amount of a substance in food or  
223 drinking-water, also expressed on a body weight basis that can be ingested daily over a  
224 lifetime without appreciable health risk (WHO, 1991). The TDI values take into account  
225 both systemic and carcinogenic effects but risk index is calculated as systemic.

226  
227  
228 The exposure assessment of this work only considers ingestion of drinking water  
229 containing pollutants through oral route as unique pathway. The oral dose for each  
230 contaminant present in water have been calculated by eq 1:

$$231 \quad D_i = \frac{C_w \times EF \times ED \times IR_w}{BW \times AT \times 365 \text{ days/year}} \quad (\text{eq 1})$$

232  
233 where  $D_i$  represents the dose of contaminant by water ingestion ( $\text{mg Kg}^{-1}\text{day}^{-1}$ ),  $C_w$  is  
234 the annual average concentration of the contaminant in water annual average ( $\text{mgL}^{-1}$ ),  
235 EF is the exposure frequency to the contaminated media ( $\text{days year}^{-1}$ ), ED is the  
236 exposure duration (year),  $IR_w$  is the rate of water intake ( $\text{L day}^{-1}$ ), BW is the body  
237 weight of the receptor (Kg), and AT is the average time (year).

238  
239 Table 2 shows the exposure values for the pathway of oral ingestion of water according  
240 to RAIS and WHO for the calculation of doses. For systemic risk  $D_i$  is calculated by  
241 using  $AT=ED$ . Then, three different indexes (systemic and carcinogenic for RAIS and  
242 an index for WHO) have been calculated:

243  
244 a) the systemic effect index according to RAIS ( $H_{Qi}$ ) is calculated on the dose basis  
245 according to RAIS reference values as a ratio between the dose (D) and the dose  
246 reference level (RfD) by eq 2:  
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249  $H_{Qi} = \frac{D_i}{RfD_i}$  (eq 2)

250

251 where the ratio of the average daily dose to a RfD below 1 implies that adverse effects  
252 are very unlikely to occur. The guideline values were calculated separately considering  
253 the risk for individual substances, without specific consideration of additivity. Although  
254 it may result in risk underestimations, unless there is evidence to the contrary, it is  
255 appropriate to assume that the toxic effects of these compounds are additive (Backhaus  
256 and Faust, 2012). Thus, a global systemic effect is obtained as contribution of the  
257 individual index values by eq 3:

258

259  $H_Q = \sum H_{Qi}$  (eq 3)

260

261 If  $H_Q$  is below 1 it implies that adverse effects are very unlikely to occur.

262

263 b) The individual carcinogenic effects are only considered in RAIS approach and the  
264 individual carcinogenic effect index ( $R_i$ ) is calculated by eq 4:

265

266  $R_i = D'_i \times SF_i$  (eq 4)

267

268 where SF is the Slope Factor (Kg day mg<sup>-1</sup>) that express a linear relationship of  $D_i$   
269 versus the risk  $R_i$  at low doses. Cancer risk is calculated by multiplying the estimated  
270 dose or exposure level by the appropriate measure of carcinogenic potency. A guideline  
271 value of 10<sup>-5</sup> means one additional cancer case per 100 000 of the population ingesting  
272 drinking-water containing the substance at the guideline value for 70 years (Cothorn et  
273 al., 1986). Following the principle of additivity of compounds, the global risk index for  
274 all compounds is calculated as an addition of individual risk indexes by eq 5:

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276  $R = \sum R_i$  (eq 5)

277

278 c) the individual WHO (W) index is developed by using eq 6.

279

280  $W_i = \frac{D_i}{TDI_i}$  (eq 6)

281

282 And then, the global risk index for all compounds is calculated as an addition of  
283 individual risk indexes by eq 7:

284

285  $W = \sum W_i$  (eq 7)

286

287

## 288 **2.4. Contaminant concentrations data treatment and filtering of raw data**

289

290 A tool was created and validated using Microsoft Excel® programme for the calculation  
291 of risk indexes according to RAIS and WHO toxicity values and doses (eq 1) for the list  
292 of compounds by using eq 2-7. The tool was programmed to determine annual average  
293 concentration of the compounds. Values representing the limit of quantitation (LOQ)  
294 for each compound were also introduced so the tool was able to discriminate between  
295 measured values and values below LOQ. Blank cells are automatically recognised as  
296 not measured parameters in the data analysis.

297

298 The scheme in Figure 2 has been followed in order to assess the risk related to the  
299 compounds present in water and incorporates filtering steps to obtain reliable risk  
300 indexes mentioned previously. When dealing with raw data concentrations in the  
301 calculation of indexes, three main issues were identified and, consequently, filtering  
302 steps were applied:

303  
304 a) The lack of existence of oral toxicity data for each contaminant. The methodology is  
305 based on risk approach, so the contaminants without toxicity values given by RAIS or  
306 WHO were excluded from index calculations. The comparison of measured  
307 contaminants with levels present in the Directive 98/83/EC is a first step that could  
308 determine the risk when toxicity is not available.

309  
310 b) Annual average concentrations were calculated with a mixture of values below the  
311 LOQ and quantified values. The election of LOQ/2 is usually applied and solves the  
312 uncertainty of a concentration that could be between zero and LOQ but, at the same  
313 time, introduces an uncertainty that has to be considered, as could lead to an  
314 overestimation of the risk (James et al., 2009). In order to have an idea of this  
315 uncertainty for the annual average values, an uncertainty index “U” has been calculated  
316 by using eq 8.

317  
318 
$$U = 1 - \frac{Avg(0)}{Avg(LOQ/2)} \quad (\text{eq 8})$$

319  
320 where Avg(0) is the average concentration when all the values below LOQ are  
321 considered as zero and Avg(LOQ/2) is the average concentration when all the values  
322 below LOQ are considered as LOQ/2. This U index is 1 if all the values are below LOQ  
323 (maximum uncertainty) and 0 if all the values are higher than LOQ (minimum  
324 uncertainty). U index will be useful to evaluate the uncertainty of final global indexes.

325  
326 c) Goodness of the analytical techniques for the sensitive measurement of risk indexes.  
327 It could happen that some analytical techniques are focused on the detection of  
328 contaminants just below the legislative values and are not sensitive enough to calculate  
329 the contribution of the contaminants to risk assessment when present at very low  
330 concentrations. Thus, an important role of the analytical techniques applied to risk  
331 indexes calculation would be to provide LOQ values able to quantify small amounts of  
332 risk.

333  
334 In order to decide which analytical techniques are sensitive enough to measure the risk  
335 properly, the calculation of the risk indexes by using LOQ levels was performed.  
336 Parameters giving values of individual indexes, based on LOQ, below a threshold (0.02  
337 for systemic risk according to RAIS, 0.01 for systemic risk according to WHO and  $5 \times 10^{-7}$   
338 for carcinogenic risk) will be included in the index. For the excluded parameters, risk  
339 assessment should be performed by comparing the annual average concentration with  
340 the limits recognised by legislation, as those thresholds have been also calculated on the  
341 basis of risk to human health studies.

342  
343 Some extra calculations have been programmed so aggregate indexes are easily  
344 calculated taking into account some variables e.g. compounds measured at the inlet  
345 during the five years and compounds measured at the outlet during the five years. The  
346 figures showing the evolution of the final indexes have been programmed and they are

347 automatically updated. The Excel tool has facilitated the index calculations based on a  
348 significant number of data and can be easily adapted to new input data.

