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

Compound depositions from the BOPEC fires on Bonaire

Measurements and risk assessment

RIVM letter report 609022067/2011

M. Mooij et al.

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

Compound depositions from the BOPEC fires on Bonaire

Measurements and risk assessment

RIVM Letter report 609022067/2011
M. Mooij et.al.

Colophon

Prof.dr.ir. D. van de Meent (ecotoxicologist, Laboratory for Ecological Risk Assessment)
Dr. C.W.M. Bodar (ecotoxicologist, Expertise Centre for Substances)
M.E. Boshuis (analytical expert, Centre for Inspection, Environment and Health Advice)
Ing. A.C. De Groot (specialist Environmental Assessment Module, member sample team)
Dr. D. De Zwart (ecotoxicologist, Laboratory for Ecological Risk Assessment)
Dr. S.M. Hoffer (coordinator, Centre for Inspection, Environment and Health Advice)
Ing. P.J.C.M. Janssen (toxicologist, Centre for Substances and Integrated Risk Assessment)
Drs. M. Mooij (coordinator, Centre for Inspection, Environment and Health Advice)
Drs. G.M. de Groot (editor, Centre for Inspection, Environment and Health Advice)
Prof. dr. W.J.G.M. Peijnenburg (ecotoxicologist, member Environmental Assessment Module, head Bonaire sample team)
Dr. E.M.J. Verbruggen (ecotoxicologist, Expertise Centre for Substances)

Contact:
M. Mooij
Advisory Service for the Inspectorate, Environment and Health (IMG)
martje.mooij@rivm.nl

This investigation has been performed by order and for the account of VROM-Inspectorate Crisis Management Department, within the framework of project M/609022/10/BO.

Abstract

Compound deposition from the BOPEC fires on Bonaire
Measurements and risk assessment

Some polycyclic aromatic hydrocarbons (PAHs) and some perfluorinated fire fighting foam constituents (especially perfluorooctane sulfonate, PFOS) were found in deposited soot and in water on Bonaire after the BOPEC oil depot fires in September 2010. In particular, the concentrations of PFOS decrease clearly with increasing distance from the BOPEC facilities. The soot deposition did not result in elevated concentrations of dioxins, PCBs and heavy metals. The probability and magnitude of human health and ecotoxicological risks were negligible for the PAHs, as well as for the dioxins, the PCBs and the metals. For PFOS ecotoxicological risks cannot be excluded. PFOS-concentrations may diminish over time due to natural removal processes, however, at an unknown speed. Furthermore there is a possibility that PFOS, used in fire fighting agents, may spread into the environment via groundwater. Additional measurements of PFCs in water, sediment, soil and biota should give more information on current PFOS occurrence from all potential exposure routes. This would allow for a more comprehensive risk assessment, including an appropriate risk management strategy. Options for active risk reduction management may be scarce, however, due to specific PFOS characteristics and the vulnerability of the area. Further investigation can give more information if active risk reduction measures at the BOPEC area are needed and feasible. When ecotoxicological responses would be observed in the nature reserve in the future, it is recommended to involve a tropical ecologist to investigate an appropriate impact reduction approach.

Key words:
fire, Bonaire, BOPEC, environment, ecosystem, human health, risk, dioxin, PCB, PAH, metal, PFC, PFOS

Contents

Executive Summary

Introduction and backgrounds

Two storage tanks at the BOPEC facilities on Bonaire caught fire on September 8, 2010. The fires, in tanks with crude oil and naphtha, lasted half a day and two and a half day, respectively. It was attempted to stop the fires using water, seawater and six fire fighting foams. The fires caused aerial emissions of smoke and soot in the environment, potentially in association with various hazardous compounds, which were in part deposited in the vicinity. Wet and dry depositions from the cloud of smoke and ash were observed amongst others in nearby protected nature reserves, as well as all over Bonaire.

The potential deposition of hazardous compounds was ground for concerns on human health and the nature reserves. On behalf of the competent authorities of Bonaire, the Environmental Assessment Module (EAM) of the Dutch National Institute for Public Health and the Environment (RIVM) was asked by the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM, since 2011 Ministry of Infrastructure and Environment, I&M) to execute a preliminary environmental risk assessment.

Sampling and measurements

The RIVM expert team visited Bonaire in the week of September 14, 2010. Given the nature of the burned substances (crude oil and nafta), and the materials used during the fire-fighting operations (seawater and fire fighting foams), the spread of PAHs and PFCs was the major concern. In addition, measurements were made on dioxins, polychlorinated biphenyls (PCBs) and metals. The EAM-team focussed on the deposition-route mainly. Samples were taken of debris/sediment, deposition, vegetation, water and fire fighting foams.

Risk assessment results

PAHs, dioxins, PCBs and metals

Measurements on deposited material resulted in increases of the concentrations of various PAHs, which reduced with increasing distance to the BOPEC facilities. The concentration levels of PAHs found in the Bonaire samples did, however, not indicate potential risks for human health or ecosystems. The probability and magnitude of impacts by the compounds after deposition are both negligible. The deposition of soot did not result in increases of the concentrations of dioxins, PCBs and metals. The concentration levels of these compounds found in the Bonaire samples did not indicate potential risks for human health or ecosystems. The probability and magnitude of impacts by the compounds after deposition are both negligible.

PFCs/PFOS

Perfluorinated compounds (PFCs) were analysed in both debris/sediment samples (first set of analyses) as in water samples (second set of analyses). The exposure assessments suggested that the deposited material resulted in increased concentrations of PFCs in debris and water samples in the nature reserves. The concentration levels were such that potential risks of these compounds could not be excluded, neither for human health and water organisms nor for birds and mammals being exposed via the food chain in the ecosystem. Perfluorooctane sulfonate (PFOS), is the most well known and frequently used representative of the PFCs. The available risk limits for PFOS are exceeded by one or two orders of magnitude. Actual risks for humans, via consumption of food sources from the lake, are considered negligible due to

absence of this route of exposure. Due to rainfall there is probably a natural depuration mechanism which will reduce PFOS exposure levels over time, however, at unknown speed. Furthermore, it is not clear whether additional distribution of PFOS takes place due to leakage and transport via groundwater from the BOPEC premises. Further investigation can give insight if there is relevant spread of PFOS from the BOPEC area into the soil and (ground)water. It is unknown to what extent aquatic life may have actually been affected. The ecological impact of this exposure to above-limit PFOS concentrations cannot be assessed without further observations.

Recommendations
Because both the speed of natural dilution of PFOS-concentrations in water, as the occurrence of PFOS-transport via groundwater, are unknown, it is not possible to estimate the actual risks of PFOS in the nature reserves. Additional measurements of current concentrations of PFOS in the local environment should give more information. Measurement of PFOS in soil/groundwater at the BOPEC area would give more specific insight into the potential risk of leakage of PFOS to groundwater and further on. Additional chemical monitoring would allow for a more comprehensive risk assessment, including an appropriate risk management strategy. It should be realised, however, that options for active risk reduction managementmay be scarce. This due to specific PFOS-characteristics and the vulnerability of the area. Further investigation can give more information if active risk reduction measures at the BOPEC area are needed and feasible.
When ecotoxicological responses would be observed in the nature reserve in the future, it is recommended to involve a tropical ecologist to derive an appropriate impact reduction approach. It should be noted that ecotoxicological impacts of low exposures are usually not easily detected. This means that impacts which do in fact occur may initially go unnoticed due to natural variability.

1 Introduction

1.1 Backgrounds

On Wednesday September 8, 2010, two storage tanks at the BOPEC (Bonaire Petroleum Corporation) facilities on Bonaire caught fire. The BOPEC facilities are located in the north-western half of the island of Bonaire. The area is situated at the southern shore, close to the water body between the saline inland Lake Goto and the Caribbean Sea (Figure 1).

Figure 1 The BOPEC facilities and the surrounding protected nature reserve, seen from the southwest.

Various nature areas of importance are situated in the vicinity of the BOPEC facilities, especially Washington Slagbaai National Park (see the maps in Figure 2).

Figure 2 The situation of the BOPEC-facilities (south middle, west of the channel to Lake Goto) and the protected nature areas. Lake Goto is the large lake northeast of the facilities.

Two oil storage tanks were caught fire, one with crude oil and one with naphtha (Figure 3). All available fire fighting capacity of Bonaire was activated to fight the fires, including the fire brigade of the airport.

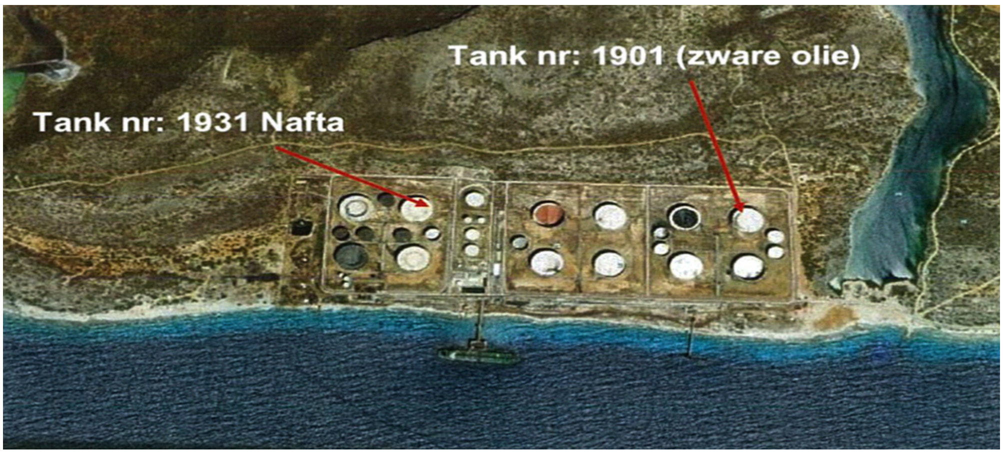

Figure 3 Detail of the BOPEC-facilities, with the naphtha tank ("1931 – Nafta") and the crude oil tank ("1901-zware olie") which caught fire.

The crude oil fire was extinguished the same day at approximately 18.00 hrs. The naphtha tank was eventually left to burn. On Friday, September 10, 2010, at approximately 22.00 hrs., the fire in the naphtha tank stopped due to lack of further fuel. After this, the tank smouldered for a further few days. An estimated amount of approximately 90,000 m^3 naphtha and crude oil has been burnt.

In the course of the fires, it was attempted to extinguish the fires with several types of fire fighting foam, water and seawater (Figure 4, Figure 5).

Figure 4 Photo impression of a later stage of the fire in the naphtha tank, including some fire fighting activities.

Figure 5 Photo impression of the sources of various fighting foams. The blue vessels contain the foam brand "Fomtec", the square ones the brand "Thunderstorm". The tanks (bottom right) are part of the permanent foam depot of BOPEC. Photos taken in the week of September 14, 2010.

The fires resulted in emissions to the premises (leakage of oil, water and foams; Figure 6). Further, there were emissions of smoke and soot to the air (Figure 7). Initially, a small column of soot and smoke was present, apparently sometimes grounding; later on, the smoke column reached high altitudes (Figure 8).

Figure 6 The situation near the burnt naphtha tank after the fire. Debris, probably of oil, water and foams, have leaked from the tank to the premises. Photos taken in the week of September 14, 2010.

Figure 7 Photo impression of various stages of the fires.

Figure 8 The smoke column reached high altitudes.

Apart from direct impacts of heat and inhalation of smoke by man and animals, concerns were voiced on the possibility that longer term risks might occur due to the emissions of hazardous compounds in the environment. Hazardous compounds may be present in the debris leaked to the soil, as well as in the smoke and associated to the soot particles. Risks of this may occur on the longer term when hazardous compounds are deposited on soil and water bodies.

Depositions may occur due to plume grounding and due to dry and wet deposition. The prevailing wind direction at the onset of the fires was from the south (various directions), triggering specific concerns for the nature areas north (various directions) of the fires. Some plume grounding in the initial stage of the fires may have occurred (see Figure 7). The smoke and soot column was spread over a broader area later on, due to changing wind directions. At that time, the smoke and soot column reached high altitudes, so that no plume grounding occurred. A low fraction of material was deposited by dry deposition on the island in that period. Visual observations in this period imply that most of the smoke and soot were transported outside the islands' borders. Heavy rains (especially on September 9, 2010) caused wet depositions on various parts of Bonaire – again including the aforementioned nature areas.

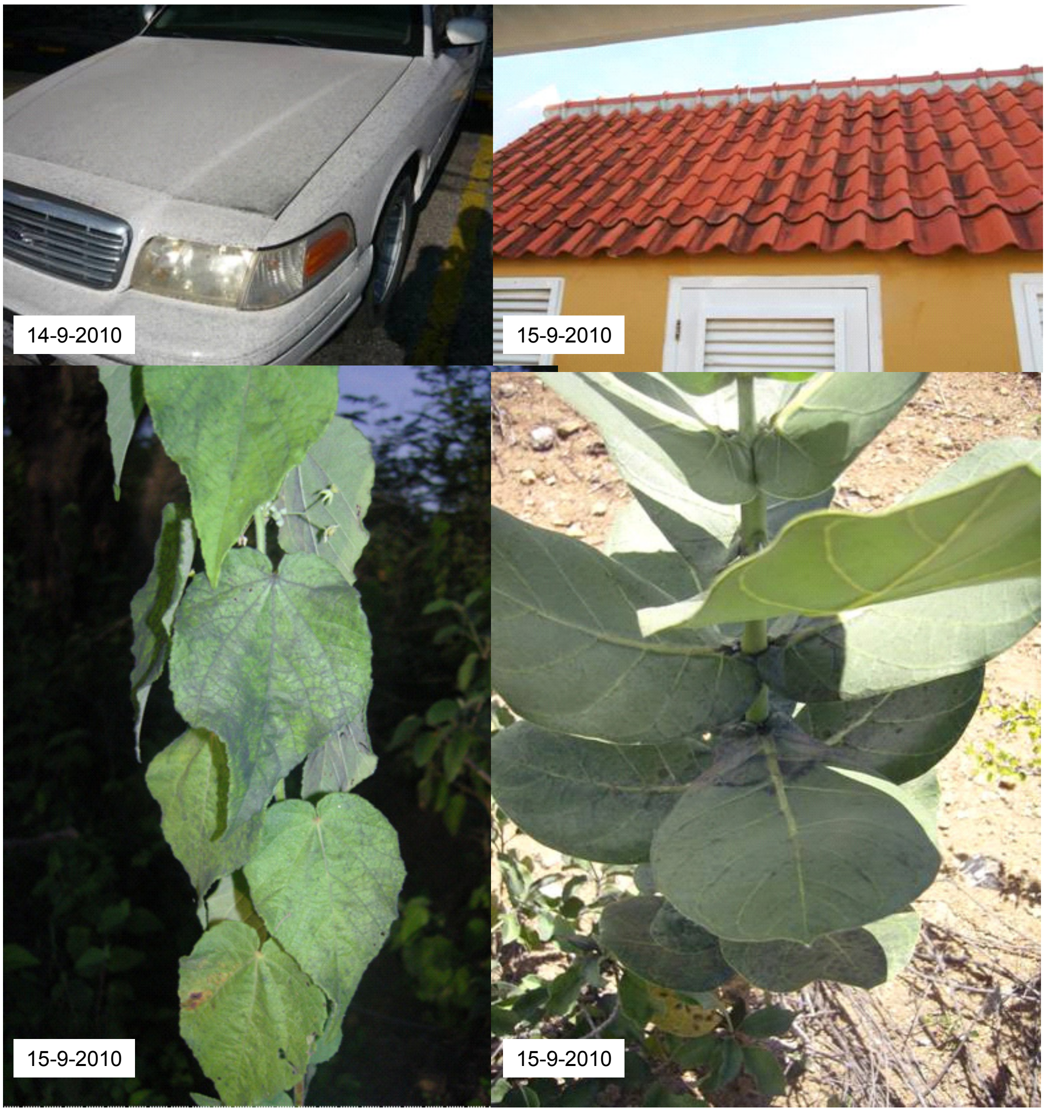

Figure 9 Pictures taken on various days after the fires, illustrating soot depositions on various materials.

