National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

Follow-up study on the chemical status of Lake Goto, Bonaire

Measurements and risk assessment

RIVM Letter Report 609224001/2012
D. de Zwart et al.

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This investigation has been performed by order and for the account of DGM, within the framework of project M/609224 Bodemonderzoek Gotomeer Bonaire

Abstract

Follow-up study on the chemical status of Lake Goto, Bonaire

On 8 and 9 September 2010 there was a big petrochemical fire at the BOPEC facility on Bonaire. In a study on the environmental impact it was concluded by RIVM that for perfluorooctane sulfonate (PFOS) environmental quality criteria were exceeded in Lake Goto and Salina Tam, two lagunas which are located in the vicinity of BOPEC. These substances originated from the fire fighting foams that were used on the BOPEC site. The study was inconclusive about the nature and size of possible ecological effects that could result from this. It was noted that concentrations might gradually decrease in time, however at an unknown speed.

At present the results from a follow-up study in 2012 performed by RIVM show that the concentrations of PFOS in water and sediments of Lake Goto and Salina Tam, although a little lower than in 2010, are still exceeding environmental quality criteria. This means that ecotoxicological riks because of this exposure that has been going on for 2 years now, can not be excluded. Examples are direct effects on waterorganisms such as mortality, or indirect effects for example when higher organisms leave because their food has disappeared. It is impossible to make any firm conclusions on the question whether the higher concentrations in Lake Goto and Salina Tam are the (only) causative factors influencing the observed ecological deterioration as indicated by a disappeared flamingo population from Lake Goto. In order to address this question an ecological study is needed, which will be performed by research institute IMARES.

This follow-up study was performed by order of The Dutch Ministry of Infrastructure and the Environment (I&M) upon request of the Public Entity of Bonaire.

Keywords:
BOPEC fire, Water quality, Lake Goto, PAH, PFOS

Rapport in het kort

Vervolgstudie naar de chemische verontreinigingstatus van het Gotomeer, Bonaire

Op 8 en 9 september 2010 woedde een grote brand op het terrein van de olieraffinaderij BOPEC op Bonaire. Destijds bleek uit onderzoek van het RIVM dat normen voor perfluoroctaansulfonaat-verbindingen (PFOS) zijn overschreden in het Gotomeer en in Salina Tam, twee zoutmeren vlakbij BOPEC. Deze verbindingen maakten deel uit van het gebruikte blusschuim op het BOPEC-terrein. Het bleek niet mogelijk om aan te geven wat de ecologische effecten van deze normoverschrijding zouden kunnen zijn. Wel werd aangegeven dat de concentraties van deze stoffen in beide meren geleidelijk zouden kunnen gaan afnemen. Hoe snel dat zou gaan, was onbekend.

Uit vervolgonderzoek in 2012 van het RIVM blijkt dat de milieukwaliteitsnormen nog steeds worden overschreden in het Gotomeer en Salina Tam. De concentraties PFOS in het water en sediment van deze meren vlakbij de brand zijn iets lager dan in 2010, maar nog duidelijk verhoogd. Risico’s voor het ecosysteem van deze inmiddels twee jaar durende blootstelling zijn hierdoor niet uit te sluiten. Hierbij valt te denken aan directe effecten op waterorganismen zoals bijvoorbeeld sterfte, of indirecte effecten wanneer hogere organismen verdwijnen doordat er niet meer voldoende voedsel voor ze is. Het is echter niet aan te geven of, en zo ja, in welke mate de verhoogde concentraties ervoor verantwoordelijk zijn dat de flamingopopulatie is verdwenen. Hiervoor is nader onderzoek naar de ecologische dynamiek van dit ecosysteem nodig. Onderzoeksinstituut IMARES gaat dit binnenkort doen.

Deze studie is uitgevoerd in opdracht van het Nederlandse ministerie van Infrastructuur en Milieu (I&M) en het bestuur van de ‘bijzondere gemeente’ Bonaire, het Openbaar Lichaam Bonaire (OLB).

Trefwoorden:
Brand BOPEC, Waterkwaliteit, Gotomeer, PAK, PFOS

Contents

Summary

The big petrochemical fire that took place in September 2010 at the BOPEC facility on Bonaire, caused a lot of potentially toxic material to be deposited on the island. Recently, the ecological condition of Lake Goto and Salina TAM, two water bodies adjacent to the BOPEC terrain are suspect of being deteriorated by these toxic depositions. The deterioration is thought to be indicated by the recent disappearance of the once thriving flamingo population in Lake Goto. By order of the Dutch Ministry of Infrastructure and the Environment (I&M) as requested by the Public Body of Bonaire, RIVM conducted a follow-up study in collaboration with IMARES to assess the present chemical condition of Lake Goto and a few other salinas (salt lakes). More explicitly, the follow-up study should answer the following questions:

1. Does the water and/or the sediments of Lake Goto contain pollutants that may be related to the BOPEC fire or the fire fighting foams used
2. Are the observed concentrations of these compounds high enough to induce ecological effects?

The follow-up study indicated that only the concentrations of fire fighting foam constituents, such as perfluoridated compounds (PFC), mainly represented by the most toxic and most bioconcentrating perfluorooctane sulfonate (PFOS), are still elevated in the water and sediments of Lake Goto and Salina Tam. These substances are not present in the two reference salt lakes evaluated in comparison. It turned out that the evaluation of the second question is affirmative. Some of the observed PFOS concentrations in the water and less in the sediment of Lake Goto are clearly indicative for secondary food chain intoxication.

In order to address the question if ecological effects in the food chain have actually taken place as a consequence of the elevated PFOS concentrations, an ecological study is needed. Such a study might elucidate the possibly contaminated food supply of the flamingo population and potential other ecologically or climatologicallly significant disturbing factors that may have caused the flamingo population (and possibly other flora and fauna) to disappear

1 Introduction

1.1 Rationale behind the follow-up study on Lake Goto, Bonaire

On 8 and 9 September 2010 there was a big petrochemical fire at the BOPEC facility on Bonaire. The BOnaire PEtroleum Corporation is a fuel oil storage and transhipment terminal that is fully owned by the Venezuelan oil company Petróleos de Venezuela S.A. (PDVSA). Allegedly, 32 million liters of crude and naphta went up in flames over a period of 2 days (http://www.beautiful-bonaire.nl/natuur/gotomeer.html). Immediately after the fire, the environmental impact resulting from the release of mainly oil, polycyclic aromatic hydrocarbons (PAH) and perfluorinated constituents of fire fighting foams were assessed and reported by RIVM (RIVM 2011).

In January 2012, an Antillean website (http://www.boneiru-awe.com/2012/01/22/awa-den-salina-di-goto-ta-kontamina/) signals a suspected contamination of Lake Goto, adjacent to the BOPEC facility. Lake Goto is historically known to be of value as a nature conservation area with, amongst others, a healthy flamingo population (*Phoenicopterus ruber*). The website reports that the flamingo's are basically gone from Lake Goto. It is indicated that the flamingo population already displayed a vast reduction of abundance within 4 months after the fire.

1.2 Objectives of the follow-up study

Two years after the fire the biological condition of Lake Goto lead to the question whether the observed deterioration of ecological values may be related to delayed ecotoxicological impact caused by the 2010 BOPEC fire and the release of fire associated chemicals. On October 15, 2012, the Dutch Ministry of Infrastructure and the Environment (I&M) as requested by the Public Body of Bonaire ordered RIVM to conduct a follow-up study to assess the present chemical condition of Lake Goto and a few other salinas (salt lakes). More explicitly, the follow-up study should answer the following questions:

1. Does the water and/or the sediments of Lake Goto contain pollutants that may be related to the BOPEC fire or the fire fighting foams used
2. Are the observed concentrations of these compounds high enough to induce ecological effects?

1.3 Cooperation between RIVM and IMARES

The study plan for this follow-up evaluation of the chemical quality of Lake Goto was designed in close cooperation with I&M and our sampling partner IMARES. IMARES expects to get an assignment from the Dutch Ministery of Economic affairs (EZ) in 2013 to evaluate the possibly contaminated food supply of the flamingo population and potential other ecologically significant disturbing factors that may have caused the flamingo population to disappear. In order to make sure that the results of the RIVM research can be used for this possible ecological follow-up study, the monitoring campaign was designed and performed together. During the sampling expedition RIVM took water and sediment samples. IMARES took samples of available small animals and algae that represent the food of the flamingo birds and stored them for analysis for the possible assignment in 2013.

