Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.30150

316 (2023) 22–33
December

Contribution to the study of seawater desalination effluents: chemical and toxicological analysis of a discharge after using a mixing basin (Martinique)

Loïk Sylvius[a,b,*], Frédéric Ferrer[a], Christelle Lemus[c], Juliette Smith Ravin[b,d], Stéphanie Morin[e]

[a]*Société Anonyme de la Raffinerie des Antilles, Le Lamentin, Quartier Californie Zone Industrielle - 97232 Le Lamentin Martinique, emails: loik.sylvius@sara-ag.fr (L. Sylvius), Frederic.FERRER@sara-ag.fr (F. Ferrer)*
[b]*Université des Antilles - Campus Universitaires de Schoelcher, 97275, Martinique, email: Juliette.Smith-Ravin@univ-antilles.fr*
[c]*SAS LAFAYETTE, 50 Rue ERNEST DEPROGE Fort-de-France, 97200, Martinique, email: c.lemus@martinique.cci.fr*
[d]*Groupe BIOSPHERES-AREBio, 11 rue Frantz Fanon, Bellevue Fort-de-France, 97200, Martinique*
[e]*BiodivMA, 12 rue Pois Doux Le Robert, 97231, Martinique, email: biodivma@gmail.com*

Received 7 August 2023; Accepted 15 November 2023

ABSTRACT

Oil production and refining require very large quantities of fresh water. Therefore, the use of unconventional methods to exploit resources, such as seawater desalination, appears to be an interesting alternative to produce a controlled and conditioned quantity of water to meet the required quality for its use. In this context, the French Company "Société Anonyme de la Raffinerie des Antilles (SARA)", as being the main industrial consumer of fresh water in Martinique, became interested in this mode of production and implemented a project to build a seawater desalination unit. However, seawater desalination generates a discharge of brine concentrate that, by its nature, could lead to environmental problems in the surrounding aquatic environment. To minimize the effects, several measures were taken in the design of the unit, in particular the installation of a mixing basin to dilute the concentrate prior to discharge. The purpose of this study is to assess the potential chemical toxicity of this effluent. The physico-chemical composition on 32 selected parameters as well as toxicity tests using controlled and standardized marine aquatic biological models (*Aliivibrio fischeri*, *Phaeodactylum tricornutum*, and *Crassostrea gigas*) are presented. No chemical elements of concern are observed for the effluent. Moreover, no toxic effect is observed under the conditions of salinity tolerance of the model organisms. These results suggest that the effluent generated by the SARA desalination unit does not present any demonstrated ecotoxicity under the studied conditions. This original work constitutes the first toxico-chemical evaluation study of discharge after dilution in a mixing basin.

Keywords: Desalination; Effluent; Ecotoxicology; Environmental impact

1. Introduction

In a context of very heavy environmental pressures, the management of fresh water supply and aqueous discharge has become a major challenge for the oil industry. Water is essential for the proper functioning of the refinery industrial activities and is required in large quantities. Securing the supply of fresh water is therefore vital [1].

Among the processes to obtain a substantial amount of fresh water, desalination of seawater emerged as a real alternative [2]. This so-called "unconventional" process makes it possible to separate the mineral salts present in the saltwater

* Corresponding author.

in conjunction with traditional resources coming from rainwater runoff. This process can be thermal (distillation) or membrane-based (reverse osmosis (RO)). The thermal process consists of bringing seawater to a boil and to condense the water vapor into salt-free water (single effect distillation, multi-effect distillation, multi-effect with vapor compression and distillation by successive expansions (or multiflash) [3]. Reverse osmosis is based on the ability of semi permeable membranes to retain salts and to allow water molecules to pass through. The use of reverse osmosis requires less energy consumption than the thermal process. In addition, it cancels out the environmental impact of high-temperature discharge [3].

Today, desalination is the most widely exploited alternative water production process in the world with approximately 95 million·m^3 of desalinated water per day [4]. That makes it possible for millions of people around the world to access to drinking water that meets the quality standards in effect. Unfortunately, this desalination is accompanied by the production of effluents with more than 141 million·m^3/d of brine discharged into the sea [5]. As well as discharges from "ion exchange resin regeneration" and discharges of "ballast" water, the discharge of brine has become one of the largest sources of wastewater produced by industry [6].

The nature of the effluent must be considered because it is made up of a "chemical universe" comprising elements that originate from the feed water and elements that can be transmitted during desalination operations. Elements from feed water are organic, naturally inorganic, and anthropogenic (contributed by human activity), and transmitted elements may consist of cleaning chemicals during processes (specific to the process and the facility), corrosion products coming from building materials, and, finally, the disinfection by-products in the form of organic halides [7,8].

In the composition of the disposal water, we do not only find coagulant injected in the pre-treatment phase (iron or aluminum salts), but also biocides (such as chlorine or other brominated agents), antiscalant agents (such as sodium sulfite), anti-scaling agents to prevent soiling of the membranes (such as polyphosphates, polyacrylic acid, etc.), cleaning solutions in case of reverse osmosis membranes (acid solutions, alkaline solutions and detergents) as well as pH and hardness correctors for the water produced (limestone). These products are necessary to treat the feed water and to maintain the efficiency of the membranes [9]. In addition, aqueous discharges can also contain high concentrations of metals from seawater, on the one hand, such as lead, manganese, copper and zinc, or from the corrosion of construction materials on the other hand, such as copper, cadmium, chromium and iron [9].

However, it is now accepted that the chemical content of a sample does not necessarily provide information as to its toxicity to living organisms, and many studies have been conducted in order to assess this issue [10,11]. Compliance with the regulations ensures that there is no acute toxicity in the receiving waters close to the discharge, but monitoring indicators must be set up and chronic impacts are closely monitored. These ecological monitoring studies have shown variable effects that range from no significant impact on benthic or fish communities [12] to generalized alterations in the structure of marine ecosystems (seagrass beds, coral reefs, sediment fauna and microbial community) for discharges into environments where the water mass is seldom renewed [12–19].