Figure 10 Impression of deposited debris on the water surface (top), on the shores of the Saliña's (middle), and an impression of debris sampling (bottom).

Due to the rains that occurred during and after the fires, the deposited material was washed away from e.g. plant leaves, and accumulated down slopes and/or in the downwind direction (e.g. towards a downwind shore line). The spatial distribution within an area is therefore inhomogeneous.

1.2 Request

At the request of Bonaire's government, RIVM was requested by the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM, since 2011 Ministry of Infrastructure and Environment, I&M, Appendix 1.) to execute:

1. an environmental risk assessment of the situation after the fires, with special focus on human health risks and the ecotoxicological risks posed by the release of potentially toxic compounds on Bonaire, with special emphasis on the nature areas
2. if possible, a systematic exploration of risk management options, for the compounds for which risks could be present.

1.3 Aims

The aims of the work were:

1) to identify which compounds have been emitted on Bonaire with a primary focus on the deposition route,
2) to establish whether this could lead to potential risks for human health or the local ecosystems, based on comparisons to generic, protective environmental quality criteria
3) if possible from previous steps: establish the probability and magnitude of risks and impacts for compounds for which potential risks could not be excluded,
4) if possible from previous steps: to explore risk management perspectives.

1.4 Research approach

The spread of soot and mixtures of unknown composition that followed from the fires may imply the presence of risks of deposited hazardous compounds for human health and for the local ecosystems in the nature areas. Such (eco)toxic risks may be present directly. They may also develop over time, when a hazardous compound would detach from the soot, and spread in the environment. The latter may also occur via other emission/exposure routes, for example, distribution from the BOPEC premises via leakage to groundwater or lake catchment run-off.

Hypothesized hazardous compound depositions

To address the concerns voiced, and based on experience (e.g., Mennen et al. (2009), and Health Protection Agency of the UK (2006)) attention was paid to a set of expected compounds, shown in Table 1. Special attention was asked for the hypothesized emissions of synthetic perfluorinated organic compounds (PFCs). PFCs were expectedly present in the fire fighting foams. Further attention focused on the possible formation of hazardous chlorine-related compounds (dioxins and polychlorinated biphenyls, PCBs) because of the use of (chloride-containing) sea water to extinguish the fires.

Table 1 Compounds of potential concern. PAH=Polycyclic Aromatic Hydrocarbons. PCB=Polychlorinated Biphenyls.

Hypothesized emissions	Reason to measure
PAHs	Oil fire
Dioxins, PCBs	Use of seawater in fire fighting
PFCs	Use of foams in fire fighting
Heavy metals	Standard screening

Risk assessment

The results of the measurements are the subject of a (preliminary) risk assessment (see Chapter 3).

1.5 Contents and readers' guide

This report describes the study results as follows:

Chapter 2	describes the results of the visual inspections in the field and the sampling campaign.
Chapter 3	describes and discusses the results of the chemical analyses and evaluates the associated potential risks (risk assessment).
Chapter 4	describes the final recommendations.
Chapter 5	describes the major conclusions.

2 Observations and sampling

2.1 Observations reported to the team

An RIVM Environmental Assessment Module expert team visited Bonaire in the week of September 14, 2010. The RIVM expert team received a copy of a written report made by Mr. S. Stapert on the basis of his visual observations on September 11 and 12, 2010, at Playa Frans and Lake Goto. The report of Mr. Stapert has been submitted to the competent authority of Washington Slagbaai National Park on September 13, 2010. The report was used – in addition to the expert team's own observations – to plan the sampling scheme.

The report of Mr. Stapert reinforced the scientific expectations on the influences of the prevailing wind conditions on the gradual decrease of depositions. The report of Mr. Stapert further mentions deposition of soot-resembling material on vegetation, soil, water and sediments, including local accumulation effects, e.g., due to wind or slope.

Regarding biotic impacts, Mr. Stapert reported on impacts of soot on leaves, and impacts on leaves due to high temperatures nearby the facilities. He further reported on substantial numbers of dead brine flies and brine shrimps in Lake Goto, an effect not observed on the previous days, September 8 and 9, 2010. An unspecified number of dead fish was reported. The behavior of the flamingos was reported as aberrant from common. Dead birds were reported as follows: Least Sandpiper (2 individuals, eastern most point in Lake Goto), Barn Swallow (five individuals, Southeast part Lake Goto).

Exposure of animals to soot was hypothesized in Staperts' report for various animals. Exposure was derived from e.g. a dark color of the excrements of snails.

2.2 Observations of the team

The visual observations and the sampling efforts of the RIVM expert team started September 14, 2010 by a visit to the BOPEC facilities.

Part of the BOPEC facilities appeared contaminated with various kinds of debris and oily remnants, including remains of the activities of the fire fighters (water, foam; see Figure 6).

Subsequently, the team visited various sites around Lake Goto. The observations made by the team there reinforced the types of observations as summarized in Section 2.1. Based on their visual observations, the team reported on depositions of soot and black substances in the environment, with local accumulations, and on the likeliness of exposures of biotic species to the debris. There were no longer observations of dead aquatic biota as reported earlier.

On September 15, 2010, sampling activities progressed further, starting at Lake Goto and the nearby Saliñas, and the terrestrial nature areas in the vicinity of BOPEC. Sampling efforts focused on water, sediment, transition layers between water and sediment, dried sediment, dry soil, and vegetation. There were again no direct observations on dead or weakened biota. The absence of birds in the different Saliñas was considered remarkable by the STINAPA experts.

The expert team confirmed on September 16 the gross pattern of reduced depositions with distance to BOPEC, when their sampling range further expanded over Bonaire. On this day, the focus was on the nature areas north of the BOPEC facilities. The team reported decreasing soot deposition as compared to sample sites nearby the facilities, and a normal appearance of the biota in the area (including the presence of birds).

On the last days of the sampling campaign, the team visited and sampled the remaining areas of Bonaire, including sites most distant to and most upwind of the BOPEC facility. These samples are considered as relative references in the remainder of the assessment. The samples included spots near the village of Rincon, near a goat farm in the central part of Bonaire, and in the west of Bonaire.

2.3 Sampling and sampling sites

Based on the scientific expectation and the report of Mr. Stapert, samples were taken by an RIVM expert team of the Environmental Assessment Module. The sampling campaign was supported by the local authorities and by the area managers of Slagbaai National Park (STINAPA). Samples were taken all over Bonaire, as depicted in Figure 11. The campaign started by a visit to the BOPEC premises. Subsequently, the team took samples from various substrates in Slagbaai National Park, and the remainder of the island. The team reported that the amount of deposited soot reduced with increasing distance to the BOPEC facilities.
For part of the time, the amounts of material that were deposited on the island were visible by bare eye, in the form of thin black layers amongst others on soil, water, sediment, vegetation, cars and roofs. Material deposited on soil and water surfaces is named ‘debris’ in the remainder of this report, since this material is in close contact with the water or the soil. An impression of the depositions is given in Figure 9 and Figure 10.

Figure 11 Bonaire-wide map showing all sample locations (yellow dots). The top of the graph is North. Generally, the prevailing wind is from Southeast, but it has been variable during the fires. The BOPEC facilities are located on the south shore in the northwest part of Bonaire. The nature areas are situated in the direct vicinity, in the northern directions from the facilities (see also Figure 2).

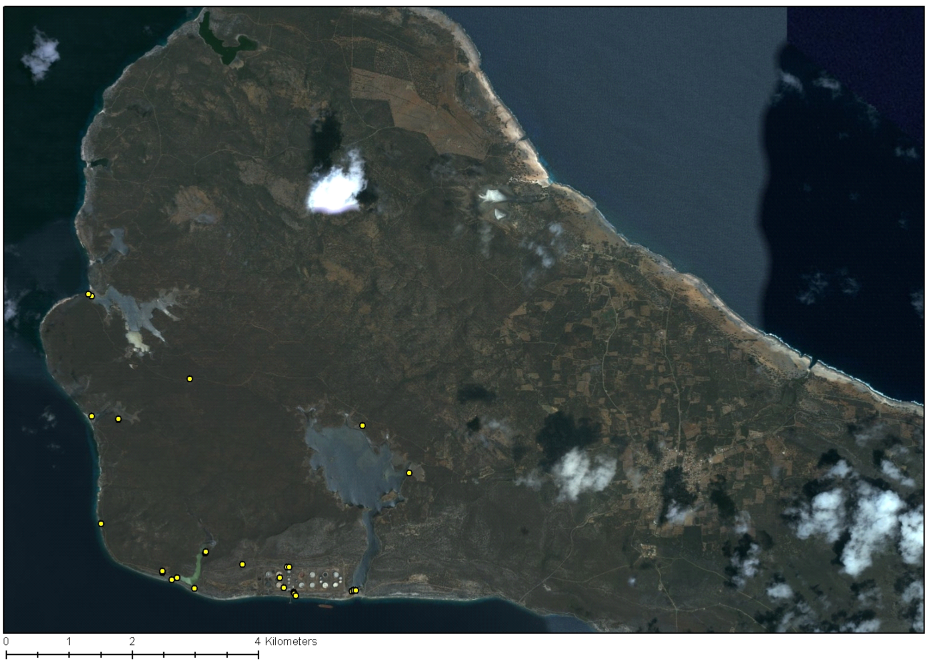

Figure 12 Detail of the map above (Figure 11), showing the sample locations (yellow dots) in north-east Bonaire around the BOPEC area and the Washington Slagbaai National Park including Lake Goto. The top of the graph is North.

The sample set consists of samples taken at the BOPEC area, including samples of two of the fire fighting foams used, and to water, soil, sediment and vegetation samples. The sample set contains samples taken at particular spots where the depositions tended to accumulate ('hot spots' debris), so as to maximize the probability of identifying compounds that may have been emitted from deposition.
Local accumulation spots were observed by the RIVM expert team, as expected:
- first, down the slopes of hills, due to effects of rainwater moving down the slopes;
- second, in the downwind areas of the larger water bodies and lakes (see Figure 10).

Samples were taken using standardized protocols.

2.3.1 *Sampling points for PAH measurements*

Samples for which PAH concentrations were determined represent samples from soil, from debris collected at the shores of Lake Goto and various Saliñas, from sediment and from vegetation. The selected samples have been taken all over Bonaire (Figure 13).

Figure 13 Map with sampling points for PAH measurements (17 samples, codes in blue).

2.3.2 *Sampling points for PFC measurements*

Samples were taken from the storage vessels of Fomtec and Thunderstorm. Further, a sample was taken from debris on the BOPEC area itself, from a local site where a mixture of water, oily substances and foams was deposited. Further samples originated from the immediate vicinity of the BOPEC facilities and Lake Goto (Figure 14).

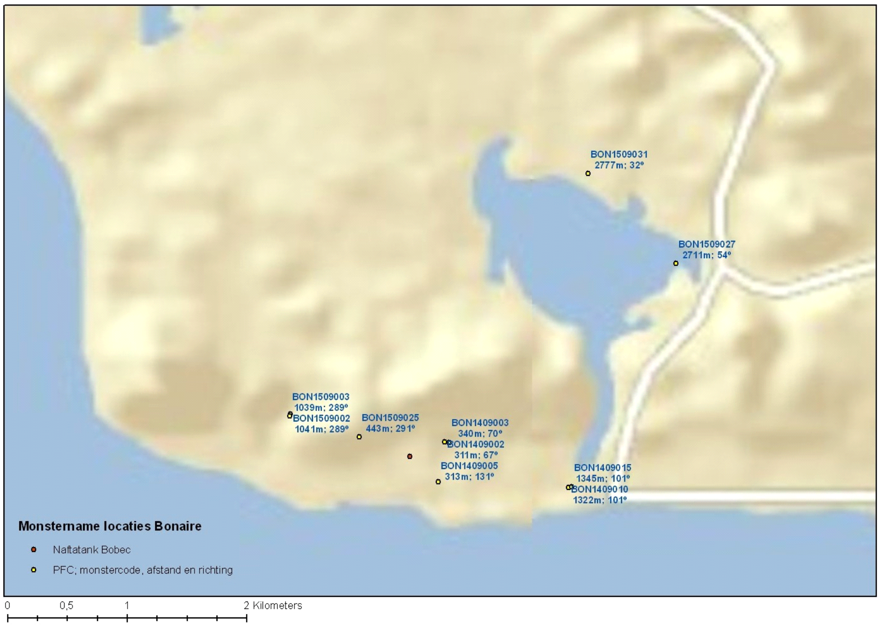

Figure 14 Map with sampling points for PFC measurements (1st set of analyses) on or near the BOPEC facility (midst of the map, south coast). See also Figure 15.