2 Study plan

Immediately after the fire, elevated concentrations of mixtures of PAHs and perfluorinated constituents of fire fighting foams were detected in Salina Tam and Lake Goto, both close to the BOPEC facility. It is proposed to restrict our sampling and analytical efforts to a minimally plausible set of samples from a limited number of surface waters and sediments. As a reference for the previously contaminated water bodies (Salina Tam and Lake Goto), a similar type of water body had to be selected where the flamingo abundance did not suffer from the date of the fire to the present time. Salinas in Bonaire are however differing from each other on specific characteristics (See: Buitrago et al. 2010). The reference Salinas to be selected will always differ in certain aspects from Lake Goto, e.g. in salinity, size, depth, organic matter, substrate. From this point of view, the selection can be pragmatic as well, and be based on the previous study results, in combination with recent observations that Flamingo is present in to be selected reference sites.

2.1 Sampling

The total number of sampling locations is therefore restricted to 10:

- Five sampling locations in Lake Goto at different distances from the BOPEC facility
- Three sampling locations in Salina Tam
- Two sampling locations in reference salinas. Prior to the sampling on Bonaire, we selected Salina Matijs and Salina Bartol as appropriate reference sites

This selection leads to 20 samples to be analyzed:

- Ten sampling locations, and
- Two compartments, namely surface water and sediment

2.2 Chemical analyses of potential fire related contaminants

In order to reduce the analytical expenditure, the analyses are restricted to the two groups of chemicals that are most likely associated to the 2010 BOPEC fire:

- Polycyclic aromatic hydrocarbons (PAH), possibly limited to naphtalene and phenanthrene as the most prominently occurring PAH compounds related to spilling and burning of mineral oil. These analyses were performed by the laboratory of TNO Earth, Environmental and Life Sciences, Utrecht, the Netherlands.
- Perfluorinated alkanoic acids and perfluorinated alkane sulfonic acids, possibly limited to perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) as the most prominently used constituents of fire fighting foams. These analyses were performed by the laboratory of our sampling partner IMARES, IJmuiden, the Netherlands.

2.3 Associated measurements

In order to be able to put the analytical contaminant results into a biological impact perspective, it is necessary to co-evaluate a small number environmental or sample characteristics, either during sampling in the field, or during analysis in the laboratory:

- Lab measurement of the fraction organic matter in sampled sediment. Needed because this sediment property influences bioavailability and toxicity of organic contaminants
- Lab measurement of dry weight of the sampled sediment. Needed because the environmental quality standards (EQS) for sediments are generally available based on dry weight
- Field measurement of sample descriptors like map coordinates, sampling depth and nature of the sample. Needed for mapping and identification of the sampled compartment

- Field measurement of electrical conductivity as a proxy for salinity, temperature, dissolved oxygen and pH at the time of sampling. Needed as estimates of environmental biocompatibility

2.4 Evaluation of ecological risk

The local risk of ecosystem deterioration as a consequence of ecosystem exposure to adverse chemical conditions is commonly expressed as risk quotient (RQ): the local available concentration of a single toxicant divided by a certified risk limit (RL), in this case defined as a near completely safe maximum permissible concentration (MPC) of the toxicant after prolonged exposure. If this RQ is below one, there is no risk for ecosystem damage. If the RQ is above unity, ecosystem damage is potentially to occur. RQs for similarly acting chemicals (e.g. PAH or PFC compounds) may be added (ΣRQ – in this report impossible for PFCs, due to absence of data) to evaluate the risk of local toxicant mixtures. Risk limits are defined for a diversity of different kinds of impacts and for different routes of exposure (water, sediment, soil, food, air, etc.). In the present report we will only evaluate the risk for general direct ecotoxicity originating from exposure to water and to sediment, as well as the risk for secondary poisoning from the toxicant contained in water and sediment propagating through the food chain. For the derivation of risk limits, a variety of toxicity observations obtained from single species lab tests, microcosm experiments and even field studies may be used as input. The risk limits for general direct ecotoxicity ($MPC_{eco,\ sediment}$ and $MPC_{eco,\ water}$) used in this study are either based on a species sensitivity distribution (SSD) approach with (sub)chronic no observed effect concentrations (NOEC) data (e.g. for PAH) and extrapolated to safe levels for the ecosystem, or, if not sufficient data of good quality are available (e.g. for PFOS), on the lowest (sub)chronic NOEC observed for any species tested extrapolated to a safe ecosystem level by applying assessment factors. The risk limits for secondary poisoning used in this study are derived from chronic food exposure experiments with warm blooded vertebrates (rat, mouse, monkey, bird, etc.). Safe intake levels (e.g. in mg/kg/day) are first transformed to safe concentrations in the food (e.g. mg/kg), and thereafter transformed to safe environmental concentrations in the environment where the food organisms are exposed to (e.g. water - -ng/L and/or sediment - -mg/kg). In every legislation, risk limits for individual substances are formulated according to stringent protocols, where uncertainty is followed by reducing the lowest observed effect endpoint or the derived hazard concentration with appropriate assessment factors (AF – sometimes also called safety factors). The use of assessment factors may reduce the RL by several orders of magnitude. It is therefore very hard to make a reliable estimate of what really will happen in terms of ecosystem damage in a particular situation where the RLs are exceeded. It is not always easy to trace the overall assessment factors that are applied in the derivation of risk limits. In order to express risk in easily understandable terms for lay people, a widely applied strategy is to divide the entire continuous risk scale (RQ or ΣRQ, theoretically ranging from zero to infinity) into three color coded parts:

1. The green part indicates very reliable estimates where the risk with **near 100% certainty** indicates that no impacts will occur even if the evaluated situation is to occur during prolonged periods of time. For this part of the risk scale we will adopt the local situation where the concentrations are below the certified risk limits.
2. The orange part, related to **possible risks**, is indicative for a situation where we can only predict impacts with a **large uncertainty**. In terms of RL this applies to the RQ range (uncertainty margin – UM) between the RL and the RL multiplied by the applied assessment factor.
3. The red part is indicative for the higher concentration range where we are **near 100% certain** that unacceptable impacts of chemical exposure will occur.

3 Sampling

The week from October 29th to November 2nd, 2012 a two person team consisting of Mr ing. Arthur de Groot (RIVM-IMG) and Dr Ir Michiel Kotterman (IMARES) traveled to Bonaire and took the required samples in collaboration with representatives of the Dutch Ministry of I&M and by the area managers of Stichting Nationale Parken Bonaire (STINAPA Bonaire). STINAPA is a non governmental, non profit foundation commissioned by the island government to manage the two protected areas of Bonaire: the Bonaire National Marine Park (BNMP) and the Washington Slagbaai National Park (WSNP). The sampling team was guided through the WSNP by a park ranger, Mr G. Thode.

3.1 Sampling procedure

Before the actual sampling took place at the preselected sampling locations, readings on depth, pH, conductivity, dissolved oxygen and temperature were taken in the field. The measurements where conducted just under the water surface and a few centimeters above the sediment layer on the bottom of the lake. Water and sediment samples were taken in duplicate. To avoid the introduction of turbidity in the water samples, the water samples were taken first by submersing a plastic beaker to approximately mid depth, and subsequently filling two glass 1 L bottles. After sampling the water, two 250 mL sediment samples were taken by carefully scraping the sediment of the bottom surface layer and transferring the collected sediment to a 250 ml glass container. After sampling the samples are labeled and stored in a cool box. After a sampling day, all samples where store in a refrigerator, until transport to the Netherlands. The water content in most initial sediment samples was very high due to the sampling technique. Some of these sediment samples settled considerably during storage at Bonaire. The overlaying water layer was discarded before transport to The Netherlands.

3.2 Sampling schedule and locations

Salinas Matijs and Bartol East where sampled on 29 October, Lake Goto on 30 October and Salina Tam on 31 October 2012.

A tabular overview of sampling data is given in Appendix 1, Table 6.

A map showing the sampling locations on the island of Bonaire is given in Figure 1.

Figure 1 Map of the north-eastern part of the island of Bonaire, showing the sampling locations by code – Loc 1 to 14, with missing numbers.

4 Chemical analyses and properties of the chemicals

4.1 Polycyclic Aromatic Hydrocarbons

At TNO, the analysis of PAH compounds is automated to quantify the concentrations of the most commonly occurring 16 EPA PAHs in a single analytical run. It proved that limiting the analyzed compounds to naphtalene and phenanthrene did not reduce the overall analytical expenditure.

4.1.1 *Analytical procedure*

The organic constituents in the water samples are extracted by speeddisk (J.T. Baker) filtration on a solid phase, which is then eluted with toluene. The organic constituents in the sediment samples were collected in toluene by Accelerated Solvent Extraction (ASE). The toluene solution is subsequently analyzed to determine the concentration of the 16 EPA PAHs by a GCMS procedure with isotope dilution.