349

### 350 **3. RESULTS**

351

#### 352 **3.1. Analysis of water quality improvement in the DWTP**

353

354 Analysis of the annual evolution, from 2008 to 2012, of the average concentrations of  
355 the contaminants is collected in Table 3 and Table 4. Only parameters at the inlet and  
356 the outlet that have routinely measured during the five years have been included. As it  
357 could be seen, the surface water quality of the inlet water works (Table 3) have  
358 improved over the years for most of the parameters, except for arsenic, barium,  
359 cyanides, chromium, selenium, tetrachloroethene and tungsten. Other compounds like  
360 boron, calcium, strontium, magnesium, nitrates and sulphates remain constant.

361

362 In the case of the outlet concentrations (Table 4), a reduction of the contaminants levels  
363 could be seen for all the compounds except for chlorates and chromium. This reduction  
364 can be explained mainly by the introduction of the RO step where at least 50% of the  
365 total waterworks capacity is treated. When the evolution of the DBPs concentrations is  
366 analysed, a reduction of 89% has been achieved for total THMs. It should also be taken  
367 into account that the DWTP is applying disinfection by using chlorine up to 2010 and  
368 by using chlorine dioxide from 2010, which is the main responsible for the formation of  
369 chlorinated DBPs. However, the presence of bromide and iodide acts as precursors for  
370 the formation of brominated and iodinated DBPs. Additionally, and due to the use of an  
371 ozonisation step, the formation of bromates from bromide occurred. The introduction of  
372 the membrane treatment unit has improved the quality and in terms of the reduction of  
373 the high salinity (ca. 0.9 g TDSL<sup>-1</sup>), the DBPs precursors and the DBPs themselves so  
374 the total content of THMs below 100 µgL<sup>-1</sup> is easily accomplished from 2009.

375

376 The increase on the chlorate content should be attributed to the substitution of the initial  
377 chlorination steps of the treatment by using chlorine dioxide instead of chlorine.  
378 Chlorate and chlorites are disinfection by products of the use of chlorine dioxide. In the  
379 case of chromium (VI) the increase is due to the contribution of a groundwater pollution  
380 plume generated by electroplating industries, for more than 30 years, at industrial areas  
381 of the Llobregat Delta. The seasonal recharge of this plume onto surface water provides  
382 the detected peaks, always below the limits fixed by the regulation (10 µgL<sup>-1</sup>).

383

#### 384 **3.2. Risk indexes comparison of raw and treated water**

385

386 Global indexes for systemic risk according to RAIS and WHO reference values and  
387 carcinogenic risk based on RAIS reference data are shown at Table 5. The global risks  
388 indexes have been calculated by addition of the individual ones. For the calculation of  
389 the global indexes, only the compounds that have been measured during the five years  
390 at the surface water (inlet) on one side, and the compounds measured for the five years  
391 at the treated water (outlet) on the other side, have been included in order to obtain  
392 comparable global indexes.

393

394 A list of compounds is not included in the global index due to the filtering steps  
395 performed, due to the unavailability of reference data or to the low sensitivity of the  
396 analytical technique. In case they are excluded, annual average concentrations are



397 compared to the thresholds established at Directive 98/83/EC. Table 6, Table 7 and  
398 Table 8 shows the concentrations of those parameters for the outlet water in the  
399 calculation of  $H_Q$ ,  $R$  and  $W$ . Only free chlorine (2008-2009), chlorides (2008-2009) and  
400 sodium (2008) show levels above Directive reference values.

401  
402 Figure 3 shows the annual evolution of the global indexes. Thresholds for the three  
403 types of indexes have also been included ( $H_Q < 1$ ;  $R < 10^{-5}$ ;  $W < 1$ ). It should be highlighted  
404 that, although the thresholds have been designed for individual parameters, they are  
405 being applied in this methodology to the global risk values. Annual evolution of indexes  
406 shows a decrease on the global risk for all situations. The biggest reduction can be seen  
407 after the first year, 2008, where a severe drought took place. The low average river flow  
408 in 2008 ( $8.12 \text{ m}^3\text{s}^{-1}$  compared to  $12.83 \text{ m}^3\text{s}^{-1}$  in 2009) may be associated to higher  
409 average concentrations of pollutants and, therefore, an increase of the risk indexes.

410  
411 From the methodology developed it is also possible to identify the main contaminants  
412 contributing to risk. Lists for the top 10 compounds contributing to every risk index for  
413 the year 2012 are shown in Table 9.  $U$  indexes shows the uncertainty related to the  
414 calculation of the individual risks. The closer  $U$  is to 1, the higher the uncertainty of the  
415 value of the annual concentration used for the risk calculation. The compounds posing  
416 major risk shows  $U$  close to 0, except for carcinogenic risk at the inlet that is based on  
417 compounds not found ( $U=1$ ), but global index shows acceptable risk.

418  
419 For systemic risk according to RAIS reference values,  $H_Q$ , the compounds posing a  
420 major risk at the inlet are nitrates and nitrites. Nitrates are found at high concentrations  
421 and the main risk is linked to their potential of becoming nitrites. Some other  
422 compounds like bromates, strontium, boron, barium and nickel are also contributing  
423 considerably to the global risk. At the outlet, boron and the halogenated  
424 chlorodibromomethane, bromoform, trichloroethene and 1,1,2-trichloroethane appears at  
425 the highest position in the list along with the former ones. Some other compounds like  
426 the fluorides, free chlorine and metals like thallium, lithium and chromium (VI) and  
427 non-metals as arsenic and antimony do not contribute to the global index calculation as  
428 the techniques for performing the analysis have been regarded as not sensitive enough.  
429 Thus indicates that LOQs should be improved so they can be included in the global risk  
430 assessment.

431  
432 The situation according to the systemic risk index based on WHO values,  $W$ , is not so  
433 different to the index based on RAIS values,  $H_Q$ , regarding the compounds showing the  
434 highest contribution to the global index. In this case, the filter has only excluded the  
435 pesticide atrazine for the inlet plus free chlorine, chlorates and chlorites in drinking  
436 water.

437  
438 For carcinogenic risk,  $R$ , no compounds have a significant risk at the inlet, and values  
439 are two order of magnitude below the threshold. Risk is higher at the outlet as DBPs can  
440 only be found at the treated water. Compounds like bromates, chromium and arsenic are  
441 discarded for contributing to the risk in a big extent due to their high LOQs but were  
442 below the values established at the Directive 98/83/CE. At the outlet, legislated THMs  
443 and 1,1,2-Trichloroethane have the maximum contribution to the general added risk. A  
444 reduction in the risk is especially remarkable beyond 2009. This improvement is  
445 associated to the implementation of the RO treatment step, where it expected a  
446 reduction of the concentrations of the DBPs precursors (bromide, iodide and dissolved

447 organic matter) and also a reduction of the DBP concentration formed in the  
448 chlorination step before coagulation (see Figure 1). This reduction is exemplified at  
449 Figure 4 where the evolution of the levels of THMs is shown.