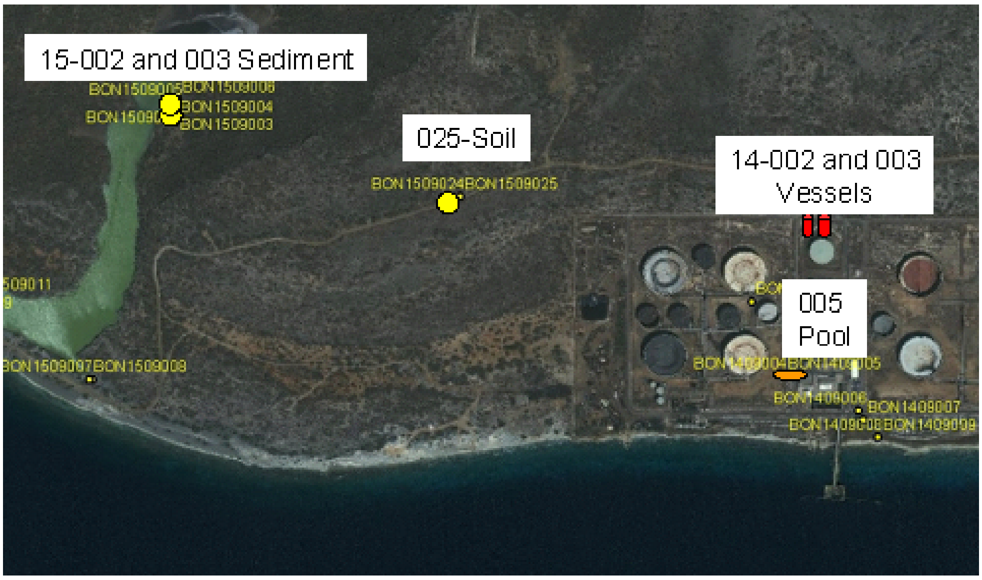

Figure 15 Detail of the map shown in Figure 14, showing the exact positions of the storage drums for the foams on the BOPEC area, the pool on the BOPEC area where fire fighting remnants were deposited as a sediment, and the nearest environmental sampling sites (1 soil and 2 sediment samples) outside the facilities. Other samples were taken at Lake Goto.

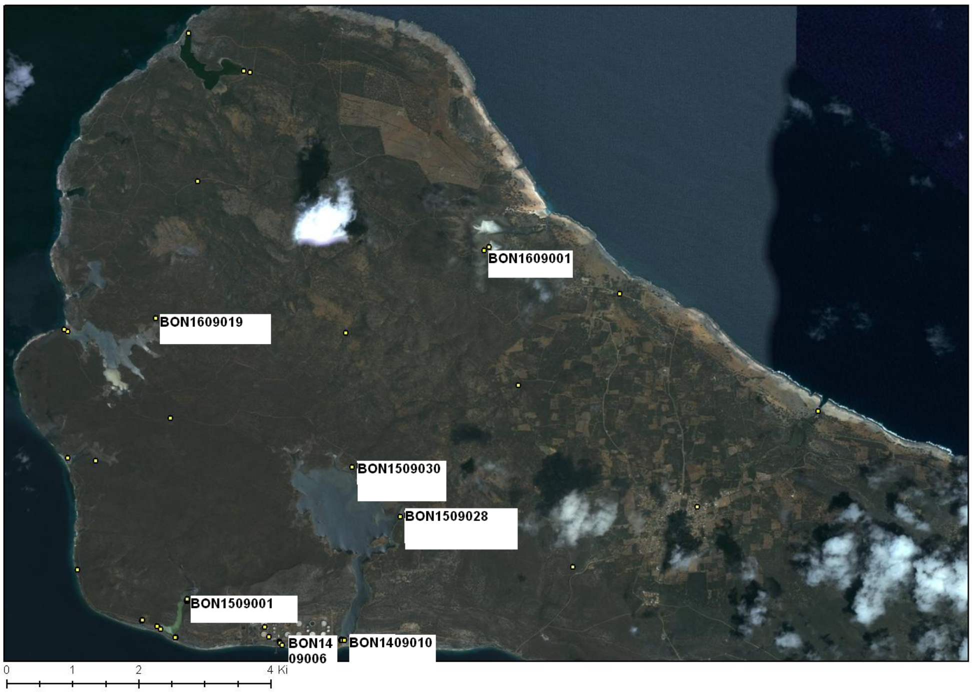

Figure 16 Sampling points for PFC-measurements (2nd set of analyses) on water and deposition.

2.3.3 *Sampling points for dioxin and PCB measurements*

Samples for dioxin and PCB measurements were taken from depositions on vegetation. Six vegetation samples were selected from the suite of samples available to be analyzed. The selection was done so as to obtain the best possible insights in the distance-concentration relationship, as basis for the preliminary risk assessment (Figure 17).

Figure 17 Map with sampling points and codes for dioxin and PCB measurements (vegetation samples; codes printed in blue).

2.3.4 *Sampling points for heavy metal measurements*

The samples for the metal measurements were taken as shown on the map in Figure 18. The samples were mainly taken to the north of the BOPEC facilities.

Figure 18 Map with sampling points for metal measurements.

3 Risk assessment

3.1 How risk assessment is done

3.1.1 Approach

Risk assessment is done by comparing actual exposure- and intake levels (concentrations of substances in air, water, soil, food; amounts of substances taken in by organisms) to safe levels. When concentrations in the environment exceed safe concentration levels, assessments are made of the expected magnitude of the effects, so that decisions can be made about the (un)acceptability and about the need to take measures.
Steps to be taken in risk assessment are:

1. *Hazard identification*
   In this case, four classes of chemical substances were identified as potential hazards: PAHs, Dioxins/PCBs, PFCs and heavy metals.
2. *Exposure assessment*
   Through measurement and reasoning, estimations are made of the concentration levels to be expected.
3. *Effects assessment*
   Sufficient knowledge exists about toxic effects of these chemical substances on human- and ecosystem health. In a first tier of risk assessment, derived safe concentrations, used in preventive environmental policy to protect from effects due to long-term exposure, are used for effects assessment.
4. *Risk characterization*
   Exposure concentrations are compared to safe levels.

Steps 2 – 4 are taken in a so-called tiered approach, iteratively refining the assessment to the level of reliability needed to serve the decision making purpose.
In this case, first-tier assessments are made by comparing actual exposure levels to maximum permissible concentrations. When the exposure concentrations are compared to these risk limits, the *safe concentration levels* are referred to as *risk limits.* When no exceedances are observed, it is concluded that the probability of unacceptable effects is low: low enough to decide that no measures are needed. In case there are exceedances, second-tier assessments are necessary, in which more detailed information is gathered on exposure levels, effects levels, or both.

3.1.2 Environmental exposure assessment

The general approach to assessing exposure concentrations follows the transport pathways and ecological receptors indicated schematically in Figure 19. The graph visualizes that different areas of Bonaire may contain different concentrations, and that different compartments (water, soil, sediment) may contain different concentrations.

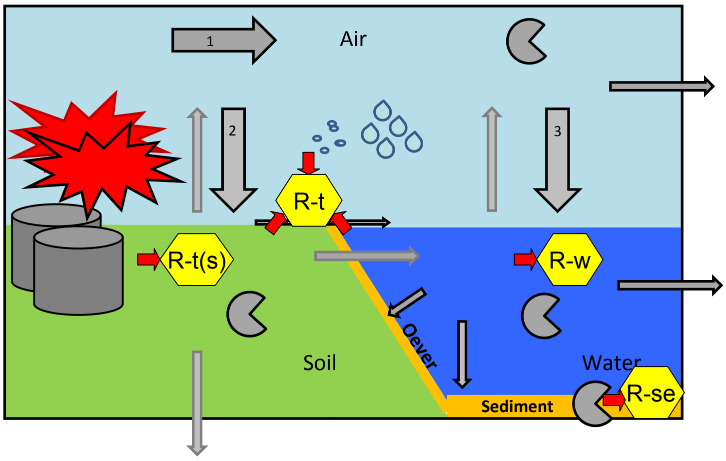

Figure 19 The conceptual model for the BOPEC fire on Bonaire. The red arrows indicate how species may be exposed: R-t(s) = terrestrial organisms living in or on the soil (exposed through soil); R – t = terrestrial mammalian and bird species (exposed through air and/or through food sources and habitat(s) [water, soil, sediment]); R-w = water inhabiting organisms (exposed through water); R-se = sediment inhabiting organisms (exposed through sediment). Numbers 1-3 indicate the initial focus of the current exposure assessment.

In case of emissions from point sources – the BOPEC incident is considered such a case – exposure concentrations are expected to decrease with increasing distance from the source. This is the result of dispersion of the chemical substance into the environment over increasingly large areas (volumes). Consequently, concentrations are expected to drop by roughly the square of the distance.
In the case of fires, when the main emissions of concern are usually to air, such exposure-distance relations have often been observed (see e.g. the reports on the environmental impacts of the emissions from the fire in the UK, at the Buncefield oil depot in 2005 (Health Protection Agency of the UK 2006; Kibble et al. 2006; Murray et al. 2006) and from the fire in the Netherlands, at a chemical storage and packaging facility near Moerdijk in 2011 (RIVM 2011a; RIVM 2011b)).
Similarly, although by different mechanisms and perhaps less pronounced, decrease of exposure levels with distance should be expected for dispersion upon emission to water and soil.

3.1.3 *Environmental effects assessment and risk characterization*

The general approach to assessing environmental effects is to compare the sensitivity of exposed organisms to the local bioavailable concentrations of compounds, taking the pathways of exposure into account (Figure 19). In this respect human beings are not different from any other species. Note that biological species may be linked to each other in the transfer of toxic compounds via predator-to-prey relationships in a so-called food chain, so that non-toxic exposures of e.g. lower organisms may be relevant for organisms higher in the food chain. This may include man, when man is eating fish from a contaminated water body, while that fish has been exposed via the water and the food.
Environmental risk assessment can be performed in a probabilistic way, relating the intensity of effects to a range of increasing concentrations. In the present study we will only perform a simple dichotomous evaluation to determine whether the locally available concentrations are exceeding the critical level where effects of a particular type may be expected to start occurring.

3.2 First-tier risk assessment

3.2.1 Use of measurements

A suite of samples was taken on Bonaire in the week after the fires. Some of these were used for the first-tier risk assessment; some were stored for later use.
In this report, measurements were used in the first-tier risk assessment using the following approaches:

- determination of spatial patterns of compound concentrations, so as to assess whether environmental concentrations of measured compounds may be associated to the fires and the subsequent depositions.
- comparison of environmental concentrations to generic, protective environmental quality criteria; this includes exploration of food chain exposure and associated risks of secondary poisoning.

Along this line, we present the results of the first-tier human- and ecological risk assessments for different compound groups. Some polycyclic aromatic hydrocarbons (PAHs) and some perfluorinated fire fighting foam constituents (especially perfluorooctane sulfonate, PFOS) were found in the soot debris deposited on Bonaire.

3.2.2 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are commonly formed during combustion. The chemical class of PAHs comprises compounds that contain two or more aromatic rings. The physical and chemical properties and toxicities of PAHs vary greatly, particularly for PAHs of different molecular size. Lower molecular weight PAHs (naphthalene, fluorene, phenanthrene, anthracene) induce higher acute toxicity in aquatic organisms than high molecular weight PAHs (e.g. chrysene, coronene). Several PAHs are carcinogenic, with benzo(a)pyrene representing the most well-studied example.

<u>Presence in the environment</u>
In general, the lower-molecular weight PAHs were most abundant in the samples, and within that subgroup detectable concentrations mostly concern naphthalene (see Appendix 2). The concentrations were below the limits of detection for many PAHs. This holds especially for the higher molecular weights. The samples were from several spots at Bonaire ranging from approximately 1.1 km from the BOPEC site to more than 19 km away. At Saliña Tam, the sampling point nearest to the BOPEC plant, the higher molecular weight PAHs were detected more frequently, and the highest PAH concentrations were observed. At greater distances, lower concentrations of all PAHs were found. Concentrations of PAHs seemed to decrease with distance from the source, but not as much as should be expected for dispersion from a point source. The clearest reduction with distance was observed for the lower PAHs and for debris. An example of this is presented in Figure 15, for debris (left) and vegetation (right). The data suggest depositions of PAHs, especially in the samples nearby BOPEC, and further with a partly decreasing, partly irregular concentration pattern.

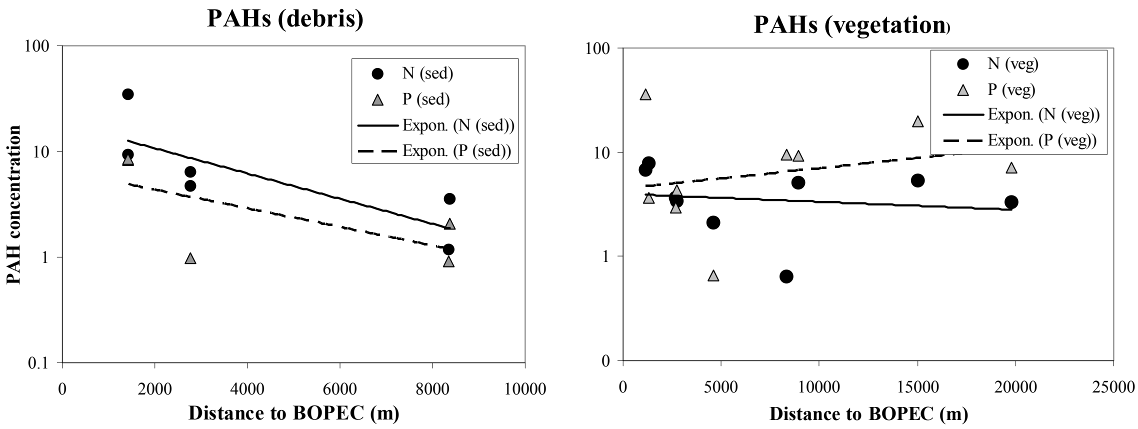

Figure 20 Concentration-distance relationship for naphthalene (N) and phenanthrene (P) in debris samples (µg/kg, left) and vegetation samples (right).

It is concluded that the PAHs are present in the environment, with a slight tendency to decrease with increasing distance from the BOPEC site. The measurements do not convincingly demonstrate that the PAHs found originate from the BOPEC fire.

Human health effects

It is well known that the critical factor in human health effects of PAHs is their carcinogenic potential. The human-toxicological evaluation proceeds by expressing exposure concentrations in terms of their potency to induce toxic (i.e. carcinogenic) effects. To this end, the effects know for benzo(a)pyrene (BaP) are used. All exposure concentrations are expressed as BaP-equivalents for carcinogenicity.
PAH concentrations in vegetation samples were maximally around 1 µg BaP-equivalents per kg plant material and usually (much) lower. Possible ingestion of such plant material (e.g. as vegetables) would result in human exposure levels below the oral maximum permissible risk (MPR) of 0.5 µg per kg body weight per day. The possible extra cancer risk associated to the concentrations found should be considered negligible: the PAH-concentrations which were found in the depositions on vegetation do not pose risks to human health beyond the MPR-criterion used by the Dutch government for long-term exposure.

Ecological effects

Maximum permissible concentrations (MPCs) for protection from toxic effects of 16 PAHs in standard sediment (organic carbon content 5%) have been proposed recently within the context of the European Union Water Framework Directive (Verbruggen, in prep.). As can be seen from Table 2 standardized soil and sediment concentrations in the Bonaire samples are well below the derived risk limits for all individual PAHs. Therefore, effects of any of the PAH-compounds alone are highly unlikely. Indicated in Table 2 is also that combined effects of the PAHs measured, expressed in toxic units (TU) fall considerably below the critical value of 1.