Toxicological studies on marine organisms are described in the literature, using simple tests (single species) [20] and multi-species tests [21] in order to assess these impacts. For example, salinity exposure tests show significant sublethal effects on the growth and survival of seagrass beds from 40 g/L but no effects on fish at 50 g/L [22]. A decrease in survivability was observed in juvenile oysters and attributed to the concentration of copper (Cu) [22]. Polyphosphate scale inhibitors cause a reduction in bacterial diversity and an increase in eukaryotic diversity, while coagulant $FeCl_3$ causes a decrease in eukaryotic diversity [23]. Regarding organic halides, it has been found that trihalomethane and haloacetic acid from RO effluent affect bivalves and aquatic macrophytes, others at low concentrations, such as monochloroacetic acid and monobromoacetic acid, inhibit the growth of green algae *Scenedesmus subspicatus* [24,25]. Overall, no effects are observed on fish, which are most likely able to avoid the plume in the immediate proximity of the discharge.

In fact, the most tested biological models are microorganisms, plants (algae and seagrass) and mollusks, the species which are most likely to be impacted and that are sensitive enough to detect any pollutants. Ideally located near a bay from Martinique's Island Atlantic Central Coast, (Baie du Cohé du Lamentin), SARA, as the main consumer of industrial water in the territory, has opted for the use of a seawater desalination unit (Fig. 1). This process leads to a freshwater production capacity of 30 m^3/h by RO and meets regular water needs of the industrial process of SARA.

This process has been identified as requiring less energy and as being less harmful to the receiving environment because it does not produce high-temperature effluent devoid of oxygen caused by the water heating and degassing stages that are only necessary for thermal processes. Several measures have been implemented to mitigate the potential impact of discharge into the environment, in particular the installation of a mixing basin in which the brine concentrate, sand filter washing water, freshwater tank purging and rainwater are mixed before discharging into the sea (Fig. 2).

In this present study, the physico-chemical properties of an effluent produced by seawater desalination were analysed and its toxic potential was characterised before release after passage through a dilution tank.

2. Materials and methods

2.1. Measurement points

The study was conducted on 4 samples (Fig. 3): a water sample from the feed seawater intake tank (SWT) a water sample from the mixing basin (MB) (and 2 solid samples from sediment around the outlet and the precipitate formed at the bottom of the mixing basin. These samples were collected using the valves installed on the water pathway. The vials used to collect and store the samples were pre-rinsed two to three times to avoid any possible interference.

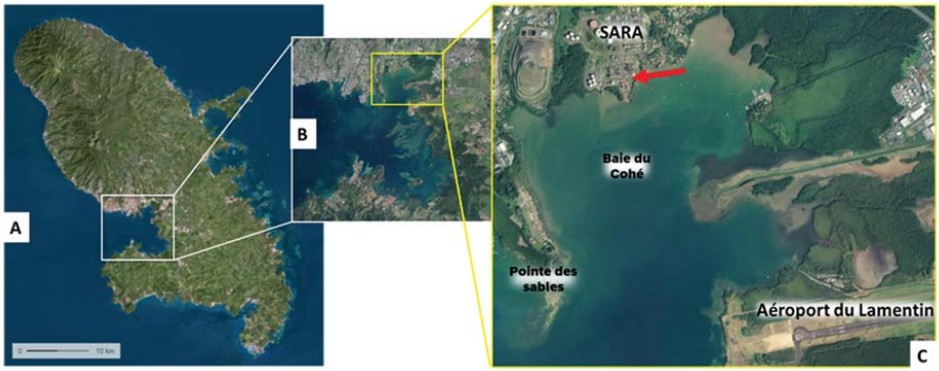

Fig. 1. Satellite image of Martinique (A), zoom in on the "Baie de Fort de France" (B) and zoom in on the Baie du Cohé du Lamentin with the SARA desalination plant location marked by a red arrow (C) (Geoportail map background).

Fig. 2. Photo of the mixing basin at SARA's seawater desalination plant. The effluent from the desalination unit is discharged into this tank before being released into the seawater.

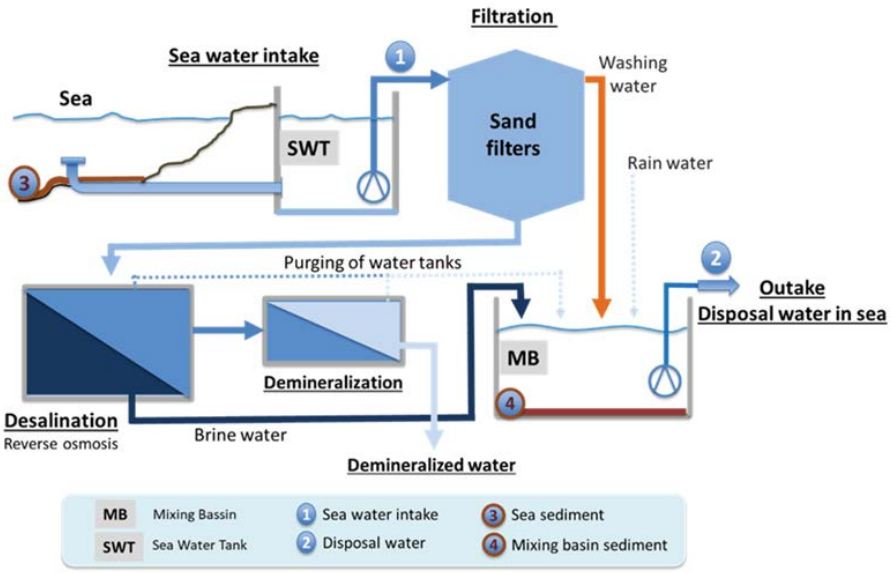

Fig. 3. Simplified diagram of the SARA seawater desalination plant. The samples analysed are identified by numbers (measurement points): 1-Seawater intake (SWT); 2-Water discharged into the sea after passing through the mixing basin (MB); 3-Sea sediment; 4-Mixing basin sediment.