450

### 451 **3.3. Contribution of disinfection by-products on risk indexes**

452

453 A special analysis has been done to disinfection by-products at drinking water. The four  
454 THM's included in the legislation (bromoform, bromodichloromethane,  
455 dibromochloromethane, chloroform) are some of the top-ranking compounds in  
456 contributing to the global carcinogenic risk. Figure 4 shows the decrease of risk over  
457 time due mainly to a reduction of the concentration of THMs. It should be stated that  
458 for the four regulated THMs, U is equal to 0, showing no uncertainty in the risk  
459 calculations as the compounds are always quantified above their LOQs.

460

461 This reduction can be explained by two main factors: the upgrade of the treatment line  
462 by inclusion of the RO desalination treatment in 2009 and the substitution of chlorine  
463 by chlorine dioxide with a weaker oxidation potential, and then, with a lower capacity  
464 for formation of DBPs. The introduction of a desalination step treating 50% of the in-let  
465 flow rate is reducing the concentration of the DBPs precursors, both inorganic species  
466 as bromide and iodide, and organic species, mainly dissolved organic matter (natural  
467 and non natural). The reduction of the DBP concentrations up to four times could only  
468 be explained by the combination of both changes on the treatment line.

469

### 470 **3.4. Risk indexes methodology advantages and constraints.**

471

472 The main advantage of these calculations is related to the fact that they are based on  
473 three accepted approaches on the assessment of health risks, differentiating between  
474 systemic and carcinogenic risk. Those indexes are considering all measured parameters  
475 even if the monthly average concentrations are below the LOQ. The obtained indexes  
476 can be recalculated as long as new substances are analyzed and WHO or RAIS is  
477 recognizing new toxicity values.

478

479 But as those global indexes integrate individual values of specific pollutants, it is  
480 noticeable that final risk values would increase as new parameters are measured, even if  
481 the results of the analytics are below the quantification limit. In order to cope with this  
482 problem, it is important to establish filters so substances presenting high-risk values  
483 when concentrations are below quantification limits do not overestimate global health  
484 risks.

485

486 Series of data show some limitations when the methodology is applied. Monthly  
487 averages are calculated on the base of different frequency of measurements depending  
488 on the specific parameter, so the number of analysis and the time where they were  
489 performed can have an influence on the results. Additionally, not the same list of  
490 parameters has been registered during the 5 years. In order to be able to perform an  
491 annual comparison, global indexes only includes the parameters that have been  
492 measured during the five years covered in the study.

493

494 Analytical techniques have their own constraints as no concentration values can be  
495 reported under LOQ. This LOQ is not only dependent on the technique, but on the  
496 specific compound, water matrix, and the methodology applied for the analytical

497 measurements. Due to some facts like the replacement of the instruments and the  
498 criteria for the calculation and acceptance of these limits, an evolution of LOQs can also  
499 be observed, making more difficult the interannual comparison.

501 Another issue to be faced is presented when trying to assess the risk of produced water  
502 in comparison with raw water at the inlet of a DWTP. This analysis can be interesting  
503 when evaluating the performance of the treatment technologies in removing certain  
504 substances. The difficulties arise when some analytes are only measured in one of the  
505 water streams as their presence is not expected in the outlet, due to the optimum  
506 removal efficiency, or in the inlet, due to their production as result of the treatment of  
507 the water flow, e.g. DBPs. The differences in the list of compounds analysed and a  
508 change in the limit of quantification, due to the analysis in different water matrixes,  
509 pose an additional difficulty in the assessment.

#### 511 4. CONCLUSIONS

512  
513 A methodology has been developed in order to assess globally the chemical risk of  
514 drinking water and its source water. Indexes have been created including those  
515 parameters that have passed all the quality filters (existence of reference toxicological  
516 values and concentration measured with a sensitive analytical technique). The average  
517 concentration of the parameters that were excluded from the hazard indexes has been  
518 compared to the threshold established at the legislation.

519  
520 The annual evolution of the global indexes at the intake and the outlet of a DWTP has  
521 reported a continuous decrease of the toxicity from 2008 to 2012. After the application  
522 of the methodology, resulting global indexes are located below the thresholds except for  
523 carcinogenic risk in the output of the DWTP, where the index is slightly above the  
524 threshold during 2008 and 2009 before the upgrade of the treatment works with  
525 membrane technologies. Annual evolution of indexes shows a decrease on the global  
526 values for all situations: H<sub>Q</sub> systemic index based on RAIS descends from 0.64 to 0.42  
527 for surface water and from 0.61 to 0.31 for drinking water; R carcinogenic index based  
528 on RAIS is negligible for input water and varies from  $4.2 \times 10^{-05}$  to  $7.4 \times 10^{-06}$  for drinking  
529 water; W systemic index based on WHO moves from 0.41 to 0.16 for surface water and  
530 from 0.61 to 0.31 for drinking water. A specific analysis for the indexes associated to  
531 trihalomethanes (THMs) shows the same pattern.

532  
533 Form the second group of parameters, not included in the calculation of the indexes,  
534 only free chlorine and chlorides at 2008 and 2009, and sodium at 2009 showed average  
535 concentrations slightly above the threshold for drinking water.

536  
537 Although risk indexes have been calculated in order to help the decision of the  
538 stakeholders in charge of water treatment works and administrations dealing with health  
539 issues, it is important not to forget that legislation (e.g. Directive 98/83/EC in Europe) is  
540 the main reference when assessing the compliance of water quality to health standards.  
541 Those indexes have been presented as a tool to show the improvement of the produced  
542 water, especially after the year 2009 where the UF and RO membrane technologies  
543 where installed.

544  
545 The methodology developed in the form of risk indexes has included more parameters  
546 than the existing in the legislation to provide a tool based on risk assessment and not

547 only on the concentration of legislated parameters. Those indexes take into account  
548 different effects (systemic and carcinogenic) and are based on reference values given by  
549 international organizations taken into account oral ingestion doses. Indexes developed  
550 provide a quantification of the quality improvement that could be integrated with Life  
551 Cycle Assessment (LCA) and Life Cycles Costing (LCC) analysis.

552

553 To summarize, the methodology introduced is able to estimate the risk reduction win  
554 when a change on the treatment line is introduced and could be used to estimate  
555 potential health benefits for such investment.

556

557

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559

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563

564

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**Table 1. Chemical parameters routinely monitored at the Sant Joan Despí DWTP (surface water and produced drinking water) in 2012**