Table 2 PAH-concentrations for soils and sediments, normalized to standard soil and sediment in order to evaluate their ecotoxicological hazards. The net risks of the PAH-mixtures in each of the samples are expressed in the last column (Toxic Units; for technical details see Verbruggen, in prep). The risk limits (MPCs) for each of the individual PAH-compounds are given in the bottom row.

				Normalized to 5% OC.														
Sample type	Sample detail	Distance to BOPEC (m)	Direction to BOPEC	Naphtalene (µg/kg)	Acenaphtylene (µg/kg)	Fluorene (µg/kg)	Phenanthrene (µg/kg)	Fluoranthene (µg/kg)	Pyrene (µg/kg)	Benz[a]anthracene (µg/kg)	Chrysene (µg/kg)	Benzo[b]fluoranthene (µg/kg)	Benzo[k]fluoranthene (µg/kg)	Benzo[a]pyrene (µg/kg)	Indenol[123-cd]pyrene (µg/kg)	Benzo[g,h,i]perylene (µg/kg)	Toxic units
Soil	Soil at Lake Goto	2777	32	0.37			0.3										0
Soil	Soil at Salina Bartol	8367	359	4.61			1.02										0.01
Sediment	Sediment at Salina Tam	1421	268	34.83	6.15	1.41	8.36	6.52	5.73	1.57		2.99	1.57	2.92	2.02	2.15	0.14
Sediment	Sediment at shore Salina Tam	1421	268	9.41			8.44	2.87	3.45		1.32	1.18		1.11	0.87		0.05
Sediment	Sediment at Lake Goto	2777	32	4.73													0.01
Sediment	Sediment at shore Lake Goto	2777	32	6.38	1.37	0.23	0.97	0.61	1		0.27	0.2		1.43			0.02
Sediment	Sediment at shore Salina Bartol	8348	360	1.17			0.9										0
Sediment	Sediment at Salina Bartol	8367	359	3.56			2.07										0.01
Risk limit (µg/kg)				400	490	580	650	800	780	1400	1200	1800	1800	1900	3500	2200	

It is concluded that PAH concentrations at the investigated sites are low enough to consider risk to aquatic organisms living in the water column, in the sediment, or in terrestrial soils, sufficiently low.
Secondary poisoning has not been considered in this ecological effects assessment, for a number of reasons:

- no limit values have been derived by Verbruggen (in prep.);
- there is hardly any evidence that the observed PAH levels are related to the BOPEC fire;
- if relevant at all for effects on ecosystems via secondary poisoning, carcinogenic effects of PAHs are expected to be low anyhow.

3.2.3 *Dioxins and PCBs*

Dioxins and PCBs are persistent, toxic, potentially carcinogenic and they can biomagnify in food chains. They are complex chemical compounds with different chemical structures, and they are always emitted as complex mixtures of so-called dioxin congeners. Some dioxins and PCBs are highly carcinogenic (e.g., TCDD), while others are (much) less potent. The compounds can be formed during the production of chemicals (especially: chlorines) and during incineration of materials. They can be formed in any combustion process where carbon, oxygen and chlorine are present, which can be the case especially for waste. In theory, their formation cannot be excluded for the fires at BOPEC, since sea water (containing sodium chloride) was used for extinguishing the fire. The compounds can be especially formed when the combustion conditions imply incomplete burning of materials. For the BOPEC case, the black smoke column which was observed indicates such incomplete combustion.

<u>Presence in the environment</u>
Concentrations of the individual congeners were above the limits of detection only in some samples (dioxins: Appendix 4 and PCBs: Appendix 5).
Results gave no indications that concentrations decreased with increasing distance to the source for any of the dioxin or PCB congeners. There is no reason to think that the dioxins and PCBs found in the environmental samples originate from the fires at BOPEC.

<u>Human health effects</u>
Based on the analyses of Van den Berg et al. (2006), the World Health Organization has established relative toxic potentials for a number of dioxin and PCB congeners. By expressing the concentration of each of the dioxin and PCB congeners as equivalent amounts of the most toxic compound (TCDD), the risks of all congeners were aggregated to obtain a single net risk level of the dioxin and PCB mixtures in each of the samples, expressed in Toxic TCDD Equivalents (TEQs). See Table 3.

Table 3 Lower and upper bounds of the total TEQ-levels of the dioxins and the PCBs in the samples as derived from the approaches formulated by the World Health Organization (Van den Berg et al. 2006).

Sample code	Compounds	Sample type	Detail	Remark	Distance to BOPEC (m)	Direction from BOPEC	WHO-PCDD/F-PCB-TEQ [lower bound]	WHO-PCDD/F-PCB-TEQ [upper bound]
BON1509024	Dioxins and PCBs	Vegetation	Vegetation near BOPEC	Vegetation black	443	291	0.01	0.20
BON1509033	Dioxins and PCBs	Vegetation	Vegetation lear Lake Goto	Vegetation black	2777	32	0.01	0.20
BON1609036	Dioxins and PCBs	Vegetation	Village Rincon	No visible deposition	6796	75	0.48	0.59
BON1709011	Dioxins and PCBs	Vegetation	Vegetation near goat farm	No visible deposition	12039	99	0.06	0.24
BON1709014	Dioxins and PCBs	Vegetation	Vegetation near Mata di Fruta	No visible deposition	15655	114	0.22	0.41
BON1709018	Dioxins and PCBs	Vegetation	Vegetation near Dos Kura	No visible deposition	26539	138	0.01	0.20

Vegetation with a clearly visible soot deposition still present at the time of sampling showed total TEQ levels similar to vegetation collected at large distance, whereby for the latter there were no visual reports of remains of deposited soot. Note that all samples were taken after a rainy period. As can be seen from Figure 21, TEQ in vegetation samples do not show a clear relationship with distance from the source. All measured concentrations are much lower than the background levels in The Netherlands.

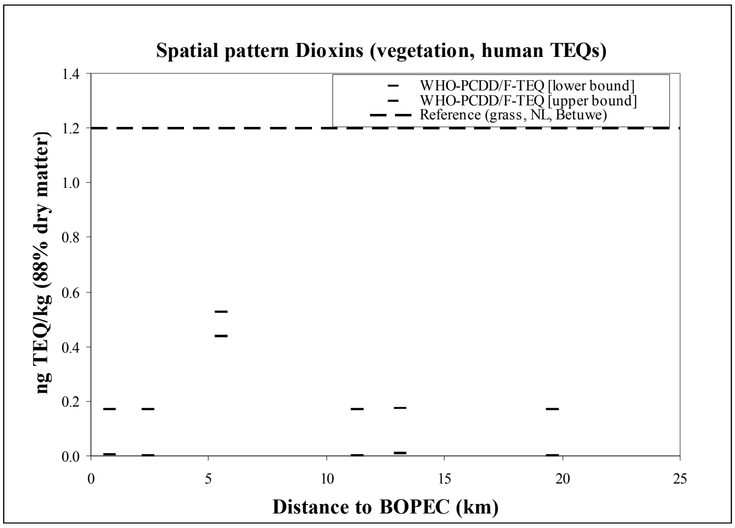

Figure 21 Distance-TEQ relationship for dioxins and PCBs based on vegetation samples analyzed for dioxins, including a sample from Rincon village. For comparison, total TEQ-values for vegetation are shown for a non-industrialized reference area in the Netherlands, in the Betuwe.

Regarding possible consumption of vegetation by cattle, e.g. at the goat farm (12 km form the fire) where one of the vegetation samples was taken, it is relevant to note that the TEQ-levels found are (far) below the EU-limit for dioxins in animal food, which is 0.75 ng TEQ/kg. As contextual information from other areas, TEQ-levels on winter grass in industrial areas in the Netherlands (e.g., Likkebaard polder) are in the range of 4-6 ng dioxin TEQ/kg (88% dry matter). In Dutch reference areas (non-industrial region), winter grass TEQ-levels are between 1.5-1.8 ng dioxin TEQ/kg. In spring and summer, these levels reduce to 0.1 till 0.4 ng dioxin TEQ/kg for both industrial and more remote areas (RIKILT 2006). The maximum values reported for vegetation on Bonaire are 0.59 ng TEQ/kg, near the village of Rincon. The vegetation near the goat farm contained an upper estimate of total TEQ of 0.24 ng/kg. The levels found in Bonaire samples are at most near and usually below the ranges found for Dutch sites used as contextual reference.
It is concluded that there is no reason for concern about human health effects from exposure to dioxins and PCBs, due to the BOPEC fires.

<u>Ecological effects</u>
A detailed ecological risk assessment has not been made for the following reasons:

- there are no relevant dioxin- or PCB enrichments related to the BOPEC fires, and local concentrations in samples from Bonaire are lower than background levels in The Netherlands;
- these exposure levels represent negligible risk to humans, known to be the most sensitive endpoint.

Without further assessment, it is assumed that there is no reason for concern about ecological effects from exposure to dioxins and PCBs, due to the BOPEC fires.

3.2.4 *Metals*

Based on standard protocols, various samples were measured for their heavy metal concentrations, to see whether levels are enhanced, perhaps as a result of the fires, and whether risk limits are exceeded.

<u>Presence in the environment</u>
Concentrations of the measured metals are summarized in Table 4 including various data on background concentrations and risk limit values used in Dutch regulations (source: website 'Risico's van Stoffen', http://www.rivm.nl/rvs/). The data give no reason to think that metal concentrations are related to the BOPEC fires, or even elevated at all.

Table 4 Summary of metal concentration data and in soil and sediment samples and various data on background concentrations in the Netherlands and risk limits for soils and sediments (in mg/kg dry weight).

Sample code	Description	Distance to BOPEC (m)	Orientation	Ni	Cu	Zn	Cd	Pb
BON1509034-1	Floating layer	2777	32	6.1	40	40	< 2.6	2.0
BON1509034-2	raw fraction	2777	32	9.6	40	39	< 3.3	2.4
BON1509032	Soil	2777	32	4.2	30	66	< 2.8	3.2
BON1609010	Soil	8348	360	8.2	26	99	< 2.7	4.0
Background concentrations for soils (NL)				35	40	140	0.6	50
Maximum Values Soil use "Housing"				39	54	200	1.2	210
BON1509010	Sediment	1421	268	4.3	39	75	< 3.1	5.3
BON1509011	Sediment	1421	268	6.3	46	76	< 2.9	4.3
BON1509031	Sediment	2777	32	5.8	30	70	< 2.8	4.0
BON1609008	Sediment	8367	359	11.5	37	118	< 2.8	4.6
BON1609009	Sediment	8367	359	7.9	24	86	< 2.8	3.3
Risk limit for sediment				44	73	620	12	530

<u>Human health effects</u>
Concentrations of nickel, copper, zinc and lead in the soil samples from Bonaire were low, compared to both the Netherlands criterion for the soil use 'Housing' and the background concentrations in The Netherlands. Cadmium levels could not be measured with sufficient sensitivity to be compared to the above references. All cadmium levels are certainly below the risk limit for soils used as "Industry", which is 4.3 mg Cd/kg dry weight.
It is concluded that there is no reason for concern about human health effects from exposure to metals, emitted during the BOPEC fires.

<u>Ecological effects</u>
Metal concentrations in the soil samples are compared specifically to the background concentrations of soil samples in The Netherlands. This comparison indicates fitness of use of the soil for the soil uses 'nature' and 'agriculture'. These comparisons indicate the absence of unacceptable ecological effects of metals in soils.
It is concluded that there is no reason for concern about ecological effects from exposure to metals, emitted during the BOPEC fires.

3.2.5 *Perfluorinated compounds*

Perfluorinated compounds (PFCs) have been used to produce aqueous film forming foam (AFFF foams (AFFFs)), used as in fire-fighting. Of this group, perfluorooctane sulfonate, commonly known as PFOS, is the most well known and the most frequently used representative. The substance persists degradation by biotic and abiotic processes, accumulates in biota by binding to proteins, biomagnifies in the food chain, and is very toxic to biota, including humans. Because of its unwanted intrinsic characteristics PFOS has received serious international policy attention during the last decade. For example, PFOS has been recently added to the list of persistent organic pollutants of the Stockholm Convention. Furthermore PFOS is recommended for inclusion as 'priority hazardous substance' in the EU Water Framework Directive. For more details about the policy status of PFOS: see Appendix 7.
Research on the samples collected by the RIVM expert team focused on the PFAAs and PFASs shown in Appendix 3. Both perfluorinated alkyl acids (PFAAs, perfluoroalkyl carboxylates) and perfluorinated alkyl sulfonates (PFASs) are compound groups that consist of various analogues. P8S is also known as PFOS.

<u>Possible emissions from use in BOPEC fire fighting</u>
During the BOPEC fires, large amounts of fire fighting foams were used. According to the competent authorities, the Dutch Ministry of Infrastructure and Environment, approximately 145,000 litres of fire fighting foam concentrates were used during the BOPEC fires (see Table 5). Unfortunately, no precise registration of the PFOS-content is available of these amounts. Various emptied foam storage vessels for foam products were observed by the RIVM sampling team. According to the vessels' labels, two of the foams that were used were "Fomtec" and "Thunderstorm". No measurements could be obtained for the materials sampled from these vessels.

On the basis of Material Safety Data Sheets of fire fighting foam concentrates, and the above information, an estimation is made of the amounts of PFOS used during the fire. According to the Material Safety Data Sheets, the content of fluoroalkyl surfactants in the fire fighting foam concentrates that were used, varies from 0% (Ajax, Thunderstorm), 0,5-1,5% (Lightwater AFFF), 0,5-2% (Universal Gold), to <5% (Fomtec) (Ajax-Chubb 2009; Chemguard 2009; 3M 2005; NF 2009; Fomtec 2005). Perfluorooctane sulfonate, PFOS/P8S, is known to be the main fluoroalkyl surfactant component of fire extinguishing foams. A debris sample and a deposition sample taken from a car, both collected on the BOPEC facilities, show that by far the highest concentrations of PFAS, were measured for P8S (=PFOS) (see Appendix 3). Therefore, it is assumed that on average 2% of the foam concentrates that contain fluoroalkyl surfactants, contains of PFOS. This means that approximately 2500 kg of PFOS have been used on a total of 145,000 L of fire fighting foam concentrates (Table 5).

Table 5 Estimated amount of PFOS present in the total volume of the six foam types reported to have been used on the BOPEC premises.