2.2. Physico-chemical analyses

2.2.1. Water measurement (mixing basin effluent and seawater)

2 types of analysis were carried out: SARA's internal monitoring analyses included daily spot measurements of conductivity and continuous measurements using dissolved oxygen probes and temperature probes immersed directly in the mixing tank. Along with a series of analyses using controlled, standardized methods, carried out by an independent, accredited laboratory based in France. As a result, 32 physico-chemical parameters were measured, including 13 metals characteristic of industrial activities and 19 based on general physico-chemical parameters of chemical and ecological water quality (Table 1). All these parameters are classically analyzed in the literature. The methods used are not detailed here.

2.2.2. Analysis of marine sediment and the mixing basin sediment

For the sediment analysis, 17 parameters were analyzed (Table 2). 13 metals and 4 chemical parameters were selected in accordance with the physico-chemical parameters in Table 1 and the needs of the study. Here again, all these analyses are commonly used and the methods used have not been detailed here.

2.3. Ecotoxicological analyses

The ecotoxic potential of the effluent was analyzed using the bacteria-based *Vibrio fischeri* luminescence inhibition assay, marine algae growth inhibition test with *Phaeodactylum tricornutum* and the bivalve embryo-larval development test using mollusks. These tests, that used controlled, standardized marine aquatic biological models, were carried out by an independent and accredited laboratory based in France.

2.3.1. Microtox test

The 2 samples were collected in 2 L plastic bottles. These samples were placed directly into an isothermal box containing eutectic plates and hermetically sealed to maintain the temperature. This sublethal and acute toxicity test consists of determining the concentration of pollutant that inhibits 50% of the light production (bioluminescence) of the luminescent bacterium *V. fischeri* compared to a control (AFNOR T 90-320 and NF EN ISO 11348-3). The luminescence, measured after a contact time of 5, 15 and 30 min, considers a correction factor (*fkt*) which represents a measure of the changes in intensity of the controls during the exposure time. The inhibitory effect of the water sample was determined as EC_{50} (effective concentration 50) values.

2.3.2. Toxicity test with diatom (P. tricornutum; EN ISO 10253)

This test consists of monitoring the increase in cell density for 72 h (growth) and the increase in cell density per unit of time (growth rate) in the presence of the sample to be tested. The test organism was a diatom of the species *P. tricornutum* from the Culture Collection of Algae and Protozoa of the Scottish Association for Marine Science, Oban, Scotland. The algae were placed in a growth medium 3–4 d before the test to obtain algae in the exponential phase of growth. The algae were placed in different sample concentrations (100%, 56%, 32%, 18%, 10%, 5.6%, and 3.2%), 6 replicates for 100%, and 3 replicates for the other concentrations. 3,5-dichlorophenol was used as a reference polluting substance. The test vessels contain 2 mL of algae in the growth medium and the sample was added depending on the target concentration. The final volume of 20 mL is obtained by supplementing with artificial seawater. After 72 h of incubation at 20°C +/–2°C, in continuous light, with agitation (110 rpm), the cell concentrations for each test condition were measured. The growth inhibition percentages were calculated relative to the control.

Table 1
List of physico-chemical characteristics analysed during the water survey. These parameters are studied to characterize the quality of the water and the impact of industrial activities

List of 13 metallics substances characteristic of industrial activities	Aluminum, arsenic, barium, lead, cadmium, chromium, iron, copper, manganese, nickel, zinc, tin, mercury
List of 19 general physico-chemical parameters for water and characteristic of industrial activities	pH, temperature, dissolved oxygen, conductivity, salinity (calculated), calcium, potassium, magnesium, sodium, total nitrogen, total phosphorus, phosphates, chlorides, AOX, TOC, total cyanides, sulfites, sulfates, fluorides

Table 2
List of physico-chemical characteristics analysed during the sediment survey. These parameters are studied to characterize the quality of marine sediment and the mixing basin sediment

List of 13 substances characteristic of industrial activities	Aluminum, arsenic, barium, lead, cadmium, chromium, iron, copper, manganese, nickel, zinc, tin, mercury
List of 4 general physico-chemical parameters for water and characteristic of industrial activities	Total nitrogen, total phosphorus, AOX, TOC

2.3.3. Toxicity test based on the embryo-larval development of the Pacific oyster (Crassostrea gigas) (NF ISO 17244 - 2015)

This test is based on the evaluation of the concentration that induces 50% of developmental anomalies of the larvae in 24 h, at 24°C in the dark. The anomalies can be characterized by a blockage at the embryo stage, or by morphological anomalies of the larvae (shell and/or hinge anomalies, mantle hypertrophy). The test organism was a Pacific oyster (*Crassostrea gigas*) from the Guernsey Sea Farms Hatchery in Great Britain, a hatchery that specializes in the production of marine organisms under controlled conditions. The oysters there undergo a conditioning cycle (high temperature and abundant food) so that they are ready to spawn as soon as they are received in the laboratory. The samples were kept cool and analyzed within a maximum period of 15 d following collection. All solutions were prepared in flasks in the amount of 50 mL for each test condition, by diluting the raw sample with synthetic seawater. The maximum tested concentration was 100% for the samples, then the interval between two dilutions was 0.25 logarithmic units, 100–56–32–18–10 etc. A test series consisted of 6 replicates for the control and 3 replicates per test concentration. Cu^{2+} in the form of copper sulphate ($CuSO_4 \cdot 5H_2O$) was used as the control substance tested in each series of tests to check the sensitivity of the larvae. The test is validated if the percentage of normal larvae in the negative control batches is greater than or equal to 80%. Here, it was 93.8%. Furthermore, the EC_{50} value of copper sulfate (EC_{50} Cu^{2+} = 12.1 μg/L) (confidence level of between 11.1 and 13.4 μg/L) was included in the validity interval of between 4 and 16 μg/L expressed as Cu^{2+}. Results were given for each flask by establishing the percentage of normal and abnormal larvae for each test condition. The Log-Prit statistical model (ToxCalc Software) was used to determine the EC_{50}, and the Bonferroni Test (Toxcalc Software) was used to determine the NOEC and LOEC.