4.1.2 *The PAH compounds analyzed and their risk limits*

The set of analyzed PAH compounds, together with justified risk limits for water and sediments is presented in Table 1 . The MPC values are derived by calculating the $MPC_{eco,\ water}$ and the $MPC_{eco,\ sediment}$ as the hazard concentration for 5% (HC5) of the tested species exposed to water or sediment, respectively. The testdata are given for a mix of fresh and saltwater taxa. The MPC calculations are based on a SSD approach with (sub)chronic NOEC data and dividing the resulting HC5 concentration by an AF of 5 (HC5/5) (Table 99, p 102 in Verbruggen 2012). Risk limits for secondary poisoning are not readily available for all 16 PAH compounds. In view of the very low concentrations now observed in the sample Bonaire waterbodies and the low associated risk of direct ecotoxic effects (Appendix 2, Table 7 and Appendix 4, Table 9), we did not evaluate the risk of secondary poisoning for PAH compounds. Risk limits are always derived from experiments with a limited exposure duration. For (sub)chronic toxicity tests, the maximum exposure duration is about a month. Potentially, the exposure time to the substances originating from the BOPEC fire in 2010 is now (december 2012) more than 27 months. Due to the fact that the concentrations of PAH were never so high that we may expect direct ecotoxic effects to occur, we did also not include considerations of prolonged exposure into the evaluation.

Table 1 The set of 16 most prominently occurring PAH compounds as selected by the USEPA. The HC5/5 for water and sediments are adopted as the maximum permissible risk limits. For sediments, the risk limits are standardized to sediments with 10% organic matter (OM) (Table 99, p 102 in Verbruggen 2012).

Compound	**CAS #**	**$MPC_{eco,\ water}$**	**Unit**	**$MPC_{eco,\ sediment}$ 10% OM**	**Unit**
Naphthalene	91-20-3	5400	ng/L	430	µg/kg DW
Acenaphthylene	208-96-8	4000	ng/L	510	µg/kg DW
Acenaphthene	83-32-9	1700	ng/L	530	µg/kg DW
Fluorene	86-73-7	1100	ng/L	580	µg/kg DW
Phenanthrene	85-01-8	580	ng/L	670	µg/kg DW
Anthracene	120-12-7	410	ng/L	710	µg/kg DW
Pyrene	129-00-0	270	ng/L	890	µg/kg DW
Fluoranthene	206-44-0	180	ng/L	990	µg/kg DW
Chrysene	218-01-9	74	ng/L	1700	µg/kg DW
Benz[a]anthracene	56-55-3	64	ng/L	1900	µg/kg DW
Benzo[k]fluoranthene	207-08-9	54	ng/L	2500	µg/kg DW
Benzo[b]fluoranthene	205-99-2	53	ng/L	2600	µg/kg DW

Compound	CAS #	$MPC_{eco, water}$	Unit	$MPC_{eco, sediment}$ 10% OM	Unit
Benzo[a]pyrene	50-32-8	53	ng/L	2600	µg/kg DW
Benzo[ghi]perylene	191-24-2	52	ng/L	3100	µg/kg DW
Dibenz[a,h]anthracene	53-70-3	36	ng/L	4700	µg/kg DW
Indeno[1,2,3-cd] pyrene	193-39-5	35	ng/L	4900	µg/kg DW

4.1.3 Analytical results

The analytical results of the PAH analyses are presented in Appendix 2, Table 7.

4.2 Perfluorinated compounds

At IMARES, the analysis of PFC compounds is automated to quantify the concentrations of the most commonly occurring 12 PFCs in a single analytical run. It proved that limiting the analyzed compounds to PFOA and PFOS did not reduce the overall analytical expenditure.

4.2.1 Analytical procedure

For all PFC analyses 50 ng of 13C4-PFOS in 350 µl of methanol and 50 ng of 13C4-PFOA in 350 µl of methanol were used as internal standards.

For water samples an internal standard was added to 1 liter of sample, after which the sample was vigorously shaken. A 1 g Oasis HLB solid phase extraction (SPE) column was prepared by activating with 10 ml of methanol followed by 20 ml of demineralized water after which the sample was introduced onto the column. Subsequently, 5 ml of acetonitrile was used to rinse the bottle and elute the column, followed by another 5 ml of acetonitrile. The samples where then dried over a glass filter containing sodium sulfate and concentrated to approximately 1 ml. Subsequently, 50 mg of ENVIcarb (Sigma Aldrich, Zwijndrecht, Netherlands) was added to the sample after which it was vortexed for 1 minute and then centrifuged for 20 minutes at 3000 rpm. The homogenate was transferred to a polypropylene auto sampler vial and concentrated under nitrogen to approximately 350 µl. The sample was made up to 700 µl by adding demineralized water after which the vial was capped and stored at 4°C until analysis by LC-MS.

For sediment samples, an internal standard was added to 2 g of (homogenized wet) sample in a 15 ml polypropylene (pp) tube. Eight ml of acetonitrile was added and the sample was shaken for 3 minutes by hand, 30 minutes on a shaker and then centrifuged for 20 minutes at 3000 rpm after which the acetonitrile was transferred to a 50 ml pp tube. The extraction was repeated 2 times. The extract was concentrated to 5 ml using a TurboVap. Subsequently, 5 ml of hexane was added and the sample was shaken vigorously for 5 minutes and then centrifuged at 3000 rpm for 5 minutes after which the hexane layer was removed. Due to the high salt content after concentration, the water and the acetonitrile did not fully mix (two separate layers). The salt water layer was removed by drying over 20 grams of sodium sulfate. This was repeated 2 times after which the acetonitrile extract was concentrated to approximately 700 µl. 50 mg of ENVIcarb was added and the sample was vortexed for 1 minute and subsequently centrifuged for 5 minutes at 10000 rpm. The extract was transferred into a auto sampler vial and concentrated under nitrogen to approximately 350 µl. The sample was made up to 700 µl by adding demineralized water after which the vial was capped and stored at 4°C until analysis by LC-MS.

The effect of high salt contents on the analysis was tested by using internal reference material (IRM) for water and sediment with and without added salt. No effect on determined levels was observed, not even with salt concentrations twice the level of the Bonaire salina samples.

Dry weight was determined gravimetrically by weight loss (103 °C, 3 hours). Dry weight in sediment samples was corrected for dry weight of water samples; due to the high salt content the mass of salt in the adhering water was significant.

Dry weight was also determined by washing sediment twice with a relative large volume of demineralized water (followed by centrifugation). The dry weight was comparable with the values obtained by correcting for calculated adhering salt.

Organic carbon was determined gravimetrically as loss on ignition (550°C, 22 h) in sediment samples previously washed twice with demineralized water to remove the salt.