Parameter	Frequency inlet measurements	Frequency outlet measurements	Parameter	Frequency inlet measurements	Frequency outlet measurements
1,1-dichloroethane	every 2 weeks	every week	Fluorides	every week	every month
1,1-dichloroethene	every year	every week	Free chlorine residual (in situ)	N/A	every hour
1,1,1-trichloroethane	every 2 weeks	every week	Gallium	every day	every day
1,1,1,2-tetrachloroethane	every year	every week	Geosmin	every 2 weeks	every 2 weeks
1,1,2-trichloroethane	every year	every week	Heptachlor	every week	every month
1,1,2,2-tetrachloroethane	every year	every week	Heptachlor epoxide	every week	every month
1,2-dibromoethane	every year	every week	Indene(1,2,3-c,d)pyrene	every week	every month
1,2-dichloroethane	every year	every week	Indium	every day	every day
1,2-dichloropropane	every year	every week	Iron	every day	every 8 hours
2-methylisoborneol	every 2 weeks	every 2 weeks	Lanthanum	every 2 weeks	every day
4,4'-DDD	every week	every month	Lead	every day	every day
4,4'-DDE	every week	every month	Lindane	every week	every month
4,4'-DDT	every week	every month	Lithium	every day	every day
Acenaphthene	every week	every month	m+p-Xylene	every 2 weeks	every month
Acenaphthylene	every week	every month	Magnesium	every day	every day
Alachlor	every week	every month	Malathion	every week	every month
Aldrin	every week	every month	Manganese	every day	every day
alpha-Endosulfan	every week	every month	Mercury	every week	every day
alpha-HCH	every week	every month	Methyl parathion	every week	every month
Aluminium	every day	every 8 hours	Metolachlor	every week	every month
Ametryne	every week	every month	Molinate	every week	every month
Ammonium	every 2 hours	every 12 hours	Molybdene	every day	every day
Anthracene	every week	every month	Naphthalene	every week	every month
Antimony	every day	every day	Nickel	every 4 hours	every day
Arsenic	every day	every day	Nitrates	every week	every month
Atrazine	every week	every month	Nitrites	every week	every month
Barium	every day	every day	Non-ionic tensioactives	every 2 weeks	N/A
Benzene	every 2 weeks	every month	o-Xylene	every 2 weeks	every month
Benzo(a)anthracene	every week	every month	Palladium	every day	every day
Benzo(a)pyrene	every week	every month	Parathion	every week	every month
Benzo(b)fluorantene	every week	every month	Pendimethalin	every week	every month
Benzo(g,h,i)perylene	every week	every month	Phenanthrene	every week	every month
Benzo(k)fluorantene	every week	every month	Phenols	every 2 weeks	N/A
Beryllium	every day	every day	Phosphorus	every day	every day
beta-Endosulfan	every week	every month	Pirimicarb	every week	every month
Bismuth	every day	every day	Potassium	every day	every day
Boron	every day	every day	Prometrine	every week	every month
Bromates	every week	every day	Propanil	every week	every month
Bromides	every day	every month	Propazine	every week	every month
Bromochloroacetoneitrile	N/A	every week	Pyrene	every week	every month
Bromoform	every year	every day	Rubidium	every day	every day
c-1,2-Dichloroethene	every year	every week	Selenium	every day	every day
c-1,3-Dichloropropene	every year	every week	Silicon	every day	every day
Cadmium	every day	every day	Silver	every day	every day
Calcium	every day	every 8 hours	Simazine	every week	every month
Cesium	every 2 months	every year	Sodium	every day	every day
Chlorates	N/A	every day	Strontium	every day	every day
Chlorfenvinphos	every week	every month	Sulfates	every day	every month
Chlorides	every day	every day	Sum 4 PAHs Dir. 98/83/CE	every week	every month
Chlorites	N/A	every day	Sum THMs Dir. 98/83/CE	every year	every month
Chlorodibromomethane	every year	every day	t-1,2-Dichloroethene	every year	every week
Chloroform	every year	every day	t-1,3-Dichloropropene	every year	every week
Chlorpyrifos	every week	every month	Terbutylazine	every week	every month
Chromium	every day	every day	Terbutryn	every week	every month
Chromium (VI)	every 4 hours	every 4 hours	Tetrachloride carbon	every year	every week
Chrysene	every week	every month	Tetrachloroethene	every 2 weeks	every week
Cobalt	every day	every day	Thallium	every day	every day
Copper	every day	every day	Tin	every day	every day
Cyanides	every 8 hours	every month	Tiobencarb	every week	every month
Diazinon	every week	every month	Titanium	every day	every day
Dibenzo(a,h)anthracene	every week	every month	Toluene	every 2 weeks	every month
Dibromoacetoneitrile	N/A	every week	Total Haloacetoneitriles	N/A	every week
Dichlobenil	every week	every month	Total Pesticides	every week	every month
Dichloroacetoneitrile	N/A	every week	Total Trihalomethanes	N/A	every day
Dichlorobromomethane	every year	every day	Trichloroacetoneitrile	N/A	every week
Dieldrin	every week	every month	Trichloroethene	every 2 weeks	every week
Endrin	every week	every month	Trichloroethene + Tetrach.	every 2 weeks	every week
Ethofumesate	every week	every month	Trifluralin	every week	every month
Ethylbenzene	every 2 weeks	every month	Tungsten	every day	every day
Fenitrothion	every week	every month	Uranium	every 2 months	every year
Fluoranthene	every week	every month	Vanadium	every day	every day
Fluorene	every week	every month	Zinc	every day	every day

662 **Table 2. Exposure parameters for oral ingestion of water according to RAIS and WHO**  
663  
664

Parameters	RAIS	WHO
EF(days year <sup>-1</sup> )	350	365
ED* (years)	24	-
IR (L day <sup>-1</sup> )	2	2
BW (kg)	70	60
AT* (years)	70	-

\*Sistemic risk: AT=ED

665



**Table 3. Annual average concentrations of the compounds at the inlet and its percentage of reduction in the year 2012 compared to 2008**

