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**
4

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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_Q 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 4.2×10^{-05} to 7.4×10^{-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 where installed.
45

46 **KEYWORDS**
47

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 1st 2009, a limit of total THMs of 100 μgL^{-1} is established in the EU

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

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

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

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

A set of water quality data registered during five years from the DWTP monitoring program has been used to implement the risk assessment methodology. The results obtained will be used to quantify numerically the improvement of the water quality by the use of risk indexes. This study should contribute to develop new managing practices based, not only on the occurrence, but also on the potential hazard of the 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^2 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^{3}s^{-1}, 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
210 **2.3. Fundamentals of the risk assessment methodology**
211
212 Chemicals that display environmental and biological persistence, bioaccumulation,
213 toxicity and long range transport have been previously assessed quantitatively by
214 national and international health agencies (Szabo and Loccisano, 2012). Among the
215 databases that offer information on the toxicity of the compounds that can be found in
216 water, two of the most widely used are the Risk Assessment Information System
217 (RAIS) and the WHO guidelines (WHO, 2011).
218
219 RAIS uses the Reference Dose (RfD), expressed as an oral dose per kilogram of body
220 weight (given in units of $mgKg^{-1}day^{-1}$), as an estimate of the lowest daily human
221 exposure that is likely to occur without appreciable risk of deleterious, non-cancerous
222 effects during a lifetime. WHO proposes a very similar reference value called the
223 Tolerable Daily Intake (TDI) as an estimate of the amount of a substance in food or
224 drinking-water, also expressed on a body weight basis that can be ingested daily over a
225 lifetime without appreciable health risk (WHO, 1991). The TDI values take into account
226 both systemic and carcinogenic effects but risk index is calculated as systemic.
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
232 $$D_i = \frac{C_w \times EF \times ED \times IR_w}{BW \times AT \times 365_{days/year}} \text{ (eq 1)}$$

233
234 where Di represents the dose of contaminant by water ingestion (mg $Kg^{-1}day^{-1}$), C_w is
235 the annual average concentration of the contaminant in water annual average (mgL^{-1}),
236 EF is the exposure frequency to the contaminated media (days $year^{-1}$) , ED is the
237 exposure duration (year), IR_w is the rate of water intake (L day^{-1}), BW is the body
238 weight of the receptor (Kg), and AT is the average time (year).
239
240 Table 2 shows the exposure values for the pathway of oral ingestion of water according
241 to RAIS and WHO for the calculation of doses. For systemic risk D_i is calculated by
242 using AT=ED. Then, three different indexes (systemic and carcinogenic for RAIS and
243 an index for WHO) have been calculated:
244
245 a) the systemic effect index according to RAIS (H_{Qi}) is calculated on the dose basis
246 according to RAIS reference values as a ratio between the dose (D) and the dose
247 reference level (RfD) by eq 2:
248

249 $H_{Qi} = \dfrac{D_i}{R_{fDi}}$ (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-1) that express a linear relationship of D_i
269 versus the risk Ri 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^{-5} 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 (Cothern 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:

275

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

277

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

279

280 $W_i = \dfrac{D_i}{TDI_i}$ (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

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

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

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

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

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

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

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

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

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

3. RESULTS

3.1. Analysis of water quality improvement in the DWTP

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

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

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

3.2. Risk indexes comparison of raw and treated water

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

A list of compounds is not included in the global index due to the filtering steps performed, due to the unavailability of reference data or to the low sensitivity of the 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.

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 m^3s^{-1} compared to 12.83 m^3s^{-1}in 2009) may be associated to higher
409   average concentrations of pollutants and, therefore, an increase of the risk indexes.

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.

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-trichlorethane 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.

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.