Information from Ministry (17-2-2011)		Information from MSDS	Assumed PFOS content	Amount PFOS (kg)
Foam information / Brand name	Volume used (L)	% Fluoroalkyl surfactants, according to MSDS		
3%[1] Fluoroprotein BOPEC foam storage tanks	77,715	Various manufacturers. Assumed 3% PFC (0.5-<5%)	2%	1554
3%[1] Fluoroprotein by airfreight from Venezuela	28,637	Various manufacturers. Assumed 3% PFC (0.5-<5%)		573
Light water 3% or 6%[1], AR AFFF foam received by tugboat from Curacao	13,079	Fluor containing analogues 0.5-1.5%		262
Universal Gold 1%-3%[1], Bonaire Fire Brigade	2067	Fluoralkyl surfactants 0.5-2.0%		41
Thunderstorm 1%-3%[1] ATC AR-AFFF, received by aircraft from St Croix	21,066	0% PFC	0%	0
Ajax HTF-1000 R20/R21/R22, foam received from coast guard at the jetty 1	799	0% PFC	0%	0
Total fire fighting foam used	143,363		1,7%	2430

The fate of the approximately 2,500 L of PFOS that were used, is unknown:

1. A fraction of this material may have been burnt in the fires. The recommended mechanism of removal of PFOS from the environment is adsorption by activated carbon, followed by burning of the dried carbonaceous material at high temperatures(>600 ^{o}C). It unlikely that temperatures in the BOPEC fires have been this high.
   For the present assessment, the fraction burnt is assumed to be negligible.

2. Considerable amounts must have survived the fires. Most likely, the unburnt PFOS will have associated with soot particles formed in the fire and transported by air, away from the BOPEC site over fairly long distances. One sample of soot dust, collected from a vehicle (20cm x 20cm = 0.04 m^2) present at the BOPEC site was reported to contain 130 ng of PFOS (see Appendix 3 (2nd set of analyses)). This would indicate a near-BOPEC deposition of soot-associated PFOS of no more than 3 g per km^2. This is likely to seriously underestimate the real depositions.

3. Considerable amounts must still be present at the BOPEC site, in the burnt remains of the storage tanks or spilled onto or into the soil/groundwater. Further investigation can give insight if there is relevant spread of PFOS from the BOPEC area into the soil and (ground)water.

Presence in the environment

Debris

The sampling team has focused on 'hot spots', expecting that this would yield the highest probability to find compounds which have been emitted. Several samples of what was reported as "sedimented debris" (material scraped from visually polluted surfaces) have been collected at various locations and analyzed for PFCs. The environmental samples taken outside the BOPEC-area contain

[1] The percentages mentioned in the brand names refer to the percentages of foam concentrates needed to make fire fighting foam, and do not indicate the PFC or PFOS content in the foam concentrates.

PFAAs and PFASs at varying concentrations, and generally contain higher concentrations of PFASs than of PFAAs (Appendix 3). The concentration of PFOS is, by far, highest amongst all PFCs. Measured concentrations in debris are plotted in Figure 22.

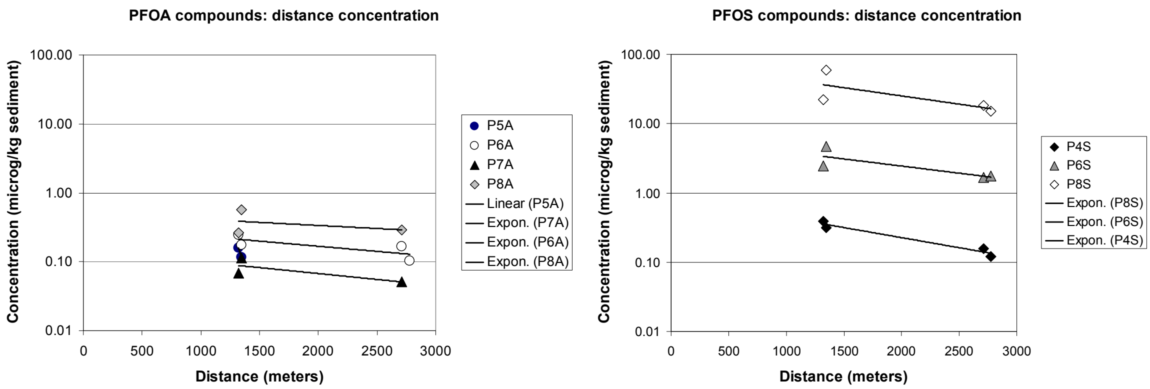

Figure 22 Concentration-distance relationships for various perfluoroalkyl compounds in sediment debris samples. The Y (concentration) axis is logarithmic.

Amongst the compounds, as expected from the debris sample of the BOPEC area, PFOS showed the highest concentrations (figure right). The measured concentrations in all these samples are further (much) lower than those measured in the foam source samples and the debris sample taken within the BOPEC area. However, extrapolation in the direction of the BOPEC facilities suggests that depositions nearer to the fires could contain PFOS-concentrations of approximately 100 μg/kg debris or higher.

Water

Water samples from various Salinas were analyzed for PFCs. Results as presented in Appendix 3 (2nd set of analyses), indicate significant concentrations of PFOS. As can be seen from Figure 23, the PFOS concentrations are much lower at greater distances from the BOPEC site.

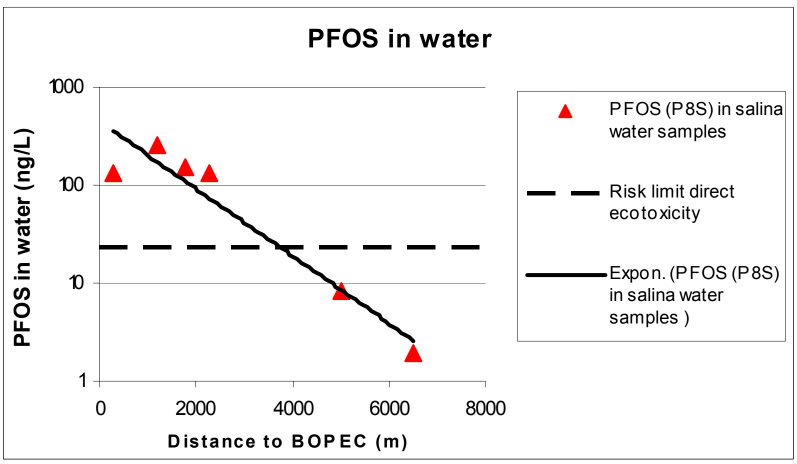

Figure 23 Concentration-distance relationships for PFOS (P8S) in water samples from Salinas. The dashed line indicates the risk limit for direct ecotoxicity of 23 ng/L (risk limits for fish consumption and secondary poisoning are lower). The Y-axis is logarithmic.

The PFOS concentrations in both water samples as debris samples, show a clear concentration-distance relationship. These observations form a strong indication that the PFOS in Salinas waters originates largely from the BOPEC fires. Measured concentrations in debris and water mutually consistent, from a perspective of expected equilibrium between them. On the basis of an organic carbon normalised partition coefficient K_{OC} of 107000 L/kg and a fraction organic carbon f_{OC} of debris of 3%, ratios of measured concentrations in debris and water water are approximately ten times smaller than the expected equilibrium ratios, which is within the error margin, lacking detailed knowledge of K_{OC} for this specific sorbent.

Only measurements on samples taken shortly after the fire event are available. It is unknown if and, if so, at what rate, concentrations in the Salinas have dropped since then. If the measured PFOS concentrations are the result of one single deposition event, concentrations in the lakes are expected to fall. On the other hand it is unknown if the measurements after 5 days already indicate the maximum levels of PFOS that are released from deposited material into the water phase. On top of that an additional flow of PFOS may (have) occur(ed) via groundwater (see below).

Groundwater
A relatively large amount of PFOS may have found its way onto the soil at the BOPEC site, as a result of the fire fighting operations. It is, at least theoretically, possible that some of this material will be transported with groundwater into the direction of Lake Goto and Salina Tam, resulting in an increase of PFOS concentrations over time. Unfortunately, nothing is known about this possible route of transport. PFOS is known to be relatively mobile. However, besides one measurement of "debris" from the BOPEC site, no PFOS measurements were made of the groundwater system.
In absence of measured data, little can be said about the possibility of future increase of PFOS concentrations, due to transport from the BOPEC site via groundwater. Further investigation can give insight if there is relevant spread of PFOS from the BOPEC area into the soil and (ground)water.

<u>Human and ecological effects</u>
Risk assessment is focused entirely on PFOS, the dominant PFC, and its targets of concern, Lake Goto and Salina Tam.
Exposure concentrations are compared to recently derived generic protective environmental risk limits (MPCs) for PFOS in water (Moermond et al. 2010). These risk limits are currently within the policy process of the EU Water Framework Directive. Within a certain time frame they are expected to be set as formal WFD Environmental Quality Standard values (EQS). The limits derived for PFOS are expressed as "truly dissolved" concentrations – much of PFOS may be present in water in other forms (associated with small particles, or in micelles) - and are based on human fish consumption direct and indirect (secondary poisoning) ecotoxicological effects to aquatic organisms and their predators in the aquatic food chain. Of these three effect types, human fish consumption is potentially the most critical effect, closely followed by secondary poisoning in the aquatic food chain (Table 6).

Table 6 Overview of relevant risk limits for PFOS in water. Data from Moermond et al. (2010).

Route	Limit [ng/L]
Human fish consumption	0.65
Direct ecotoxicity	23
Secondary poisoning	2.6

Measured concentrations in water of Lake Goto and Salina Tam clearly exceed the risk limits for human fish consumption (0,65 ng/l), secondairy poisoning (2.6 ng/l) and direct ecotoxicity of 23 ng/L.

The exceedance of the fish consumption risk limit of 0.65 ng/L could lead to human effects only if (i) PFOS concentrations would remain at this level for extended periods of time, and (ii) if fish, shellfish or other products from the lakes would be consumed by people. The exposure period of PFOS is difficult to assess due to various uncertainties as described above. However, a report obtained from the Ministry of Infrastructure and Environment, based on local information, states that human consumption of products from the lakes is excluded. It is therefore concluded that no unacceptable human health effects of PFOS are to be expected from the BOPEC fires.
Measured concentrations of PFOS in Salina Tam and Lake Goto exceed the risk limits of direct ecotoxicity (23 ng/L), in Salina Tam by more than an order of magnitude. This means that some of the aquatic species in these lakes have experienced concentrations that must be regarded as possibly unsafe, during and immediately after the fire event. The ecological impact of this exposure to above-limit PFOS concentrations cannot be assessed without further observation of the response of organisms. It should be pointed out, however, that the risk limit values are meant to prevent ecologic effects at all times, under all conditions, with sufficient certainty. When organisms are exposed to the risk limit concentrations during their entire lifetime, less than 5% of the species are expected to suffer from an effect (e.g. growth inhibition). Temporary exeedance of risk limits does not necessarily lead to irreversible ecological effects. The problem is, however, that both the actual magnitude of PFOS exposure in water and its exposure time are unknown.
Risk limits for secondary poisoning (2.6 ng/L) are being exceeded in Salina Tam and Lake Goto by one or two orders of magnitude. Secondary poisoning is a relevant exposure route for these waters (in any case Lake Goto) as birds (e.g. flamingo) largely collect their feed from these waters. The question is if problems may indeed arise from such PFOS levels in water. Here again, the actual magnitude and exposure time is unknown. Furthermore there is no information on the actual uptake (bioconcentration) of PFOS from water to specific biota, like shrimps.

For comparison, the concentrations of PFOS in other surface waters are mentioned here. Recent monitoring data from Western Europe (09/2007-02/2009) show that dissolved concentrations of PFOS were 0.9-10 ng/L in the River Rhine and tributaries in Germany, 13-19 ng/L in the River Scheldt in Belgium, 1.1 to 25 ng/L in the Rhine-Meuse delta in the Netherlands, and 0.13-0.70 in the North Sea along the Dutch coast (Möller, 2009). Other recent samples from the Netherlands show PFOS concentrations in Channel Lekkanaal (2006-2007) of 5.0-26 ng/L and in Channel Amsterdam-Rijnkanaal (2007) <d.l.(detection limit)-26 ng/L (RIWA, 2007-2008) and in several water bodies (09-10/2008) of 9-52 ng/L (www.helpdeskwater.nl). Comparing with older monitoring data, concentrations appear to have declined over the last years. In

general, concentrations in excess of 150 ng/L seem to be linked to local discharge points, e.g. a fluorochemical plant (EFSA, 2008).

Uncertainties
The uncertainties in the ecological risk assessment for PFCs are large, mainly due to uncertainty about ecological responses to the observed exeedances of risk limits of PFOS in water.
As already partly discussed above, the main reasons are:
1. Lack of knowledge of the time scale (hours, days, weeks or months?) of the present exeedance of risk limits based on the initial set of PFOS surface water measurements related to deposition. The environmental removal rate of PFOS is an important topic in this respect. Abiotic degradation and biodegradation rates are expected to be low for PFOS. Physical removal of PFOS in the lakes may be relevant (e.g. owing to water refreshment), but quantitative estimates on this are lacking. Local hydrological, geological and meteorological conditions are important parameters for such assessment.
2. Absence of information about the possible transport of spilled PFOS from the BOPEC site to the nearby lakes. This uncertainty has not been explored, but it is important to estimate both the actual magnitude and time scales of PFOS exposure from this potential, additional source. Exposure may (have) occur(ed) either via direct run-off (rainfall) or via seepage to groundwater and transport further on. One should realize that it takes a small amount of PFOS only (viz. approximately 20 g) to raise the PFOS concentration in the lake to levels that meet the risk limits, irrespective of the currently observed water PFOS levels from deposition. Further investigation can give insight if there is relevant spread of PFOS from the BOPEC area into the soil and (ground)water.

3.3 Field impact observations until February, 2011

Responses of secondary poisoning as an event chain might become overt only over prolonged time frames. To check on the risk assessment outcomes an inventory was made on the observations on impacts some months after the fires. Two sources of information were checked. Neither the official reporting systems used in disaster management and follow-up (updated till mid-February 2011), nor a deliberation on the situation between the Ministry of Infrastructure and Environment and the competent authorities (in December 2010) suggested the presence of any adverse ecotoxicological effect in the nature reserve until mid February. The latter deliberations still reported the presence of soot debris.

Despite the apparent absence of ecotoxicological impacts so far, it is noted that ecotoxicological impacts of low exposures are usually not easily detected. This means that impacts which do in fact occur may initially go unnoticed due to natural variability. The influence on next generations population effects may turn out to be an issue (for example breeding success of flamingo). The latter fact has implications for the final recommendations (next Chapter).