3. Results and discussion

3.1. Physico-chemical analyses

3.1.1. Environmental parameters

The first objective of this study was to compare the chemical profile of the feed seawater (intake) to the aqueous discharge (outlet) of the desalination unit. To make sure that the test samples were representative of our model, taking test samples during one-off events, such as heavy rain or contamination (which could affect interpretations), was avoided. To do this, we chose environmental parameters known to influence the distribution of marine species, such as salinity, pH, temperature and dissolved oxygen (Table 3). These environmental parameters collected from internal SARA monitoring data and physico-chemical monitoring data of research programs or monitoring of marine surveillance networks of Baie du Cohé du Lamentin from which the seawater comes, such as the Observation Network (ex-RNO).

The pH values observed for the seawater are similar to those of the effluent and are both consistent with the last campaign that was carried out between January and December 2018 by the RNO Observation Network (between 7.4 and 8.6) corresponding to good ecological water quality. The salinity recorded for the water in the mixing basin (effluent) during the sampling is 37.8 g/L and that of the intake seawater is 34.8 g/L. A salinity consistent with the average of 38.9 g/L and values between 32.4 and 44.3 g/L observed over a period of 5 months of operation of the unit. The salt concentration of the seawater is also consistent with the data recorded by the Observation Network's Monitoring with an annual average ranging from 33.1 to 37.8 g/L in 2016. The temperature obtained for the effluent is 28.5°C and that obtained for the seawater is approximately 26.1°C, that are consistent with the results obtained from the monitoring of the mixing basin with values between 28°C and 29.7°C and that of the Observation Network in the Bay with an annual average fluctuating from 27.7°C to 30.3°C between 2002 and 2016. The dissolved oxygen concentration is 6.4 mg/L for the effluent and 6.9 mg/L for the feed seawater, and once again, these results are consistent with the basin monitoring results with an average of 6.63 mg/L, ranging from 4.55 and 8.98 mg/L, and with those obtained by the monitoring network in the bay ranging from 3.8 to 6.9 mg/L in 2016. All the results obtained for temperature, and dissolved oxygen suggest that they do not seem to be a cause for environment concern, as they are consistent with all the results previously observed. This confirms that the desalination process in question does not involve a decrease in dissolved oxygen or a significant increase in the temperature of the effluent [26,27]. Moreover, knowing that the salt concentration of the brine is on average 48 g/L for values between 41.7 and 53.09 g/L, we determine that the basin allows an average dilution factor of 1.2. This does not make it possible yet to reach the concentration of seawater, but the installation of an additional continuous source of fresh water to reach a dilution factor of 1.4 would be a necessary measure to obtain a salt concentration close to that of seawater.

Table 3
Characteristics of seawater from the intake basin (SWT) and effluent from the mixing basin (MB) according to 5 environmental parameters known to influence the distribution of marine biodiversity

	Seawater intake (SWT)	Effluent mixing basin (MB)	Difference
Temperature (°C)	26.1	28.5	+3.5 (15.2%)
pH	7.8	7.6	–0.2 (2.6%)
Dissolved oxygen (mg/L)	6.99	6.4	–0.4 (8.5%)
Conductivity (μS/cm)	52,900	56,770	3,870 (6.8%)
Salinity (calculated) (g/kg)	34.8	37.8	+3 (8.6%)

3.1.2. Chemical composition

To investigate the quality of the disposal water and its potential chemical toxicity compared to the intake seawater, analysis of the 14 selected general parameters (Table 4) and 13 metal parameters (Table 5) was carried out. As for the general parameters, the chemical compositions were similar, although there were a few differences. No total nitrogen was detected; a phosphorus concentration of 0.52 mg/L for the mixing tank sample was detected, but not in the seawater, and it was below the regulatory threshold of 10 mg/L. In addition, an overall higher concentration was observed in the mixing basin for most of the other analyzed elements, in particular the salt concentration. The results showed a higher concentration than in the input seawater for potassium, magnesium, sulphates, and total organic carbon.

Conversely, the concentration obtained for the organic halides parameter (adsorbable organic halides (AOX)) is at a much lower level than in the feed water. A decrease of 70%, while we expected to find a value at least equal to that obtained for the intake. This suggests a degradation of AOX [28], due to the evaporation of the more volatile part of the AOX and/or even a phenomenon of precipitation of the less soluble ones. Besides this, we also observed the disappearance or significant decrease in the concentration of 3 of the 4 metals detected (Al, Mn and Fe) despite a very close metal profile (Table 5) between the two types of water studied. Once again, these results suggest that the precipitation

Table 4
Chemical characteristics of seawater from the intake basin (SWT) and effluent from the mixing basin (MB)

	Seawater intake (SWT)	Effluent mixing basin (MB)	Difference	Regulatory thresholds
Total nitrogen (mg·N/L)	ND	ND	/	30
Total phosphorus (mg·P/L)	ND	0.52	+0.52 (100%)	10
Phosphates (mg·PO_4/L)	ND	ND	/	–
Chlorides (mg/L)	20,000	22,830	+2,830 (14%)	Na + Cl 48,000 (1)
AOX (µg/L)	320	97	–223 (69.7%)	1,000
TOC (mg/L)	2.1	3.0	+0.8 (42.8%)	40
Total cyanides (mg/L)	ND	ND	/	0.1
Sulfites (mg/L)	ND	ND	/	20
Sulfates (mg/L)	3,900	6,200	+2,300 (58%)	2,000
Fluorides (mg/L)	0.98	0.98	/	15
Calcium (mg/L)	260	280	+20 (7.7%)	–
Potassium (mg/L)	320	350	+30 (9.4%)	–
Magnesium (mg/L)	950	1,000	50/5	–
Sodium (mg/L)	7,900	8,700	800 (10.1%)	–