Parameter (inlet)	Units	2008		2009		2010		2011		2012		2008/2012 Reduction*
		Avg Conc	U	Avg Conc	U	Avg Conc	U	Avg Conc	U	Avg Conc	U	
Aluminium	µg/l	110,285	0,000	108,792	0,000	76,006	0,000	70,283	0,000	65,689	0,000	40%
Antimony	µg/l	1,386	0,030	0,864	0,289	0,500	1,000	0,750	1,000	0,750	1,000	100%
Arsenic	µg/l	0,838	0,298	0,816	0,358	0,927	0,225	1,024	0,488	1,851	0,068	-121%
Barium	µg/l	129,628	0,000	135,570	0,000	149,878	0,000	146,448	0,000	166,529	0,000	-28%
Boron	µg/l	198,792	0,000	154,549	0,000	175,617	0,000	196,130	0,000	211,309	0,000	-6%
Bromates	µg/l	16,584	0,014	6,432	0,034	2,173	0,072	2,500	1,000	2,500	1,000	100%
Bromides	mg/l	0,894	0,000	0,627	0,000	0,580	0,000	0,644	0,000	0,632	0,000	29%
Calcium	mg/l	110,442	0,000	110,509	0,000	112,958	0,000	109,647	0,000	106,272	0,000	4%
Cyanides	µg/l	0,542	0,846	0,500	1,000	0,500	1,000	0,815	0,460	3,905	0,320	-621%
Chlorides	mg/l	390,809	0,000	268,052	0,000	254,409	0,000	255,901	0,000	263,749	0,000	33%
Chromium	µg/l	2,125	0,343	1,512	0,689	1,926	0,379	1,846	0,395	2,487	0,293	-17%
Chromium (VI)	µg/l	4,067	0,461	2,924	0,712	3,374	0,556	2,712	0,845	2,723	0,842	33%
Diazinon	µg/l	0,034	0,009	0,024	0,066	0,031	0,081	0,056	0,028	0,006	0,410	82%
Strontium	mg/l	1,658	0,000	1,689	0,000	1,790	0,000	1,733	0,000	1,708	0,000	-3%
Iron	µg/l	61,401	0,000	55,864	0,000	57,235	0,000	47,908	0,000	50,766	0,000	17%
Phosphorus	µg/l	267,809	0,000	175,152	0,000	182,537	0,000	163,824	0,000	181,920	0,000	32%
Gallium	µg/l	1,370	0,836	1,250	1,000	1,250	1,000	1,250	1,000	1,250	1,000	100%
Geosmin	ng/l	9,492	0,077	1,250	1,000	2,500	1,000	3,727	0,610	8,250	0,253	13%
Lithium	µg/l	27,402	0,000	19,406	0,000	21,095	0,000	18,575	0,000	20,731	0,000	24%
Magnesium	mg/l	33,988	0,000	32,559	0,000	32,955	0,000	33,250	0,000	32,485	0,000	4%
Malathion	µg/l	0,006	0,573	0,004	1,000	0,004	1,000	0,004	1,000	0,004	1,000	100%
Manganese	µg/l	54,221	0,000	32,831	0,000	27,360	0,000	24,742	0,000	26,520	0,000	51%
Mercury	µg/l	0,059	0,000	0,018	0,487	0,014	0,805	0,014	0,837	0,014	0,812	76%
Molybdene	µg/l	2,100	0,020	1,457	0,029	1,521	0,000	1,383	0,000	1,400	0,030	33%
Nickel	µg/l	10,669	0,000	6,888	0,000	5,083	0,000	6,189	0,000	8,924	0,000	16%
Nitrates	mg/l	9,949	0,000	9,810	0,000	11,818	0,000	10,422	0,000	9,372	0,000	6%
Nitrites	mg/l	0,491	0,000	0,339	0,000	0,290	0,000	0,328	0,000	0,164	0,038	67%
Potassium	mg/l	37,768	0,000	26,167	0,000	24,248	0,000	26,619	0,000	29,519	0,000	22%
Rubidium	µg/l	30,274	0,017	13,611	0,230	21,171	0,049	9,978	0,365	12,261	0,127	59%
Selenium	µg/l	0,799	0,365	0,611	0,682	0,500	1,000	0,818	0,840	1,029	0,486	-29%
Silicon	mg/l	1,740	0,000	1,830	0,000	2,159	0,000	1,720	0,000	1,375	0,000	21%
Sodium	mg/l	199,810	0,000	142,642	0,000	133,269	0,000	144,095	0,000	147,260	0,000	26%
Sulphates	mg/l	170,747	0,000	167,688	0,000	176,347	0,000	170,975	0,000	164,838	0,000	3%
Thallium	µg/l	1,779	0,527	1,391	0,824	1,250	1,000	1,603	0,585	1,486	0,701	16%
Non-ionic tensioactives	mg/l	0,090	0,000	0,068	0,000	0,092	0,000	0,081	0,000	0,083	0,000	8%
Terbutylazine	µg/l	0,042	0,000	0,072	0,000	0,012	0,161	0,020	0,108	0,018	0,136	56%
Terbutryn	µg/l	0,007	0,796	0,005	0,665	0,004	1,000	0,004	0,795	0,004	1,000	100%
Tetrachloroethene	µg/l	0,138	0,264	0,260	0,022	0,125	1,000	0,145	0,788	0,156	0,735	-13%
Titanium	µg/l	1,938	0,000	1,837	0,023	1,232	0,135	1,745	0,072	1,608	0,078	17%
Total Pesticides	µg/l	0,150	0,764	0,125	1,000	0,141	0,815	0,141	0,007	0,020	0,063	87%
Vanadium	µg/l	2,388	0,000	1,492	0,056	1,295	0,064	1,137	0,073	1,002	0,166	58%
Tungsten	µg/l	2,241	0,232	1,495	0,697	1,368	0,838	1,837	0,397	3,332	0,031	-49%

\*Percentage of reduction of the concentration of the parameter comparing 2008 and 2012. 100% of reduction means that the concentration in 2012 has fallen below LOQ

**Table 4. Annual average concentrations of the compounds at the outlet and its percentage of reduction in the year 2012 compared to 2008**

Parameter (outlet)	Units	2008		2009		2010		2011		2012		2008/2012 Reduction*
		Avg Conc	U	Avg Conc	U	Avg Conc	U	Avg Conc	U	Avg Conc	U	
1,1,1-trichloroethane	µg/l	0,200	0,042	0,025	1,000	0,025	1,000	0,125	1,000	0,125	1,000	100%
1,1,2-trichloroethane	µg/l	3,857	0,001	0,397	0,026	1,117	0,000	1,939	0,000	2,265	0,009	41%
1,2-dichloroethane	µg/l	0,281	0,111	0,119	0,480	0,083	0,630	0,225	1,000	0,225	1,000	100%
Aluminium	µg/l	44,761	0,000	86,387	0,000	57,931	0,000	53,135	0,000	34,908	0,000	22%
Antimony	µg/l	0,564	0,812	0,551	0,831	0,500	1,000	0,750	1,000	0,750	1,000	100%
Silver	µg/l	0,669	0,560	0,500	1,000	0,500	1,000	0,750	1,000	0,750	1,000	100%
Barium	µg/l	54,383	0,000	52,663	0,000	36,219	0,000	31,276	0,000	31,261	0,000	43%
Boron	µg/l	195,303	0,000	129,547	0,000	154,589	0,000	137,830	0,000	147,601	0,000	24%
Bromates	µg/l	5,745	0,011	7,893	0,000	7,867	0,008	3,636	0,458	4,161	0,350	28%
Bromoform	µg/l	39,647	0,000	35,545	0,000	19,724	0,000	20,063	0,000	16,126	0,000	59%
Bromides	mg/l	0,136	0,123	0,216	0,029	0,165	0,076	0,097	0,107	0,074	0,198	46%
Calcium	mg/l	134,535	0,000	108,935	0,000	97,789	0,000	92,806	0,000	90,362	0,000	33%
Free chlorine residual (in situ)	mg/l	1,006	0,000	1,007	0,000	0,837	0,000	0,828	0,000	0,858	0,000	15%
Total chlorine residual (in situ)	mg/l	1,192	0,000	1,183	0,000	0,967	0,000	0,931	0,000	0,980	0,000	18%
Chlorates	µg/l	85,201	0,039	954,511	0,001	1012,222	0,000	857,978	0,000	822,752	0,000	-866%
Chlorites	µg/l	13,000	0,353	13,339	0,187	17,021	0,171	14,978	0,111	9,026	0,231	31%
Chlorodibromomethane	µg/l	28,842	0,000	19,148	0,000	6,204	0,000	4,891	0,000	4,277	0,000	85%
Chloroform	µg/l	9,373	0,000	6,023	0,000	0,483	0,000	0,745	0,000	0,619	0,000	93%
Chlorides	mg/l	414,610	0,000	280,842	0,000	186,797	0,000	179,581	0,000	183,703	0,000	56%
Cobalt	µg/l	0,625	0,667	0,500	1,000	0,500	1,000	0,500	1,000	0,500	1,000	100%
Chromium	µg/l	2,171	0,384	1,956	0,479	2,631	0,277	2,239	0,326	3,921	0,027	-81%
Chromium (VI)	µg/l	2,500	1,000	2,922	0,713	3,240	0,579	3,623	0,403	3,073	0,678	-23%
Dibromoacetonitrile	µg/l	0,281	0,119	0,050	1,000	0,102	0,287	0,050	1,000	0,089	0,469	68%
Dichlorobromomethane	µg/l	18,654	0,000	10,881	0,000	0,797	0,000	0,633	0,000	0,634	0,000	97%
Strontium	mg/l	1,852	0,000	1,626	0,000	1,226	0,000	1,098	0,000	1,103	0,000	40%
Ethylbenzene	µg/l	0,038	0,000	0,045	0,000	0,050	1,000	0,125	1,000	0,250	1,000	100%
Iron	µg/l	9,205	0,000	8,831	0,000	8,999	0,000	8,389	0,000	8,751	0,014	5%
Fluorides	mg/l	0,151	0,000	0,114	0,055	0,119	0,035	0,127	0,016	0,106	0,059	29%
Phosphorus	µg/l	24,928	0,017	13,242	0,063	10,617	0,196	11,174	0,149	13,343	0,094	46%
Lithium	µg/l	28,483	0,000	17,996	0,000	13,654	0,000	11,287	0,000	12,522	0,000	56%
m+p-Xylene	µg/l	0,071	0,000	0,052	0,000	0,050	1,000	0,250	1,000	0,500	1,000	100%
Magnesium	mg/l	43,063	0,000	31,344	0,000	24,860	0,000	22,281	0,000	23,147	0,000	46%
Manganese	µg/l	1,920	0,000	1,176	0,142	1,061	0,118	0,901	0,185	0,995	0,168	48%
Mercury	µg/l	0,046	0,045	0,014	0,794	0,013	1,000	0,013	1,000	0,013	1,000	100%
Molybdene	µg/l	1,104	0,189	0,975	0,214	0,500	1,000	0,846	0,246	0,636	0,589	42%
Nickel	µg/l	5,108	0,000	3,263	0,000	2,527	0,000	2,747	0,000	3,763	0,000	26%
Nitrates	mg/l	10,755	0,001	10,313	0,000	9,138	0,000	7,700	0,000	7,458	0,000	31%
Potassium	mg/l	34,802	0,000	23,162	0,000	16,988	0,000	17,182	0,000	19,175	0,000	45%
Rubidium	µg/l	18,471	0,056	9,556	0,436	8,933	0,525	8,302	0,565	7,398	0,704	60%
Selenium	µg/l	0,569	0,805	0,500	1,000	0,500	1,000	0,876	0,713	0,750	1,000	100%
Silicon	mg/l	2,507	0,000	1,643	0,000	1,463	0,000	1,169	0,000	1,249	0,000	50%
Sodium	mg/l	203,257	0,000	129,339	0,000	98,539	0,000	99,359	0,000	106,460	0,000	48%
Sulphates	mg/l	197,292	0,000	158,333	0,000	127,833	0,000	110,333	0,000	109,917	0,000	44%
Thallium	µg/l	1,446	0,793	1,406	0,815	1,250	1,000	1,474	0,707	1,474	0,706	-2%
Terbutylazine	µg/l	0,005	0,708	0,004	1,000	0,004	1,000	0,004	1,000	0,004	1,000	100%
Tetrachloroethene	µg/l	0,395	0,047	0,084	0,822	0,119	0,472	0,125	1,000	0,213	0,342	46%
Toluene	µg/l	0,063	0,000	0,093	0,000	0,080	0,573	0,250	1,000	0,250	1,000	100%
Total Haloacetonitriles	µg/l	0,414	0,242	0,150	1,000	0,243	0,360	0,150	1,000	0,188	0,733	55%
Total Trihalomethanes	µg/l	96,449	0,000	46,296	0,000	13,267	0,000	12,766	0,000	11,044	0,000	89%
Trichloroethene	µg/l	0,562	0,000	0,173	0,000	0,356	0,000	0,249	0,293	0,163	0,638	71%
Trichloroethene + Tetrachloroethene	µg/l	0,953	0,000	0,305	0,000	0,301	0,249	0,360	0,521	0,317	0,658	67%
Vanadium	µg/l	1,067	0,234	0,835	0,349	0,558	0,821	0,586	0,711	0,500	1,000	100%