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.
500
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.
510
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_Q 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 $4.2x10^{-05}$ to $7.4x10^{-06}$ 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
558   **ACKNOWLEDGEMENTS**
559

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565   **REFERENCES**
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657

658 **Table 1. Chemical parameters routinely monitored at the Sant Joan Despí DWTP (surface**
659 **water and produced drinking water) in 2012**
660

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-trichlorethane	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-trichlorethane	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 day	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
Bromochloroacetonitrile	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	Terbuthylazine	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
Dibromoacetonitrile	N/A	every week	Total Haloacetonitriles	N/A	every week
Dichlobenil	every week	every month	Total Pesticides	every week	every month
Dichloroacetonitrile	N/A	every week	Total Trihalomethanes	N/A	every day
Dichlorobromomethane	every year	every day	Trichloroacetonitrile	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

661

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

Parameters	RAIS	WHO
EF(days year^{-1})	350	365
ED* (years)	24	-
IR (L day^{-1})	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 Avg Conc	U	2009 Avg Conc	U	2010 Avg Conc	U	2011 Avg Conc	U	2012 Avg Conc	U	2008/2012 Reduction*
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%
Terbuthylazine	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 Avg Conc	U	2009 Avg Conc	U	2010 Avg Conc	U	2011 Avg Conc	U	2012 Avg Conc	U	2008/2012 Reduction*
1,1,1-trichlorethane	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-trichlorethane	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%
Terbuthylazine	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_Q calculation when reference values from Directive 98/83/CE exist