ND: not detected

Table 5
Chemical characteristics of seawater from the intake basin (SWT) and effluent from the mixing basin (MB) - dissolved metals study

	Seawater intake (SWT)	Effluent mixing basin (MB)	Difference	Regulatory thresholds
Aluminum (ug/L)	130	ND	–130 (100%)	2.5
Arsenic (ug/L)	ND	ND	/	25
Barium (ug/L)	ND	ND	/	3
Cadmium (ug/L)	ND	ND	/	25
Chromium (ug/L)	ND	ND	/	50
Copper (ug/L)	ND	ND	/	150
Tin (ug/L)	ND	ND	/	2,000
Iron (ug/L)	0.20	0.12	–0.8 (40%)	2,500
Manganese (ug/L)	9.2	5.3	–3.9 (42.4%)	1,000
Mercury (ug/L)	ND	ND	/	25
Nickel (ug/L)	ND	ND	/	100
Lead (ug/L)	ND	ND	/	100
Zinc (ug/L)	ND	ND	/	800

ND: not detected

of these elements is certainly due to the presence of ferric chloride in the mixing basin [29]. The other metals analyzed (As, Ba, Cd, Cr, Cu, Sn, Hg, Ni, Pb and Zn) are not detected.

To explain the somewhat surprising contents of the discharge water and to confirm the hypothesis of the precipitation of certain chemical elements, we characterized the precipitate formed at the bottom of the basin, limiting the study to 17 select parameters, including the 13 metals, with particular attention to the levels of AOX, phosphorus, aluminum, and manganese (Tables 6 and 7). The seabed sediment around the seawater outlets was also analyzed for information and comparison purposes, but no conclusion can be drawn as to the origin of the elements because of the possible dual origin of the compounds [9,30]. We thus found the 3 chemical compounds that we were looking for, but also others which were not detected in the effluent such as N_{total}, Al, As, Ba, Pb, Cr, Cu, Ni, Zn, and Sn, confirming the precipitation of several chemical elements at the bottom of the basin.

A natural and possibly chemical gravitation of elements at rates sufficiently low to not be detected in either the effluent or the feed water. Moreover, most of the other elements detected in the precipitate are also detected in the marine sediment, but at rates up to 27 times more concentrated for total phosphorus, except for manganese in a quantity that is twice less. The Cl and Cu even exceed the N_2 contamination levels of French regulations on the discharge of marine or estuarine sediments. Notable indicators that may be a sign of a potential negative impact. The most probable hypothesis is that we are dealing with accumulated materials from the sea which are transmitted during the desalination process after a year of operation and decomposition of organic matter (organophosphates) deposited at the bottom of the basin. However, this is just a hypothesis and does not fall within the scope of this present study.

In any case, one of the benefits of using the mixing basin is to permit the precipitation of a set of chemical compounds that do not end up then in the discharge water. However, this in no way predicts the ecotoxic potential of this water, that we are going to study now.

3.1.3. Ecotoxicology

Toxic potential of the water from the mixing basin (MB) was assessed using 3 marine organisms with a maximum salinity tolerance of approximately 35‰, the limit of the study of a sample's study was its salt concentration. Water from the SWT was also tested. The seawater feed samples were taken at the same time as the mixing basin samples so as not to introduce any bias into the study. The first series includes an MB1 sample at a measured concentration of 35‰ and an SWT1 sample of seawater at a concentration of 30‰. For the 2nd series, our MB2 sample has a concentration of 43.8‰ and the SWT2 sample has a concentration of 33.9‰.

3.1.4. Microtox test: V. fischeri luminescence inhibition assay

The percentage of inhibition observed for the MB1 sample on bioluminescence remained below the significant

Table 6
Chemical characteristics for the precipitate obtained at the bottom of the mixing basin (mixing basin sediment) and for the sediment collected around the seawater (marine sediment) sampling site

	Marine sediment (sampling site)	Mixing basin sediment (precipitate)
Total nitrogen (mg/kg)	500	780
Total phosphorus (mg/kg)	410	11,000
AOX (mg/kg)	ND	390
TOC	8,300	5,800

ND: not detected

Table 7
Chemical characteristics for the precipitate obtained at the bottom of the mixing basin (mixing basin sediment) and for the sediment collected around the seawater (marine sediment) sampling site – metals study

	Marine sediment (sampling site)	Mixing basin sediment (precipitate)	Regulatory threshold, contamination level N_2
Aluminum (mg/kg)	42,000	24,000	–
Arsenic (mg/kg)	21	31	50
Barium (mg/kg)	5	17	–
Cadmium (mg/kg)	ND	ND	2.4
Chromium (mg/kg)	11	370	180
Copper (mg/kg)	47	320	90
Tin (mg/L)	3	3	–
Iron (mg/kg)	47,000	200,000	–
Manganese (mg/kg)	1,300	560	–

ND: not detected

inhibition threshold of 20% for concentrations of effluent ranging from 10% to 80% of the total effluent (Table 8) for the entire duration of the test (0–30 min). There was therefore no inhibiting effect of the effluent on bioluminescence and the EC 50% was greater than the maximum concentration tested. The same observation applied to the results obtained for the feed seawater.

For the MB2 sample, the percentage of inhibition observed on bioluminescence remains below the significant inhibition threshold of 20% for effluent concentrations of up to 80% of the total effluent (Table 9) for the entire duration of the test (0–30 min). There was therefore no visible inhibiting effect of the effluent on bioluminescence and the EC 50% was greater than the maximum concentration tested. The same observation applied to the results obtained for the feed seawater. It should nonetheless be noted that at a sample concentration of 80% corresponding to the salinity of greater than 35‰, and that the value measured exceeds 10% inhibition for all the samples taken at 5, 15 and 30 min. An effect onset therefore seemed to be felt most likely due to the concentration of salts, but overall, there was no acute toxicity revealed by the microtox test in line with results previously obtained [31].