\*Percentage of reduction of the concentration of the parameter comparing 2008 and 2012. 100% of reduction means that the concentration in 2012 has fallen below LOQ

**Table 5. Global risk indexes calculation for systemic risk according to RAIS reference values ( $H_Q$ ) and WHO values ( $W$ ) and carcinogenic risk ( $R$ )**

	Inlet			Outlet		
	$H_Q$	$R$	$W$	$H_Q$	$R$	$W$
2008	0,64	4,62E-07	0,41	0,61	4,21E-05	0,32
2009	0,50	4,51E-07	0,31	0,50	2,66E-05	0,25
2010	0,49	4,68E-07	0,30	0,41	8,18E-06	0,19
2011	0,47	5,11E-07	0,32	0,33	8,06E-06	0,17
2012	0,42	5,24E-07	0,16	0,31	7,40E-06	0,17

**Table 6. Annual averages of the compounds excluded from the H<sub>Q</sub> calculation when reference values from Directive 98/83/CE exist**

Parametre (excluded from H <sub>Q</sub> )	Unit	2008	2009	2010	2011	2012
Antimony	µg/l	0,564	0,551	0,500	0,750	0,750
Arsenic	µg/l	0,558	0,500	0,500	0,750	0,907
Bromates	µg/l	-	-	-	3,636	4,161
Free chlorine residual (in situ)	mg/l	1,006*	1,007*	0,837	0,828	0,858
Chlorides	mg/l	414,610*	280,842*	186,797	179,581	183,703
Chromium	µg/l	2,171	1,956	2,631	2,239	3,921
Fluorides	mg/l	0,151	0,114	0,119	0,127	0,106
Lindane	µg/l	0,006	0,004	0,004	0,004	0,004
Pirimicarb	µg/l	0,006	0,006	0,006	0,006	0,006
Sodium	mg/l	203,257*	129,339	98,539	99,359	106,460
Sulfates	mg/l	197,292	158,333	127,833	110,333	109,917
Terbutylazine	µg/l	0,005	0,004	0,004	0,004	0,004
Trichloroethene + Tetrachloroethene	µg/l	0,953	0,305	0,301	0,360	0,317

\*Average concentrations above the thresholds established at Directive 98/83/EC: free chlorine (1 mg/L), chlorides (250 mg/L) and sodium (200 mg/L)

**Table 7. Annual averages of the compounds excluded from the R calculation when reference values from Directive 98/83/CE exist**