Parametre (excluded from H_Q)	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
Terbuthylazine	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
Terbuthylazine	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_{Qi} inlet	U	Parameter	Ri inlet	U	Parameter	Wi inlet	U	Parameter	H_{Qi} 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	Terbuthylazine	<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
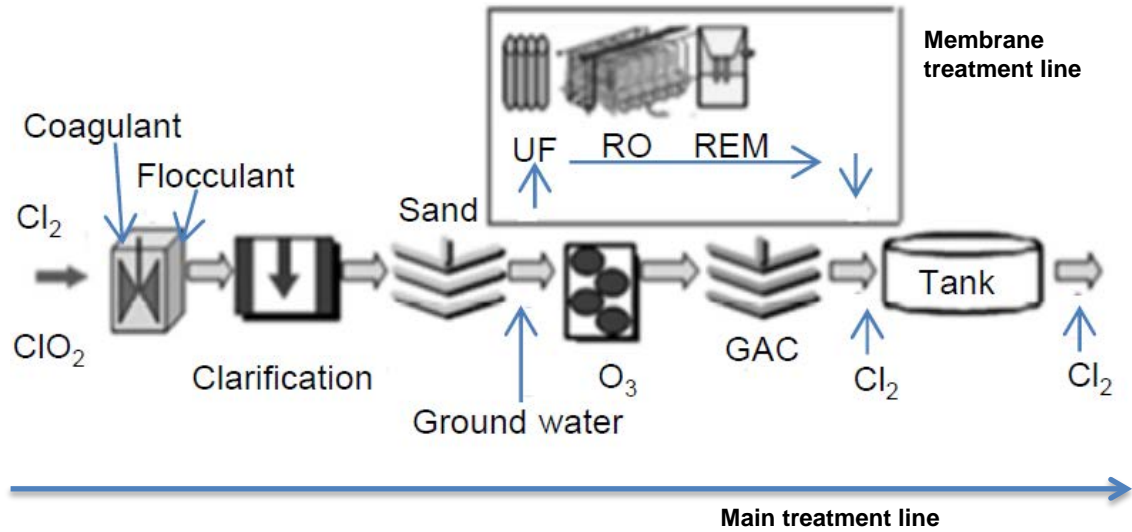
Fig 2. Chart flow representing the methodology for risk assessment and previous filtering steps
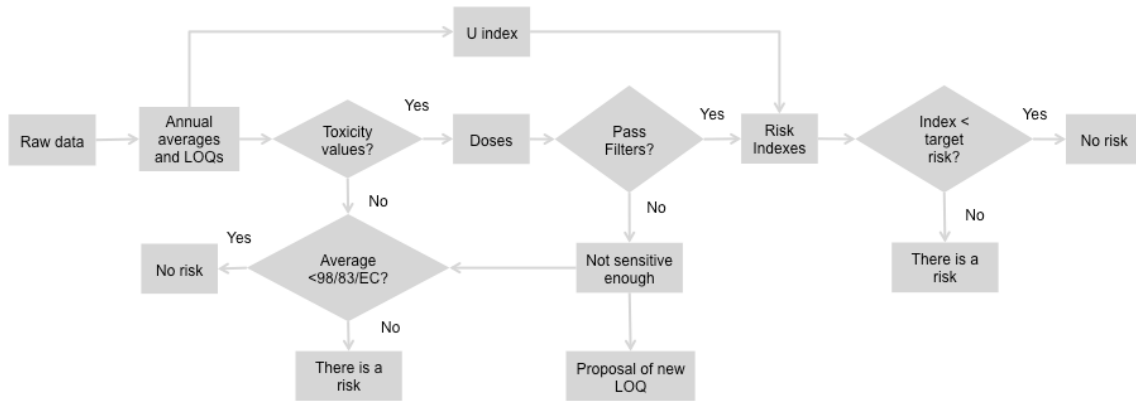
Fig 3. Annual evolution of the global indexes for systemic and carcinogenic risk assessment according to RAIS and WHO reference data
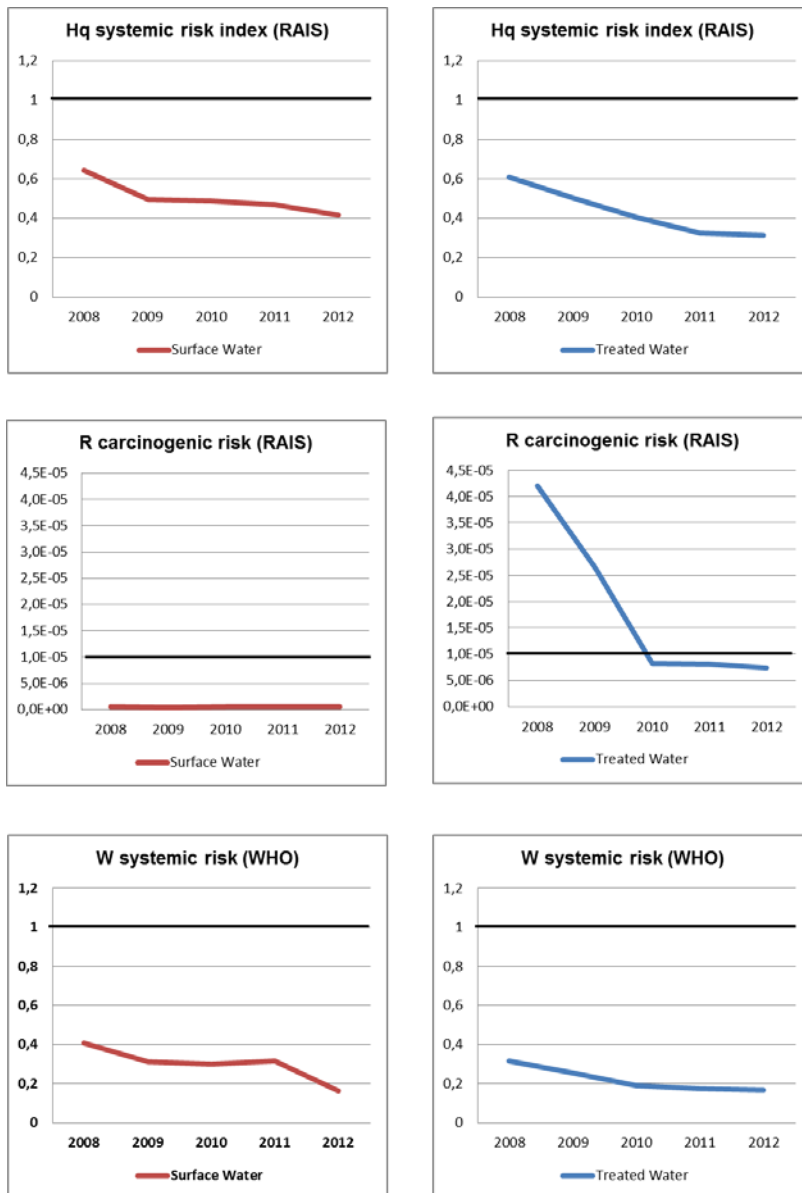
Fig 4. Annual evolution of risk indexes for systemic and carcinogenic risk assessment for the four regulated THMs (bromoform, chlorodibromomethane, chloroform, dichlorobromomethane) at the outlet