3.1.5. Growth inhibition of P. tricornutum (marine diatom)

After measuring the cellular density (number of cells/mL) at 72 h in the test cultures and the control cultures (Malassez cell counts), the specific growth rate (μ) was calculated. Regarding the MB1 sample, the cell concentration and the cell growth rate obtained for a maximum concentration of 100% of the total effluent was equal to that obtained for the control sample (Table 10). There were therefore no toxic effects to report under the conditions of the study. No differences were observed between the control sample and the "total effluent" sample. As a result, the inhibition EC_{50}, 72-h growth EC_{50} and NOEC values were above 100% in line with the results previously obtained [31].

Regarding the MB2 sample, the physico-chemical measurements taken within the framework of the test indicated that the sample was very saline, with a reading of 43.9‰ at a 100% sample concentration. This was the reason why only concentrations of less than or equal to 18% had a salinity corresponding to acceptable levels for *P. tricornutum*.

By only considering the concentrations acceptable for the species (concentrations ≤ 18%), we obtained an EC_{50}-72 h of less than 18% and a NOEC of 18%; there was no

Table 8
Microtox tests performed in duplicate at 0, 5, 15 and 30 min for effluent from the mixing basin sample (MB1) and for seawater from the intake basin sample (SWT1). Samples MB1 and SWT1 designate the first sampling series

Time	Concentration	Test 1 (% inhibition)	Difference (%/average)	Test 2 (% inhibition)	Average
			Effluent (MB1)		
5 min	10	4	2	1	2,5
	20	7	2	4	5,5
	40	0	0	0	0
	80	7	1	5	6
15 min	10	1	0	0	0,5
	20	0	0	0	0
	40	3	2	0	1,5
	80	8	2	3	5,5
30 min	10	5	3	0	2,5
	20	5	1	3	4
	40	0	0	1	0,5
	80	10	0	9	9,5
			Seawater intake (SWT1)		
5 min	10	2	0	3	2,5
	20	0	1	2	1
	40	5	3	0	2,5
	80	7	0	6	6,5
15 min	10	1	0	0	0,5
	20	0	0	0	0
	40	3	2	0	1,5
	80	8	2	3	5,5
30 min	10	4	1	6	5
	20	0	2	3	1,5
	40	3	1	1	2
	80	8	1	6	7

Table 9
Microtox tests performed in duplicate at 0, 5, 15 and 30 min for effluent from the mixing basin sample (MB2) and for seawater from the intake basin sample (SWT2). Samples MB2 and SWT2 designate the second sampling series

Time	Concentration	Test 1 (% inhibition)	Difference (%/average)	Test 2 (% inhibition)	Average
		Effluent (MB2)			
5 min	10	2	1	1	1,5
	20	3	1	4	3,5
	40	2	1	0	1
	80	10	1	5	7,5
15 min	10	2	0	1	1,5
	20	3	1	0	1,5
	40	1	2	2	1,5
	80	14	1	13	13,5
30 min	10	0	0	0	0
	20	3	2	0	1,5
	40	3	0	3	3
	80	15	0	14	14,5
		Seawater intake (SWT2)			
5 min	10	0	0	0	0.0
	20	0	0	0	0.0
	40	0	0	0	0.0
	80	0	0	0	0.0
15 min	10	0	0	0	0.0
	20	0	0	0	0.0
	40	0	0	0	0.0
	80	0	0	0	0.0
30 min	10	0	0	0	0.0
	20	0	0	0	0.0
	40	0	0	0	0.0
	80	0	0	0	0.0

Table 10
Impact of the effluent sample (MB1) on cell concentration and cell growth rate of *Phaeodactylum tricornutum*

Concentration %	Cellular concentration × 10^6						Average number of cells	Cell inhibition		
	1	2	3	4	5	6				
0	0.23	0.25	0.22	0.22	0.24	0.22	0.22			
100	0.21	0.22	0.23	0.23	0.22	0.25	0.22	0%		
Concentration %	Growth rate						Average growth rate	Cell inhibition	Standard deviation	Coefficient of variation (%)
0	1.04	1.07	1.02	1.03	1.05	1.01	1.04		0.021	2.05
100	1.01	1.03	1.04	1.05	1.02	1.07	1.04	0%	0.022	2.16

observable effect. Yet by considering all the possible concentrations, we obtained an EC_{50}-72 h of 100% and a NOEC of 56% (Table 11).

3.1.6. Impact on embryo-larval development of bivalves

At concentrations of 56% and 100% of effluent for sample MB1, the net percentage of abnormal larvae obtained was below the significant threshold of 10%, with 1.2% and 2.3%, respectively (Table 12). As a result, the inhibition EC_{50}, NOEC and LOEC values were above 100%. No effect was observed, especially as the results for the feed water were higher.

Regarding the sample MB2, the physico-chemical measurements carried out as part of the test indicated that the sample was highly saline, as seen above, with a value of

Table 11
Impact of the effluent sample (MB2) on cell concentration and cell growth rate of *Phaeodactylum tricornutum*

Concentration %	Cellular concentration × 10^6						Average number of cells	Cell inhibition		
	1	2	3	4	5	6				
0	0.24	0.23	0.19	0.21	0.19	0.23	0.21			
56	0.24	0.24	0.19				0.22	–4%		
100	0.09	0.12	0.14				0.11	47%		
Concentration %	Growth rate						Average growth rate	Cell inhibition	Standard deviation	Coefficient of variation (%)
0	1.05	1.04	0.02	1.03	1.05	1.01	1.04		0.034	3.32
56	1.06	1.05	0.97				1.03	–1%	0.048	4.69
100	1.01	1.03	1.04				1.04	21%	0.022	10.44

Table 12
Raw data obtained for the MB1 and SWT1 toxicity test on the embryo-larval development for bi-valves