Parametre (excluded from R)	Unit	2008	2009	2010	2011	2012
Aldrin	µg/l	0,004	0,004	0,004	0,004	0,004
alpha-Endosulfan	µg/l	0,006	0,004	0,004	0,004	0,005
Aluminium	µg/l	44,761	86,387	57,931	53,135	34,908
Ammonium	mg/l	0,038	0,038	0,041	0,038	0,038
Antimony	µg/l	0,564	0,551	0,500	0,750	0,750
Arsenic	µg/l	0,558	0,500	0,500	0,750	0,907
beta-Endosulfan	µg/l	0,004	0,004	0,004	0,004	0,006
Boron	µg/l	195,303	129,547	154,589	137,830	147,601
Bromates	µg/l	5,745	7,893	7,867	3,636	4,161
Free chlorine residual (in situ)	mg/l	1,006*	1,007*	0,837	0,828	0,858
Chlorfenvinphos	µg/l	0,004	0,004	0,004	0,004	0,004
Chlorides	mg/l	414,610*	280,842*	186,797	179,581	183,703
Chromium	µg/l	2,171	1,956	2,631	2,239	3,921
Dieldrin	µg/l	0,004	0,004	0,004	0,004	0,004
Iron	µg/l	9,205	8,831	8,999	8,389	8,751
Fluorides	mg/l	0,151	0,114	0,119	0,127	0,106
Heptachlor	µg/l	0,006	-	-	-	-
Heptachlor epoxide	µg/l	0,004	0,004	0,004	0,004	0,004
Lindane	µg/l	0,006	0,004	0,004	0,004	0,004
Malathion	µg/l	0,004	0,004	0,004	0,004	0,004
Manganese	µg/l	1,920	1,176	1,061	0,901	0,995
Mercury	µg/l	0,046	0,014	0,013	0,013	0,013
Metolachlor	µg/l	0,004	0,004	0,004	0,004	0,004
Molinate	µg/l	0,004	0,004	0,004	0,004	0,004
Nickel	µg/l	5,108	3,263	2,527	2,747	3,763
Nitrates	mg/l	10,755	10,313	9,138	7,700	7,458
Nitrites	mg/l	0,010	0,010	0,010	0,010	0,010
Pendimethalin	µg/l	0,006	0,004	0,004	0,004	0,004
Pirimicarb	µg/l	0,006	0,006	0,006	0,006	0,006
Propazine	µg/l	0,006	0,006	0,006	0,006	0,006
Selenium	µg/l	0,569	0,500	0,500	0,876	0,750
Sodium	mg/l	203,257*	129,339	98,539	99,359	106,460
Sulfates	mg/l	197,292	158,333	127,833	110,333	109,917
Terbutylazine	µg/l	0,005	0,004	0,004	0,004	0,004
Terbutryn	µg/l	0,006	0,004	0,004	0,004	0,004
Tiobencarb	µg/l	0,006	0,004	0,004	0,004	0,004
Trichloroethene + Tetrachloroethene	µg/l	0,953	0,305	0,301	0,360	0,317

\*Average concentrations above the thresholds established at Directive 98/83/EC: free chlorine (1 mg/L), chlorides (250 mg/L) and sodium (200 mg/L)

**Table 8. Annual averages of the compounds excluded from the W calculation when reference values from Directive 98/83/CE exist**

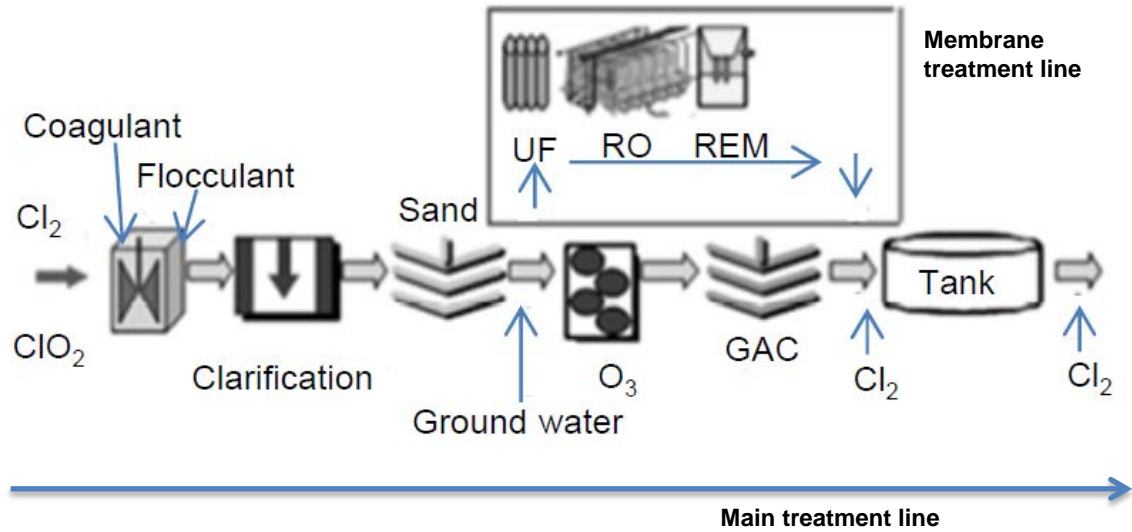
Parametre (excluded from W)	Unit	2008	2009	2010	2011	2012
1,2-dichloroethane	µg/l	0,281	0,119	0,083	0,225	0,225
Alachlor	µg/l	0,006	0,004	0,004	0,004	0,004
alpha-Endosulfan	µg/l	0,006	0,004	0,004	0,004	0,005
Aluminium	µg/l	44,761	86,387	57,931	53,135	34,908
Ammonium	mg/l	0,038	0,038	0,041	0,038	0,038
Arsenic	µg/l	0,558	0,500	0,500	0,750	0,907
Atrazine	µg/l	0,006	0,006	0,006	0,006	0,006
Benzene	µg/l	0,023	0,035	0,050	0,125	0,125
beta-Endosulfan	µg/l	0,004	0,004	0,004	0,004	0,006
Bromates	µg/l	5,745	7,893	7,867	3,636	4,161
Free chlorine residual (in situ)	mg/l	1,006*	1,007*	0,837	0,828	0,858
Chlorfenvinphos	µg/l	0,004	0,004	0,004	0,004	0,004
Chlorides	mg/l	414,610*	280,842*	186,797	179,581	183,703
Chromium	µg/l	2,171	1,956	2,631	2,239	3,921
Iron	µg/l	9,205	8,831	8,999	8,389	8,751
Fluorides	mg/l	0,151	0,114	0,119	0,127	0,106
Heptachlor	µg/l	0,006	0,004	0,004	0,004	0,004
Heptachlor epoxide	µg/l	0,004	0,004	0,004	0,004	0,004
Malathion	µg/l	0,004	0,004	0,004	0,004	0,004
Manganese	µg/l	1,920	1,176	1,061	0,901	0,995
Pirimicarb	µg/l	0,006	0,006	0,006	0,006	0,006
Propazine	µg/l	0,006	0,006	0,006	0,006	0,006
Selenium	µg/l	0,569	0,500	0,500	0,876	0,750
Sodium	mg/l	203,257*	129,339	98,539	99,359	106,460
Sulfates	mg/l	197,292	158,333	127,833	110,333	109,917
Terbutryn	µg/l	0,006	0,004	0,004	0,004	0,004
Tiobencarb	µg/l	0,006	0,004	0,004	0,004	0,004
Trichloroethene + Tetrachloroethene	µg/l	0,953	0,305	0,301	0,360	0,317

\*Average concentrations above the thresholds established at Directive 98/83/EC: free chlorine (1 mg/L), chlorides (250 mg/L) and sodium (200 mg/L)

**Table 9. Lists for the compounds having a higher contribution for every risk index and their associated uncertainty in the year 2012**