4.2.2 *The PFC compounds analyzed, their risk limits and partitioning*

The set of analyzed PFC compounds for water and sediments is presented in Table 2, together with molecular mass, chain length and an estimate of the partitioning coefficient (Koc) of the compounds between water and the organic carbon content in the sediment (Sepulvado et al. 2011). Table 3 gives the justified risk limits that are only derived for PFOS (Moermond et al. 2011) in water. Bodar et al. (2011) derive risk limits for PFOS in terrestrial soil. We adopted these risk limits without modification for sediments. Properly derived risk limits for the other PFCs analyzed are simply not available, because these compounds have never been subject to formal toxicity testing. However, PFOS is by far the most toxic and the most bioconcentrative constituent of the fire fighting foam formulations used to extinguish the BOPEC fires. The ecotoxicological effectivity of PFOA is considered to be less than that of PFOS by a factor of approximately 50 (Hekster et al. 2003). Sulfonates accumulate in biota to a greater extent than the corresponding carboxylates (Kwadijk et al. 2010). This is most probably the only reason for PFOS to be more toxic than PFOA (personal communication Eric Verbruggen). The extent of bioconcentration of PFCs appears to be highly structure dependent. Martin et al. (2003) showed that carboxylates with less than 7, and sulfonates with less than 6 perfluoroalkyl carbons did hardly accumulate in rainbow trout. For longer PFCs than PFOS, bioconcentration factors increase with increasing length of the perfluoroalkyl chain. Luckily, the compounds with a chain length longer than 8 were not present in the samples taken in 2010 nor in 2012 (Appendix 3, Table 8). It has become clear that PFCs behave differently from non-polar and slightly polar organic micropollutants (Hekster et al. 2003). The perfluoroalkylated chain is oleophobic as well as hydrophobic (Key et al. 1997). Therefore, the partitioning process of PFCs to lipids in biota or to organic matter in sediments is not fully governed by hydrophobic interactions. PFCs are intrinsically polar chemicals. For example, PFOS is present in the environment as the dissociated salts. Therefore, electrostatic interactions may play an important role in their distribution. Both biotic membranes and sediment surfaces have various polar parts with which such interactions are plausible. For these reasons the prediction of ecotoxicity through quantitative structure-activity relationships (QSAR) based on octanol-water partitioning is not applicable to PFC compounds. Although the partitioning between water and the organic material contained in the sediments is not fully governed by partitioning between water and organic carbon, there is a marked gradient in the Koc values (Sepulvado et al. 2011) and also in the overall sediment partitioning Kd values (Möller 2009) for the PFCs associated with different chain lengths. In Figure 2 the chain length is related to the Koc value for carboxylates and sulfonates separately. Due to the fact that there are only few data available, the risk limits for PFOS are all characterized by the application of rather large assessment factors. For the determination of the risk limit for direct ecotoxicity upon (sub)chronic exposure, eleven NOEC/EC10 values are available for the combined freshwater and marine datasets (Moermond et al. 2011), the lowest of which is 27 μg/L for *Pimephales promelas*. According to the guidance, an assessment factor of 10 would normally be applied to the lowest NOEC when long-term NOECs are available from at least three species across three trophic levels. This is only sufficient, however, if the species tested can be considered to represent one of the more sensitive species groups. In the available data are several lowest observed effect concentrations (LOEC - specified by a less than sign – "<") that are far below the lowest NOEC, and substantial effects are observed at the level of these LOECs. Applying an assessment factor of 10 to the lowest NOEC of 27 µg/L would lead to an $MPC_{eco, water}$ of 2.7 µg/L. This value is highly underprotective, since considerable effects on emergence of *Chironomus tentans* were present at 2.3 µg/L. Moreover, 18% effect on metamorphosis of the insect *Enallagma cyathigerum* (Bots et al. 2010) and 80% effect on larval survival of *Oryzias latipes* (Ji et al. 2008) were observed at 10 µg/L. Therefore, an assessment factor of 100 is put on the lowest available endpoint (the LOEC of 2.3 µg/L) and the $MPC_{eco, water}$ using the assessment factor method becomes 2.3 / 100 = 0.023 µg/L = 23 ng/L. The $MPC_{eco, sediment}$ is derived with a similar method from the measured (sub)chronic toxicity in terrestrial soil for earth worm (14 day NOEC of 77 mg/kg DW at 10% organic matter (OM)) and lettuce (EC10 approx. 1 mg/kg DW). With chronic data available for only a single species of plants a assessment factor of 100 is to be applied, leading to an MPCeco, sediment of 10 µg/kg DW. Aquatic toxicity studies revealed that insect larvae are highly sensitive towards PFOS exposure. The MPC based only on earth worms and terrestrial plants may not be very protective for sediment dwelling species. The $MPC_{sp, water}$ for secondary poisoning in water is derived from the lowest MPC_{oral} of 0.037 mg/kgbiota ww for rabbits. This value is based on a no observed adverse effect level (NOAEL) of 0.1 mg/kg bw/d for maternal weight gain from a teratogenicity study where exposure lasted from gestation day 6 to day 20. The applied assessment factor is 90. Normally, the factor of 90 is applied to subchronic toxicity studies with an exposure duration of minimally 90 days. From similar studies with rats exposed during the gestation period compared with full chronic studies, it can be concluded that the assessment factor of 90 can also be applied to teratogenicity studies. The assessment factor of 90 is composed of a factor of 3 to correct for the high caloric content of fodder given in lab experiments, a factor of 3 to extrapolate from subchronic to chronic exposure and a factor of 10 as a real assessment factor. Subsequently, the $MPC_{sp, water}$ can be calculated using the bioconcentration factor (BCF) from water to food organisms of 2800 L/kg and the biomagnification factor (BMF) from food to predator of 5 kg/kg. The $MPC_{sp, water}$ thus becomes 0.037 / (2800 × 5) = 2.6 × 10-6 mg/L = 0.0026 µg/L = 2.6 ng/L. The $MPC_{sp, sediment}$ for secondary poisoning in sediments is derived from the same data with a biota-to-soil-accumulation-factor (BSAF = the ratio between the concentration in earth worms and soil) instead of the aquatic BCF. The BSAF is 2.5 kg/kg dw. With a correction for the specific mass of sediments, the $MPC_{sp, sediment}$ becomes: 3.2 µg/kg dw for sediments with 10 % of OM. For both risk limits for secondary poisoning, the assessment factor for the concentration ranges with uncertain impact is therefore set to 30. As for PAH compounds, the risk limits for PFOS are derived from experiments with a limited exposure duration. For (sub)chronic toxicity tests, the maximum exposure duration is about a month. Potentially, the exposure time to the substances originating from the BOPEC fire in 2010 is now (december 2012) more than 27 months. It is virtually impossible to account for the potential effects that may be caused by this prolonged exposure times.

Table 2 The set of the most prominently occurring PFC compounds as selected by the US EPA, together with their molecular mass, chain length and the Koc (Sepulvado et al. 2011). - = not available.

Abbreviation	Name compound	CAS#	MW (g/Mole)	Chain Length	^{10}log Koc
PFHxA	Perfluorohexanoic acid	307-24-4	314.05	6	1.91
PFOA	Perfluorooctanoic acid	335-67-1	414.07	8	2.31
PFNA	perfluorononanoic acid	375-95-1	464.08	9	2.33
PFDcA	Perfluorodecanoic acid	335-76-2	514.08	10	3.17
PFUnA	Perfluoroundecanoic acid	2058-94-8	564.09	11	-
PFDoA	Perfluorododecanoic acid	307-55-1	614.10	12	-
PFTrA	Perfluorotridecanoic acid	72629-94-8	664.11	13	-
PFBS	Perfluorobutanesulfonic acid	375-73-5	300.10	4	-
PFHxS	Perfluorohexanesulfonic acid	355-46-4	400.11	6	2.7

Abbreviation	Name compound	CAS#	MW (g/Mole)	Chain Length	^{10}log Koc
PFHpS	perfluoroheptanesulfonic acid	375-92-8	450.12	7	-
PFOS	Perfluorooctanesulfonic acid	1763-23-1	500.13	8	3.34
PFDS	Perfluorodecanesulfonic acid	335-77-3	600.14	10	-

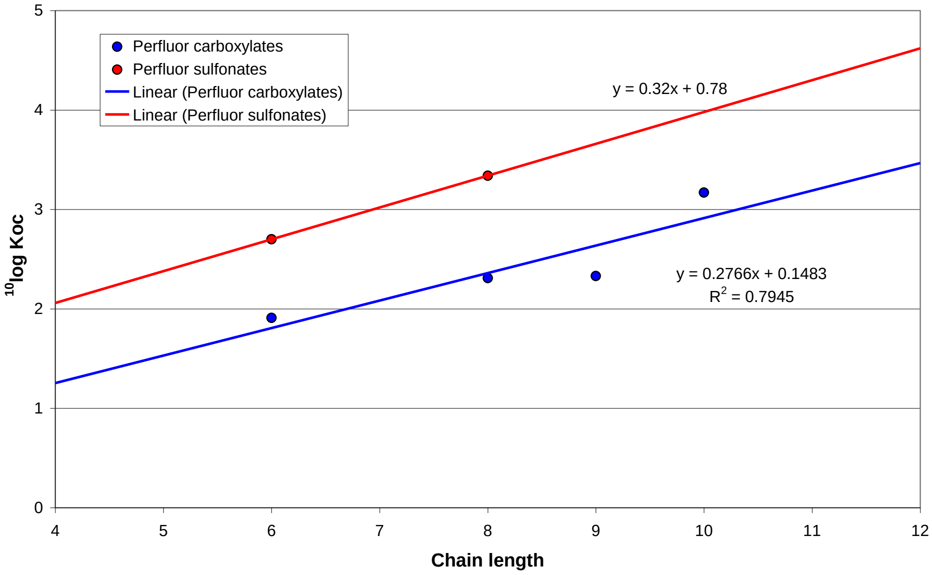

Figure 2 The relationship between chain length and Koc value (Sepulvado et al. 2011).

Table 3 The risk limits defined for PFOS as the Maximum Permissible Concentration (MPC) based on assessment factors (AF) for direct ecotoxicological effects (eco) and for secondary poisoning (sp) (Bodar 2011, Moermond et al. 2011). For sediments, the risk limits are standardized to dry sediments with 10% organic matter (OM).