Concentration	Normal	Abnormal	Gross percentage of abnormal larvae	Net percentage of abnormal larvae
			Effluent (MB1)	
100%	94	6	6.0%	–0.2%
	92	8	8.0%	2.0%
	89	11	11.0%	5.2%
Average	92.7	7.3	7.3%	1.2%
56%	93	7	7.0%	0.9%
	92	8	8.0%	2.0%
	93	7	7.0%	0.9%
Average	91.7	8.3	8.3%	2.3%
			Seawater intake (SWT1)	
100%	89	11	11.0%	5.2%
	88	12	12.0%	6.2%
	93	7	7.0%	0.9%
Average	90	10.0	10.7%	4.1%
56%	93	7	7.0%	0.9%
	91	9	9.0%	3.0%
	93	7	7.0%	0.9%
Average	92.7	7.7	7.3%	1.6%

43.4‰ for a sample concentration of 100%. For this reason, only concentrations less than or equal to 18% had a salinity corresponding to acceptable levels for *C. gigas* (Table 13).

If we consider all the concentrations of the effluent, even those that are not acceptable for the species (above 35‰), we obtained a EC_{50} of 27.6%, NOEC of 18%, and LOEC of 32%. All such concentrations were above the tolerable salinity threshold for the test organisms corresponding to a concentration of 18% of effluent. We can conclude that for any salt concentration below the tolerance threshold, no effect is observed for these three tests with EC_{50} and LOEC > at 18% and NOEC of 18%.

4. Conclusion

Seawater desalination is now a common means of producing fresh water. This type of freshwater production generates an effluent that can cause environmental problems. Currently, the goal is to understand better this type of discharge to minimize or even to completely eliminate these negative impacts. The dilution of the salt concentrate upstream of the discharge into the sea is one of the measures that can make it possible to achieve this, which is why SARA has opted for dilution carried out in a basin before discharge into the sea. This present study of the disposal water demonstrates that the concentration of salts is not only reduced, but also many chemical elements such as metals (Mn, Fe, Mo, etc.) that may be of concern for the environment, precipitate on the bottom of the basin and are not released. Thus, no ecotoxic potential appears either in the chemical composition for the 33 parameters selected, or in the results of the 3 ecotoxicological tests of acute and chronic toxicity chosen for salt concentrations appropriate for the test organisms under the conditions of the study. The *V. fischeri*

Table 13
Raw data obtained for the MB2 and SWT2 toxicity test on the embryo-larval development for bi-valves

Concentration	Normal	Abnormal	Gross percentage of abnormal larvae	Net percentage of abnormal larvae
			Effluent (MB2)	
	0	100	100.0%	100.0%
100%	0	100	100.0%	100.0%
	0	100	100.0%	100.0%
Average	0.0	100	100.0%	100.0%
	7	93	93.0%	92.8%
56%	6	94	94.0%	93.8%
	7	93	93.0%	92.8%
Average	6.7	93.3	93.3%	93.1%
	16	84	84.0%	83.4%
32%	17	83	83.0%	82.4%
	18	82	82.0%	81.4%
Average	17	83.0	83.0%	82.4%
	94	6	6.0%	2.8%
18%	95	5	5.0%	1.7%
	96	4	4.0%	0.7%
Average	17.0	83.0	5.0%	1.7%
			Seawater intake (SWT2)	
	98	2	2.0%	–1.4%
100%	98	2	2.0%	–1.4%
	94	6	6.0%	2.8%
Average	96.7	3.3	3.3%	4.1%

luminescence inhibition assay (microtox), indicates that no toxicity is observed up to the maximum concentration of 80% of effluent that can be analyzed for this test. For the algae growth inhibition test with *P. tricornutum*, the tests show an EC_{50} and NOEC always above the effluent concentration within the acceptable salinity limit. The same observation applies regarding the toxicity test on the embryo-larval development of bivalves (*C. gigas*), as we obtained an EC_{50}, NOEC, and LOEC of 100% when the salinity was adapted. The study therefore shows that within the saline tolerance limits of the species studied, no toxic potential is demonstrated. Other ecotoxic tests will need to be carried out to confirm this observation, such as passive biomonitoring of indigenous sentinel organisms or by toxicity tests on carefully chosen marine organisms such as *Artemia* type euryhaline species, so as to be able to assess the influence of the other constituents of the mixture at higher concentrations. We can therefore conclude that the use of the mixing basin seems to be a good effluent management measure, but it also reveals that it would be ideal to be capable to add an additional source of fresh water to this basin to maintain salinity at a rate of less than 35‰. Moreover, the precipitate found at the bottom of the basin that is potentially dangerous for the environment should be eliminated using suitable methods to avoid any transfer into the target environment. For example, by drying and disposing of sand filter backwash products "on land" to avoid discharging these residues with the effluent.

References

[1] L. Nabzar, J.-L. Duplan, L' eau dans la production de carburants: production pétrolière et raffinage, Point Sur., Energies Nouvelles, Panorama, 2011.
[2] N.C. Darre, G.S. Toor, Desalination of water: a review, Curr. Pollut. Rep., 4 (2018) 104–111.
[3] J.-M. Rovel, Dessalement de l'eau de mer, Tech. Ing., Veolia, 2015. Available at: https://doi.org/10.51257/a-v1-w5700
[4] E. Jones, M. Qadir, M.T.H. van Vliet, V. Smakhtin, S. Kang, The state of desalination and brine production: a global outlook, Sci. Total Environ., 657 (2019) 1343–1356.
[5] J.M. Arnal, M. Sancho, I. Iborra, J.M. Gozálvez, A. Santafé, J. Lora, Concentration of brines from RO desalination plants by natural evaporation, Desalination, 182 (2005) 435–439.
[6] D. Ariono, M. Purwasasmita, I.G. Wenten, Brine effluents: characteristics, environmental impacts, and their handling, J. Eng. Technol. Sci., 48 (2016) 367–387.
[7] J. Le Roux, N. Nada, M.T. Khan, J.-P. Croué, Tracing disinfection byproducts in full-scale desalination plants, Desalination, 359 (2015) 141–148.
[8] C.J.L. Taylor, The effects of biological fouling control at coastal and estuarine power stations, Mar. Pollut. Bull., 53 (2006) 30–48.
[9] S. Lattemann, T. Höpner, Environmental impact and impact assessment of seawater desalination, Desalination, 220 (2008) 1–15.
[10] R. Angerville, Evaluation des risques écotoxicologiques liés au déversement de Rejets Urbains par Temps de Pluie (RUTP) dans les cours d'eau: application à une ville française et à une ville haïtienne, Thèses, Chimie, INSA de Lyon, Français, 2009.
[11] C. Boillot, Évaluation des risques écotoxicologiques liés aux rejets d'effluents hospitaliers dans les milieux aquatiques. Contribution à l'amélioration de la phase "caractérisation des effets", Thèses, INSA de Lyon, Français, 2008.