4 Recommendations and risk management perspectives

4.1 Recommendations

Potential and actual ecotoxicological risks of PFOS could not be excluded (paragraph 3.2.5). This conclusion is, however, based on a preliminary risk assessment. At present it is not clear what actual PFOS concentrations are in water, sediment and biota. PFOS-concentrations may have diminished, due to natural removal processes. On the other hand, insight into another possible exposure route (i.e. via groundwater) is lacking. It is not clear if such leaching from the BOPEC grounds towards surface water has indeed occurred and, if yes, whether this ‘flow’ is still active. Additional measurements of PFCs in water, sediment and biota in the lakes can give more information on current PFOS levels from all potential exposure routes. Measurement of PFOS in soil at the BOPEC-area would give more specific information of the potential risk of leakage of PFOS to groundwater.
Besides further chemical monitoring continued ecological monitoring is recommended as well. In the case that species would show aberrant population development or any unexpected individual impacts, it is recommended to involve local ecological experts, to investigate appropriate counteractive measures. It should be noted that long-term ecotoxicological impacts of low exposures are usually not easily detected. This means that impacts which do in fact occur may initially go unnoticed due to natural variability.

4.2 Measures

The above risk estimations constitute no reason to consider human health risk management measures.
The ecological risk assessment concludes that, although environmental PFOS risk limits are exceeded, there is no certainty that aquatic ecosystems have been affected to an unacceptable extent. However, there is uncertainty about the present PFOS levels in the area (see above). Therefore the final balance on potential ecotoxicological risk cannot be made yet. A comprehensive risk assessment, including an appropriate risk management strategy, could only be made after further chemical monitoring. Anticipating that active risk reduction measures would be theoretically needed, one should realize that such measures, may be very difficult, if feasible at all. This due to a combination of both specific characteristics of PFOS (e.g. its persistence) and the vulnerability of the nature reserves. Further investigation can give more information if active risk reduction measures at the BOPEC area are needed and feasible.

PFOS is a chemical that has been adopted in various (inter)national policy frameworks. This because of its unwanted intrinsic characteristics (PBT, POP). These frameworks aim at eliminating or seriously reducing the release of PFOS in the environment. When considering any risk reduction strategy for PFOS, current PFOS sanitation activities in the Netherlands should be taken into account for reasons of consistency (see also Appendix 7).

5 Conclusions

Measurements after the BOPEC fire on Bonaire in 2011 have shown there are no human or ecotoxicological risks to be expected due to deposition of PAHs, dioxins and heavy metals. However, measurements of PFCs in water and deposition have shown that ecotoxicological risks of PFOS-deposition cannot be excluded. PFOS-concentrations in water samples taken from Lake Goto and Salina Tam a week after the fire, exceed environmental risk levels.
PFOS-concentrations will diminish over time due to natural removal processes, however, at an unknown speed. Furthermore there is a possibility that PFOS, used as fire fighting agents, may (have been) additionally spread into the environment via groundwater from the polluted BOPEC area. Additional measurements of PFCs in water, sediment and soil and biota could give more information on PFOS occurrence and risks from all potential exposure routes.
It should be realised that options for active risk reduction management may be scarce, due to PFOS-characteristics and the vulnerability of the area. Further investigation can give more information if active risk reduction measures at the BOPEC area are needed and feasible.
Continued ecological monitoring is considered relevant. In the case that species would show aberrant population development or any unexpected individual impacts, it is recommended to involve local ecological experts, to investigate appropriate counteractive measures.

References

3M. 2005. Material Safety Data Sheet. FC-203CF LIGHT WATER(TM) AFFF 3%.

Ajax-Chubb. 2009. Technical specififications and properties of the foam making agents of Ajax-Chubb Fire & Safety.

Chemguard. 2009. Material Safety Data Sheet. Thunderstorm F-601B. Last Updated 9/08/2009.

EFSA. 2008. Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts. Scientific Opinion of the Panel on Contaminants in the Food chain. The EFSA Journal 653: 1-131.

Fomtec. 2005. Material Safety Data Sheet. Fomtec AFFF 3% S.

Health Protection Agency of the UK. 2006. The public health impact of the Buncefield oil depot fire - 2005.

Kibble A, Smith T, Fisher P. 2006. T he public health impact of the Buncefield oil depot fire. 2006. Appendix 1. Environmental impacts of the Buncefield oil depot explosion.

Mennen MG, Kooi ES, Heezen PAM, Van Munster G, Barreveld HL. 2009. Verspreiding van stoffen bij branden: een verkennende studie (Fire-related spread of compounds in the environment: an exploratory study). Bilthoven, The Netherlands: RIVM-Dutch National Institute for Public Health and the Environment. Report nr RIVM-report 609022031.

Moermond CTA, Verbruggen E.M.J., Smit CE. 2010. Environmental risk limits for PFOS: A proposal for water quality standards in accordance with the Water Framework Directive. . RIVM - Dutch National Institute for Public Health and the Environment. Report nr RIVM report 601714013.

Möller A. 2009. Analysis of poly- and perfluoroalkyl compounds (PFCs) in surface water of the River Rhine using HPLC-MS/MS. Diplomarbeit Fachhochschule Lübeck, Fachbereich Angewandte Naturwissenschaften Studiengang Chemieingenieurwesen. Hamburg. .

Murray V, Mohan R, Aus C, Wilson J. 2006. The public health impact of the Buncefield oil depot fire - 2006. Appendix 4. Atmospheric modelling and monitoring.

NF. 2009. Material Safety Data Sheet #NMS420. Universal Gold 1% / 3%. National Foam.

OECD. 2002. Hazard assessment of perfluorooctane sulfonate (PFOS) and its salts. Organisation for Economic Co-Operation and Development. Report nr ENV/JM/RD(2002)17/FINAL.

RIKILT. 2006. Onderzoek dioxines in gras en bodem in de Rijnmond en de overdracht naar melk. Report nr RIKILT report 2006.015. http://www.rikilt.wur.nl/NR/rdonlyres/BDEEDD31-F58C-47EB-A0AA-23CB9956CE18/34272/R2006015.pdf (page view October 5, 2010).

RIVM. 2011a. Meetresultaten MOD Brand Moerdijk voor gebied tot 10 km Benedenwinds en met uitzondering van bedrijventerrein (Measurement results of the Environmental Accidents Division for the chemical depot fire at Moerdijk, for the area up till 10 km downwind, except the industrial area itself). RIVM - Dutch National Institute for Public Health and the Environment. Report nr RIVM Letter report 609022073, version January 25, 2011.

RIVM. 2011b. Risicobeoordeling brand Moerdijk voor gebied tot 10 km. Benedenwinds en met uitzondering van bedrijventerrein (Risk

assessment for the chemical depot fire at Moerdijk for the downwind area up till 10 km, with the exception of the industrial area itself). Report nr RIVM Letter Report 609022074, version January 21, 2011.
RIWA. 2007. Jaarrapport 2006. De Rijn. Nieuwegein, The Netherlands: RIWA-Rijn.
RIWA. 2008. Jaarrapport 2007. De Rijn. Nieuwegein, The Netherlands: RIWA-Rijn.
Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L et al. 2006. The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. . Toxicological Sciences 93 (2):223–241.
Verbruggen EMJ. In prep. Environmental risk limits for polycyclic aromatic hydrocarbons (PAHs). RIVM - Dutch National Institute for Public Health and the Environment. Report nr RIVM report 601714013 (draft).

Appendix 1. The research plan of RIVM, commissioned by VROM

Postbus 1
3720 BA Bilthoven
A. van Leeuwenhoeklaan 9
Bilthoven
Tel (030) 274 91 11
Fax (030) 274 29 71
info@rivm.nl
www.rivm.nl

rivm
Rijksinstituut
voor **Volksgezondheid**
en Milieu

VROM-Inspectie - Stafafdeling Crisismanagement
Drs. C.J. Dijkens
Postbus 16191
2500 BD Den Haag

Onderwerp
Aanbieding voor het uitvoeren van een verkenning naar milieuschade in Bonaire

Geachte heer Dijkens,

Hierbij ontvangt u het plan van aanpak, betreffende de verkenning naar de huidige toestand van de natuurgebieden nav de nafta- en zware stookoliebrand op Bonaire.

Zoals afgesproken maken wij op basis van nacalculatie de kosten inzichtelijk.

Ik vertrouw erop dat ik u hiermee een passende aanbieding heb gedaan en zie uit naar een prettige samenwerking. U kunt ons schriftelijk opdracht geven door een getekend afschrift van het voorblad van deze offerte aan ons terug te sturen of te faxen.

Datum
13 september 2010
Ons kenmerk
20100329 IMG SH
Blad
1/5

Tel (030) 274 3143
Fax (030) 229 0919

IMG vraagnummer
3931

RIVM
t.a.v. dr. Sally Hoffer, pb21
Postbus 1
3720 BA Bilthoven
Fax nummer 030-2290919

Met vriendelijke groet,

Dr. Sally Hoffer

Voor akkoord contactpersoon:
Drs. C.J. Dijkens

Datum:

Handtekening :

Kosten van deze activiteit komen ten laste van:

Onderzoek in dienst van mens en milieu

rivm

Datum
13 september 2010
Ons kenmerk
20100329 IMG SH
Blad
2/5

Verkenning naar de huidige toestand van de natuurgebieden nav de nafta- en zware stookoliebrand op Bonaire

- Opstellers : Leo Posthuma, Arthur de Groot en Sally Hoffer
- IMG Vraagnummer : 3931
- Naam opdrachtgever : Drs. C.J. Dijkens
- Instelling opdrachtgever : VROM-Inspectie - Stafafdeling Crisismanagement
- Contactpersoon RIVM : dr. S.M. Hoffer

Een crisisteam op Bonaire, waaraan ook VROM functionarissen deelnemen, heeft op vrijdag 10 september gesproken met ecologische deskundigen van het RIVM. Er werd gevraagd naar de mogelijke risico's, effecten en maatregelen ten aanzien van natuur en milieu op Bonaire. Dit naar aanleiding van een brand die verontreiniging van natuurgebieden op Bonaire kan hebben veroorzaakt.

Uit dit gesprek kwam naar voren dat zonder visuele inspectie van de omvang van de milieubelasting, en van aard/concentraties van de stoffen en de lokale of diffuse verspreiding van de stoffen, het moeilijk is om telefonisch adviezen te verstrekken over het nemen van maatregelen die de schade aan natuur en milieu kan doen verminderen. De identiteit van de stoffen is namelijk enerzijds bepalend voor het gedrag in het milieu (autonome afbraak oplosbaarheid, mobiliteit, zowel van bv. water naar sediment, als van milieu naar organismen) en anderzijds de ecotoxiciteit. Opgemerkt wordt overigens, dat de zwarte vlekken die waargenomen zijn op Bonaire niet alleen uit mogelijk ecotoxische stoffen kan bestaan (zoals PAKs, of eventueel bestanddelen van het blusschuim), maar ook uit roet. Van roet (koolstof) is bekend dat het uiterst effectief is in het immobiliseren van toxische stoffen (vergelijk: Norit). In hoeverre de zwarte vlekken 'roet' zijn, of 'roet gemengd met toxische stoffen', of eventueel 'met name toxische stoffen' is van groot belang voor de ecologische risico's en effecten.

Wel zijn enkele voorstellen voor handelingen aangereikt zoals het verzamelen van biotische monsters en milieumonsters. Met de biotische monsters kan, mocht dit wenselijk zijn, achteraf met behulp van analyses het optreden van ecologische risico's bepaald worden.

Visuele waarneming is ook van belang, denk hierbij een effecten van:

- *Acute toxiciteit*:
  Acute inhalatoire toxiciteit van stoffen in de roetwolk die per direct dieren treft, met sterfte als waarneembaar gevolg (gedurende passeren roet/rookwolk).
- *Chronische toxiciteit*:
  Melding laten maken / actieve observatie van eventuele dode of verzwakte dieren na het passeren van de wolk, in relatie tot de zwarte plekken, is relevant. Indien er zonder andere aanwijsbare reden sterfte op gaat treden, kan er sprake zijn van lokale oplading van de stoffen op plekken in het milieu die door bepaalde soorten als foerageerplekken gebruikt worden, gevolgd door ophoping van de stoffen via de voedselketen (van lagere organismen in het sediment naar bv. predatoire vogels).

Bij dit soort waarnemingen dient er een nadere aandacht te komen.

In een vervolg gesprek op zaterdag 11 september met een VROM functionaris van het crisisteam is aangegeven dat een grofmazige verkenning toegespitst op het **het beoordelen van de ecologische risico's en het volgen van de effecten** een zeer wenselijke is.

Wat is de situatie:
Een blikseminslag zorgde woensdag 8 september 2010 bij het Venezolaanse overslagbedrijf BOPEC voor een brand. Hierbij vatte twee tanks vlam, een met zware stookolie erin en een met

nafta. De brand in de tank met zware stookolie was na een paar uur geblust, maar de brand in de tank met het licht ontvlambare nafta bleek een stuk hardnekkiger. Omdat de brand in deze tank niet meer onder controle te krijgen was, is besloten de tank gecontroleerd uit te laten branden. Rookpluimen en regen hebben gezorgd voor depositie in de nabijgelegen omgeving waar zich ook natuurgebieden bevinden.

De opdracht aan het RIVM is:
Voer een verkenning uit naar de risico's en effecten voor het ecologische systeem in de natuurgebieden die door de BOPEC-brand zijn verontreinigd en geef waar mogelijk advies over maatregelen ter bestrijding of vermindering van de effecten.

Aanpak:
Er wordt een twee-sporenaanpak gevolgd:

1. Overzichts-verkenning van de ruimtelijke milieubelasting (eenmalige monsterneming in het gebied; monsters van water, bodem, sediment); hiermee wordt het mogelijk uitsluitsel te geven op de aard en mogelijke omvang van de ecologische risico's.
2. Indien de overzichtsverkenning op risico's duidt, is het wenselijk om – in de opslag – al monsters te hebben van het milieu (water, bodem, sediment) en van organismen (lagere organismen) die op verschillende tijdstippen genomen zijn (typische reeksen zouden zijn: 1, 3, 7, 14, 35… dagen); deze monsters kunnen de risico's die op basis van de overzichtsverkenning vermoed worden nader specificeren of valideren.

Ad 1. Overzichtsverkenning en vaststelling aan- of afwezigheid van risico's.
In eerste instantie dient de maximale omvang van de kwetsbare gebieden waar risico's (kans op effecten, acuut en op termijn) te verwachten zijn en waar effecten die al opgetreden zijn in kaart gebracht te worden via een eenmalige monsterneming in het gebied. Risico's en effecten kunnen pas optreden als er milieubelasting was (roet/rookwolk) of is (achtergebleven stoffen in het milieu). Het door eenmalige monsterneming vaststellen van de ruimtelijke verspreiding en concentraties in water, bodem en sediment en van de identiteit van de betreffende stoffen is van belang. Immers, die identiteit bepaalt zowel het milieugedrag als de mate van toxiciteit (acuut en op langere termijn).