Abbreviation	Name	MPC$_{eco, water}$	MPC$_{sp, water}$	MPC$_{eco, sediment}$	MPC$_{sp, sediment}$
PFOS	Perfluorooctanesulfonic acid	23 ng/L	2.6 ng/L	10 µg/kg DW	3.2 µg/kg DW
AF	Assessment factors applied (AF)	100	30	100	30

4.2.3 *Analytical results*

The analytical results of the PFC analyses are presented in Appendix 3, Table 8.

Scrutinizing the analytical results for the PFCs, the large difference between the water and sediment accommodated concentrations immediately jumps into the eye. At the locations 7 to 11, the concentrations in the water phase for the PF-carboxylates is relatively high (above 100 ng/L) for PFHxA and around 10 ng/L for PFOA. In the sediments, the concentrations of these substances are below the detection limit. This can only be explained by a relatively low hydrophobicity (low Koc, see Figure 2) and high polarity, resulting in a low adsorption to soil particulates and a high solubility. This holds for all the PF-carboxylates as compared to the PF-sulfonates. For the PF-sulfonates the situation is different. At the locations 7 to 11, we see high (>100 ng/L) water concentrations for PFBS, PFHxS and PFOS, while the concentrations for PFHpS are detectable, but below 10 ng/L. In the sediments, only the concentrations for PFHxS and PFOS are above the detection limit, but generally below a concentration of 10 µg/kg WW. The PFOS concentration in the sediment sample of location 9, with 26 µg/kg WW is deviating. At this location, sediment was very hard to collect between the hard sediment (consisting of large chunks of coral and rocks), a large part of the collected soft upperlayer of sediment was therefor collected about 50 meters from the water samples. These two spots were divided by a very low, porous dam of rocks and coral This sample is characterized by a high water content of more than 90% and a high % of organic matter. Similar to the PF-carboxylates, the low adherence of PFBS to sediment particulates prevents the high concentration in the water phase to reflect in high concentrations in the sediment.

5 Risk analysis and discussion

5.1 Polycyclic Aromatic Hydrocarbons

5.1.1 The 2012 concentrations as compared to 2010

The 2012 concentrations in water and sediments for 16 US EPA PAH compounds are presented in Appendix 2, Table 7. Immediately after the fire in 2010 the analyses of PAH compounds from water bodies in Bonaire was restricted to the sediments of Salina Tam, Lake Goto and Salina Bartol. Water samples were not taken for PAH analysis in 2010. The dataset from 2010 also relates to a subset of 12 of the 16 different PAH compounds: Acenaphthene, Anthracene, Benzo[ghi]perylene and Dibenz[a,h]anthracene were not measured in 2010. Of all the sediment concentrations measured in 2010 the highest value was 20 µg/kg DW found for naphtalene in Salina Tam. In 2012 the highest concentration was 9.9 µg/kg DW found for fluoranthene also in Salina Tam. In general the concentrations went down in the period between 2010 and 2012. Salina Matijs (Location 1) is characterized by comparatively high PAH concentrations (Appendix 2, Table 7) for acenaphtylene in water and sediment. This may be explained by a different origin and exposure route than in the other water bodies. Salina Matijs may be exposed to airborne PAH compounds, rather than the water related PAHs in Salina Tam and Lake Goto.

5.1.2 The risk of ecological damage in 2012

In tabular form the risk analysis by the sigma RQ approach of the PAH compounds contained in water and sediments of the sampled water bodies on Bonaire are presented in Appendix 4, Table 9. The RQ for a particular compound is defined as the concentration (Appendix 2, Table 7) divided by the risk limit (Table 1), both expressed in the same units. In case of sediments, the risk limits (RL) are corrected for the local organic carbon content of the sediments. The risk limit is quantified as µg/kg DW for sediments containing 10% of organic matter (OM). If the local sediment then contains x% of organic matter, the risk limit is recalculated according to $RL_{new} = RL_{old} * x\%OM/10\%OM$.

For all sampling locations in both sediments and water, the sum of the risk quotients (ΣRQ) for the different PAHs is considerably below unity (1), indicating a complete absence of risk in terms of ecosystem impact caused by exposure to PAHs. This is why we did not evaluate the risk of secondary poisoning, as wel as the assessment factors that have been applied in the derivation of the risk limits.

5.2 Perfluorinated compounds

5.2.1 The 2012 concentrations as compared to 2010

Table 4. gives a color coded comparison of the results of the maximum PFC measurements in water and sediments generated for the different water bodies immediately after the fire in 2010 (RIVM 2011) and in October 2012 (Table 8). This evaluation is only valid if the limits of detection for the 2010 and 2012 PFC concentration data are similar. The 2010 and 2012 detection limits appear to be of the same order of magnitude. A more statistical approach does not seem to be possible, because the data for 2010 and 2012 are derived from different locations. As an overall conclusion it can be stated that the concentrations of the measured PFC compounds show a slight, but for most compounds a consistent decrease since 2010. This does not mean that the PFCs are subject to degradation, but mainly that some of it is diluted by rain or sea water, or relocated to a pool of PFC in the subsoil, the groundwater, or the biota. From a comparison of individual PFC measurements (not presented), it is obvious that the PFC concentrations in the 2012 evaluation are more evenly distributed within the different water bodies.

Table 4 Color coded comparison of the maximum analytical results for sampled PFC compounds immediately after the fire in 2010 and in the month of October 2012, based on the maximum concentrations observed in the water bodies.

	Year	**2010**	**2010**	**2010**	**2010**	**2010**	**2010**	**2010**	**2010**	**2010**	
		Max. conc.	**Max. conc.**	**Max. conc.**	**Max. conc.**	**Max. conc.**	**Max. conc.**	**Max. conc.**	**Max. conc.**	**Max. conc.**	
Water body	**Medium**	**PFHxA**	**PFOA**	**PFNA**	**PFDcA**	**PFDoA**	**PFTrA**	**PFHxS**	**PFOS**	**PFDcS**	**Unit**
Lake Goto	water	140	-	0.98	<DL	<DL	<DL	383	156	<DL	**ng/L**
Salina Tam	water	4.2	-	2.24	<DL	<DL	0.2	27	254	<DL	**ng/L**
Salina Matijs	water	0.14	-	<DL	<DL	<DL	0.31	<DL	1.9	<DL	**ng/L**
Lake Goto	sediment	0.18	0.57	0.14	0.07	0.06	0.1	4.6	58.5	<DL	**µg/kg DW**
Salina Tam	sediment	0.09	0.28	0.12	0.4	0.33	0.35	0.34	-	<DL	**µg/kg DW**
Salina Matijs	sediment	-	-	-	-	-	-	-	-	-	**µg/kg DW**
	Year	**2012**	**2012**	**2012**	**2012**	**2012**	**2012**	**2012**	**2012**	**2012**	**Unit**
Lake Goto	water	180	14	<DL	<DL	<DL	<DL	210	130	<DL	**ng/L**
Salina Tam	water	<DL	5.2	2.4	<DL	<DL	<DL	18	37	<DL	**ng/L**
Salina Matijs	water	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	**ng/L**
Lake Goto	sediment	<DL	<DL	<DL	<DL	<DL	<DL	499.65	20.62	<DL	**µg/kg DW**
Salina Tam	sediment	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.6	<DL	**µg/kg DW**
Salina Matijs	sediment	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	**µg/kg DW**

- means Not Measured

Comparison
2012 < 2010
2012 ≅ 2010 (± 20%)
2012 > 2010

5.2.2 *The risk of ecological damage in 2012*

The evaluation of ecological risk associated with the observed exposure to PFOS is given as risk quotients (RQ) in *Table 5*. With respect to the risk quotient of direct ecotoxicity in water it is important to realize that a number of specific aspect should, additionally be taken into account when discussing the possibility that effects will actually occur. These aspects are 1) the simultaneously co-exposure of the organisms to other PFCs than PFOS, 2) the very long exposure time of organisms to PFCs (two years) and 3) the RL is not based on a NOEC divided by an assessment factor, but on a LOEC (i.e. concentration level at which effects will occur). It is difficult to precisely quantify the total impact of these extra factors, but they definitely point towards a larger possibility that adverse effects will become manifest, than when exceeding the risk limits for PFOS only. The reference salinas Matijs en Bartol are exposed to PFOS to a green level, indicating the complete absence of risk. For Salina Tam the exceedences op risk limits are relatively low, with a complete absence of risk for the sediments and a very modest exceedence of the risk limits for water exposure with a maximum risk of RQ = 1.6 for direct intoxication and a RQ = 14.2 for secondary poisoning. All sampling locations in Lake Goto indicate a possible risk in the uncertain orange RQ-range, for direct ecotoxicological effects induced by sediment exposure with a maximum RQ of 16.8 and an average RQ of 5.1, and for water exposure a maximum RQ of 5.7 with an average RQ of 4.8. This direct ecotoxicity may have reduced the small organisms (*Artemia*, brine fly larvae and algae) that previously served as a source of food for the disappeared flamingo population. With respect to secondary food chain poisoning, the risk is in the red zone zone for water exposure with a maximum RQ of 50 (average RQ = 42.7). For secondary poisoning originating from sediment exposure the observations are generally in the uncertain orange zone with an average RQ of 15.8. However, the maximum RQ of 52.4 for secondary poisoning from sediment exposure is the only observation with a red risk indication. For sediments the RQ maxima of 16.8 for direct ecotoxicity and of 52.4 for secondary poisoning are clear outliers with respect to the average RQ in the samples from Lake Goto of 5.2 and 15.8, respectively. These outlying RQ values are both coming from a sediment sample with a high water content taken at location 9. There is also a clear gradient that correlates with the distance to the BOPEC facility: the water samples taken at locations 7 and 8 are both characterized by a lower RQ than deducted for the locations 9 – 11.