[12] N. Raventos, E. Macpherson, A. García-Rubiés, Effect of brine discharge from a desalination plant on macrobenthic communities in the NW Mediterranean, Mar. Environ. Res., 62 (2006) 1–14.
[13] M. Ahmed, R. Anwar, An assessment of the environmental impact of brine disposal in marine environment, Int. J. Mod. Eng. Res., 2 (2012) 2756–2761.
[14] J.A. de-la-Ossa-Carretero, Y. Del-Pilar-Ruso, A. Loya-Fernández, L.M. Ferrero-Vicente, C. Marco-Méndez, E. Martinez-Garcia, F. Giménez-Casalduero, J.L. Sánchez-Lizaso, Bioindicators as metrics for environmental monitoring of desalination plant discharges, Mar. Pollut. Bull., 103 (2016) 313–318.
[15] Y. Fernández-Torquemada, J.L. Sánchez-Lizaso, J.M. González-Correa, Preliminary results of the monitoring of the brine discharge produced by the SWRO desalination plant of Alicante (SE Spain), Desalination, 182 (2005) 395–402.
[16] E. Gacia, O. Invers, M. Manzanera, E. Ballesteros, J. Romero, Impact of the brine from a desalination plant on a shallow seagrass (*Posidonia oceanica*) meadow, Estuarine Coastal Shelf Sci., 72 (2007) 579–590.
[17] D.A. Roberts, E.L. Johnston, N.A. Knott, Impacts of desalination plant discharges on the marine environment: a critical review of published studies, Water Res., 44 (2010) 5117–5128.
[18] Y.D.P. Ruso, J.A.D. la Ossa Carretero, F.G. Casalduero, J.L.S. Lizaso, Spatial and temporal changes in infaunal communities inhabiting soft-bottoms affected by brine discharge, Mar. Environ. Res., 64 (2007) 492–503.
[19] J.L. Sánchez-Lizaso, J. Romero, J. Ruiz, E. Gacia, J.L. Buceta, O. Invers, Y. Fernández Torquemada, J. Mas, A. Ruiz-Mateo, M. Manzanera, Salinity tolerance of the Mediterranean seagrass *Posidonia oceanica*: recommendations to minimize the impact of brine discharges from desalination plants, Desalination, 221 (2008) 602–607.
[20] J.L. Dupavillon, B.M. Gillanders, Impacts of seawater desalination on the giant Australian cuttlefish Sepia apama in the upper Spencer Gulf, South Australia, Mar. Environ. Res., 67 (2009) 207–218.
[21] S. Iso, S. Suizu, A. Maejima, The lethal effect of hypertonic solutions and avoidance of marine organisms in relation to discharged brine from a destination plant, 97 (1994) 389–399.
[22] T. Hoepner, S. Lattemann, Chemical impacts from seawater desalination plants — a case study of the northern Red Sea, Desalination, 152 (2003) 133–140.
[23] N. Belkin, E. Rahav, H. Elifantz, N. Kress, I. Berman-Frank, The effect of coagulants and antiscalants discharged with seawater desalination brines on coastal microbial communities: a laboratory and in situ study from the southeastern Mediterranean, Water Res., 110 (2017) 321–331.
[24] R. Kühn, M. Pattard, Results of the harmful effects of water pollutants to green algae (*Scenedesmus subspicatus*) in the cell multiplication inhibition test, Water Res., 24 (1990) 31–38.
[25] M.E. Stewart, W.J. Blogoslawski, R.Y. Hsu, G.R. Helz, By-products of oxidative biocides: toxicity to oyster larvae, Mar. Pollut. Bull., 10 (1979) 166–169.
[26] M.A. Dawoud, M.M. Al Mulla, Environmental impacts of seawater desalination: Arabian Gulf case study, Int. J. Environ. Sustainability, 1 (2012) 22–37.
[27] A.K. Omar, A. Khaldi, Dessalement de l'eau de mer et impacts environnementaux: cas de la station d'EL-MACTAÂ, J. Water Environ. Sci., 1 (2017) 6.
[28] W. Jin, J. Zhou, B. Chen, X. Zhu, C. Cui, Modeling volatilization and adsorption of disinfection byproducts in natural watersheds, J. Environ. Monit., 14 (2012) 2990–2999.
[29] A.J. Hargreaves, P. Vale, J. Whelan, L. Alibardi, C. Constantino, G. Dotro, E. Cartmell, P. Campo, Coagulation–flocculation process with metal salts, synthetic polymers and biopolymers for the removal of trace metals (Cu, Pb, Ni, Zn) from municipal wastewater, Clean Technol. Environ. Policy, 20 (2018) 393–402.
[30] N. Kress, B. Galil, Chapter 8 – Impact of Seawater Desalination by Reverse Osmosis on the Marine Environment, in: Efficient Desalination by Reverse Osmosis, 2018, pp. 175–179.
[31] T. Hurley, Onslow Seawater Desalination Plant, Desalination Brine Toxicity Assessment, Environmental Protection Authority, 2021.