Ad 2. Zonodig: nadere specificatie risico's (opgeslagen monsters)
Het nemen van monsters op diverse tijdstippen na de ramp kan eventueel van belang zijn voor het volgen van de autonome afbraak of (omgekeerd) lokale accumulatie van de stoffen. Monsters van latere tijdstippen moeten dan bevroren worden opgeslagen. Analyse volgt als uit de verkennende metingen noodzaak toe blijkt.

Indien de identificatie van de stoffen en de lokale concentraties aanduiden dat er risico's op langere termijn kunnen optreden (bijvoorbeeld voor stoffen die langzaam afbreken, mobiel zijn in de richting van milieu naar organismen en/of van lagere organismen naar hogere organismen) dan kunnen waarnemingen aan daadwerkelijke opname in de lagere organismen van belang zijn. Dit om vast te stellen of er daadwerkelijk blootstelling van hogere organismen via de lagere organismen op kan treden, en zo ja, of deze toe- of afneemt in de tijd. De opname kan in de praktijk bijvoorbeeld laag zijn, doordat de lagere organismen de 'zwarte vlekken' in het milieu ontwijken, waardoor de risico's voor de hogere organismen lager zullen zijn dan verwacht. Hetzelfde effect treedt op als de zwarte vlekken met name uit roet bestaat. De biotische monsters, die evenals de milieumonsters op verschillende tijdstippen na de milieubelasting kunnen worden genomen, zullen wanneer nodig uitsluitsel geven over daadwerkelijke opname, en toe- of afname in de tijd.

rivm

Het is van belang te bepalen welke sleutelorganismen er in het gebied leven. Dit kan het beste worden vastgesteld aan de hand van overleg met de rangers. Vragen die zullen worden gesteld zijn:

- welke (hogere) soorten (zoals de flamingo's) er in het gebied vóórkomen,
- in welke mate *dít* specifieke natuurgebied cruciaal is voor de instandhoudingsdoelen van die soorten,
- en wat de dominante voedselbronnen van die soorten zijn.

Die voedselbron-soorten zouden dan bemonsterd kunnen worden; de monsters worden dan opgeslagen in de vriezer, en eventueel geanalyseerd indien daar een noodzaak toe blijkt.

Resultaten en gebruik ervan
Door de verkennende milieugegevens kan worden ingeschat in welk gebied de grootste effecten van vrijgekomen chemische stoffen voor het milieu te verwachten zijn. Daarop kan zonodig met prioriteit worden gehandeld.
Door de beschikbaar gehouden monsters van milieu en de organismen in de voedselketen kan worden gevalideerd of de verwachte risico's daadwerkelijk optreden, en kan nadere actie worden afgeleid. Daar waar mogelijk zal advisering over eventuele te treffen maatregelen plaatsvinden.

Te verwachten ruimtelijke verspreiding
Er wordt van uitgegaan dat de belasting van het ecologisch systeem afneemt met toenemende afstand tot de bron. Maar er zal rekening gehouden worden met van de bergen afstromende water/roetstromen die lokaal tot verhoogde concentraties kunnen leiden.

Activiteiten, quick-wins en no-regret acties
Hoewel de ecologische risico's en effecten feitelijk pas na vaststelling van de identiteit en concentraties van de stoffen vastgesteld kunnen worden zijn er twee activiteiten die direct kunnen worden uitgevoerd:

1. Waarnemingen aan de lokale flora en fauna: treden er na het passeren van de rook/roetwolk alsnog effecten op die gerelateerd zijn aan lokale belasting met stoffen (zwarte vlekken etc); denk niet alleen aan sterfte of verzwakking van bijvoorbeeld vogels, maar ook aan fysieke nadelige effecten zoals olie op de veren van vogels (zoals bij olierampen).
2. Quickwins. Vanuit het perspectief 'geen blootstelling = geen risico = geen effect" kan de aandacht gericht worden op locaties met geconcentreerde 'zwarte vlekken'. Indien die door een geringe inspanning (gericht op de ergste plekken) weggehaald kunnen worden, dan neemt dit de ecologische risico's ook weg. Let op: het ingezette middel moet niet erger zijn dan de kwaal. Het gaat om niet-invasieve aanpak van bestaande vlekken, en over het indammen van vlekken die zich naar kwetsbare objecten in het gebied zouden verspreiden (voorkómen van verspreiding). De leidraad voor dergelijke maatregelen kunnen het best worden geformuleerd door de rangers zelf, die het gebied het beste kennen. Door toepassing van de logica van 'geen blootstelling – geen effect' kan soms eenvoudig veel milieuwinst worden behaald.

Monstername
Bovenstaande informatie zal ook bepalend zijn voor de monstername strategie in de verkennende fase. Om de mate van verontreiniging in de natuurgebieden vast te stellen zullen de volgende monsters genomen worden:

- Bronmateriaalbemonstering (zowel nafta als het schuim dat gebruikt is voor het blussen)
- Bodem, water, sediment en stof (en vegetatie indien nodig)
- Biotische monsters (body residues prooien)

Analyse
Analyse van de monsters op nafta, blusschuim en de verbrandingsproducten zal in Nederland plaatsvinden. Enkele milieumonsters (water, bodem, sediment) en enkele bronmonsters volstaan als "eerste ronde". Bij gebleken noodzaak kunnen de opgeslagen monsters geanalyseerd worden.

rivm

Datum
13 september 2010
Ons kenmerk
20100329 IMG SH
Blad
5/5

Wie zijn er bij deze verkenning betrokken?
Namens VROM crisismanagement fungeert dhr Chris Dijkens als opdrachtgever en zal dhr. Ruud de Krom deze opdracht monitoren en als contactpersoon fungeren.

De heer Willie Peijnenburg, hoogleraar Environmental Toxicology and Biodiversity, is teamleider en zal worden ondersteund door de heer Arthur de Groot, deskundige veldmeting en monsterneming. Beide deskundigen hebben de "Environmental Emergency Training"gevolgd van de VN en hebben jarenlange operationele veldervaring met de Milieuongevallendienst van het RIVM.

Mevr. Sally Hoffer zal de missie vanuit het RIVM coördineren. De heren Dick de Zwart, Christian Mulder en Leo Posthuma (allen gepromoveerde ecologen / ecotoxicologen, met jarenlange ervaring in de kwantitatieve risicobeoordeling en betrokken bij de ontwikkeling van de UNDAC-methodiek voor het optreden bij milieurampen met toxische stoffen, assisteren bij de interpretatie van de gegevens uit de verkennende monsterneming.

Hoeveel tijd vraagt deze verkenning en wanneer vindt deze plaats?
Naar verwachting zal binnen 4-5 dagen de activiteiten op Bonaire afgerond kunnen worden. Analyses in Nederland nemen 1 week in beslag, evenals een eindrapportage. De eindrapportage van de verkennende fase omvat aard en concentraties van de stoffen in ruimtelijk perspectief, alsmede een conclusie over de mogelijke aard en omvang van de ecologische risico's die daarbij verwacht mogen worden.

De inzet zal maandag 13 september (aankomst in Bonaire dinsdag 14 september om 03h25) starten en zondag 19 september (vertrek vanuit Bonaire om 14h00) eindigen. Getracht wordt om al tijdens de inzet in Bonaire monsters naar Nederland te sturen.

Hoe rapporteren wij?
Resultaten, bevindingen en conclusies zullen via het RIVM direct gerapporteerd worden aan de opdrachtgever VROM, stafafdeling crisismanagement. De kontakten met het eilandbestuur, vertegenwoordigers van de Nederlandse overheid en de lokale overheid zijn uitsluitend bedoeld voor het inwinnen van de nodige informatie voor het uitvoeren van het onderzoek. Er vindt géén rapportage vanuit het RIVM-onderzoek plaats aan het lokaal bevoegd gezag.

Wat zijn de kosten?
Op basis van nacalculatie maken wij de kosten inzichtelijk, met als onderdelen 1) voorbereiding, 2) inzettijd, 3) analysekosten, 4) verzekering, 5) rapportage, 6) hotel- en onkostenvergoeding 7) transport van middelen/mosnters. Op een wijze zoals wij ook altijd doen bij een MOD inzet.

Op basis van onze ervaring geven wij hier een schatting. Als uitgangspunt dient de missie van RIVM/EAM naar de Oekraïne in maart 2010 welke werd uitgevoerd in opdracht van VROM en BZ. Deze missie had een gelijkwaardige aanpak waarbij bemonstering ter plaatse door een RIVM-team werd uitgevoerd en analyses in Nederland werden gedaan. Ook de uurtarieven zijn onveranderd. Maar een correctie van de kosten moet worden doorgevoerd vanwege een inzet van 3 personen voor 9 dagen in de Oekraine, terwijl nu 2 personen 6 dagen naar Bonaire zullen gaan. En er zijn verschillen in reistijd. Als schatting voor de richtbegroting komt het RIVM dan uit op €45.000.

Appendix 2. Concentration results: PAHs

Sample sites, sample characteristics, sample distances (measured in relation to the naphtha tank) and orientations in comparison to the BOPEC facilities, and measured concentrations of dioxin congeners for vegetation samples. Samples were sorted according to Sample Type and (increasing) distance.

Sample code	Measurement	Sample type	Sample detail	Remark	Distance to BOPEC (m)	Direction to BOPEC	Naphtalene (µg/kg)	Acenaphtylene (µg/kg)	Fluorene (µg/kg)	Phenanthrene (µg/kg)	Fluoranthene (µg/kg)	Pyrene (µg/kg)	Benz[a]antracene (µg/kg)	Chrysene (µg/kg)	Benzo[b]fluoranthene (µg/kg)	Benzo[k]fluoranthene (µg/kg)	Benzo[a]pyrene (µg/kg)	Indeno[123-cd]pyrene (µg/kg)
BON1509010	PAKs	Sediment	Sediment at Salina Tam		1421	268	20.0	3.5	0.8	4.8	3.8	3.3	0.9	< 0,5	1.7	0.9	1.7	1.2
BON1509011	PAKs	Sediment	Sediment washed at Salina Tam		1421	268	5.5	< 0,5	< 0,5	4.9	1.7	2.0	< 0,5	0.8	0.7	< 0,5	0.7	0.5
BON1509031	PAKs	Sediment	Sediment at Lake Goto		2777	32	2.7	< 0,5	n.d.	< 0,5	< 0,5	< 0,5	n.d.	n.d.	n.d.	n.d.	< 0,5	n.d.
BON1509034	PAKs	Sediment	Sediment at shore Lake Goto		2777	32	16.8	3.6	0.6	2.6	1.6	2.6	< 0,5	0.7	0.5	< 0,5	3.8	n.d.
BON1609009	PAKs	Sediment	Sediment at shore Salina Bartol		8348	360	1.8	n.d.	n.d.	1.4	n.d.	< 0,5	< 0,5	n.d.	n.d.	n.d.	n.d.	n.d.
BON1609008	PAKs	Sediment	Sediment at Salina Bartol		8367	359	2.5	n.d.	< 0,5	1.5	< 0,5	< 0,5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BON1509032	PAKs	Soil	Soil at Lake Goto		2777	32	1.3	n.d.	< 0.5	1.0	n.d.	< 0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BON1609010	PAKs	Soil	Soil at Salina Bartol		8367	359	2.4	n.d.	< 0.5	0.5	n.d.	< 0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BON1509008	PAKs	Vegetation	Vegetation at Salina Tam	Black deposition	1174	260	6.8	0.6	1.8	35.9	n.d.	21.4	n.d.	4.0	< 0.5	< 0.5	< 0.5	n.d.
BON1409014	PAKs	Vegetation	Vegetatie at Lake Goto near BOPEC	Black deposition	1317	101	7.8	< 0.5	< 0.5	3.6	0.8	1.0	< 0.5	0.5	< 0.5	< 0.5	< 0.5	< 0.5
BON1509029	PAKs	Vegetation	Vegetation at Lake Goto (Northeast)	Black deposition	2711	54	3.6	n.d.	0.5	2.9	0.6	0.7	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	n.d.
BON1509015	PAKs	Vegetation	Vegetatie extreme South West		2727	287	3.4	0.9	< 0.5	4.3	1.0	1.3	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	n.d.
BON1609026	PAKs	Vegetation	Vegetation Before Ua Pass	No visible deposition	4604	18	2.1	n.d.	n.d.	0.7	< 0.5	< 0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BON1609011	PAKs	Vegetation	Vegetaton at Salina Bartol		8348	360	0.6	n.d.	0.8	9.6	1.1	2.8	n.d.	< 0,5	n.d.	n.d.	n.d.	n.d.
BON1709005	PAKs	Vegetation	Vegetatie at Boka Onima	No visible deposition	8957	69	5.1	n.d.	0.7	9.2	n.d.	3.4	< 0.5	0.5	< 0.5	< 0.5	< 0.5	n.d.
BON1709021	PAKs	Vegetation	Vegetation at Kralendijk		15030	124	5.3	n.d.	1.3	19.7	n.d.	7.4	0.7	2.7	0.7	< 0.5	< 0.5	0.7
BON1709016	PAKs	Vegetation	Vegetation at Sorobon		19800	126	3.4	n.d.	0.5	7.2	n.d.	2.2	n.d.	< 0.5	n.d.	n.d.	n.d.	n.d.

Appendix 3. Concentration results: PFOS

Results 1st set of analyses

Sample sites, sample characteristics, sample distances (measured in relation to the naphtha tank) and orientations in comparison to the BOPEC facilities, and measured concentrations of PFOA and PFOS compounds in various sample types, including samples of fire-fighting foams (Fomtech and Thunderstorm) storage vessels and a pool containing fire fighting products run-off (water and foam, sedimented).