Table 5 RQ risk analysis as performed for the measured PFOS in the sampled water bodies on Bonaire. The RQ values are calculated by dividing the measured concentrations (Appendix 2, Table 8*) by the compound and medium specific risk limit (RL as specified in Table 3), for water and sediment and for direct effects of intoxication and the occurrence of secondary poisoning in the food chain. Concentrations below the limit of detection (DL) are omitted. For the different RLs the applied assessment factor is used as an uncertainty margin (UM) for the orange RQ range. For sediments the risk limits are corrected for the organic matter content of the local sediments.*

					Matijs	**Bartol**	**Goto**					**Tam**			
PFC	**Medium**	**RL**	**Unit RL**	**Value RL**	**Loc. 1**	**Loc. 3**	**Loc. 7**	**Loc. 8**	**Loc. 9**	**Loc. 10**	**Loc. 11**	**Loc. 12**	**Loc. 13**	**Loc. 14**	**Unit**
PFOS	Water	**$\text{MPC}_{\text{eco, water}}$**	ng/L	23		0.7	85	100	130	120	120	28	30	37	ng/L
PFOS	Water	**$\text{MPC}_{\text{sp, water}}$**	ng/L	2.6		0.7	85	100	130	120	120	28	30	37	ng/L
PFOS	Sediment	**$\text{MPC}_{\text{eco, sed.}}$**	µg/kg DW OM=10%	10			18.53	20.62	499.65	13.97	11.55		4.25	5.62	µg/kg DW
PFOS	Sediment	**$\text{MPC}_{\text{sp, sed.}}$**	µg/kg DW OM=10%	3.2			18.53	20.62	499.65	13.97	11.55		4.25	5.62	µg/kg DW
			Organic matter in sediment (OM)		7.2%	10.0%	8.2%	7.4%	29.8%	5.6%	12.0%	25.5%	22.6%	21.7%	%DW
PFOS	Water	**$\text{MPC}_{\text{eco, water}}$**	Uncertainty margin (UM) = 100			0.03	3.7	4.3	5.7	5.2	5.2	1.2	1.3	1.6	RQ
PFOS	Water	**$\text{MPC}_{\text{sp, water}}$**	Uncertainty margin (UM) = 30			0.27	32.7	38.5	50.0	46.2	46.2	10.8	11.5	14.2	RQ
PFOS	Sediment	**$\text{MPC}_{\text{eco, sed.}}$**	Uncertainty margin (UM) = 100			🟩	2.3	2.8	16.8	2.5	1.0	🟩	0.2	0.3	RQ
PFOS	Sediment	**$\text{MPC}_{\text{sp, sed.}}$**	Uncertainty margin (UM) = 30			🟩	7.1	8.7	52.4	7.8	3.0	🟩	0.6	0.8	RQ

Coding of RL exceedence
🟩 **RQ below RL** **NO risk**
🟧 **RQ within uncertainty margin** **POSSIBLE risk**
🟥 **RQ beyond uncertainty margin** **HIGH risk**

6 Conclusions and recommendations

6.1 Conclusions

The results derived from the October 2012 mission on the determination of the chemical water quality for Lake Goto, Salina Tam and the reference salinas Matijs en Bartol on the island of Bonaire are inconclusive for Lake Goto and Salina Tam with respect to the two study question to be answered:

1. The concentrations PFC-compounds PFOS, PFOA, PFHxA, PFHxS, PFBS and PFHpS in the water of Salina Tam and Lake Goto are still exceeding the risk limits, but within the margin of uncertainty (Appendix 3, Table 8). For sediments the concentarations of PFHxS and PFOS are similarly exceeding the risk limits for direct ecotoxicity within the uncertainty margin only in Lake Goto. For secondary poisoning the PFOS concentrations in the water from Lake Goto and a single sediment sample from location 9 are such that the margins of uncertainty are exceeded. All of these PFC compounds are certainly related to the use of fire fighting foams (used to extinguish the BOPEC fire in 2010, or used during earlier fire incidents at the BOPEC facility). However, the concentrations for all PFC compounds show a more even distribution and a decrease in time as compared to 2010 (Table 4). For the PAH compounds, the situation is completely different. The concentrations were all well below the quality criteria for water and sediment already in 2010, but the concentrations went further down (near half) over the two years preceeding October 2012. For both types of contaminants, the reference salinas Matijs (location 1) and Bartol (location 3) have very low concentrations, not exceeding any quality criterion.
2. For all measured water bodies this implies that there are no adverse biological effects to be expected from the exposure to the very low PAH concentrations. Only for Lake Goto and Salina Tam, the exposure to PFC compounds, and mainly the exposure to PFOS as the most toxic and most bioconcentrative of all the PFCs, demonstrated to have relatively high concentrations in the range where biological effects, both directly as well as in the food chain, cannot be excluded.

6.2 Recommendations

In order to address the question if ecological effects in the food chain because of the elevated PFOS concentrations have actually taken place, an ecological study is needed. Such a study might elucidate the possibly contaminated food supply of the flamingo population and potential other ecologically or climatologicallly significant disturbing factors that may have caused the flamingo population to disappear. Some of the samples required for this evaluation are already taken by our sampling and analytical partner IMARES, awaiting an assignment in this direction by the Dutch Minstery of Economic affairs (EZ) in 2013.

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Appendix 1

Table 6 Description of samples taken, together with field measured site characteristics.

Date dd/mm/yyyy	**Sampling location**	**Sample code**	**Northing** degree	**Easting** degree	**Sample taken**	**Water Temp.** ºC	**Conductivity** ms/cm	**Barometric pressure** hPa	**DO** mg/L	**pH** unit	**Sample depth** cm	**Avifauna observations**
29/10/2012	Salina Matijs	Loc. 1	12.27497	68.35562	Sed 2x250 ml	34.91	49.9	1025.0	9.8	9.21	10-15	ca 400 flamingo's
					Water 2x1 L	34.87	49.7	102.4	9.84	9.40	5-7.5	
29/10/2012	Salina Bartol	Loc. 3	12.29925	68.38962	Sed 2x250 ml	32.44	93.2	1023.6	3.86	8.34	15-20	3 flamingo's + 1 pelican
					Water 2x1 L	32.4	104.2	1023.5	5.17	8.35	7.5=10	
30/10/2012	Lake Goto in the park	Loc. 7	12.24280	68.37103	Sed 2x250 ml	32.34	123.1	1026.9	4.25	7.96	10	4 flamingo's + 1 silver heron + 2 grey herons
					Water 2x1 L	32.34	123.1	1026.9	4.25	7.96	5	
30/10/2012	Lake Goto polluted spot according to STINAPA ranger	Loc. 8	12.23507	68.36933	Sed 2x250 ml	31.63	123.7	1026.9	3.79	7.97	30-40	no flamingo's present
					Water 2x1 L	31.68	124.8	102.9	5.1	7.99	15-20	
30/10/2012	Lake Goto near BOPEC	Loc. 9	12.22213	68.37563	Sed 2x250 ml	34.14	125.8	1026.4	6.22	7.99	30-40	no flamingo's present
					Water 2x1 L	35.19	122.7	1026.4	6.73	7.97	15-20	
30/10/2012	Lake Goto	Loc. 10	12.23342	68.37175	Sed 2x250 ml	33.01	122.4	1023.7	5.16	7.99	30-40	no flamingo's present
					Water 2x1 L	33.29	114.6	1023.7	5.06	7.97	15-20	