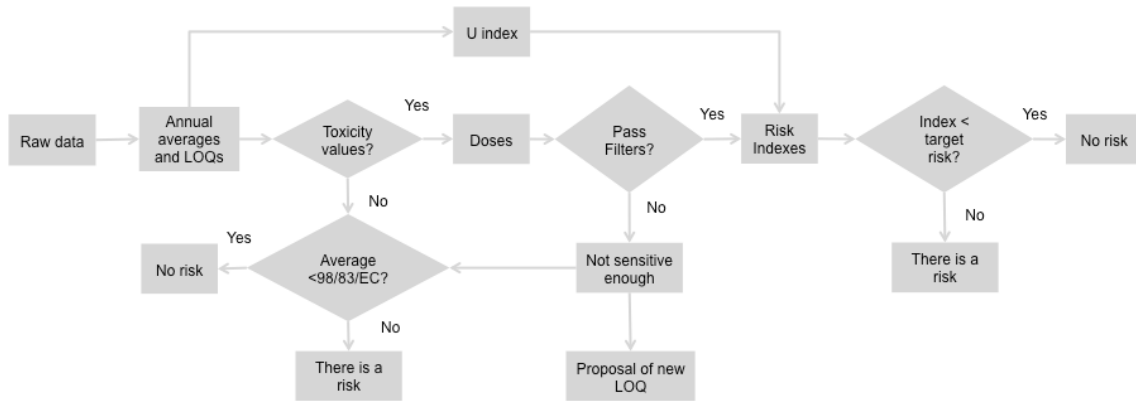
Parameter	H <sub>Qi</sub> inlet	U	Parameter	Ri inlet	U	Parameter	Wi inlet	U	Parameter	H <sub>Qi</sub> outlet	U	Parameter	Ri outlet	U	Parameter	Wi outlet	U
Nitrates	0.160	0.00	Heptachlor	1.59E-07	1.00	Nitrates	0.084	0.00	Nitrates	0.128	0.00	Chlorodibromomethane	3.37E-06	0.00	Nitrates	0.067	0.00
Strontium	0.078	0.00	Benzo(a)pyrene	8.57E-08	1.00	Boron	0.041	0.00	Strontium	0.050	0.00	1,1,2-trichlorethane	1.21E-06	0.01	Bromoform	0.030	0.00
Nitrites	0.045	0.04	Dibenzo(a,h)anthracene	8.57E-08	1.00	Nickel	0.025	0.00	Bromoform	0.022	0.00	Bromoform	1.20E-06	0.00	Boron	0.029	0.00
Boron	0.029	0.00	Benzene	6.46E-08	1.00	Antimony	0.004	1.00	Boron	0.020	0.00	Dichlorobromomethane	3.70E-07	0.00	Nickel	0.010	0.00
Barium	0.023	0.00	Trichloroethene	5.40E-08	1.00	Trichloroethene	0.003	1.00	1,1,2-trichlorethane	0.016	0.01	1,1,2,2-tetrachloroethane	2.35E-07	1.00	Chlorodibromomethane	0.007	0.00
Nickel	0.012	0.00	Ethylbenzene	2.58E-08	1.00	Aldrin	0.001	1.00	Trichloroethene	0.009	0.64	1,2-dichloroethane	1.92E-07	1.00	Nitrites	0.005	1.00
Heptachlor epoxide	0.008	1.00	Atrazine	1.35E-08	1.00	Dieldrin	0.001	1.00	Heptachlor epoxide	0.008	1.00	Chloroform	1.80E-07	0.00	Antimony	0.004	1.00
Molybdene	0.008	0.03	Benzo(a)anthracene	8.57E-09	1.00	Simazine	<0.001	1.00	Beryllium	0.007	1.00	1,2-dichloropropane	1.69E-07	1.00	Trichloroethene	0.004	0.64
Beryllium	0.007	1.00	Benzo(b)fluorantene	8.57E-09	1.00	Tetrachloroethene	<0.001	0.74	Chlorodibromomethane	0.006	0.00	Heptachlor	1.59E-07	1.00	Tetrachloride carbon	0.003	1.00
Trichloroethene	0.007	1.00	Indene(1,2,3-c,d)pyrene	8.57E-09	1.00	Terbutylazine	<0.001	0.14	Nickel	0.005	0.00	Tetrachloride carbon	8.22E-08	1.00	Chloroform	0.001	0.00

**Fig 1. Diagram of the DWTPs involved in the study. GAC: Granular Activated Carbon; MF: Micro Filtration; REM: Remineralization; RO: Reverse Osmosis; UF: Ultra Filtration. The box indicates the modification introduced on the treatment line including an step of Reverse osmosis**

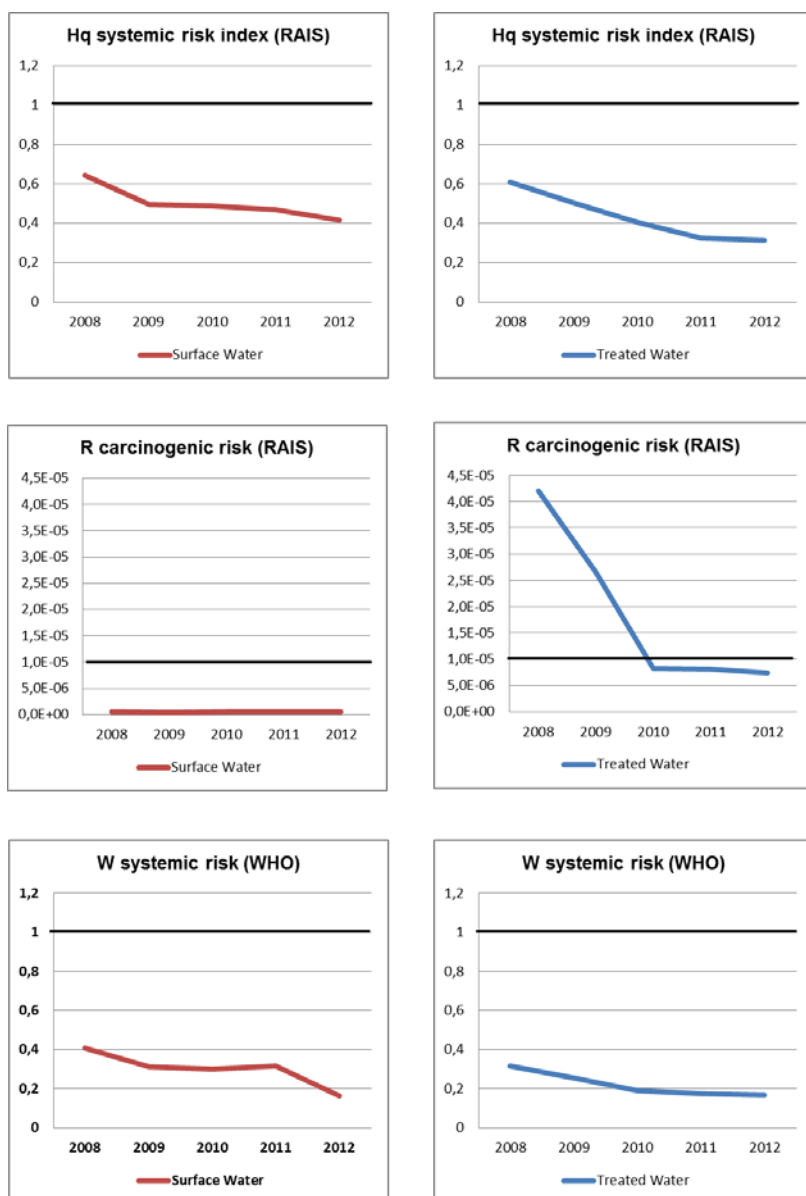




**Fig 2. Chart flow representing the methodology for risk assessment and previous filtering steps**



**Fig 3. Annual evolution of the global indexes for systemic and carcinogenic risk assessment according to RAIS and WHO reference data**



**Fig 4. Annual evolution of risk indexes for systemic and carcinogenic risk assessment for the four regulated THMs (bromoform, chlorodibromomethane, chloroform, dichlorobromomethane) at the outlet**