(orange) =maximum value amongst foams AND higher than environmental samples
(yellow) =maximum value amongst foams AND higher than environmental samples

PFOS-compounds

					µg/kg															
					PFOA-analogues												PFOS-analgues			
Sample code	Sample type	Detail	Distance to BOPEC (m)	Direction	P5A	P6A	P7A	P8A	P9A	P10A	P11A	P12A	P13A	P14A	P16A	P18A	P4S	P6S	P8S	P10S
Foam Storage Container samples																				
BON1409002	FomTec	likely 200 liter drums			<0.1	4.5	0.45	11.1	<0.1	0.93	1.01	1.1	2.5	4.3	119	24	ur	ur	ur	ur
BON1409003	Thunderstorm	likely 200 liter drums			<0.1	>500 (1100)	113	>100 (360)	ur	>100 (170)	56.4	108	6.6	158	>500 (970)	58	ur	ur	ur	ur
BOPEC area sample																				
BON1409005	Pool on BOPEC area	Sedimented debris	0		1.0	34.8	10.8	21.8	2.3	7.0	3.0	5.0	1.2	2.1	4.7		21.7	>100 (130)	>1000 (6000)	>100 (228)
Environmental samples																				
BON1509025	Soil sample near BOPEC	Top soil scraped	443	291	0.70	0.40	0.13	0.28	<0.1	<0.05	0.07	<0.05	<0.05	<0.2	0.31	<5	<0.1	0.58	7.5	<0.1
BON1509003	Sediment at Saline Tan	Sediment ("uitspoeling"), top scraped	1039	289	<0.1	0.09	<0.05	0.28	0.12	0.14	0.40	0.33	0.35	<0.2	0.41	<5	<0.1	0.34	ur	ur
BON1509002	Sediment at Salina Tan	Sediment ("waterbodem"), top scraped	1041	289	<0.1	<0.05	<0.05	0.25	<0.1	<0.05	0.05	<0.05	<0.05	<0.2	0.38	<5	<0.1	<0.1	ur	<0.1
BON1409010	Water + flocks sample	Goto, near Caribbean Sea (water fraction), East of BOPEC	1322	101	<0.1	0.08	<0.05	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.2	<0.2	<5	<0.1	<0.1	ur	<0.1
BON1409010	Water + flocks sample	Goto, near Caribbean Sea (sediment fraction), East of BOPEC	1322	101	0.16	0.25	0.07	0.26	<0.1	<0.05	<0.05	<0.05	<0.05	<0.2	0.30	<5	0.39	2.4	22.4	<0.1
BON1409015	Sediment near Lake Goto	Goto, near Caribbean Sea	1345	101	0.12	0.18	0.11	0.57	0.14	0.07	<0.05	<0.05	<0.05	<0.2	<0.2	<5	0.31	4.6	58.5	<0.1
BON1509027	Sediment near Lake Goto	North east in Lake	2711	54	<0.1	0.17	0.05	0.29	<0.1	<0.05	0.08	<0.05	0.05	<0.2	<0.2	<5	0.16	1.7	18.3	<0.1
BON1509031	Sediment near Lake Goto	North in Lake	2777	32	<0.1	0.10	<0.05	0.33	<0.1	<0.05	0.09	0.06	0.10	<0.2	<0.2	<5	0.12	1.8	15.1	<0.1
Level of Quantification (µg/kg)					0.1	0.05	0.05	0.1	0.1	0.05	0.05	0.05	0.05	0.2	0.2	5	0.1	0.1	0.5	0.1
Values in red are indicative.		Measurement uncertainty here is 40-50%																		
ur = analysis not succesful																				

Measurements of PFOA and PFOS compounds are complex, in part due to the lack of appropriate standards and analytically difficult procedures. Empty cells: compound not detected. “ur” = unclear result; not sure whether compound is absent or present. Concentrations marked in red: level of uncertainty is 40 – 50%. Values between brackets are raw estimates of possible concentrations.

Results 2[nd] set of analyses

					ng/L															
					PFOA-analogues											PFOS-analogues			
Sample code	Sample ttype	Detail	Distance to BOPEC (m)	Direction	P5A	P6A	P7A	P8A	P9A	P10A	P12A	P13A	P14A	P16A	P18A	P4S	P6S	P8S	P10S
BON1409010	Water sample	Goto near Caribean Sea, East of BOPEC	300	100	170	140	17	ur	0,98	< 0.1	< 0.1	< 0.1	2,6	0,72	<5	164	184	130	< 0.25
BON1509001	Water sample	Salina Tam	1.200	290	< 0.1	4,2	1,2	ur	2,24	< 0.1	< 0.1	0,2	1,2	0,29	<5	2,5	27	254	< 0.25
BON1509028	Water sample	Lake Goto north-east	1.800	35	130	130	19,2	ur	0,56	< 0.1	< 0.1	< 0.1	1,3	0,13	<5	196	323	156	< 0.25
BON1509030	Water sample	Lake Goto north	2.300	17	130	130	20	ur	0,61	< 0.1	< 0.1	< 0.1	1,1	0,43	<5	193	383	131	< 0.25
BON1609001	Water sample	Salina Matijs	6.500	29	< 0.1	0,14	0,12	ur	< 0.1	< 0.1	< 0.1	0,31	0,65	0,34	<5	< 0.25	0,43	1,9	< 0.25
BON1609019	Water sample	Salina Slagbaai-back	5.000	333	7	0,7	0,12	ur	< 0.1	< 0.1	< 0.1	< 0.1	0,46	0,38	<5	0,56	4,6	8,4	< 0.25
					ng/m2														
BON1409006	Deposition sample from car	BOPEC area	300	137	150	375	70	ur	2	0	0	1	3	1	<0,125	295	550	3250	23

“ur” = unclear result; not sure whether compound is absent or present.

PFAA analogues (the compounds ending on 'A') and PFASs analogues (compounds ending on "S") in this research.

Abbreviation	Systematic name
P4A	Perfluoro-n-butanoic acid
P5A	Perfluoro-n-pentanoic acid
P6A	Perfluoro-n-hexanoic acid
P7A	Perfluoro-n-heptanoic acid
P8A	Perfluoro-n-octanoic acid
P9A	Perfluoro-n-nonanoic acid
P10A	Perfluoro-n-decanoic acid
P11A	Perfluoro-n-undecanoic acid
P12A	Perfluoro-n-dodecanoic acid
P13A	Perfluoro-n-tridecanoic acid
P14A	Perfluoro-n-tetradenoic acid
P16A	Perfluoro-n-hexadecanoic acid
P18A	Perfluoro-n-octadecanoic acid
P4S	Perfluoro-1-butanesulfonate
P6S	Perfluoro-1-hexanesulfonate
P8S	Perfluoro-1-octanesulfonate
P10S	Perfluoro-1-decanesulfonate

Deriving ad hoc criteria for PFOS in sediments of Lake Goto.

A reference value for the partition coefficient of PFOS between suspended matter and water is 10,300 L/kg, which is the geometric mean based on 65 samples for suspended matter from German, Dutch and Belgian rivers (Möller 2009). The geometric mean of the partition coefficient normalized to organic carbon (Koc), available for 61 of these 65 samples, was 111,000 L/kg (Möller 2009). This is in good agreement with the Koc of 66,000 L/kg, which can be derived from data for four soils (OECD, 2002). From all these samples, an organic carbon partition coefficient of 107,000 L/kg can be derived. This value was used to derive the concentrations of PFOS in water and sediment upon equilibrium partitioning of the compounds between the water and the sediment phase, given the debris concentration data. Standard sediment has a default of 5% organic carbon, standard suspended matter has a default of 10% organic carbon. The data from sediments and suspended matter from Bonaire were normalized to these default organic carbon contents, based on Loss on Ignition measurements (Appendix 6), measuring total organic matter in the samples.

Appendix 4. Concentration results: dioxins

Sample sites, sample characteristics, sample distances (measured in relation to the naphtha tank) and orientations in comparison to the BOPEC facilities, and measured concentrations of dioxin congeners for vegetation samples and the sample in Rincon.

Sample code	Compounds	Sample type	Detail	Remark	Distance to BOPEC (m)	Direction from BOPEC
BON1509024	Dioxins and PCBs	Vegetation	Vegetation near BOPEC	Vegetation black	443	291
BON1509033	Dioxins and PCBs	Vegetation	Vegetation lear Lake Goto	Vegetation black	2777	32
BON1609036	Dioxins and PCBs		Village Rincon	No visible deposition	6796	75
BON1709011	Dioxins and PCBs	Vegetation	Vegetation near goat farm	No visible deposition	12039	99
BON1709014	Dioxins and PCBs	Vegetation	Vegetation near Mata di Fruta	No visible deposition	15655	114
BON1709018	Dioxins and PCBs	Vegetation	Vegetation near Dos Kura	No visible deposition	26539	138

	Dioxins (concentrations, ng/kg product, 88% dry wt, totaal gehaltes in ng TEQ/kg product (88% [illegible]													
Sample code	2,3,7,8-TCDF(ng/kg product)	1,2,3,7,8-PeCDF (ng/kg product)	2,3,4,7,8-PeCDF (ng/kg product)	1,2,3,4,7,8-HxCDF (ng/kg product)	1,2,3,6,7,8-HxCDF (ng/kg product)	2,3,4,6,7,8-HxCDF (ng/kg product)	1,2,3,7,8,9-HxCDF (ng/kg product)	1,2,3,4,6,7,8-HpCDF (ng/kg product)	1,2,3,4,7,8,9-HpCDF (ng/kg product)	OCDF (ng/kg product)	2,3,7,8-TCDD (ng/kg product)	1,2,3,7,8-PeCDD (ng/kg product)	1,2,3,4,7,8-HxCDD (ng/kg product)	[illegible]
BON1509024	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.302	<0.05	<0.10	<0.05	<0.05	<0.05	<0.05
BON1509033	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.10	<0.05	<0.05	<0.05	<0.05
BON1609036	<0.05	<0.05	<0.05	0.068	0.113	0.087	<0.05	0.425	<0.05	0.127	<0.05	0.310	0.201	0.3[illegible]
BON1709011	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.10	<0.05	<0.05	<0.05	<0.05
BON1709014	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.148	<0.05	0.161	<0.05	<0.05	<0.05	<0.05
BON1709018	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.10	<0.05	<0.05	<0.05	<0.05

Appendix 5. Concentration results: PCBs

Sample sites, sample characteristics, sample distances (measured in relation to the naphtha tank) and orientations in comparison to the BOPEC facilities, and measured concentrations of PCB congeners for vegetation samples.

							non-ortho-PCB's (concentrations, ng/kg product, 88% dry wt)					mono-ortho-PCB's (concentrations, ng/kg product, 88% dry wt))						
Sample code	Compounds	Sample type	Detail	Remark	Distance to BOPEC (m)	Direction from BOPEC	PCB 81 (ng/kg product)	PCB 77 (ng/kg product)	PCB 126 (ng/kg product)	PCB 169 (ng/kg product)		PCB 123 (ng/kg product)	PCB 118 (ng/kg product)	PCB 114 (ng/kg product)	PCB 105 (ng/kg product)	PCB 167 (ng/kg product)	PCB 156 (ng/kg product)	PCB 157 (ng/kg product)
DON1509024	Dioxins and PCDs	Vegetation	Vegetation near DOPEC	Vegetation black	443	291	0.23	0.39	0.00	<0.05		<10	15.00	<10	<10	<10	<10	<10
BON1509033	Dioxins and PCBs	Vegetation	Vegetation lear Lake Goto	Vegetation black	2777	32	<0.05	0.34	0.08	<0.05		<10	17.66	<10	<10	<10	<10	<10
BON1609036	Dioxins and PCBs	Vegetation	Village Rincon	No visible deposition	6796	75	<0.05	1.15	0.41	0.06		<10	12.88	<10	<10	<10	<10	<10
BON1709011	Dioxins and PCBs	Vegetation	Vegetation near goat farm	No visible deposition	12039	99	0.19	4.52	0.55	<0.05		<10	<10	<10	<10	<10	<10	<10
BON1709014	Dioxins and PCBs	Vegetation	Vegetation near Mata di Fruta	No visible deposition	15655	114	0.30	11.39	2.13	0.13		<10	<10	<10	<10	<10	<10	<10
BON1709018	Dioxins and PCBs	Vegetation	Vegetation near Dos Kura	No visible deposition	26539	138	<0.05	0.37	0.09	0.06		<10	<10	<10	<10	<10	<10	<10

Appendix 6. Loss on Ignition data, for assessing organic carbon contents

Loss on Ignition data for sediment samples collected at various sites, used to assess water-sediment partitioning of compounds as needed in the process of risk assessment.

Monstercode	Site	Loss on Ignition (%)
BON1509010	Salina Tam (near sea)	4.89
BON1509011	Salina Tam (near sea)	5.97
BON1509031	Lake Goto (North)	4.86
BON1509032	Lake Goto (North)	4.48
BON1609008	Salina Bartol	12.87
BON1609009	Salina Bartol	9.40

Appendix 7. PFOS in (inter)national policy frameworks

Because of its unwanted intrinsic characteristics PFOS has received serious policy attention during the last decade. Below a short overview is given on a number of (inter)national policy frameworks addressing PFOS, including their general policy targets.

Stockholm Convention
In May 2009 PFOS was adopted as Persistent Organic Pollutant (POP) to the Stockholm Convention. This Convention is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. Exposure to POPs can lead to serious health effects including certain cancers, birth defects, dysfunctional immune and reproductive systems, greater susceptibility to disease and even diminished intelligence. Given their long range transport, no one government acting alone can protect is citizens or its environment from POPs. In response to this global problem, the Stockholm Convention, which was adopted in 2001 and entered into force in 2004, requires Parties to take measures to eliminate or reduce the release of POPs into the environment.

REACH
PFOS is included in Annex XVII of REACH (restrictions). A restriction of a substance is any condition for prohibition of or concerning, its manufacture, use or placing on the market. Restrictions enable risk management measures beyond those already implemented by manufacturers, importers and downstream users, to be introduced across the Community, where they are determined to be necessary. Restrictions can also impose a harmonized level of risk management measures. Restrictions apply to all manufacturers, importers, downstream users and distributors of a substance if the manufacture, use or placing on the market (activity) of this substance is included in Annex XVII.

Water Framework Directive (WFD)
PFOS is recommended for inclusion as ‘priority hazardous substance’ in the Water Framework Directive (WFD). This because of its PBT-characteristics. The target of WFD is to establish proper conditions for the European surface and ground water. The WFD makes a distinction between ‘priority substances’ and ‘priority hazardous substances’. For the latter category more stringent policy targets are set than for ‘priority substances’ (i.e. complete ending of emissions to the environment).

Dutch priority chemicals
PFOS is included on the list of ‘priority substances’ in the Netherlands. The Dutch policy on substances aims at reducing the risks of 'priority substances' that pose a potential risk to human health and the environment. The substances on the list have been selected because their dangerous characteristics, their emission or their level in the environment could introduce an unacceptable risk for human health and environment. The current target is to reach environmental concentrations lower than the so-called Negligible Concentration, where possible, by the year 2010.

Rotterdam Convention
PFOS was very recently (April 2011) recommended for inclusion in the Rotterdam Convention Prior Informed Consent procedure. The recommendation was based on a review of national regulatory actions taken by various countries to ban or restrict the use of chemicals that pose an unacceptable risk to human health and the environment. The Rotterdam Convention does not introduce bans but fosters information exchange mechanisms to help improve decision making about the trade of hazardous chemicals. It enables member Governments to alert each other to potential dangers by exchanging information on chemicals and to take informed decisions with regard to whether they want to import such chemicals in the future.

Published by:

National Institute for Public Health
and the Environment
P.O. Box 1 | 3720 BA Bilthoven
The Netherlands
www.rivm.com