Date dd/mm/yyyy	**Sampling location**	**Sample code**	**Northing** degree	**Easting** degree	**Sample taken**	**Water Temp.** ºC	**Conductivity** ms/cm	**Barometric pressure** hPa	**DO** mg/L	**pH** unit	**Sample depth** cm	**Avifauna observations**
30/10/2012	Lake Goto	Loc. 11	12.22825	68.37233	Sed 2x250 ml	33.8	122.7	1023.0	5.59	8.03	30-40	no flamingo's present
					Water 2x1 L	34.82	121.8	1023.1	5.91	7.99	15-20	
31/10/2012	Salina Tam	Loc. 12	12.22200	68.39873	Sed 2x250 ml	31.23	48.6	1028.0	3.09	8.20	30-40	no flamingo's present
					Water 2x1 L	31.31	49.0	1028.0	5.36	8.32	15-20	
31/10/2012	Salina Tam	Loc. 13	12.22263	68.39967	Sed 2x250 ml	31.92	52.6	1028.1	2.72	8.04	30-40	no flamingo's present
					Water 2x1 L	30.73	48.8	1028.1	5.38	8.36	15-20	
31/10/2012	Salina Tam	Loc. 14	12.22293	68.40028	Sed 2x250 ml	30.86	48.2	1027.3	4.2	8.37	30-40	no flamingo's present, but some small birds foraging
					Water 2x1 L	30.79	48.2	1027.5	5.52	8.37	15-20	

Appendix 2

Table 7 Analytical results of the PAH measurements as performed by TNO. Yellow highlighted cells are above the limit of detection (LD).

PAH compound	**Medium**	**Loc. 1**		**Loc. 3**		**Loc. 7**		**Loc. 8**		**Loc. 9**		**Loc. 10**		**Loc. 11**		**Loc. 12**		**Loc. 13**		**Loc. 14**		**Unit**
Naphthalene	Water	<	0.34	<	0.29	<	0.32		1.84	<	0.32	<	0.32	<	0.31	<	0.28	<	0.27	<	0.28	ng/L
Acenaphthylene	Water		11.21		3.57		1.58		1.67		1.73		1.40		1.71		3.41		3.41		3.07	ng/L
Acenaphthene	Water	<	0.92	<	0.92	<	1.05	<	0.92	<	0.95	<	1.00	<	1.00	<	0.97	<	0.94	<	1.06	ng/L
Fluorene	Water		1.23		1.73		0.95		0.86		0.88		0.84		0.65		1.12	<	0.54		1.30	ng/L
Phenanthrene	Water		0.59		2.31		0.50	<	0.38	<	0.43		0.84	<	0.41		0.88		0.89	<	0.42	ng/L
Anthracene	Water	<	0.25	<	0.27	<	0.32	<	0.31	<	0.35	<	0.34	<	0.33		0.43	<	0.28	<	0.34	ng/L
Pyrene	Water	<	0.28	<	0.33		0.92		0.59	<	0.51	<	0.48	<	0.51	<	0.35	<	0.35	<	0.43	ng/L
Fluoranthene	Water	<	0.30	<	0.34		0.63	<	0.46	<	0.52	<	0.49	<	0.50	<	0.36	<	0.37	<	0.45	ng/L
Chrysene	Water	<	0.54	<	0.50	<	0.61	<	0.67	<	0.83	<	0.69	<	0.68	<	0.59	<	0.57	<	0.77	ng/L
Benz[a]anthracene	Water	<	0.65	<	0.63	<	0.83	<	0.90	<	1.06	<	0.91	<	0.96	<	0.73	<	0.72	<	1.01	ng/L
Benzo[k]fluoranthene	Water	<	0.71	<	0.57	<	0.66	<	0.69	<	0.84	<	0.74	<	0.73	<	0.70	<	0.64	<	1.04	ng/L
Benzo[b]fluoranthene	Water	<	1.18	<	1.01	<	1.27	<	1.38	<	1.65	<	1.41	<	1.52	<	1.30	<	1.19	<	1.62	ng/L
Benzo[a]pyrene	Water	<	0.95	<	0.76	<	0.88	<	0.92	<	1.07	<	0.94	<	1.00	<	0.97	<	0.90	<	1.37	ng/L
Benzo[ghi]perylene	Water	<	1.04	<	0.75	<	0.81	<	0.85	<	1.04	<	0.86	<	0.86	<	0.88		0.93		1.67	ng/L
Dibenz[a,h]anthracene	Water	<	1.24	<	0.84	<	0.91	<	1.01	<	1.14	<	0.99	<	1.01	<	0.98	<	0.92	<	1.60	ng/L
Indeno[1,2,3-cd]pyrene	Water	<	1.16	<	0.83	<	0.89	<	0.96	<	1.14	<	0.97	<	0.96	<	0.94	<	0.87	<	1.55	ng/L
Naphthalene	Sediment	<	1.79		7.17	<	1.42	<	1.01	<	1.13	<	0.35	<	1.27	<	1.23		1.77	<	0.62	µg/kg DW
Acenaphthylene	Sediment		1.45	<	0.54		0.85	<	0.34		0.65		0.64	<	1.98		3.69		1.99		3.98	µg/kg DW
Acenaphthene	Sediment		16.10	<	1.07		3.96	<	0.65	<	0.60		0.49		2.64		0.80	<	0.86		1.15	µg/kg DW

PAH compound	**Medium**	**Loc. 1**	**Loc. 3**	**Loc. 7**	**Loc. 8**	**Loc. 9**	**Loc. 10**	**Loc. 11**	**Loc. 12**	**Loc. 13**	**Loc. 14**	**Unit**
Fluorene	Sediment	1.86	< 0.40	< 0.32	< 0.30	< 0.25	< 0.15	0.46	0.95	< 0.41	0.67	µg/kg DW
Phenanthrene	Sediment	< 0.29	< 0.23	< 0.19	0.24	< 0.17	< 0.10	0.30	5.69	2.67	3.61	µg/kg DW
Anthracene	Sediment	< 0.34	< 0.24	< 0.24	0.27	< 0.17	0.21	0.46	3.82	2.86	3.44	µg/kg DW
Pyrene	Sediment	< 0.23	< 0.17	< 0.13	< 0.15	< 0.13	< 0.08	< 0.12	4.90	0.95	2.75	µg/kg DW
Fluoranthene	Sediment	< 0.18	< 0.13	< 0.10	< 0.12	2.19	< 0.06	< 0.09	9.90	4.03	6.62	µg/kg DW
Chrysene	Sediment	< 0.19	0.40	0.43	0.73	2.85	0.57	0.81	5.97	4.72	5.57	µg/kg DW
Benz[a]anthracene	Sediment	< 0.19	< 0.15	< 0.12	0.21	1.92	< 0.08	0.22	2.87	2.47	2.56	µg/kg DW
Benzo[k]fluoranthene	Sediment	< 0.17	< 0.15	< 0.12	0.21	2.00	0.11	0.22	4.11	2.37	3.39	µg/kg DW
Benzo[b]fluoranthene	Sediment	< 0.17	0.27	0.19	0.51	2.12	0.52	1.08	6.78	3.61	5.47	µg/kg DW
Benzo[a]pyrene	Sediment	< 0.22	< 0.16	< 0.15	< 0.16	2.03	< 0.10	0.20	5.29	2.93	5.35	µg/kg DW
Benzo[ghi]perylene	Sediment	< 0.17	< 0.15	< 0.13	0.46	1.54	1.35	0.35	4.45	2.47	5.86	µg/kg DW
Dibenz[a,h]anthracene	Sediment	< 0.16	< 0.16	< 0.14	< 0.15	< 0.13	0.22	< 0.11	1.15	0.58	0.89	µg/kg DW
Indeno[1,2,3-cd]pyrene	Sediment	< 0.15	0.21	0.15	0.29	1.74	< 0.09	0.51	4.39	2.28	4.28	µg/kg DW

< = Below the limit of detection (LD). LD varies with dilution factor and the recovery of internal standards.

Appendix 3

Table 8 Analytical results of the PFC measurements as performed by IMARES for water samples and wet sediment samples. The sediment concentrations calculated on a dry weight basis (lower block of data) are calculated from wet weight by a correction for sample dry weight, excluding the salt content, mainly attributable to the water phase of the sample. Yellow highlighted cells are above the limit of detection (LD). The orange highlight indicates a sediment sample with a relatively high water content.

PFC compound	**Medium**	**Loc. 1**	**Loc. 3**	**Loc. 7**	**Loc. 8**	**Loc. 9**	**Loc. 10**	**Loc. 11**	**Loc. 12**	**Loc. 13**	**Loc. 14**	**Unit**
PFHxA	Water	<3.1	<3.0	100	140	130	180	160	<3.0	<3.1	<3.0	ng/L
PFOA	Water	<0.3	<0.3	8.7	14	11	3.5	6.4	2.1	5.2	<0.3	ng/L
PFNA	Water	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	2.4	ng/L
PFDcA	Water	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	ng/L
PFUnA	Water	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	ng/L
PFDoA	Water	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	ng/L
PFTrA	Water	<3.1	<3.0	<2.9	<2.9	<2.9	<2.9	<3.0	<3.0	<3.1	<3.0	ng/L
PFBS	Water	<0.3	<0.3	160	190	170	150	160	3.1	2.4	2.6	ng/L
PFHxS	Water	<0.3	<0.3	170	210	210	210	200	18	16	14	ng/L
PFHpS	Water	<0.3	<0.3	3.4	6.1	8.3	5.7	5.3	0.3	<0.3	0.5	ng/L
PFOS	Water	<0.3	0.7	85	100	130	120	120	28	30	37	ng/L
PFDS	Water	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	ng/L
PFHxA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg WW
PFOA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg WW
PFNA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg WW
PFDcA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg WW
PFUnA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg WW
PFDoA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg WW

PFTrA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg WW
PFBS	Sediment	<0.1	<0.1	<0.10	<0.1	<0.07	<0.1	<0.1	<0.1	<0.1	<0.1	µg/kg WW
PFHxS	Sediment	<0.1	<0.1	1.3	0.1	0.4	0.2	3.4	<0.2	<0.1	<0.1	µg/kg WW
PFHpS	Sediment	<0.1	<0.1	<0.1	<0.1	<0.07	<0.1	<0.1	<0.2	<0.1	<0.1	µg/kg WW
PFOS	Sediment	<0.1	<0.1	8.1	8	26	7.4	5.4	<0.2	0.5	0.6	µg/kg WW
PFDS	Sediment	<0.1	<0.1	<0.1	<0.1	<0.07	<0.1	<0.1	<0.2	<0.1	<0.1	µg/kg WW
Dry matter in sediment		54.1%	38.4%	49.7%	45.4%	9.9%	57.6%	52.3%	15.0%	16.6%	15.5%	% W/W
Dry matter minus salt in sediment		52.4%	32.7%	43.7%	38.8%	5.2%	53.0%	46.8%	10.0%	11.8%	10.7%	% W/W
PFHxA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg DW[a]
PFOA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg DW[a]
PFNA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg DW[a]
PFDcA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg DW[a]
PFUnA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg DW[a]
PFDoA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg DW[a]
PFTrA	Sediment	<0.2	<0.2	<0.1	<0.2	<0.10	<0.2	<0.2	<0.2	<0.2	<0.2	µg/kg DW[a]
PFBS	Sediment	<0.1	<0.1	<0.10	<0.1	<0.07	<0.1	<0.1	<0.1	<0.1	<0.1	µg/kg DW[a]
PFHxS	Sediment	<0.1	<0.1	2.97	0.26	7.69	0.38	7.27	<0.2	<0.1	<0.1	µg/kg DW[a]
PFHpS	Sediment	<0.1	<0.1	<0.1	<0.1	<0.07	<0.1	<0.1	<0.2	<0.1	<0.1	µg/kg DW[a]
PFOS	Sediment	<0.1	<0.1	18.53	20.62	499.65	13.97	11.55	<0.2	4.25	5.62	µg/kg DW[a]
PFDS	Sediment	<0.1	<0.1	<0.1	<0.1	<0.07	<0.1	<0.1	<0.2	<0.1	<0.1	µg/kg DW[a]
< = Below the limit of quantification (LQ). LQ varies with dilution factor and the recovery of internal standards.												
🟧	Sediment sample with relatively high water content											
🟨	Observations above the detection limit											
[a] Dry weight calculations based on dry matter in sediment, excluding salt												

Appendix 4

Table 9 Sigma RQ risk analysis as performed for the measured PAH compounds in the sampled water bodies on Bonaire. The RQ values are calculated by dividing the measured concentrations (Appendix 2) by the compound and medium specific risk limit (RL as specified in Table 1. Concentrations below the limit of detection (DL) are omitted. For sediments the risk limits are corrected for the organic carbon content of the local sediments. The green color indicates complete absence of the risk for ecosystem damage.

PAH compound	**Medium**	**RL**	**Unit RL**	**Loc.1**	**Loc. 3**	**Loc. 7**	**Loc. 8**	**Loc. 9**	**Loc. 10**	**Loc. 11**	**Loc. 12**	**Loc. 13**	**Loc. 14**	**Unit**
Naphthalene	Water	5400	ng/L				0.000				0.000			RQ
Acenaphthylene	Water	4000	ng/L	0.003	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	RQ
Acenaphthene	Water	1700	ng/L											RQ
Fluorene	Water	1100	ng/L	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001	RQ
Phenanthrene	Water	580	ng/L	0.001	0.004	0.001			0.001		0.002	0.002		RQ
Anthracene	Water	410	ng/L								0.001			RQ
Pyrene	Water	270	ng/L			0.003	0.002							RQ
Fluoranthene	Water	180	ng/L			0.004								RQ
Chrysene	Water	74	ng/L									0.008		RQ
Benz[a]anthracene	Water	64	ng/L									0.011		RQ
Benzo[k]fluoranthene	Water	54	ng/L									0.012		RQ
Benzo[b]fluoranthene	Water	53	ng/L									0.022		RQ
Benzo[a]pyrene	Water	53	ng/L									0.017		RQ
Benzo[ghi]perylene	Water	52	ng/L									0.018	0.032	RQ
Dibenz[a,h]anthracene	Water	36	ng/L									0.026		RQ
Indeno[1,2,3-cd]pyrene	Water	35	ng/L									0.025		RQ
			ΣRQ	**0.005**	**0.006**	**0.009**	**0.004**	**0.001**	**0.003**	**0.001**	**0.004**	**0.142**	**0.034**	RQ
Organic matter content	**Medium**	**RL 10% OM**	**Unit RL**	7.2%	10.0%	8.2%	7.4%	29.8%	5.6%	12.0%	25.5%	22.6%	21.7%	OM%
Naphthalene	Sediment	430	µg/kg DW		0.017							0.002		RQ
Acenaphthylene	Sediment	510	µg/kg DW	0.004		0.002		0.000	0.002		0.003	0.002	0.004	RQ
Acenaphthene	Sediment	530	µg/kg DW	0.042		0.009			0.002	0.004	0.001		0.001	RQ
Fluorene	Sediment	580	µg/kg DW	0.004						0.001	0.001		0.001	RQ
Phenanthrene	Sediment	670	µg/kg DW				0.000			0.000	0.003	0.002	0.002	RQ
Anthracene	Sediment	710	µg/kg DW				0.001		0.001	0.001	0.002	0.002	0.002	RQ
Pyrene	Sediment	890	µg/kg DW								0.002	0.000	0.001	RQ

PAH compound	**Medium**	**RL**	**Unit RL**	**Loc.1**	**Loc. 3**	**Loc. 7**	**Loc. 8**	**Loc. 9**	**Loc. 10**	**Loc. 11**	**Loc. 12**	**Loc. 13**	**Loc. 14**	**Unit**
Fluoranthene	Sediment	990	µg/kg DW					0.001			0.004	0.002	0.003	RQ
Chrysene	Sediment	1700	µg/kg DW		0.000	0.000	0.001	0.001	0.001	0.000	0.001	0.001	0.002	RQ
Benz[a]anthracene	Sediment	1900	µg/kg DW				0.000	0.000		0.000	0.001	0.001	0.001	RQ
Benzo[k]fluoranthene	Sediment	2500	µg/kg DW				0.000	0.000	0.000	0.000	0.001	0.000	0.001	RQ
Benzo[b]fluoranthene	Sediment	2600	µg/kg DW		0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	RQ
Benzo[a]pyrene	Sediment	2600	µg/kg DW					0.000		0.000	0.001	0.000	0.001	RQ
Benzo[ghi]perylene	Sediment	3100	µg/kg DW				0.000	0.000	0.001	0.000	0.001	0.000	0.001	RQ
Dibenz[a,h]anthracene	Sediment	4700	µg/kg DW						0.000		0.000	0.000	0.000	RQ
Indeno[1,2,3-cd]pyrene	Sediment	4900	µg/kg DW		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	RQ
			ΣRQ	**0.051**	**0.017**	**0.012**	**0.002**	**0.003**	**0.006**	**0.007**	**0.021**	**0.013**	**0.020**	RQ

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